Phosphinines as Precursors for Phosphabarrelenes and Phosphinine Anions

Matthias Blug

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THÈSE

Présentée pour obtenir le titre de

DOCTEUR DE L'ÉCOLE POLYTECHNIQUE

Spécialité CHIMIE

Par

Matthias Blug

Phosphinines as Precursors for Phosphinine Anions and Phosphabarrelenes: Coordination Chemistry, Catalysis and Stabilization of Nanoparticles.

Soutenue le 23 septembre 2009, devant le jury composé de:

Mouâd Alami	Directeur de Recherche au CNRS	Président
Christian Müller	Professeur à l'Université d'Eindhoven	Rapporteur
Fréderic Paul	Directeur de Recherche au CNRS	Rapporteur
J. Chris Slootweg	Professeur à l'Université d'Amsterdam	Examinateur
Nicolas Mézailles	Directeur de Recherche au CNRS	Directeur de thèse
Pascal Le Floch	Professeur à l'École Polytechnique	

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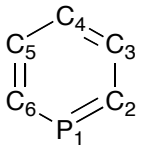
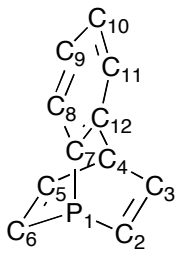
PREFACE

This manuscript contains the results of experimental work and theoretical calculations. To prevent the confusion between experimental results and theoretical structures, the following numbering was used:

- For synthesized compounds latin numbers were used in combination with the number of the section, for example **IV-15** (refers to compound 15 in part IV)
- For optimized structure that were obtained from theoretical calculations characters were used, for example **IV-A** (refers to structure A in part IV)

The following numbering is used throughout the manuscript for the positions in phosphinines and phosphabarrelenes in NMR spectra. (The numbering, that is used for the phosphabarrelenes is related to that in the phosphinines). The numbering of the molecules in X-Ray crystal structures is arbitrary and may be different from that described here.





A part of this work and related work has already been published:

1. M. Doux, P. Thuery, **M. Blug**, L. Ricard, P. Le Floch, T. Arliguie, N. Mézailles. *Anions of tridentate SPS ligands: Synthesis, X-ray structures and DFT calculations. Organometallics* **2007**, *26*, 5643 - 5653.

2. **M. Blug**, O. Piechaczyk, M. Fustier, N. Mézailles, P. Le Floch. *Protodesilylation of 2,6-Disubstituted Silylphosphinines. Experimental and Theoretical Study. J. Org. Chem.* **2008**, *73*, 3258 - 3261.

3. T. Arliguie, **M. Blug**, P. Le Floch, N. Mézailles, P. Thuéry, M. Ephritikhine. *Organouranium Complexes with Phosphinine-Based SPS Pincer Ligands. Variations with the Substituent at the Phosphorus Atom. Organometallics* **2008**, *27*, 4158–4165.

4. **M. Blug**, C. Guibert, X.-F. Le Goff, N. Mézailles, P. Le Floch. *1-Phosphabarrelene Complexes of Palladium and their use in Suzuki-Miyaura Coupling Reactions. Chem. Commun.* **2008**, 201-203.

5. **M. Blug**, H. Heuclin, T. Cantat, X.-F. Le Goff, N. Mézailles, P. Le Floch. *A Strained S~C~S Ir Pincer Complex: Intramolecular C-H Activation of an Aromatic Ring. Organometallics* **2009**, *28,* 1969-1972 .

6 **M. Blug**, M. Doux, X.-F. Le Goff, F. Ribot, P. Maitre, P. Le Floch, N. Mezailles. *The Effect of a fourth Binding Site on the Stabilization of Cationic SPS Pincer Palladium Complexes: Experimental, DFT and Mass Spectrometric Studies. Organometallics,* **2009***, 28, 2020-2027.*

7. **M. Blug**, X.-F. Le Goff, N. Mézailles, P. Le Floch. *A 14 VE Pt(0) Phosphabarrelene Complex in the Hydrosilylation of Alkynes. Organometallics,* **2009***, 28, 2360-2362.*

8. **M. Blug**, D. Grünstein, G. Alcaraz, X.-F. Le Goff, P. Le Floch, S. Sabo-Etienne, N. Mézailles. *Bonding Mode of a New Bis Phosphine-Borane Alkyl Ligand to a Rh(I) Species. Chem. Commun.* **2009,** *4432-4434.*

LIST OF ABBREVIATIONS

acac	Acetylacetonate
Ar	Aryl
ATR	Attenuated Total Reflection
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
BINOL	1,1'-Binaphthyl-2,2'-diol
BPPLED	Bipolar Pulse Longitudinal Eddy Current Delay
^{t}Bu	*tert*-Butyl
^{i}Bu	i*so*-Butyl
Bu	*n*-Butyl
cat	Catalyst
CDA	Charge Decomposition Analysis
CI	Chemical Ionization
CID	Collision-Induced Dissociation
COD	1,5-Cyclooctadiene
COE	Cyclooctene
Cp	Cyclopentadienyl
CTAB	Cethylammonium bromide
Cy	Cyclohexyl
dba	Dibenzylideneacetone
DCM	Dichloromethane
DFT	Density Functional Theory
DOSY	Diffusion Ordered Spectroscopy
dppe	Bis(diphenylphosphino)ethane
dppm	Bis(diphenylphosphino)methane
DVDS	Bis(divinyltetramethyldisiloxane)
E	Electronic energy
ee	Enantiomeric excess
ESI	Electrospray
Et	Ethyl
HOFO	Highest Occupied Fragment Orbital
G	Gibbs Free Energy
HOMO	Highest Occupied Molecular Orbital
HRMS	High Resolution Mass Spectrometry
ICR	Ion Cyclotron Resonance
^{i}Pr	*iso*-Propyl

IR	Infrared
L	Ligand
LUFO	Lowest Unoccupied Fragment Orbital
LUMO	Lowest Unoccupied Molecular Orbital
M	Metal
Me	Methyl
MeCN	Acetonitrile
MS	Mass Spectroscopy
NBD	Norbornadiene
NMR	Nuclear Magnetic Resonance
NP	Nanoparticle
NTf_2^-	Triflimide
NHC	*N*-Heterocyclic Carbene
ODE	1-Octadecene
OTf	Trifluoromethanesulfonate
o-tol	*ortho*-Tolyl
PB	Phosphabarrelene
Pic	α-Picoline
Pin	Pinacol
PCM	Polarized Continuum Model
Ph	Phenyl
ppm	Parts per million
SQUID	Superconducting Quantum Interference Devices
THF	Tetrahydrofurane
tht	Tetrahydrothiophene
TMS	Tetramethylsilane
TOF	Turnover frequency
TON	Turnover number
TS	Transition State
r.t.	Room temperature
SPS	2,6-Bis(diphenylphosphinesulfide)-3,5-diphenylphosphinine
SP	2-Diphenylphosphinesulfide-3-methyl-5,6-diphenylphosphinine

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PART I:
Introduction

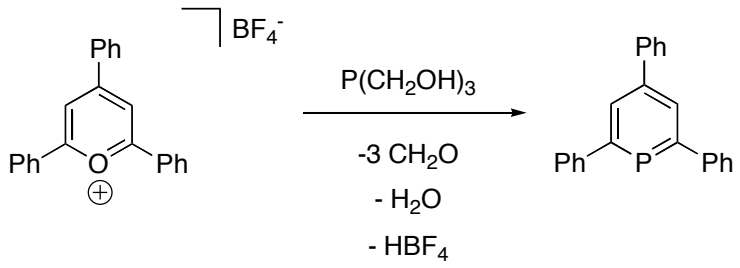
INTRODUCTION

I. PHOSPHININES

In this work we are espacially interested in molecules derived from phosphinine (C_5H_5P). These molecules are the phosphorus analogues of pyridines. To understand the particularity of these heterocycles it is important to know about the synthesis and the electronic properties of these molecules. The coordination chemistry of phosphinine ligands as well as their applications in catalysis will be presented. Finally this overview will allow for the definition of the work, that I have carried out during the last 3 years.

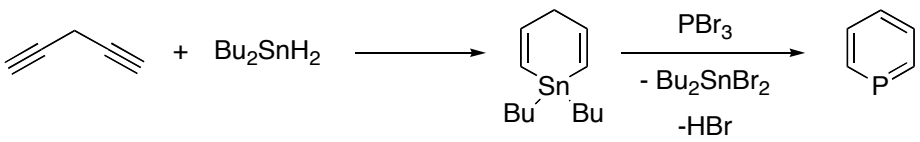
I.1. Synthesis

The first synthesis of a phosphinine was realized by Märkl in 1966. The synthesis of 2,4,6-triphenylphosphinine was achieved by the reaction of the corresponding pyryrilium salt with $P(CH_2OH)_3$ in analogy to the synthesis of pyridines (Scheme 1).[1]



Scheme 1: *First synthesis of 2,4,6-triphenylphosphinine.*

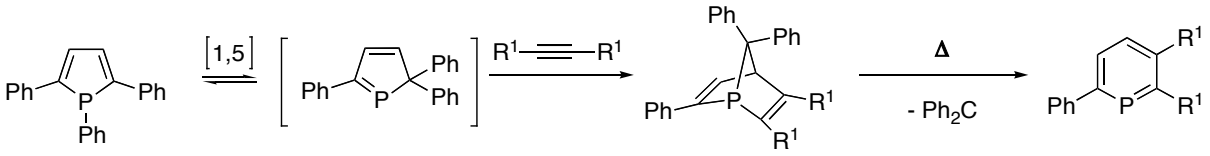
The synthesis of the parent-phosphinine C_5H_5P was reported by Ashe and coworkers in 1971 by the reaction of dibutyltinhydride with dipent-1,4-yne and subsequent metathesis with PBr_3 (Scheme 2).[2]



Scheme 2: *Synthesis of the parent-phosphinine C_5H_5P by Ashe.*

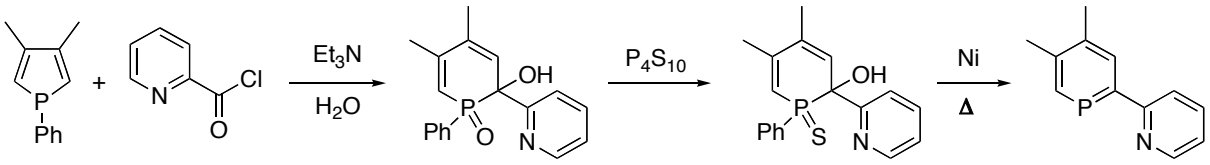
These two methods remained the only methods available for the synthesis of phosphinines until 1979. Since then, a large variety of procedures for the synthesis of functional phosphinine

derivatives have been developed. Several examples of the extension of the 5-membered cycle of phospholes have been reported. One of these methods is based on the 1,5-sigmatropic shift of a 1-Ph-phosphole with its 2-Ph-isomer that undergoes a [4+2]-cycloaddition reaction in the presence of alkynes to give the corresponding phosphanorbornadiene. Finally the elimination of diphenylcarbene leads to the formation of the desired phosphinine.[3-5]



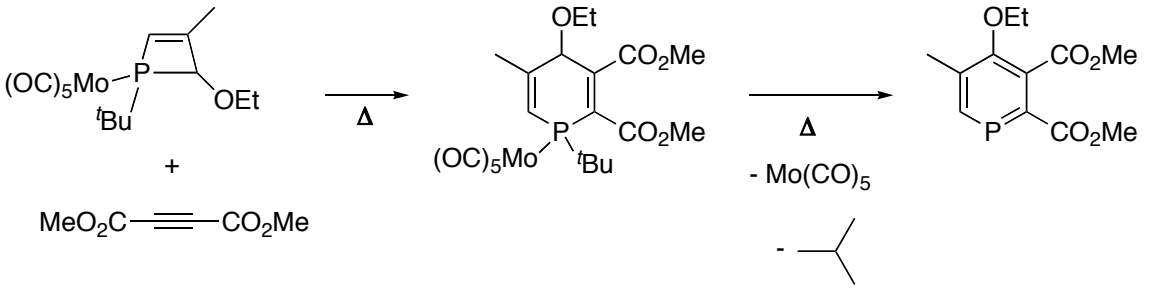
Scheme 3: *Synthesis of a phosphinine via a phosphanorbornadiene.*

Another method is the reaction of a phosphole with an acylchloride in the presence of triethylamine and the subsequent treatment with water. This method allowed for the synthesis of a mixed phosphinine-pyridine analogue of 2,2'-bipyridine after sulfurization and reduction of the intermediate phosphine oxide(Scheme 4).[6]



Scheme 4: *Synthesis of 2-(pyridyl)-phosphinine.*

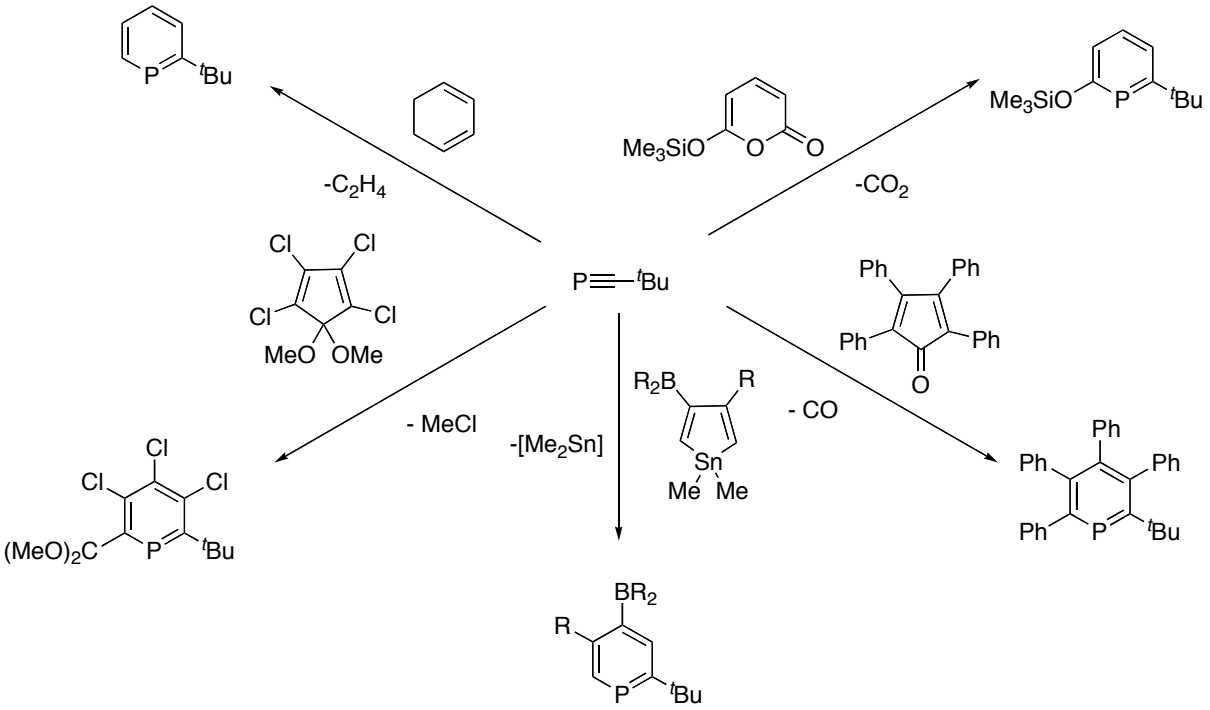
A large number of procedures for the synthesis of phosphinines using cycloaddition reactions has been reported also. For example, molybdenum carbonyl complexes of 1,4-dihydrophosphetes, a masked form of 1,3-phosphabutadienes can react with activated alkynes under thermal conditions to give phosphinines.[7]



Scheme 5: *Synthesis of phosphinines by cycloaddition of an alkyne on a 1,4-dihydrophosphete.*

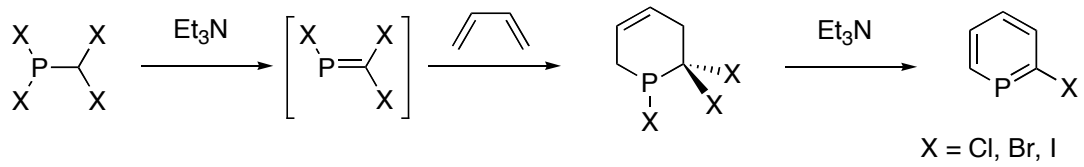
The variety of phosphinines that can be prepared by this method remains relatively restricted as due to the limited choice of alkynes that can be used for in this reaction.

The use of phosphaalkynes as dienophiles is more advantageous in this regard as phosphinines with different substitution patterns and various functionalities can be obtained (Scheme 5).[8, 9]



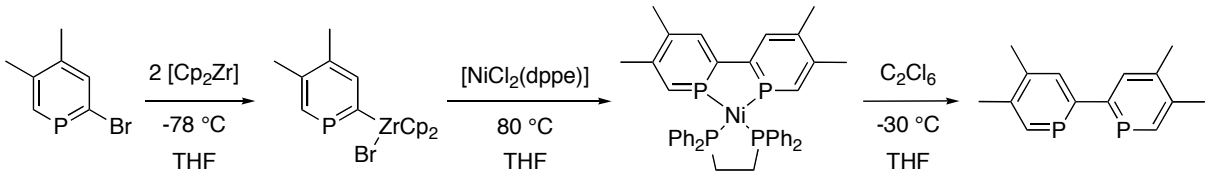
Scheme 6: *Synthesis of phosphinines from ᵗBu-phosphaalkyne.*

Highly reactive, *in situ* generated trihalogenoalkenes, obtained from the reactions of tetrahalogenoalkanes with triethylamine, were reacted with dienes in a [4+2] cycloaddition reaction, to lead to the 6 membered ring, which was aromatized in the same pot to form the desired 2-halogenophosphinines. This very elegant reaction developed in our laboratories, that can be carried out on a multigram scale (~ 30 g) provided an entry to many other derivatives. (Scheme 7).[10, 11]



Scheme 7: *Synthesis of 2-halophosphinines.*

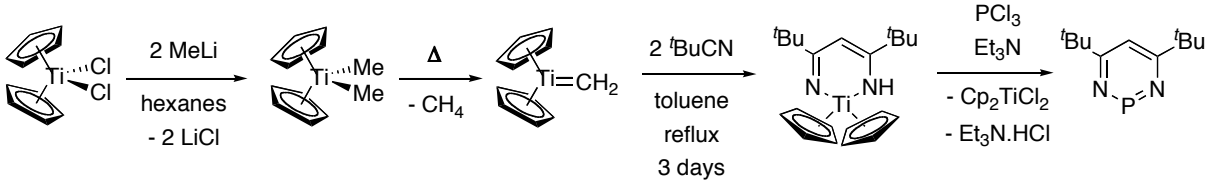
They posses the reactivity of other halogenoarene derivatives and can be used for example in various cross coupling reactions. Especially 2-bromophosphinines have shown to be versatile intermediates that allow for the synthesis of bidentate phosphinine-phosphine,[12] phosphinine-phosphole[13] and more importantly biphosphinine ligands (Scheme 8).[14]



Scheme 8: *Synthsis of a 2,2'-biphosphinine.*

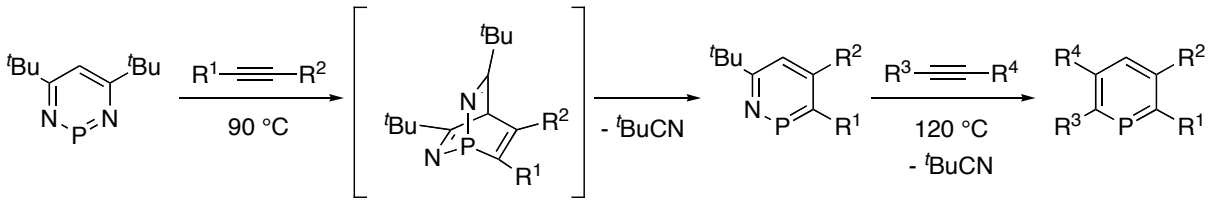
A few years ago, a synthetic strategy allowing for the synthesis of tetrafunctional phosphinine derivatives was reported from our group. This method is based on the reactivity of 1,3,2-diazaphosphinines.[15, 16]

The first step of the synthesis of 1,3,2-diazaphosphinine is the reaction of pivalonitrile with the Petasis reagent which leads to the formation of a diaza-titanacycle. In the second step, the reaction of the diaza-titanacycle with trichlorophosphine in the presence of a base then affords the desired product, which is highly sensitive towards moisture (Scheme 9).



Scheme 9: *Synthesis of 1,3,2-diazaphosphinine.*

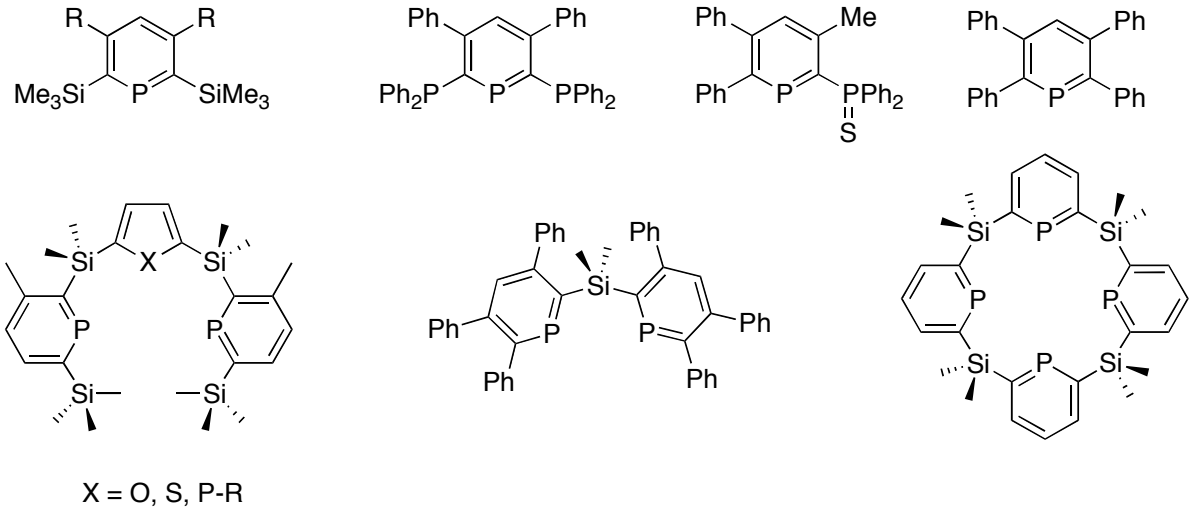
The reaction of 1,3,2-diazaphosphinine with alkynes *via* a sequence of a Diels-Alder and a Retro-Diels Alder reaction leads to the formation of a monoazaphosphinine derivative that can be converted to a phosphinine by reaction with a second equivalent of alkyne (Scheme 10).



Scheme 10: *Synthesis of phosphinines from 1,3,2-diazaphosphinine.*

This reaction is driven by thermodynamics and phosphinines are more stable than 1,3,2-diazaphosphinine or the corresponding monoaza-intermediates

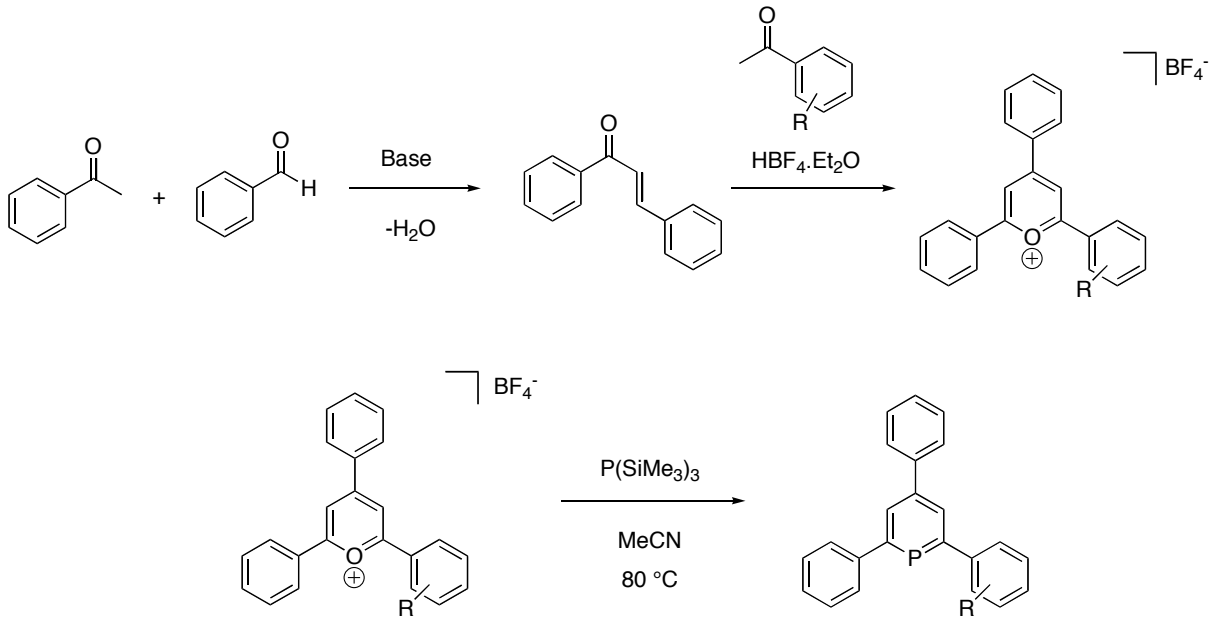
By this method a large variety of tetra-substituted phosphinines,[16, 17] polydentate phosphinines[18] and the first phosphorus macrocycles [19, 20] could be prepared during the last 13 years in our group (Scheme 11).



Scheme 11: *Several phosphinines synthesized via 1,3,2-diazaphosphinine.*

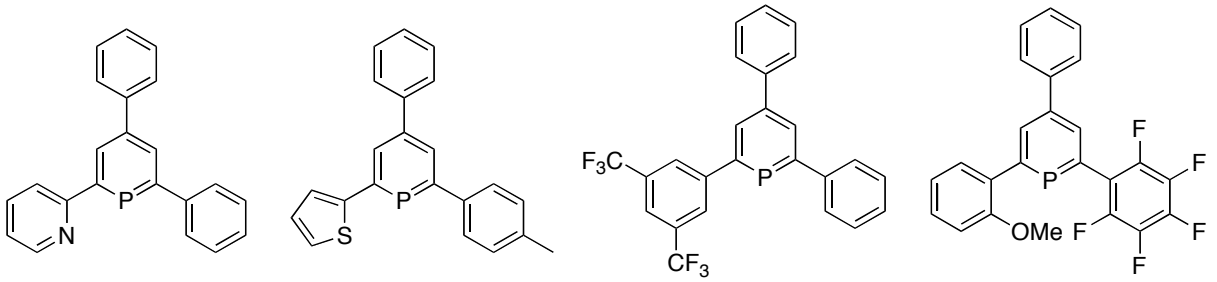
Interestingly, it could be observed that the use of silyl-substituted alkynes in this reaction sequence selectively provides phosphinines with silyl groups in the α-position of the phosphorus atom. This observation could be explained by the dipolar character of the diazaphosphinine.[21]

In 2006, Müller and coworkers, as well as Breit and coworkers, reported that asymmetrically substituted phosphinines can be prepared from pyrilium salts. For this, the preparation of the pyrilium salts from acetophenone and benzaldehyde derivatives has to be carried out in a stepwise manner (Scheme 12).[22, 23]



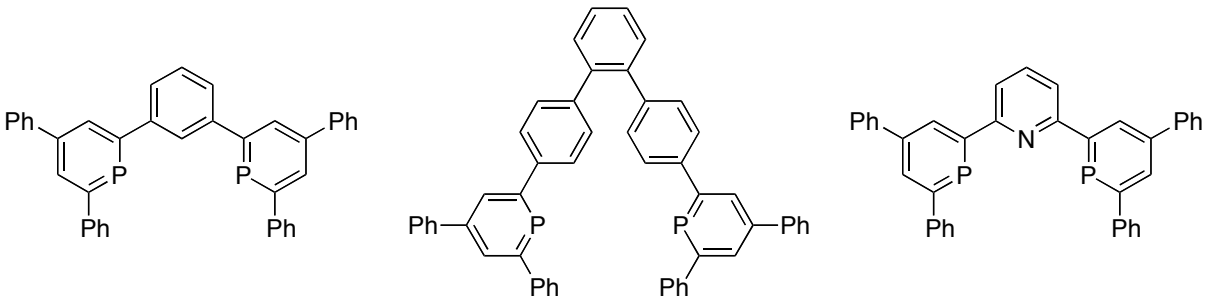
Scheme 12: *Synthesis of asymmetrically substituted phosphinines via pyrilium salts.*

A large variety of asymmetrically substituted phosphinines could be prepared by Müller and coworkers using this method. In this manner pyridyl and thienyl, as well as acceptor substituted aryl groups, could be introduced in the 2 and 6 position of the phosphinine (Scheme 13).[24]



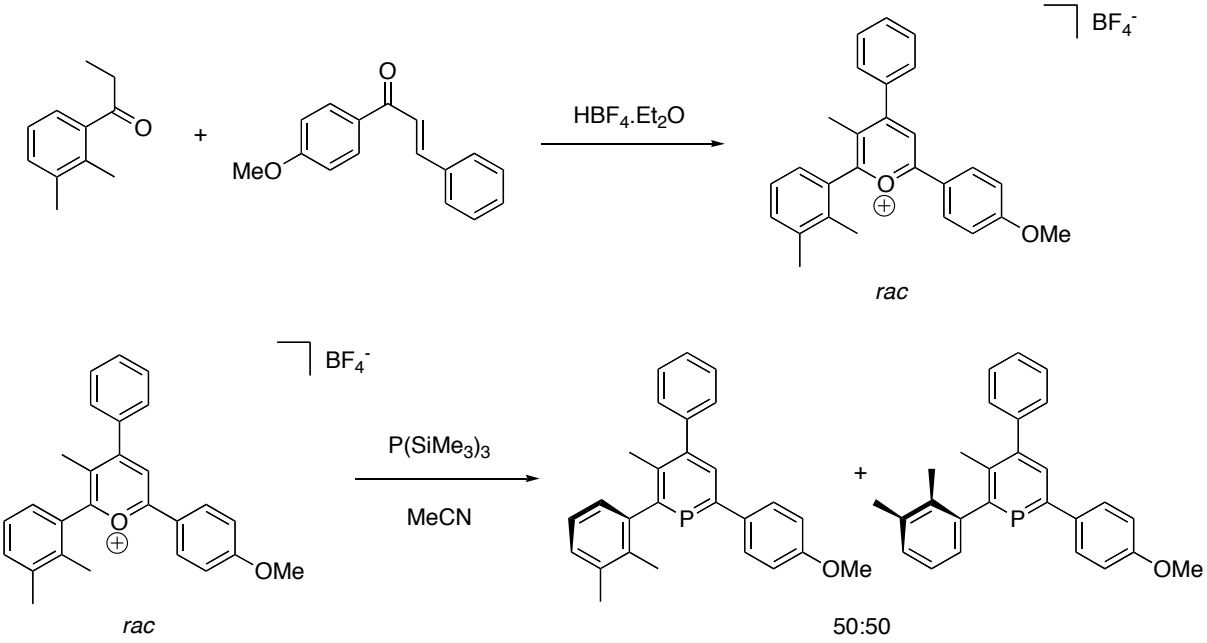
Scheme 13: *Phosphinines with pyridyl, thienyl and fluoro and trifluormethyl-arene substituents.*

Additionally the synthesis of bidentate bis-phosphinines with a large bite angle[25] and a bisphosphinine analogue of terpyridine[26] could be achieved by this method (Scheme 14).



Scheme 14: *Wide bite angle bis-phosphinines and bis-phosphinine analogue of terpyridine.*

The use of ethyl-phenyl-ketone in the synthesis allowed for the preparation of atropoisomeric pyrilium salts and subsequent phosphinines. It could be shown using chiral analytical HPLC that the rotational barrier is sufficiently high, to allow for the separation of the enantiomers at 25 °C (Scheme 15).[27]



Scheme 15: *Synthesis of atropoisomeric pyrilium salts and phosphinines.*

I.2. Electronic Properties

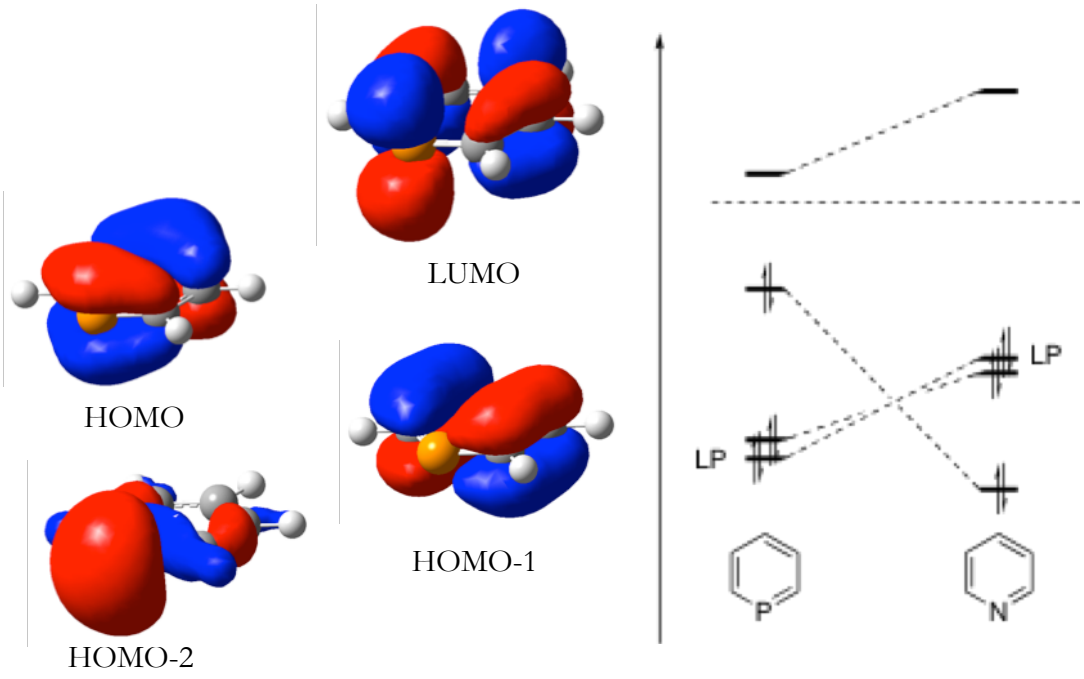
Phosphinines are planar, heterocyclic molecules[2] with an aromaticity that is comparable to that of benzene.[28] $\lambda^3\sigma^2$-phosphorus derivatives (trivalent phosphorus atom with a coordination number of two) containing a P=C double bond are often compared to carbon systems since phosphorus is isoelectronic to the C-H fragment.[29] This analogy does not simply rely on this crude electronic equivalency and, actually, some striking parallels can be drawn between the chemistry of the two systems. The fact that phosphorus is reluctant to give sp and sp^2 hybridization has been widely discussed and it is now well established that the weak overlap

between 3s and 3p atomic orbitals of the element is mainly responsible for this situation (large difference in the spatial distribution of AOs).[30]

A consequence of the difference in the hybridization of the phosphorus compared to the carbon analogue is the smaller CPC angle of 101 ° in the parent phosphinine compare to a CCC angle of 120 ° in benzene. This variation of the angle is accompanied with the observation of an augmentation of the C-X (X= P, C) bond length in the phosphinine compared to benzene.

Another important consequence of this weaker hybridization concerns the spatial distribution of lone pair on phosphorus.

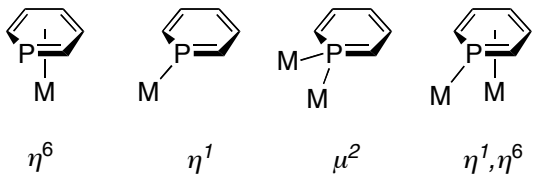
Theoretical calculations show that the orbital describing the lone pair on the phosphorus atom in phosphinines is not the highest occupied molecular orbital (HOMO) but rather the HOMO-2 orbital with an important s-character (61 % of 3s AO and 39 % of 3p AO at the phosphorus atom) compared to pyridine (HOMO, 29 % of 2s AO and 71 % 2p AO at the nitrogen atom). The important s-character of the heteroatom lone-pair, which is more diffuse in the case of the phosphinine than in pyridine, should lead to a weaker basicity in phosphinines compared to pyridines. This could be proved by gas phase proton affinities that could be obtained by ion-cyclotron resonance techniques for pyridine (195.8 kcal mol^{-1}) and the parent phosphinine (219.4 kcal mol^{-1}). Additionally the LUMO is much lower in energy in phosphinines than in pyridine. Consequently phosphinines are weaker σ-donor but better π-acceptor ligands than pyridines. [31]



Scheme 16: *Frontier orbitals of the parent phosphinine C_5H_5P (left) and frontier diagram for phosphinine and pyridine (right).*

I.3. Coordination Chemistry

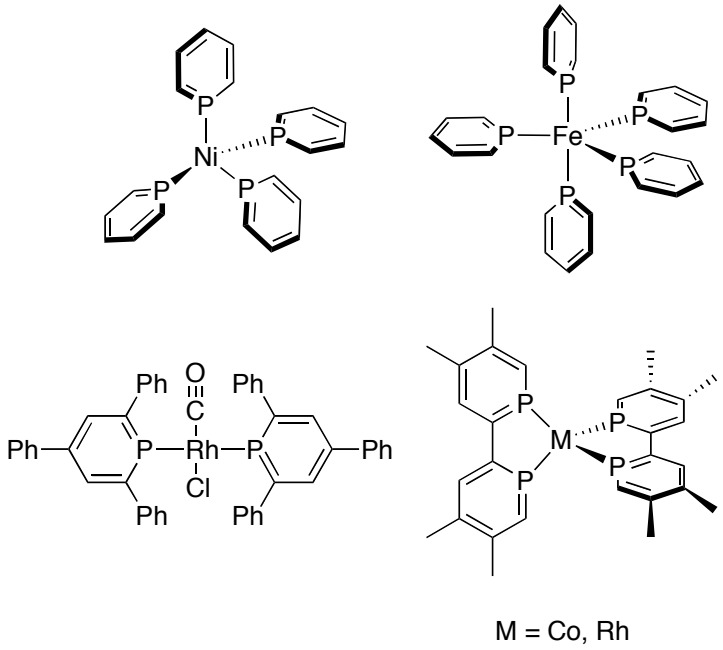
As their nitrogen analogues, phosphinines can coordinate transition metal centers through their lone pair. As it was mentioned above, the HOMO-2 orbital of phosphinines displays a σ-symmetry and can therefore act as a $2e^-$ donor. Furthermore, the HOMO-1 and HOMO orbitals of the aromatic system of the phosphinine are close in energy and allow the phosphinine to act as $6e^-$ donors. Additionally the capacity of phosphorus to accept hypervalence allows a bridging coordination mode. This leads to a wide range of different coordination modes (Scheme 17).



Scheme 17: *Common coordination modes in phosphinine-transition-metal complexes.*

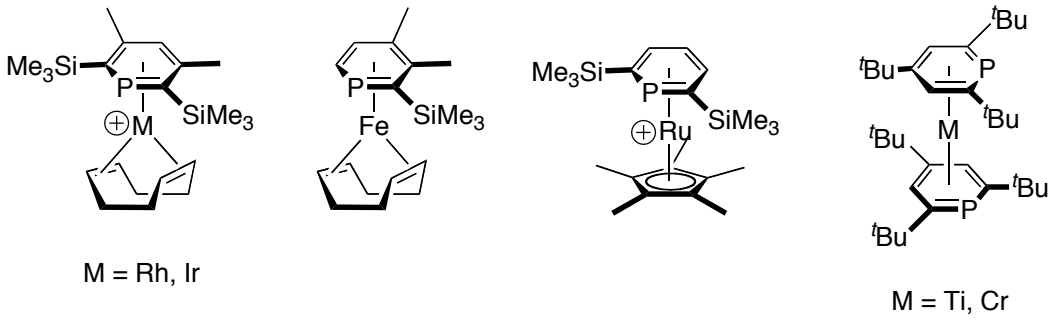
The following examples will give a brief overview about the different kind of complexes that can be stabilized with phosphinines. For more details, exhaustive summaries about the coordination chemistry of phosphinines can be found in some recent reviews by Le Floch[32, 33] and Müller.[34]

The η^1-coordination *via* the phosphorus can be observed especially in low valent complexes of late transition metals. For example Elschenbroich and coworkers reported the synthesis of homoleptic nickel(0) and iron(0) complexes $[Ni(PC_5H_5)_4]$ and $[Fe(PC_5H_5)_5]$.[35, 36] A Rh(I) complex with η^1-coordinated phosphinines was reported by Breit and coworkers.[37] The stabilization of highly reduced cobalt and rhodium complexes of a biphosphinine ligand (biphos = 4,4',5,5'-tetramethyl-2,2'-biphosphinine) with a formal oxidation state of the transition metal of (-I) has been reported by our group[38] as well as other highly reduced metal complexes such as $[M(biphos)_3]^{2-}$ (M= Zr, Ti, Hf),[39] $[M(biphos)_2]^{2-}$ (M= Ru, Fe)[40] and using the the calix[4] macrocycle a Rh(I) and Au(I) and Au(0) complex.[20] This later complex is the most stable Au(0) complex reported to date (Scheme 18).



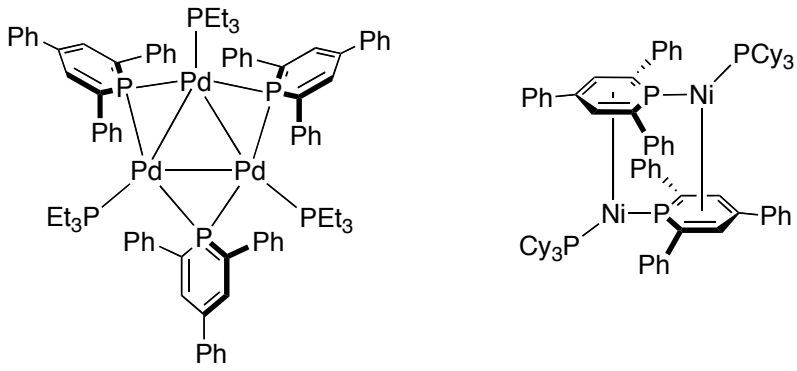
Scheme 18: *σ-coordinated transition metal complexes with phosphinine ligands.*

The formation of η^6-coordinated complexes is typically observed for early transition metals an can be additionally favored by the use of ligand with sterically demanding substituents in the 2 and 6 positions of the phosphinine (Scheme 19).[41]



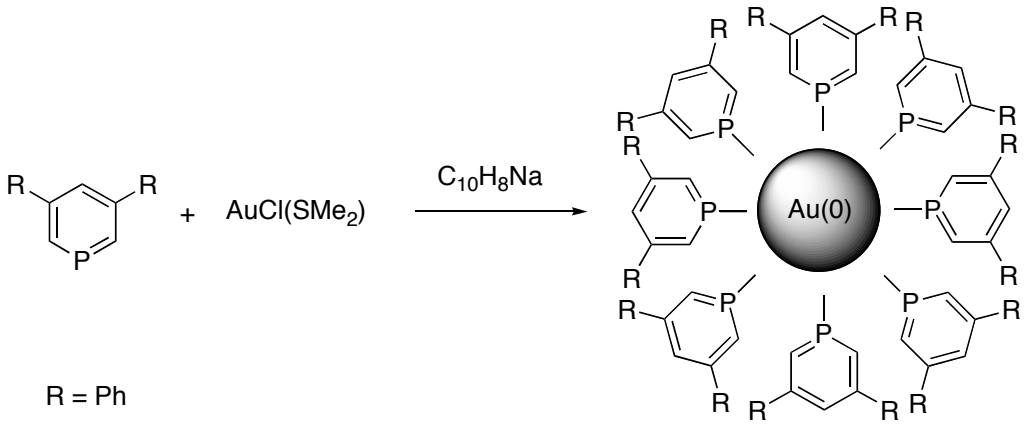
Scheme 19: *π-coordinated transition metal complexes with phosphinine ligands.*

Additionally, phosphinines can act as bidentate ligands, on the one hand by an (η^1,η^6)-coordination[42] of the phosphorus lone pair and the π-system, or on the other hand, by a (η^1,η^1)-coordination[43] of the diffuse lone pair to two metal centers (Scheme 20).



Scheme 20: *Bridging coordination modes of phosphinine ligands.*

In addition to the application in coordination chemistry, it has been shown recently in our group that phosphinines can be used to stabilize gold nanoparticles.[44]

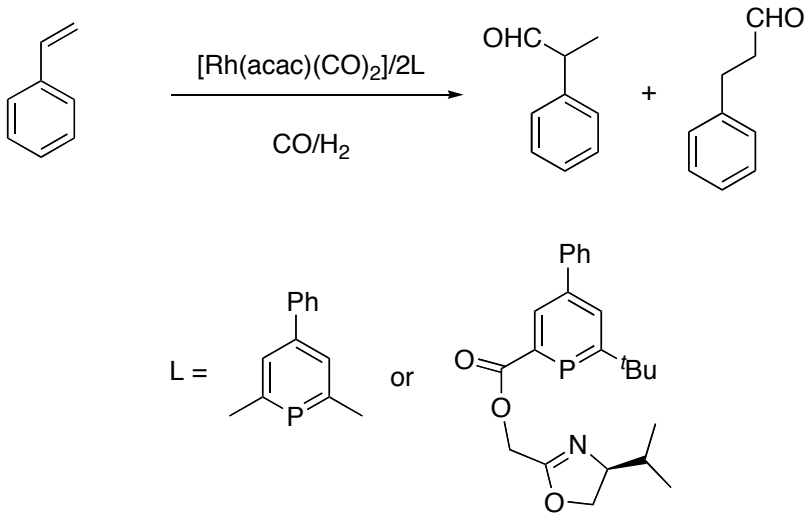


Scheme 21: *Synthesis of gold nanoparticles stabilized by phosphinines.*

I.4. Catalysis

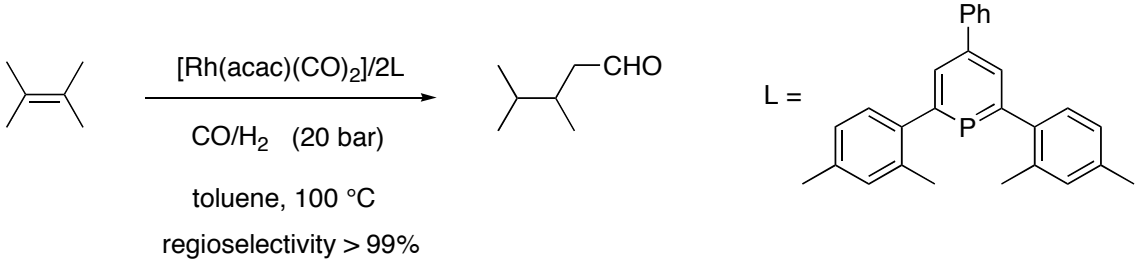
Although the synthesis and coordination chemistry of phosphinines is well-established only few applications of phosphinines as ligands in homogeneous catalysis have been reported to date, the most prominent example being the rhodium catalyzed hydroformylation of alkenes.

In 1996, Breit reported for the first time that rhodium complexes of monodentate phosphinine and bidentate phosphinine-oxazoline ligands are more active and selective catalysts than the industrially used Rh/PPh_3 catalyst.[45]



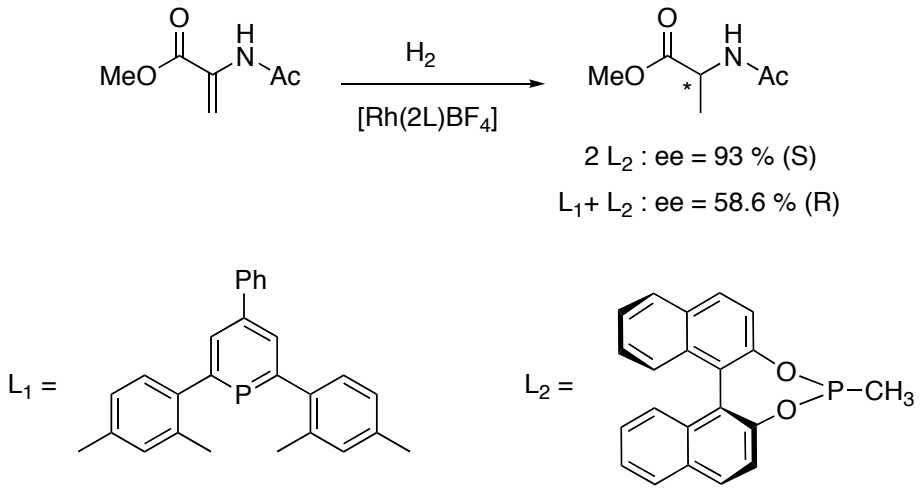
Scheme 22: *Hydroformylation of styrene by rhodium-phosphinine complexes.*

In further studies Breit and coworkers tested the influence of the phosphinine substitution pattern on the activity in the hydroformylation reaction. They reported that 2,6-xylylsubstituted phosphinines show the highest reactivity in the rhodium catalyzed hydroformylation of styrene and additionally allow for the hydroformylation of internal olefins (Scheme 21).[37, 46, 47]



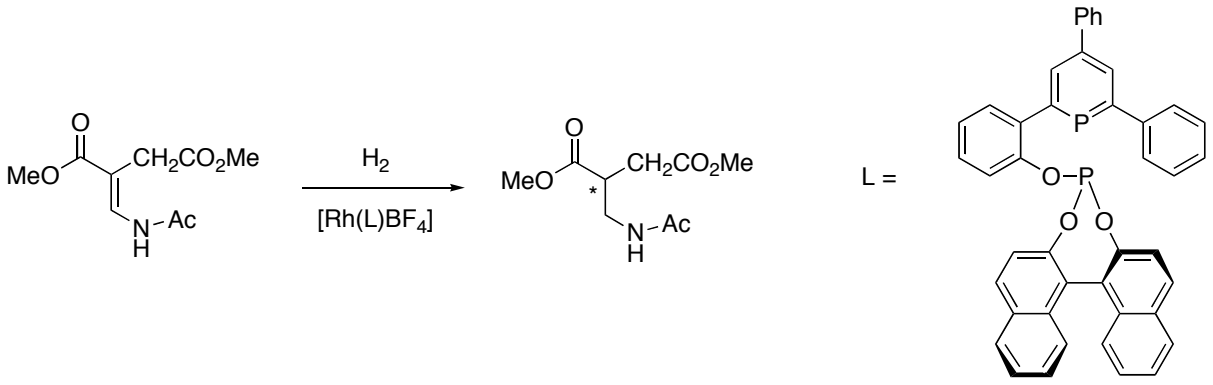
Scheme 23: *Hydroformylation of tetramethyl-ethylene by a rhodium phosphinine complex.*

The use of combinations of 2,6-dixylyl-4-phenyl-phosphinine (L_1) and a chiral, binol-based phosphite ligand (L_2) was studied by Reetz and coworkers in the rhodium-catalyzed asymmetric hydrogenation of acetamidoacrylate. Interestingly, the combination of an achiral phosphinine ligand and a chiral phosphite ligand leads to a reversal of the enantioselectivty compared to the homocombination of two chiral phosphite ligands (Scheme 24).[48]



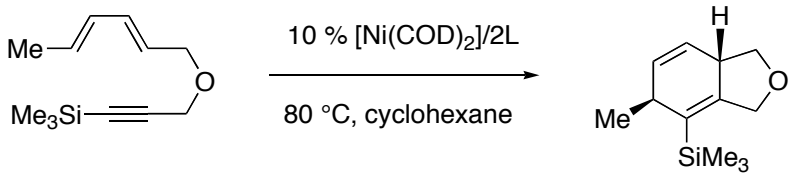
Scheme 24: *Rh-catalyzed hydrogenation of acetamidoacrylate*

Chiral bidentate phosphinine-phosphite ligands have been applied in the rhodium catalyzed hydrogenation reactions by Müller and coworkers.[23] Appreciable enantioselectivities (ee = 79 %) were obtained and high activites were observed (TOF = 2500 h^{-1}) in the hydrogenation of dimethylitaconate with an *S*-BINOL-phosphite-phosphinine ligand (Scheme 25).



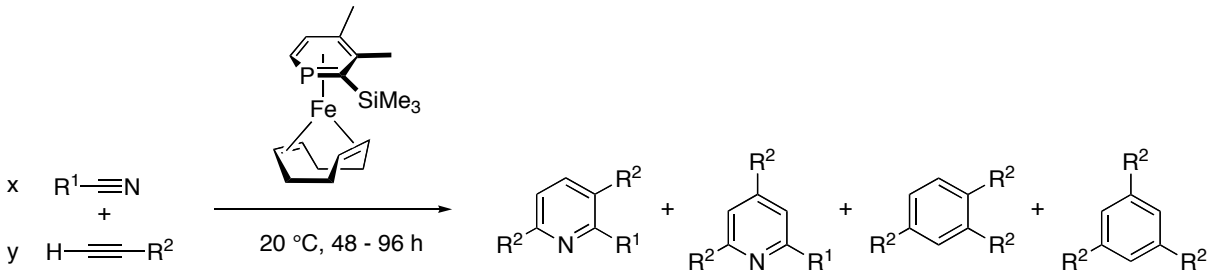
Scheme 25: *Rh-Catalyzed hydrogenation of dimethylitaconate.*

2,4,6-triphenylphosphinine in combination with $[Ni(COD)_2]$ was used as a catalyst in intramolecular [4+2]-cycloaddition reactions. Due to their strong π-accepting capacity, phosphinines tend to favor reductive elimination, a step which is rate determining in this process (Scheme 26).[49]



Scheme 26: *Ni-catalyzed intramolecular cycloaddition reaction.*

The use of a η^6-coordinated phosphinine iron(0)-complex in the cyclotrimerization of alkynes and nitriles for the synthesis of substituted pyridines was described by Zenneck, Le Floch and coworkers (Scheme 27).[49]



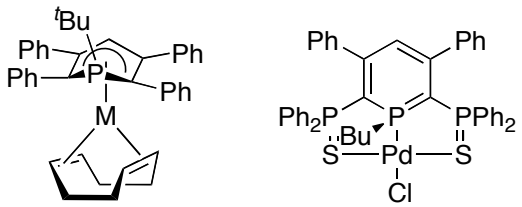
Scheme 27: *Cyclotrimerization of alkynes and nitriles catalyzed by an η^6-iron(0)-phosphinine complex.*

In these examples, the metal centers are in a low oxidation state. However, the reactivity of the P=C systems of phosphinines upon coordination to transition metals of a positive oxidation state is an important problem and often precludes the use of phosphinines as ligands in homogeneous catalysis. In general , when the phosphinines are bound to a metal center in a relatively high oxidation state, such as Rh(III) for example, the elecrophilicity of the phosphorus atom is enhanced resulting in the nucleophilic attack even from traces of H_2O in the solvents.

However, during the last years it could be shown that low coordinated phosphorus species featuring P=C bonds could be used as efficient precursors for cyclic and bicyclic phosphines.

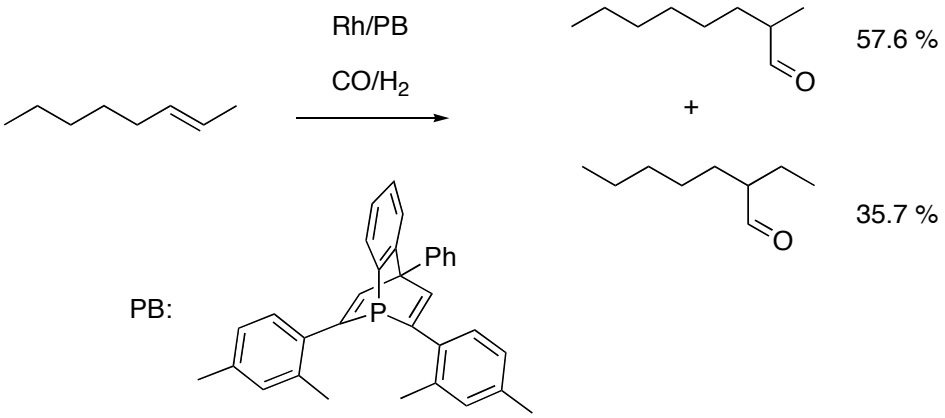
An idea that was developed in our group to circumvent the electrophilic behavior of the coordinated phosphinines was to generate a new anionic ligand system, by the reaction of phosphinines with organolithium reagents.

During her doctoral studies, A. Moores from our group showed that rhodium complexes of η^5-cooridnated phosphinine anions, obtained using this method, are highly active catalysts for the hydroformylation of olefins.[50] Additionally, it was shown by M. Doux from our group that palladium complexes of an anionic phosphinine-based pincer ligand are good catalysts in the borylation of bromoarenes.[51]



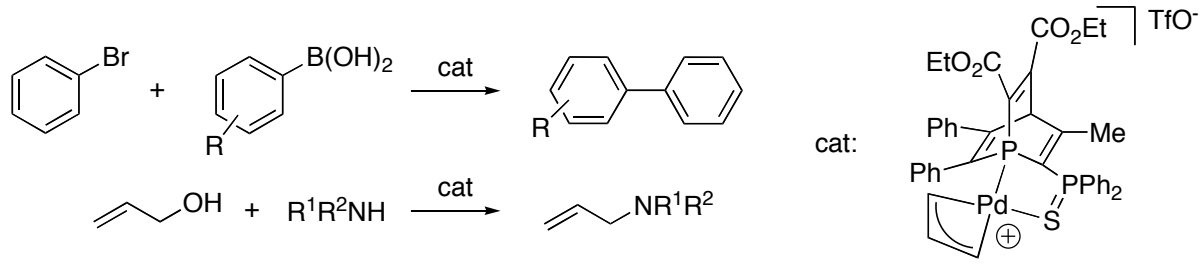
Scheme 28: *Complexes with anionic phosphinine ligands for the use in hydroformylation and borylation reactions.*

Another way of turning phosphinines into more stable ligands for the use as ligands in homogeneous catalysis is the [4+2]-Diels-Alder reaction with alkynes that yields bicylic 1-phosphabarrelenes. These ligands were successfully applied by Breit and coworkers in the hydroformylation of internal olefins (Scheme 29).[52]



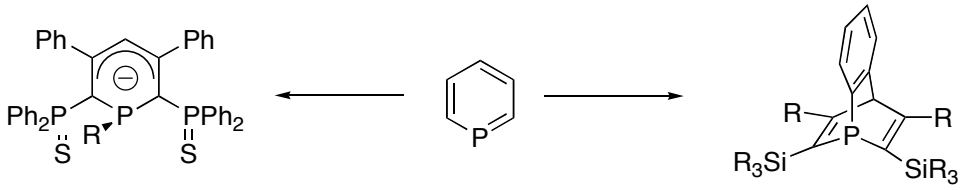
Scheme 29: *Application of 1-phosphabarrelenes as ligands in hydroformylation of internal alkynes.*

In parallel to these studies, a bidentate phosphabarrelene-phosphinesulfide ligand was developed by O. Piechaczyk and M. Doux from our group, that is a very efficient ligand in palladium catalyst Suzuki coupling reactions using bromoarenes or for the allylation of secondary amines (Scheme 30).[18]



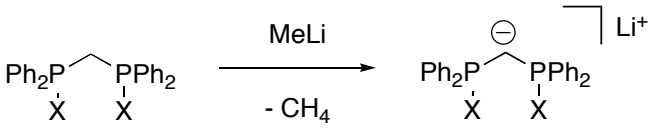
Scheme 30: *Use of a bidentate phosphabarrelene in cross-coupling and allylation reactions.*

In the present study we will be interested in the development of these highly promising approach of using phosphinines as intermediates for the generation of phosphines *via* a nucleophilic attack or *via* cycloaddition reactions (Scheme 31). Furthermore, the coordination chemistry and application of these ligands in homogeneous catalysis will be studied.



Scheme 31: *Envisaged use of phosphinines as intermediates in the synthesis of cyclic and bicyclic phosphines.*

Furthermore the coordination chemistry of monoanionic pincer complexes derived from dppm that can be readily obtained by the reaction of $dppmX_2$ (X= S, BH_3) with MeLi was studied (Scheme 32).



Scheme 32: *Envisaged synthesis of anionic pincer ligands derived from dppm.*

Additionally the synthesis of 2,6-unsubstituted phosphinines and their use in the stabilization of transition metal nanoparticles will be reported.

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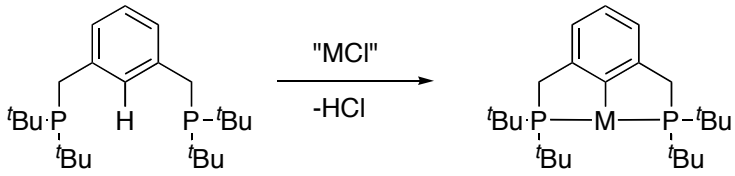
PART II:

Polydentate Anionic Ligands

CHAPTER 1: PALLADIUM COMPLEXES OF THE SPS^R-LIGAND: COORDINATION CHEMISTRY AND CATALYSIS.

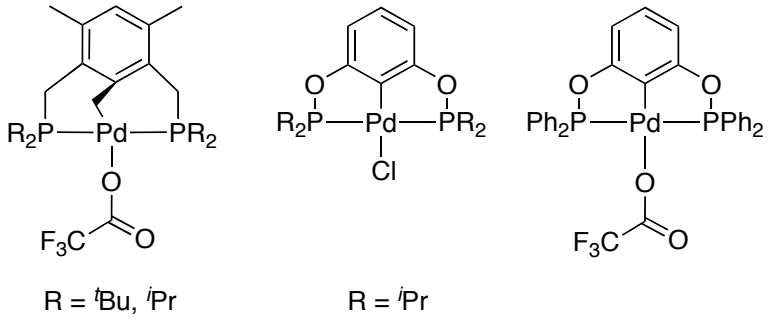
I. INTRODUCTION

The chemistry of pincer ligands has been intensely studied since the pioneering work of Shaw in the 1970's.[1] The structure that has been studied early on [2,6-(^{t}Bu$_2$PCH$_2$)C$_6$H$_3$] includes an anionic aromatic ring bearing two ancillary phosphine ligands in the 2 and 6 position, connected *via* a methylene unit (Scheme 1).



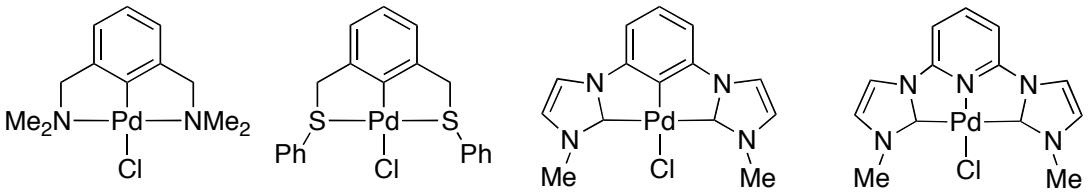
Scheme 1: *First pincer ligand studied by Shaw.*

Since then a great variety of transition metal complexes coordinated to pincer ligands with different combinations of donor atoms (C, N, P, S, O) has been reported.[2] Phosphine and phosphite PCP pincer-complexes have found numerous applications as catalyst-precursors e.g. for highly efficient cross-coupling reactions such as the Heck[3, 4] and the Suzuki-Miyaura-coupling reactions (Scheme 2).[5]



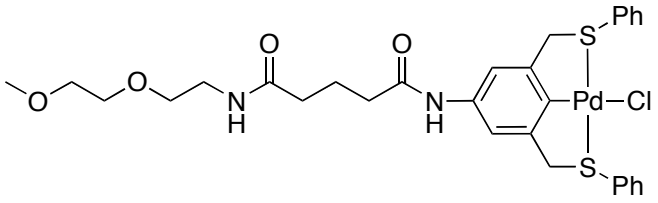
Scheme 2: *PCP-Palladium pincer complexes used in Heck and Suzuki-Miyaura coupling reactions.*

Several other types of pincer complexes with NCN, CNC, CCC and SCS pincer ligands, e.g. replacing the central phenyl moiety by a pyridine or with pendant thioether, amine or *N*-heterocyclic carbene ligands could be successfully be applied to the Heck reaction [6-9] (Scheme 3).



Scheme 3: *NCN, SCS, CCC and CNC palladium pincer complexes.*

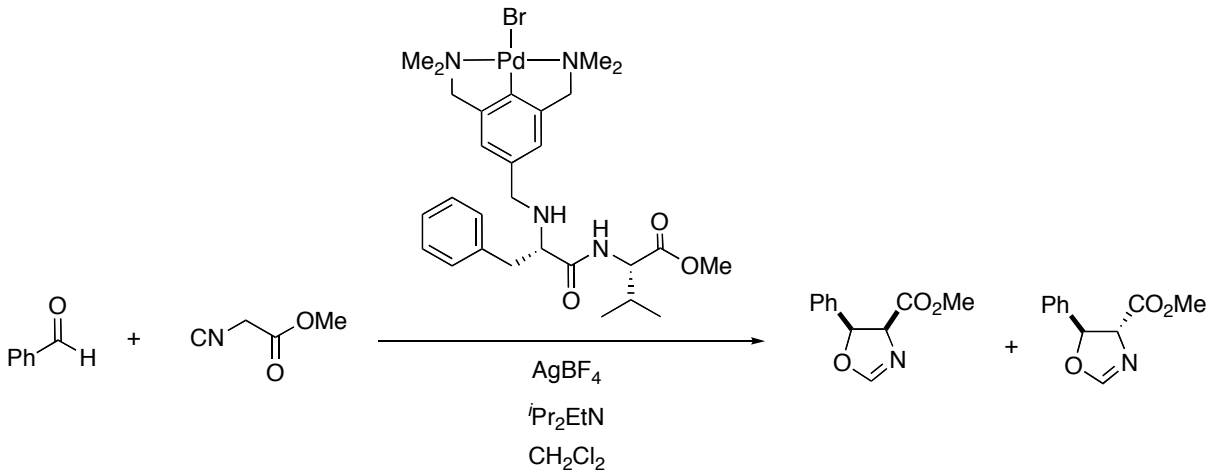
Morales-Morales reported on the possibility of functionalizing the central phenyl moiety of a SCS pincer complexes by polyethylene glycol, allowing for the easy recycling of the catalyst at least for 3 further cycles without loss of activity in the Heck reaction (Scheme 4).[6]



Scheme 4: *SCS palladium pincer complex substituted with ethylene glycol on the central phenyl moiety.*

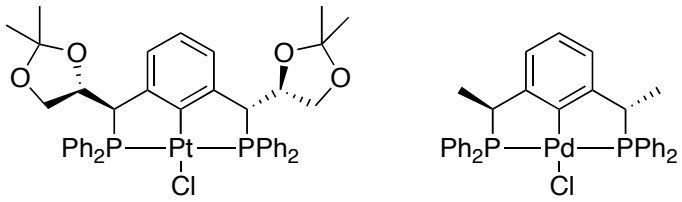
The mechanism of C-C coupling reactions involving pincer complex catalysts is still a matter of debate. Due to the fact that pincer complexes show a high thermal stability and an excellent activity in the Heck reaction, Jensen and Morales-Morales supposed an alternative catalytic cycle involving Pd(II)/Pd(IV)-intermediates in contrast to the traditional mechanism involving Pd(0)/Pd(II) species.[4, 10] Mechanistic studies by Eberhard using poisoning experiments[11] and Gladysz, using electron microscopy,[12] prove the formation of palladium nanoparticles from palladium pincer complexes. Therefore the intermediacy of Pd(IV) species might be considered as unlikely and the formed nanoparticles might serve as a source of highly reactive Pd(0)-species.[13] Overall it must be concluded, that despite of the extensive studies that have been carried out throughout the last decades it remains challenging to develop a conclusive catalytic cycle, that is compatible with the results that were obtained so far.

Apart from the Heck-reaction palladium pincer complexes have also been succesfuly applied to other reactions. Pincer complexes incorporating peptides were used by van Koten and coworkers in aldol condensation reactions(Scheme 5).[14]



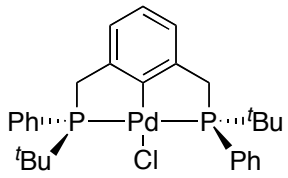
Scheme 5: *NCN palladium pincer complex substituted with a peptide chain.*

However in this case the stereogenic centers of the ligand are far away from the reactive site of the catalyst and therefore do not have any influence on the stereoselectivity. Chiral pincer complexes with the chiral center on the methylene groups of the pendant phosphine ligands were synthesized by the groups of Venanzi[15, 16] and Zhang[17] (Scheme 6). Whereas the platinum complexes reported by Venanzi only lead to a moderate enantiomeric excess in the aforementioned aldol condensation reactions, the palladium complexes reported by Zhang selectively lead to cis-oxazolines. This ligand could also be successfully applied in the allylic substitution reaction leading to high yield and good ee's of up to 80 % in the presence of a base, that is acting as a cocatalyst.



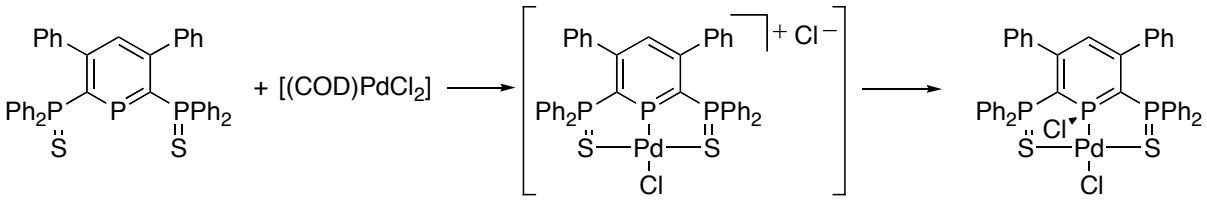
Scheme 6: *Chiral PCP palladium pincer complexes.*

The synthesis of a *P*-stereogenic pincer ligands was recently reported by Morales-Morales (Scheme 7) and the corresponding palladium complexes were employed as well in the aforementioned aldol condensation reaction. Surprisingly only poor ee's of 9 % were obtained in this case. The authors attributed this to the insufficient steric demand of the substituents.



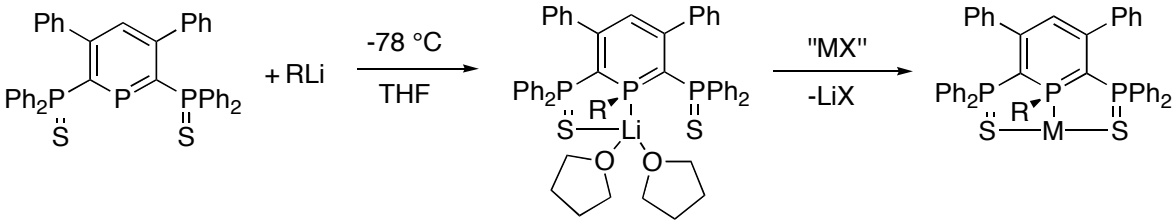
Scheme 7: *P-Chiral PCP palladium pincer complex.*

A first example of a pincer ligand incorporating a phosphinine as a central unit was reported by our group in 2002.[18] The coordination of a transition metal center to 2,6-bis(diphenylphosphine sulfide)-3,5-diphenylphosphinine (SPS) reduces the electron density on the central phosphorus atom and provokes a nucleophilic attack of the chloride atoms and the subsequent formation of a σ^4-λ^5-phosphinine (Scheme 8). The resulting chlorophosphinine ligand is sensitive towards the attack of nucleophiles and can be transformed into the corresponding phosphites by the reaction with alcohols.



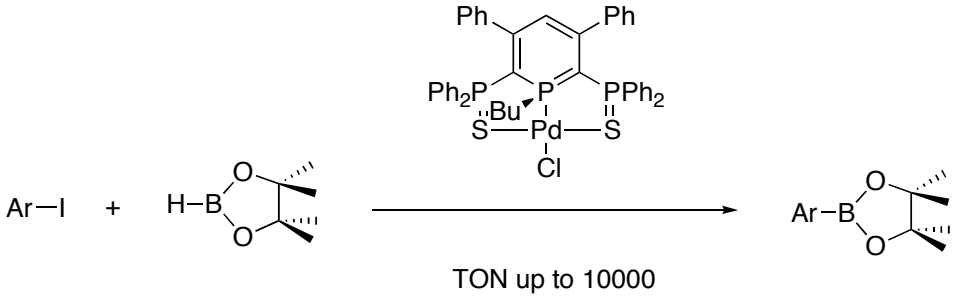
Scheme 8: *Reaction of SPS with [(COD)PdCl$_2$].*

In order to avoid the formation of sensitive chlorophosphinines, straightforward route for the synthesis of the anionic SPS^R by the reaction of SPS with organolithium reagents was developed (Scheme 9). The reaction of the lithium salts of the SPS^R-ligand with transition metal precursors allowed the synthesis of a large variety of complexes.



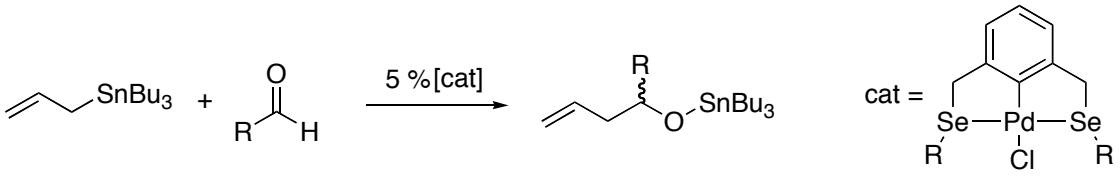
Scheme 9: *Synthesis of SPS^R –pincer complexes by reaction of SPS with alkyllithium reagents and subsequent coordination to transition metals.*

Especially palladium complexes of the SPS^{R}-ligand show an interesting activity in catalytic reactions such as the Miyaura borylation of bromo- and iodoarenes and the Heck reaction (Scheme 10).[19]



Scheme 10: *Borylation of iodoarenes catalyzed by a SPS^{Bu} palladium pincer complex.*

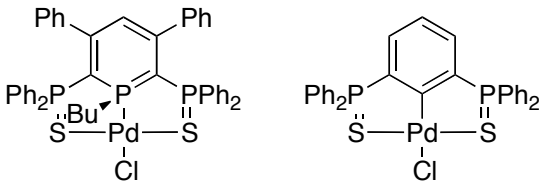
In 2003 it was shown by Szabo and coworkers, that pincer palladium complexes were suitable catalysts for the conversion of aldehydes to homoallylalcohols by the reaction with allylstannanes.[20, 21] In their studies the authors showed, that SeCSe pincer ligands have the optimal electronic properties for the desired transformation (Scheme 11).



Scheme 11: *Allylation of aldehydes with tributylallyltin catalyzed by a SeCSe palladium pincer complex***.**

Szabo *et al.* proposed a very rare η^1-allyl species as an intermediate in the catalytic cycle, based on the strong coordination behavior of the tridentate pincer ligand, occupying three of the coordination sites of the Pd(II)-complex.

Based on these results in our group a joint experimental and theoretical study with SPS^{R} and SCS pincer ligands[22] was carried out (Scheme 12).

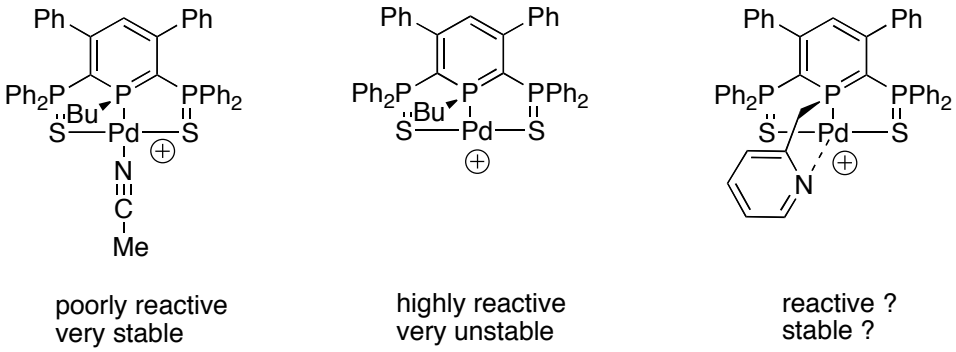


Scheme 12: *SPS^{Bu} and SCS palladium pincer complexes.*

In these studies it could be shown, that these catalysts are as active as the SeCSe-catalyst and that upon addition of a silver salt an increase of the reactivity was observed. Furthermore their theoretical study ruled out η^1-allyl species as intermediates due to the superior energetic demand compared to a Lewis-acid catalyzed process.

II. INTRODUCTION OF A FOURTH BINDING SITE TO THE ANIONIC SPS^R-PINCER-LIGAND

Due to its high reactivity, the cationic $[(SPS^{Bu})Pd]^+$ complex could not be isolated and needed to be generated *in-situ* by the addition of silver salt to the corresponding $[(SPS^{Bu})PdCl]$complex. Therefore we became interested in the design of a more stable cationic complex, that would be active in catalysis. A way to stabilize cationic complexes is the addition of a coordinating solvent (e.g. acetonitrile, pyridine), leading to the formation of very stable square-planar Pd(II) complexes that can easily be isolated. However this would lead to a reduced lewis-acidity of the metal center and reduce the reactivity of the catalyst due to the competition between the stabilizing ligand and the substrate. It was therefore desirable to synthesize complexes that would be (1) more electrophilic than the chloride derivative, allowing the direct incorporation in the catalytic cycle; (2) more stabilized than the cationic complex; (3) yet more reactive than the cationic complex stabilized with acetonitrile; (4) finally if possible allowing to finely tune the catalytic activity. Point 2 clearly requires the presence of a labile two-electron donor, and point 3 implies a weaker two-electron donor than a nitrile ligand. We thus envisioned the incorporation of an α-picoline moiety on the central phosphorus atom of the SPS-ligand, in a way to prevent the formation of a stable square planar complex (Scheme 13).

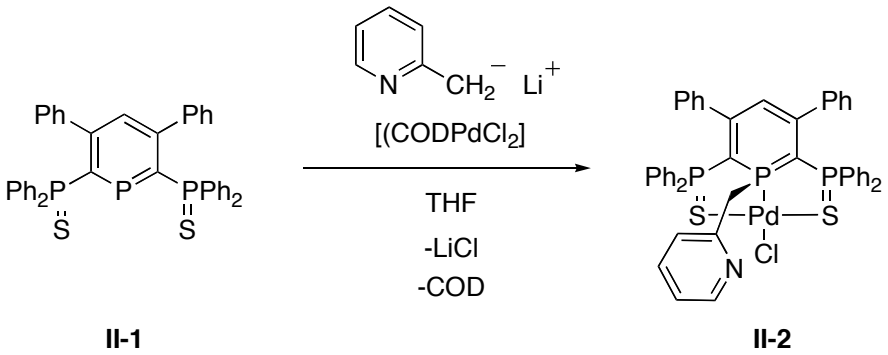


Scheme 13: *Cationic SPS^R palladium pincer complexes.*

II.1. Synthesis and Characterization

The synthesis of the potentially tetradentate ligand was reported recently and the related palladium complex could be readily achieved by the addition of $[(COD)PdCl_2]$ to a solution of

the in-situ generated ligand in THF at room temperature. Complex **II-2** could be isolated in 74 % yield as a brick red powder (Scheme 14).



II-1 **II-2**

Scheme 14: *Synthesis of SPS^{Pic} palladium pincer complex* ***II-2***.

In the ^{31}P NMR spectrum a characteristic AB_2-spin pattern (δ 48.4 ppm and 51.9 ppm with $^{2}J_{PP}$= 89.0 Hz) was observed for **II-2**. In the ^{1}H NMR spectrum ($CDCl_3$) the signal for the H4 is found at rather high field δ 5.46 ppm compared to the starting anion (Δδ 0.34 ppm) and in a similar region compared to similar [(SPS^{R})PdCl] complexes reported by our group.[18, 23] The signal shows the usual coupling pattern (t, $^{4}J_{PH}$= 4.3 Hz) due to the coupling with the two equivalent PPh_2S-groups. Single crystals suitable for X-Ray crystal structure analysis were grown from a concentrated solution of **II-2** in $CHCl_3$. The molecular structure of **II-2** is shown in Figure 1.

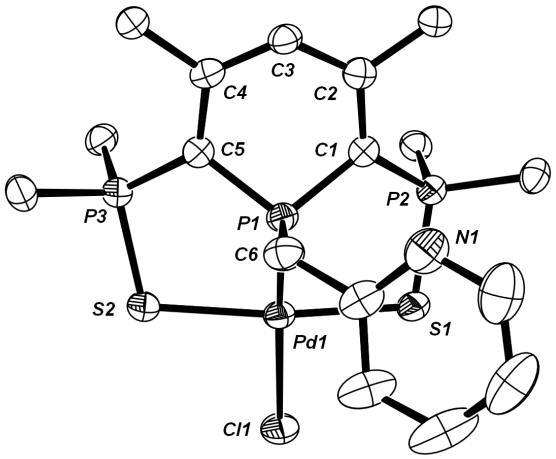
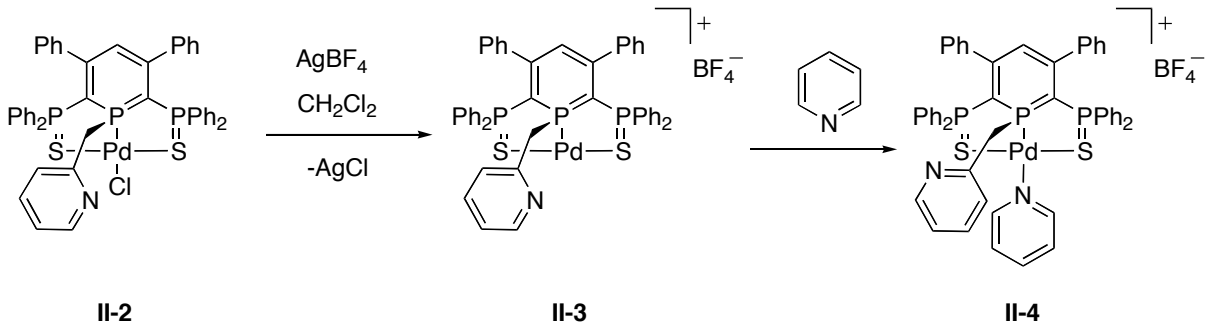


Figure 1: *Molecular structure of complex* ***II-2*** *(ORTEP-Plot, thermal ellipsoids with 50 % probability, phenyl groups and hydrogen atoms were omitted for clarity) Selected bond lengths[Å] and angles[°]: Pd(1)-P(1) 2.1783(8), Pd(1)-S(1) 2.3207(8), Pd(1)-S(2) 2.332(1), Pd(1)-Cl(1) 2.3894(8), S(1)-P(2) 2.033(1), S(2)-P(3) 2.043(1), P(1)-C(1) 1.761(3), P(1)-C(5) 1.760(3), P(1)-C(6) 1.839(3), P(1)-Pd(1)-S(1) 87.93(3), P(1)-Pd(1)-S(2) 87.17(3), S(1)-Pd(1)-S(2), 172.76(3), P(1)- Pd(1)-Cl(1) 170.25(3).*

As expected for a Pd(II) complex with a d^8 electron configuration, the coordination geometry of the palladium atom is square planar and no interaction between the pyridine moiety and the palladium atom could be observed.

The abstraction of the chloride ion was the attempted on complex **II-2** with 1 equivalent of $AgBF_4$ in methylene chloride (Scheme 15).[a] In the $^{31}P\{^1H\}$ NMR spectrum, the conversion of **II-2** to a new compound characterized by a complex spin-system between δ 45.4 and 49.8 ppm was observed. The ^1H NMR spectrum in CD_2Cl_2 of this product also shows a triplet for the H4 proton at δ 6.08 ppm ($^4J_{PH}$ = 4.7 Hz). This complex, unlike the $[(SPS^{Bu})Pd]^+$-complex, is stable in solution for extended periods of time and insensitive towards air and moisture. This clearly points towards the coordination of the pyridine fragment to the Pd-center.



Scheme 15: *Formation of cationic SPS^{Pic} palladium pincer complexes **II-3** and **II-4**.*

Despite many efforts it was not possible to grow single crystals of **II-3**. Pyridine was added to a solution of complex **II-3** leading to an AB_2 spin pattern in the $^{31}P\{^1H\}$ NMR spectrum (δ 45.7 ppm and 47.6 ppm, $^2J_{PP}$ = 79.6 Hz). Single crystals suitable for X-Ray crystal structure analysis were obtained from the diffusion of hexanes to a solution of **II-4** in CH_2Cl_2 (Figure II.2).

[a] The synthesis of complex **II-3** was already described by M. Doux (reference 59) but the precise structure of **II-3** remained unclear. Furthermore, the synthesis and X-Ray Crystal structures of **II-2** and **II-4** were described as well by M. Doux in her thesis and are included here to allow for the discussion on a complete set of data.

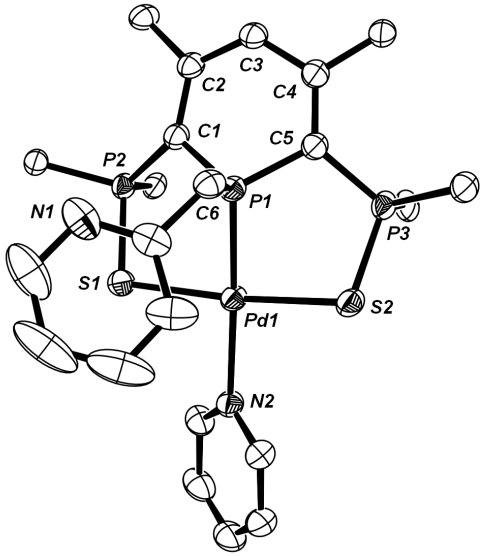


Figure 2: *Molecular structure of complex* ***II-4*** *(ORTEP-Plot, thermal ellipsoids with 50 % probalbilty, phenyl groups and hydrogen atoms were omitted for clarity) Selected bond lengths[Å] and angles[°]:Pd(1)-P(1) 2.2040(6), Pd(1)-S(1) 2.3126(6), Pd(1)-S(2) 2.3359(6), S(1)-P(2) 2.0313(8), S(2)-P(3) 2.036(1), P(1)-C(1) 1.776(2), P(1)-C(5) 1.771(2), P(1)-C(6) 1.841(2), P(1)-Pd(1)-S(1) 87.49(2), P(1)-Pd(1)-S(2) 86.83(2), S(1)-Pd(1)-S(2), 173.78(2), P(1)- Pd(1)-N(2) 175.43(5).*

The quantitative formation of **II-4** is very interesting as this clearly shows, that the pyridine moiety, that is attached to the ligand can be replaced from the palladium center by a free pyridine molecule and could be replaced by a coordinating substrate molecule in a catalytic experiment. This points to a weak stabilization, yet efficient in terms of stabilization in time of the cationic palladium center. For instance it was possible to verify the cationic nature of **II-3** but it was still needed to establish a correct structure to explain the stabilization of the cationic complex through the pyridine moiety (*vide supra*).

In parallel, in order to probe the possibility of tuning the catalytic activity, quaternarization of the lone pair of the pyridine was attempted. The overall increase of the charge of the complex should in turn increase the Lewis acidity of the palladium center. The quaternarization of the pyridine moiety was readily achieved by the addition of few equivalents of HCl in ethereal solution to a solution of **II-2** in dichloromethane. The complete formation of **II-6** could be observed in the $^{31}P\{^{1}H\}$ NMR spectrum (m, AB_2, δ 48.2 ppm and 51.9 ppm, $^{2}J_{PP}$ = 91.0 Hz). The electronic influence of the protonation on the complete ligand backbone was clearly observed. The CH_2 group of the picoline moiety experienced a downfield shift of 0.46 ppm (from 3.83 ppm in **II-2** to 4.29 ppm in **II-6**). Complex **II-6** was isolated in nearly quantitative yield after evaporation of the volatiles. The molecular structure of **II-6** is represented in Figure 3.

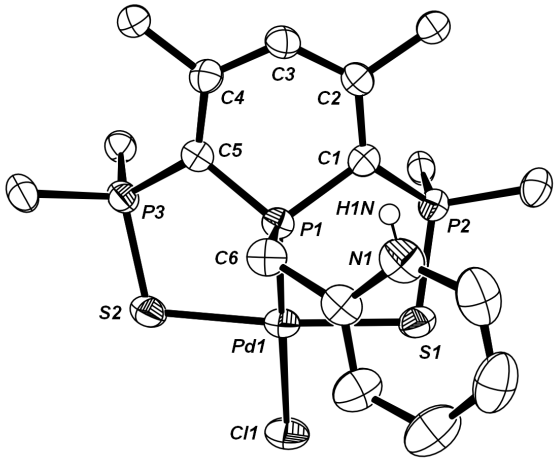
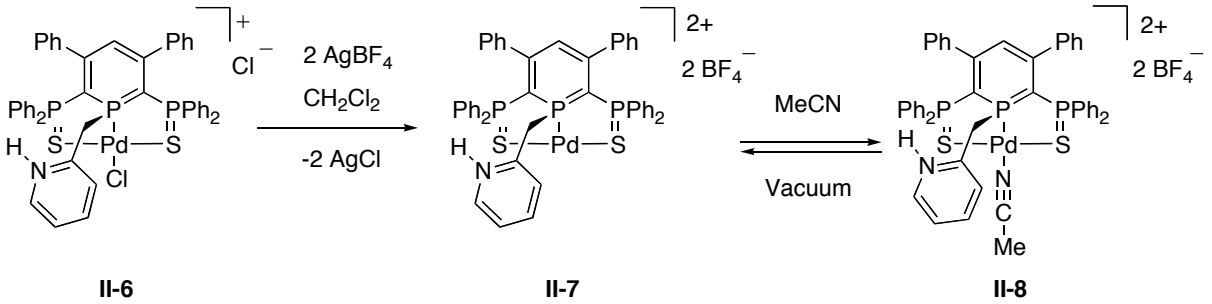


Figure 3: *Molecular structure of the cationic part of complex* ***II-6*** *(ORTEP-Plot, thermal ellipsoids with 50 % probability, phenyl groups and hydrogen atoms were omitted for clarity) Selected bond lengths[Å] and angles[°]: Pd(1)-P(1) 2.184(1), Pd(1)-S(1) 2.323(1), Pd(1)-S(2) 2.319(1), Pd(1)-Cl(1) 2.380(8), S(1)-P(2) 2.023(1), S(2)-P(3) 2.041(1), P(1)-C(1) 1.777(3), P(1)-C(5) 1.762(3), P(1)-C(6) 1.853(3), P(1)-Pd(1)-S(1) 88.39(3), P(1)-Pd(1)-S(2) 86.55(3), S(1)-Pd(1)-S(2), 174.37(3), P(1)- Pd(1)-Cl(1) 173.92(4).*

As in the case of **II-2** the synthesis of a stable cationic complex was attempted. Upon addition of two equivalents of $AgBF_4$ to a solution of **II-6** the precipitation of AgCl was observed (Scheme 16).



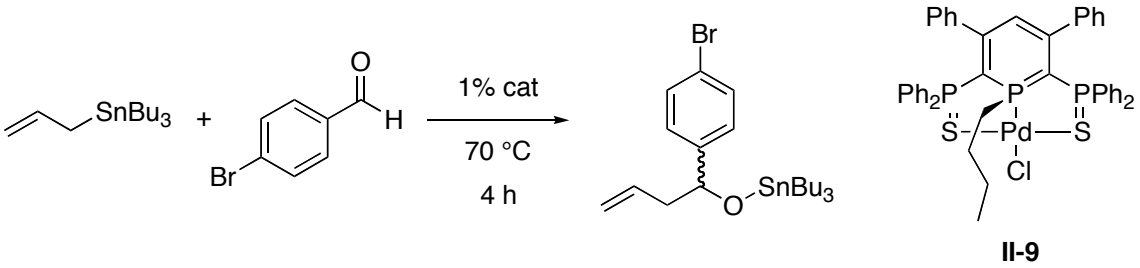
Scheme 16: *Synthesis of dicationic complexes* ***II-7*** *and* ***II-8*****.**

Surprisingly the AB_2 pattern of **II-6** disappeared in the $^{31}P\{^1H\}$ NMR spectrum in favor of a broad singlet at δ 47.7 ppm. The fact that this species **II-7** is unique could be verified by the addition of 10 equivalents of acetonitrile. The resulting complex **II-8** is characterized by an AB_2 spin pattern and was isolated in 75 % yield. Exhaustive drying of this complex under vacuum resulted in the partial loss of acetonitrile and the re-formation of **II-7**.

II.2. Catalytic studies

Having in hand several complexes it became possible to test the influence of the pyridine moiety, the use of an isolated cationic complex and the increase of the overall charge on the catalytic activity of the synthesized palladium complexes in the allylation of aldehydes.

The reaction of *p*-bromobenzaldehyde with allyltributyltin was conducted in $CHCl_3$ using 1 % of catalyst, at 70 °C for 4 h was used as a benchmark. To evaluate the influence of the picoline on the catalytic activity, catalyst **II-9** (Scheme 17) was used as a reference.



II-9

Scheme 17: *Lewis-acid catalyzed allylation of bromobenzaldehyde with allyltributyltin.*

Table 1: *Catalytic results*[a]

Entry	Catalyst	Yield %
1	**II-9**	18.2
2	**II-9 + $AgBF_4$**	37.8
3	**II-2**	10.4
4	**II-3**	18.9
5	**II-6**	15.3
6	**II-6 + $AgBF_4$**	30.2

[a]*Reaction conditions*: *p*-bromobenzaldehyde (92.5 mg, 0.5 mmol), catalyst (0.005 mmol, 1mol %), THF (0.5 mL), allyltributyltin (186 μL, 0.6 mmol), 70 °C, 4h. [b]determined by ^{1}H NMR.

Entries 1, 3 and 5 allow the direct comparison of neutral PdCl fragments, whereas the entries 2, 4 and 6 are related to cationic complexes. As reported before,[22] the addition of silver salt to catalyst **II-9** leads to an increase of product formation, due to the fast formation of the active species (Entries 1 and 2). Entry 3 allows to the direct assessment of the role of the pyridine, complex **II-2** is the least active pre-catalyst. Reasonably postulating a similar kinetic formation of the active cationic species as for **II-9** it becomes clear, that the picoline moiety has a stabilizing influence, thereby reducing the Lewis-acidity of the palladium center. The cationic complex **II-3**, isolated after chloride abstraction, performs almost twice as well as **II-2** (Entry 4).

This shows, that complex **II-3** is not only stable once isolated, but is a more active catalyst than the corresponding neutral "PdCl" complex. Complex **II-6** is also more efficent than complex **II-2**, which results from the expected increase of the Lewis-acidity of the palladium center due to the protonation of the picoline (Entry 5). However its reactivity is comparable to that of complex **II-9**, which would point to a negligible influence of the overall charge. Eventually, in situ chloride abstraction from complex **II-6** was done and the resulting complex was directly engaged in the catalytic process (Entry 6). As in the case of complex **II-9**, this resulted in doubling the catalytic activity (30.2 % vs. 15.3 %), but as previously mentioned the dicationic complex does not perform better than complex **II-9** in the presence of one equivalent of $AgBF_4$. Finally, the protonation of the picoline moiety does not seem to have a positive effect on the catalytic performance. Overall, the isolated cationic complex **II-3** provides the best compromise between catalytic performance, kinetic stability and ease of handling (no need for activation). It is obvious from these results, that the picoline moiety brings stability to the cationic palladium center and does not suppress catalytic activity.

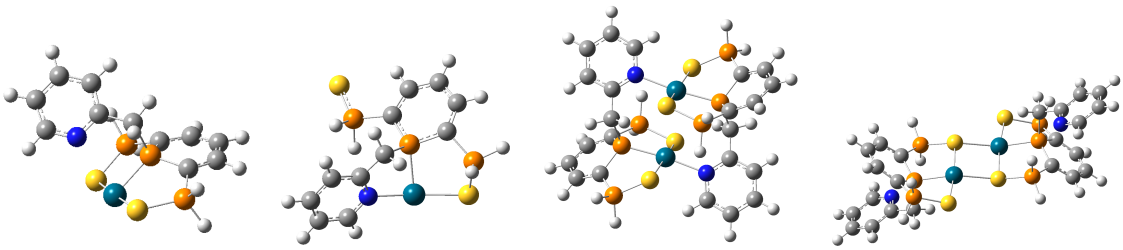
II.3. DFT-studies

The question of the precise nature of the cationic complex **II-3** remained. A DFT study was performed to investigate the possible conformations. All calculations were carried out using the Gaussian03 set of programs[24] with the B3PW91 functional,[25, 26] the 6-31G* basis-set for all nonmetallic atoms (C, H, P, S, N) and the Hay-Wadt electron core potential [27] for palladium with an additional f-polarization function.[28] A model compound replacing all phenyl groups by protons was used for this study in order to preserve calculations time (**Note:** this model has shown to be appropriate in theoretical studies reported before[22, 29-33]) As the studied model complexes are charged species, solvation effects had to be taken into account in these DFT studies. This was achieved by using the polarized continuum model (PCM)[29-32] considering CH_2Cl_2 as the solvent. A major drawback of this method is the fact that entropic factors are not incorporated in this PCM energy. Generally these entropic effects play an important role in bimolecular reactions where the number of reactants does not equal the number of product molecules and should therefore not be neglected. Therefore free energies G were calculated. However, the related relative free energies ΔG are related to systems in the gas phase and the extrapolation to the condensed phase is delicate and subject to intense debate.[33-35] In particular Maseras and coworkers proposed the use of a free energy ΔG_{PCM} taking into account solvation effects,[33] which is defined by:

$$\Delta G_{PCM} = \Delta G + (\Delta E_{PCM} - \Delta E).$$

Two monomeric species were envisaged: an SPS^{Pic}-bound monomeric complex, **II-A**, and an SPN-bound monomeric complex, **II-B** and two dimeric structure: one in which the pyridine

fragment of one ligand is coordinated to a second Pd center, complex **II-C**, and another in which sulfur atoms are bridging, complex **II-D.** This latter coordination mode has not yet been observed in phosphinine-based SPS-pincer complexes. Pictures of the optimized structures are shown in Figure 4.



II-A **II-B** **II-C** **II-D**

Figure 4: *Calculated structures* ***II-A - II-D*** *for the conformation of cationic compound* ***II-3****. Selected bond lengths [Å] and angles [°] for* ***II-A****: Pd(31)-P(17): 2.201, Pd(31)-S(15): 2.393, Pd(31)-S(16): 2.402, Pd(31)-N(23): 3.013, P(17)-Pd(31)-S(15): 86.1, P(17)-Pd(31)-N(23): 76.7, N(23)-Pd(31)-S(15): 97.7 S(15)-P(31)-S(16): 176.0. For* ***II-B****: Pd(31)-P(17): 2.278, Pd(31)-S(15): 2.383, Pd(31)-S(16): 6.176, Pd(31)-N(23): 2.086, P(17)-Pd(31)-S(15): 96.3, P(17)-Pd(31)-N(23): 83.4, N(23)-Pd(31)-S(15): 167.6. For* ***II-C****: Pd(31)-P(17): 2.249, Pd(31)-S(15): 2.418, Pd(31)-S(16): 2.379, Pd(31)-N(32): 2.182, P(17)-Pd(31)-S(15): 83.6, P(17)-Pd(31)-N(32): 173.4, N(32)-Pd(31)-S(15): 90.7. For* ***II-D****: Pd(31)-P(17): 2.239, Pd(31)-S(15): 2.393, Pd(31)-S(16): 2.414, Pd(31)-N(23): 4.943, Pd(31)-Pd(62): 3.777, Pd(31)-S(60): 2.558, P(17)-Pd(31)-S(15): 84.6, P(17)-Pd(31)-S(60): 151.6, S(15)-P(31)-S(16): 170.7.*

It should be noted that in complex **II-A** there is a weak interaction between the pyridine moiety and the Pd center, as shown by the long distance between these atoms of 3.013 Å. This distance is definitely longer than a true bond, yet the particular orientation of the pyridine pointing toward the Pd center is unambiguous. Structure **II-A** is used as a reference. Not considering the weak interaction of the pyridine ligand, the overall geometry around the palladium center is T shaped, with the two S-Pd-P angles of 86.1°. The geometry of complex **II-B** was optimized in distorted T-shape, with the pending phosphinesulfide ligands pointing in the opposite direction. In this complex, the peculiar arrangement of the ligand leads to angles significantly different from the expected 90°: P(17)-Pd(31)-S(15) = 96.3° and P(17)-Pd(31)-N(23) = 83.4°.

Interestingly, this complex is lower in energy (ΔE_{PCM}) than **II-A**, by 2.4 kcal/mol, but the free energy of this complex is slightly higher (3.1 kcal/mol), showing that the phosphine sulfide is as good a ligand as pyridine for this Pd(II) cationic center. The potential energy E, of compound **II-C** was found to be lower than that of the monomers, whereas compound **II-D** was found at higher energy relative to the monomeric compounds. It should be noted that both dimeric

structures were stabilized by ca. 6 kcal/mol, when the contribution of the solvation is added to the potential energy (ΔE_{PCM}), whereas the monomeric structures were only slightly stabilized (0-4.1 kcal/mol). However, dimerization is obviously entropically unfavorable, and the Gibbs free energies, ΔG, for the dimers **II-C** and **II-D** are found higher than that of the monomers. Of these dimers, the sulfur- bridged complex **II-D** is less stable than complex **II-C** by 8.0 kcal/mol. In complex **II-D**, the coordination deviates significantly from the expected square planar, as shown by the P(17)-Pd(31)-S(60) angle of 151.6°. This probably results from geometrical constraints. The geometry of the two "(SPS^{Pic})Pd" fragments in **II-C** is very similar to the one found in the monomeric complex **II-A**. In the dimer, the expected more favored square-planar geometry of Pd(II) is achieved by the coordination of a pyridine moiety of the opposite ligand. Finally, when ΔG_{PCM} is calculated, compounds **II-A**, **II-B**, and **II-C** all are within 1.1 kcal/mol. In the end, taking only ΔE_{PCM} into account, the dimeric- dicationic species **II-C** is predicted to be more stable and would be the only one to be observed in solution. On the other hand, ΔG predicts the monomeric-monocationic species **II-A** to be more stable and would be the only one to be observed in solution. Finally, the difference in energy ΔG_{PCM} predicted the coexistence of the three complexes **II-A**, **II-B**, and **II-C** in solution. Therefore DFT calculations did not allow for conclusively elucidating the most stable conformation of **II-3** in solution and experimental techniques were used to quantify the amount of the different complexes in solution.

II.4. TANDEM ESI-MS Study

Electrospray ionization tandem mass spectrometry (tandem ESI-MS) was used to further characterize the palladium complexes present in solution. Indeed, soft ionization tandem mass spectrometry appears to be a sensitive and rapid technique for the determination of molecular weight of organometallic compounds.[36] Electrospray ionization allows for a soft transfer to the gas phase of existing ions in solution. Short-lived reactive intermediates can also be analyzed, thus providing a method of choice for mechanistical studies.[37] The aim of this study was to determine the nature of the Pd complex **II-3**, postulating that the electrospray ionization technique would not result in the splitting of a dimeric complex if present in solution. The mass spectrum of a CH_2Cl_2 solution of the complex **II-3** is shown in Figure 5, and a detailed view of the isotopic pattern of the most intense signal at m/z of 879.0 is provided in Figure 5b. The observed isotopic pattern nicely matches the theoretical isotopic pattern calculated for a dicationic, dimeric complex modeled by **II-C** or **II-D**. A numerical fit of the experimental data however shows that a small fraction (2.5 %) of the monocationic monomeric complex (isotopic pattern given in Figure 5d) is also present.

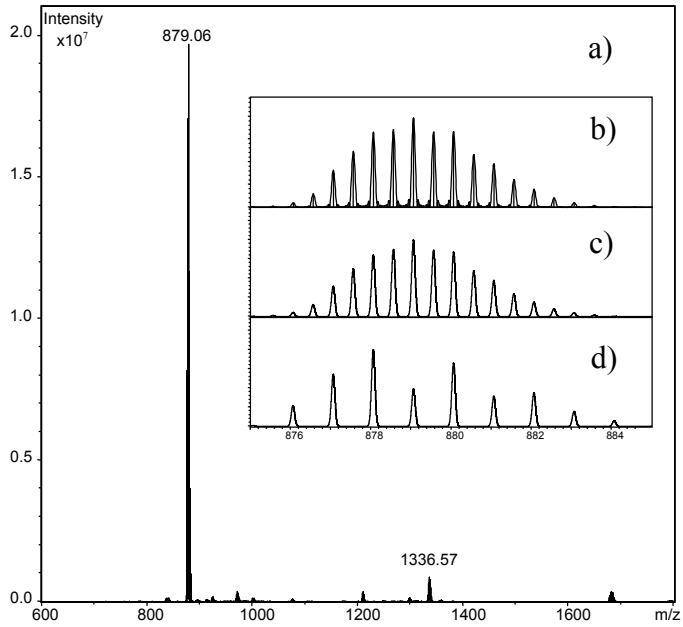


Figure 5: *Mass spectra of a sample solution of Pd complex* ***II-3*** *in CH_2Cl_2 at 10^{-5} mol.l^{-1}. Full mass spectrum recorded without mass selection (a), and detailed view of the isotopic distribution of the dominant peak at m/z 879.06 (b). Theoretical isotopic patterns calculated for the dicationic dimer (c) and monocationic monomer complexes (d).*

When used in conjunction with collision-induced dissociation (CID), ESI-MS/MS can provide additional insights. After mass selection of the ions at *m/z* 879.06 with an isolation width 10 Da, a CID experiment was performed for 100 ms. The resulting mass spectrum suggests that the dicationic dimeric species $[(SPS^{Pic})Pd]_2^{2+}$ fragments into two monocationic monomers $[(SPS^{Pic})Pd]^+$. At the ion/argon collision energies used (20 V), loss of C_6H_5N from the monomeric species was also observed. The results of this study nicely complement the result of the DFT study. Indeed, the DFT calculations did not allow settling conclusively between a monomeric and a dimeric structure. This ESI-MS study nicely shows the possibility of the formation of a dimeric form of complex **II-3**. Nevertheless, it has been reported in specific cases that the dimerization of monocationic transition metal complexes bearing halide ions, leading to halide-bridged dimmer complexes could occur in a mass spectrometer using the electrospray ionization technique.[38, 39] Therefore further studies had to be undertaken to prove the dimeric structure of complex **II-3** not only after the transfer to the gas phase but also in solution.

II.5. ^{1}H DOSY NMR Study

To finally prove the dimeric structure of complex **II-3** in solution a DOSY-NMR-study[40, 41] using the bipolar pulse longitudinal eddy current delay (BPPLED) pulse sequence[42, 43] was performed. This technique allows measuring diffusion constants of molecules in solution. In

recent studies it was shown that the hydrodynamic radii of these compounds might be estimated from the diffusion constants via the Stokes-Einstein equation.[44]

$$D = (k_B T)/(C\pi\eta r_H)$$

The diffusion constants of tetramethylsilane (TMS) and complexes **II-2** and **II-3**, as well as the corresponding hydrodynamic radii, are listed in Table 2. In all cases the diffusion constant of TMS was determined to be $D_{TMS} = 2.51 \times 10^{-9}$ m^2s^{-1}. This shows that the viscosity of the solutions is not influenced by complexes **II-2** and **II-3**. As the size of the observed samples is relatively close to the size of the solvent molecules, the frictional constant C was set to 4.[44] The difference of the diffusion constants of complexes **II-2** and **II-3** reveals an important change in the structure of the cationic complex **II-3**. The increase of the calculated hydrodynamic radius (r_H(**II-3**)/r_H(**II-2**) = 1.78) is in excellent agreement with the existence of a dimeric structure in solution. This final result clearly proves that the dimeric complex is present in solution and not formed during the ionization process.

Table 2: *Diffusion constants and Hydrodynamic radii*

Compound	Diffusion constant 10^{-10} m^2 s^{-1}	Hydrodynamic radius Å
TMS	25.1	2.95
II-2	9.5	7.76
II-3	5.4	13.8
For T = 285.16 K and $\eta = 3.14*10^{-4}$ Pa s		

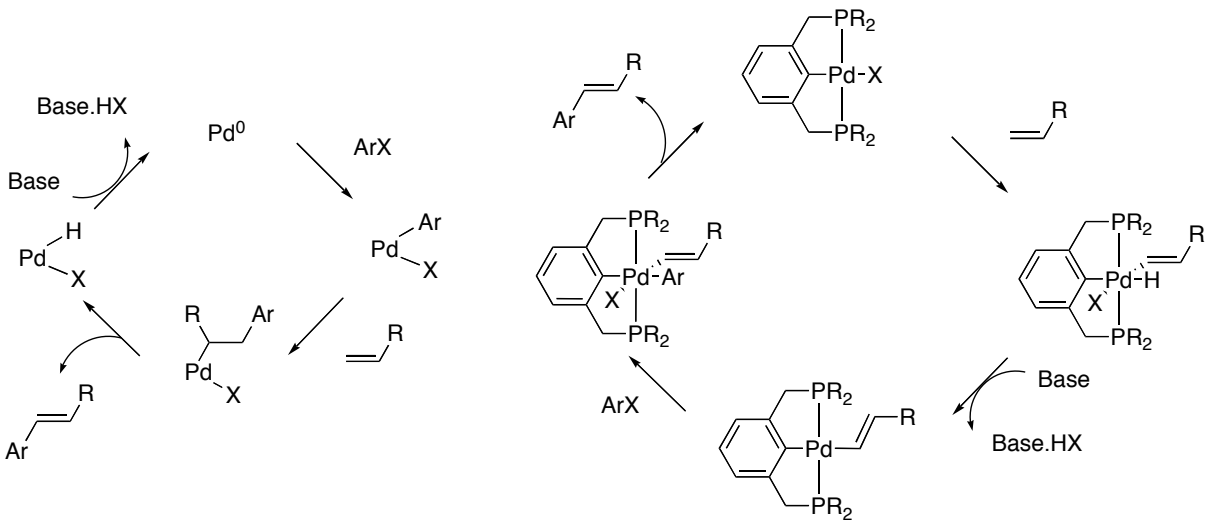
II.6. Conclusion

In this study, an anionic potentially tetradentate ligand, based on an in-house-developed SPS^R ligand, was coordinated to a Pd(II) center. Several cationic complexes have been isolated and fully characterized. In particular, complex **II-3**, unlike other related cationic "[(SPS^R)Pd]" species, is kinetically stable and isolable. Catalytic tests in the known allylation of aldehydes were performed. The stabilization of the Pd center in complex **II-3** results in lower catalytic activity than *in situ* generated cationic complexes from complex **II-6** or **II-9**, yet this complex is easy to handle and does not need to be activated. It is obvious from these results that the pyridine moiety does indeed bring stability to a cationic Pd center, without completely suppressing catalytic activity, as expected. The precise nature of complex **II-3** was not accessible by usual NMR spectroscopy, which prompted us to carry out a combined DFT and tandem ESI-MS spectroscopic study. The DFT study, taking into account the solvation effects on a model

complex, predicts a dimeric species, **II-C**, to be more stable than a monomeric species by ca. 8 kcal/mol, which would imply the sole presence of the dimer in solution. Free energy calculations on the other hand favor the monomeric form **II-A** by ca. 5 kcal/mol. Finally, the use of a recently introduced free energy G_{PCM} calculation, adding solvation effects, predicted the three complexes to lie within 1.1 kcal/mol (monomer **II-B** most stable, and, therefore, that they would coexist in solution. A precise quantification of the isomers in solution was obtained by the FT-ICR technique: about 97.5% to 2.5% (dimer **II-C** to monomers **II-A** and/or **II-B**). This corresponds to a difference in energy of ca. 2 kcal/mol in favor of the dimer. Our study points to an overestimation of the entropic factors by DFT calculations and confirms the importance of carrying out PCM calculations for charged species. In the case presented here, the recently proposed free energy ΔG_{PCM} calculation also overestimated the entropic factors and did not lead to the accurate prediction of the experimental system. Finally, our study clearly shows the interest of using combined experimental, in this case mass spectrometric techniques, and theoretical studies when the precise nature of complexes cannot be solved by usual NMR techniques or X-Ray crystallography.

III. STRUCTURE AND REACTIVITY OF A DIMERIC SPS^R-PD(I)-COMPLEX

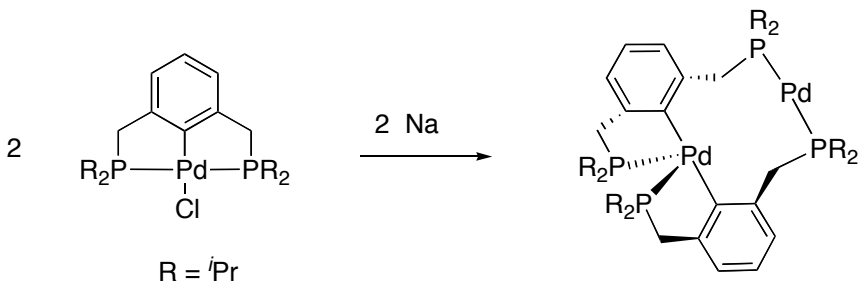
As it was mentioned before, PCP-pincer complexes are highly active catalysts for C-C coupling reactions such as the Heck reactions and the Suzuki-Miyaura reaction. Different mechanisms have been proposed for the Heck reaction based on Pd(0)/Pd(II)[3] as well as on Pd(II)/Pd(IV)[10] intermediates (Scheme 18).



Scheme 18: *Postulated mechanisms for the Heck reaction. Left: Classical mechanism based on Pd(0)/Pd(II) intermediates. Right: Mechansim proposed by Morales-Morals and Jensen based on Pd(II)/Pd(IV) intermediates.*

Furthermore PCP-palladium pincer complexes were supposed to be very robust, and due to their high stability they tolerate drastic reaction conditions.[10]

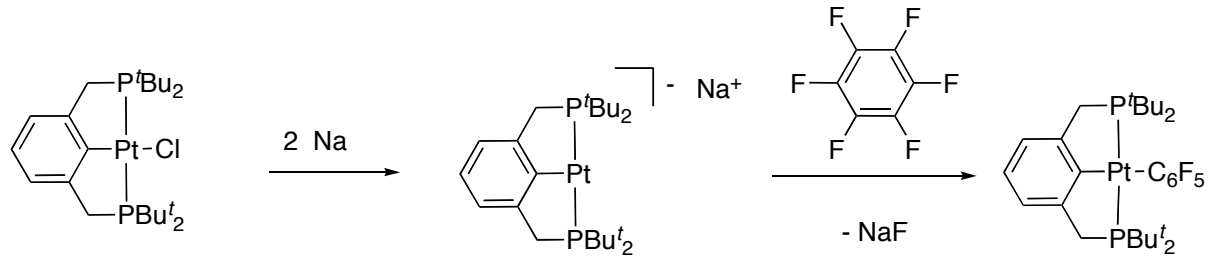
Mechanistic studies by Milstein and coworkers revealed, that the reduction of the well known PCP-palladium pincer complexes with sodium leads to a rearrangement and the formation of a mixed dimeric Pd(II)/Pd(0) (Scheme 19).



Scheme 19: *Reduction of a PCP-palladium pincer complex with sodium.*

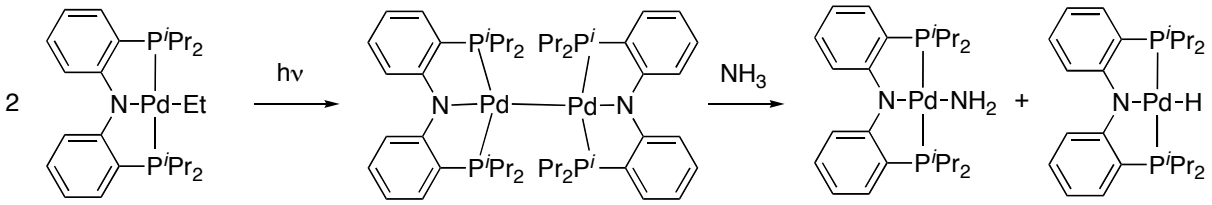
Interestingly, the dimeric complex shows a lower activity in the Heck reaction than the starting compound and no evidence could be found for the intermediacy of a reduced species palladium species in the catalytic cycle.

In further studies, Milstein ad coworkers reported that the reduction of the corresponding platinum complex does not yield the analogous dimer but rather leads to a monomeric anionic platinum complex.[45] This complex is highly reactive and capable of activating a CF bond in fluorobenzene at low temperature (Scheme 19).



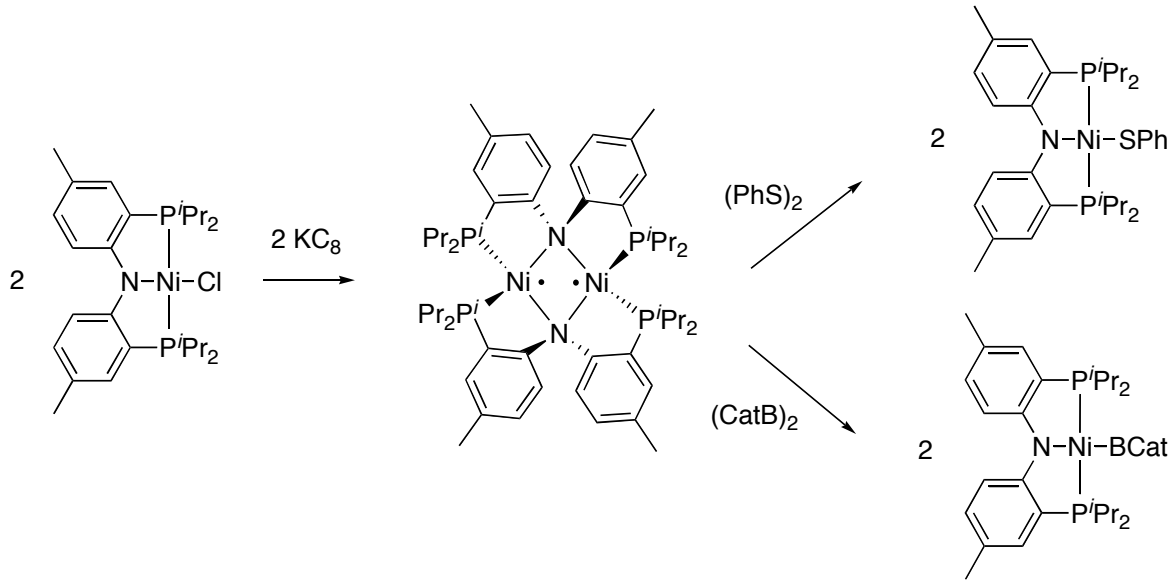
Scheme 20: *Reduction of a PCP-platinum pincer complex and activation of a CF bond in hexafluorobenzene.*

Ozerov and coworkers showed that the photolysis of a [(PNP)PdEt] complex leads to the formation of a dimeric diamagnetic Pd(I)-species (Scheme 21).[46] This complex is highly reactive and is able to activate small molecules such as H_2O, H_2, NH_3. Since the development of this anionic PNP system by Ozerov,[47] several groups have investigated its use with almost every transition metal. [48-54]



Scheme 21: *Generation of a dimeric Pd(I)-complex by photolysis and activation of NH_3.*

Mindiola and coworkers investigated the reduction of the analogous nickel complex with potassium graphite (Scheme 22).[55] This method yields a paramagnetic dimeric nickel(I) complex. This complex was used to activate diphenyldisulfide or biscatecholborane.

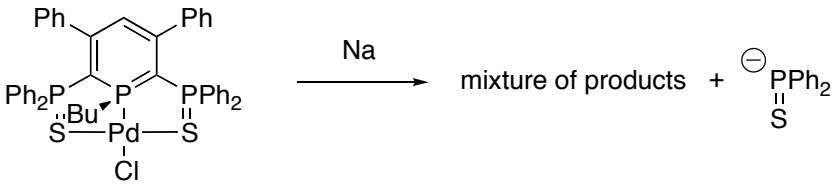


Scheme 22: *Reduction of a PNP-nickel pincer complex and activation of disulfide and Biscatecholborane.*

III.1. Synthesis and Characterization

As it was mentioned before, complex **II-9** is an active catalyst in the Heck reaction and the Miyaura borylation of iodoarenes. Due to the flexible structure of the SPS^R ligand, that allows the stabilization of various coordination geometries (square-planar, octahedral, trigonal bipyramidal,…). Therefore we wondered if it would be possible to isolate reduced palladium complexes and test their role in cross coupling reactions.

In our initial studies, we tested the reduction of the **II-9** with elemental sodium in THF. No reaction could be observed at room temperature, therefore the reaction mixture was heated to 60 °C, in analogy to the method reported by Milstein and coworkers. Under these conditions a complex mixture of products was obtained. The only product that could be readily identified by its characteristic ^{31}P NMR signal, was the anionic PPh_2S^--fragment, that was formed by the degradation of the SPS-ligand (Scheme 23).

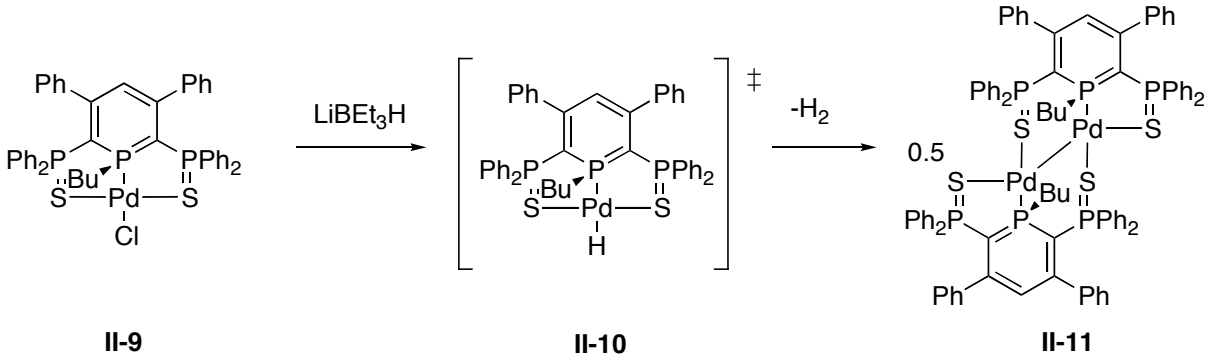


II-9

Scheme 23: *Attempted reduction of **II-9** with sodium.*

In contrast to that, the treatment of complex **II-9** with $LiBEt_3H$ as a reducing agent in THF at -78 °C led to the formation of a dark red product **II-11** after slow warming to room

temperature (Scheme 23). The expected palladium hydride intermediate **II-10** could not be observed during the reaction.



Scheme 24: *Formation of **II-11** upon reduction of **II-9** with lithium triethylborohydride.*

The $^{31}P\{^1H\}$ NMR spectrum of complex **II-11** shows three distinct signals in $^{31}P\{^1H\}$ NMR atoms with chemical shifts of 19.5 ppm (dd, $^2J_{PP}$ = 96.1 Hz) for the central phosphorus atom and two doublets at 44.4 ppm ($^2J_{PP}$ = 87.9 Hz) and 46.0 ppm ($^2J_{PP}$ = 104.2 Hz) (Figure 6). In the ^1H NMR spectrum no hydride resonance could be observed.

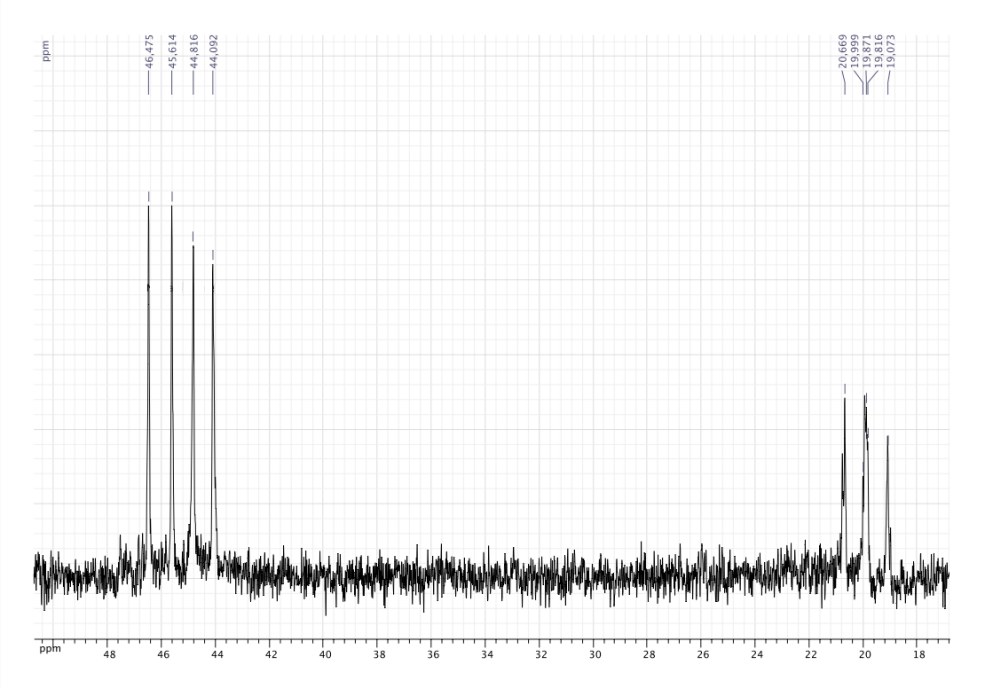


Figure 6: *$^{31}P\{^1H\}$NMR spectrum of complex **II-11**.*

This spectrum already pointed to two different environments of the phosphinesulfide moieties. Complex **II-11** is stable towards oxygen and moisture. Single crystals suitable for X-

Ray-crystal structure analysis could be obtained by slow evaporation of a concentrated solution of complex **II-11**. Its molecular structure is presented in Figure 7.

The X-Ray crystal structure reveals the distorted square planar coordination geometry of both palladium centers. The angles S(1)-Pd(1)-Pd(2) and P(1)-Pd(1)-S(3) with 174.02 ° and 167.37 ° show important deviation from theoretically expected 180 ° for a square planar coordination mode. The Pd-Pd bond length of 2.5815 Å is comparable to that of other structurally characterized Pd(I) dimers.[50, 56-58] The SPS^{Bu}-ligand acts as a bridging ligand between the two palladium centers. This coordination mode has not been observed before for the SPS-ligand and shows its structural flexibility. Interestingly, only one isomer was observed, with both butyl substituents pointing into the same direction.

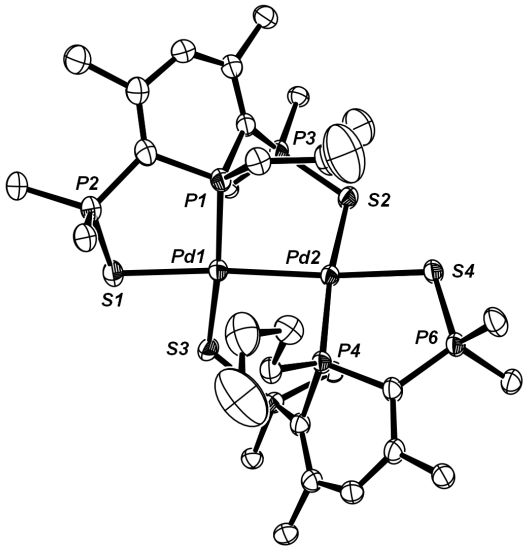


Figure 7: *Molecular structure of complex* ***II-11*** *(ORTEP-Plot, thermal ellipsoids with 50 % probability, phenyl groups and hydrogen atoms were omitted for clarity) Selected bond lengths[Å] and angles[°]: Pd(1)-Pd(2): 2.5815(3), P(1)-Pd(1): 2.2515(8), Pd1-S1: 2.4171(8), Pd(1)-S(3): 2.3540(8), S(1)-Pd(1)-Pd(2): 174.02(2), P(1)-Pd(1)-S(3): 167.37(3).*

To check whether or not **II-11** displays radical character, EPR measurements were performed, that proved **II-11** to be completely EPR silent even at 298 and 100 K.

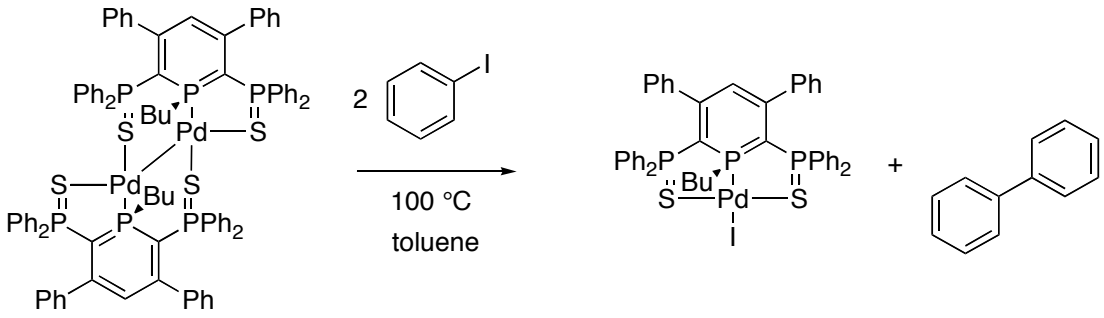
This can be explained by the antiferromagnetic coupling of the unpaired electrons in the two Pd(I)-fragments, as was observed in the case of dimeric palladium complexes by Ozerov for [(PNP)Pd(I)] complexes (Scheme 20).[46]

In order to see whether or not complex **II-11** could possibly be reduced to an anionic Pd(0)-species, the redox potentials of complex **II-11** were studied by means of cyclovoltammetry. Surprisingly no signals of reduction or oxidation could be detected in the range of -2 V to 2 V relative to the Standard-Calomel-Electrode for a 0.1 mM solution of complex **II-11** in a 0.5 M solution of tetrabutylammonium tetrafluoroborate in THF as electrolyte.

Preliminary catalytic tests with **II-11** in cross-coupling reactions showed a higher activity for **II-11** in cross coupling reactions than for **II-9**. Therefore we wondered if **II-11** might be an intermediate in the catalytic cycle and decided to carry out stoichiometric reactions to get information about the reactivity of **II-11**.

III.2. Reactivity

The test the ability of complex **II-11** to undergo oxidative addition, its reactivity toward iodobenzene was tested. At room temperature, no reaction could be observed with iodobenzene or other reagents. In contrast, at 100 °C, complex **II-11** reacted with iodobenzene to give a single phosphorus containing product in quantitative yield after 4 h as judged by ^{31}P NMR. Due to the characteristic coupling pattern of the [SPS^{Bu}Pd] fragment, this new compound was readily identified as [SPS^{Bu}PdI]. Additionally, biphenyl was identified as a product in this reaction by means of GC (Scheme 25).



II-11 **II-12**

Scheme 25: *Reaction of II-11 with iodobenzene.*

Single crystals of **II-12** could be grown from a concentrated solution of $CHCl_3$. The X-Ray crystal analysis confirms the expected molecular structure of complex **II-12** (Figure 8).

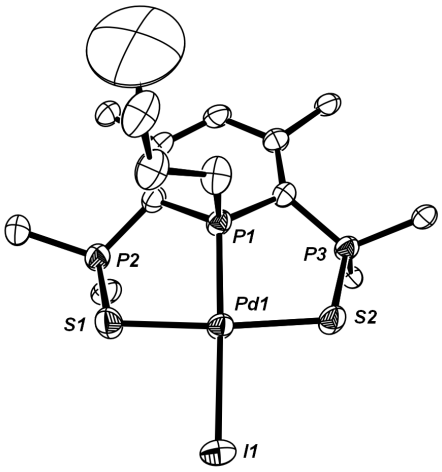


Figure 8: *Molecular structure of complex* ***II-12*** *(ORTEP-Plot, thermal ellipsoids with 50 % probability, phenyl groups and hydrogen atoms were omitted for clarity) Selected bond lengths[Å] and angles[°]: Pd1-P1: 2.207(1), Pd1-S1: 2.330(1), Pd1-S2: 2.325(1), Pd1-I1: 2.6922(4), P2-S1: 2.037(1), P3-S2: 2.033(2), P1-Pd1-I1: 171.92(3), S1-Pd1-S2: 174.52(4).*

The X-Ray crystal structure reveals the expected square planar coordination mode expected for this type of complex with the iodide ion trans to the central phosphorus atom.[59]

When the reaction was followed by ^{31}P NMR, a mixture of two complexes could be observed: **II-12** and another complex. With the aim of understanding whether this complex was formed form **II-11** by heating or because of the reaction with iodobenzene, another reaction was carried out, heating **II-11** in the absence of iodobenzene to 100 °C in toluene.

The same intermediate could be observed when heating compound **II-11** alone, in toluene for 1h. The ^{31}P{^{1}H} NMR reveals the formation of a single species bearing five clearly separated signals (Figure 8). One of them at a chemical shift δ = 46.5 ppm ($^{2}J_{PP}$ = 95 Hz), is much less complicated than the others and can be identified as decoordinated PPh_2S-moiety (Figure 9).

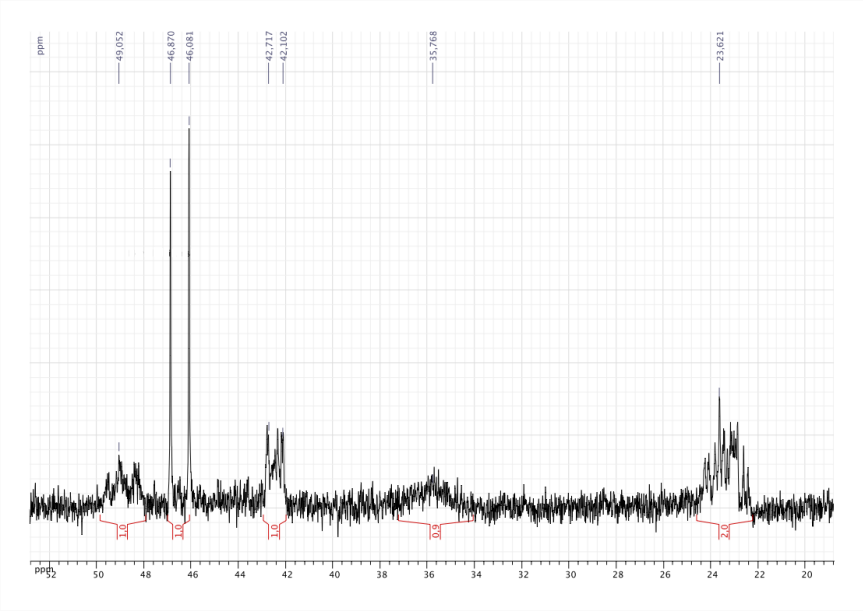
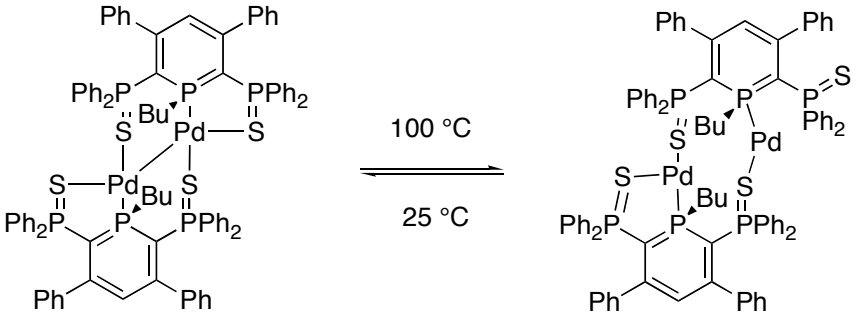


Figure 9: *$^{31}P\{^{1}H\}$ NMR Spectrum of **II-11** after 1h at 100 °C in toluene.*

After 24 h at room temperature the quantitative reformation of complex **II-11** is observed, therefore it must be supposed, that a reversible rearrangement occurs upon heating of complex **II-11**. A possible structure for this compound is drawn in Scheme 26. Despite of numerous attempts no X-Ray crystal structure of product **II-13** could be obtained, because of the relatively fast rearrangement to the starting product at room temperature.



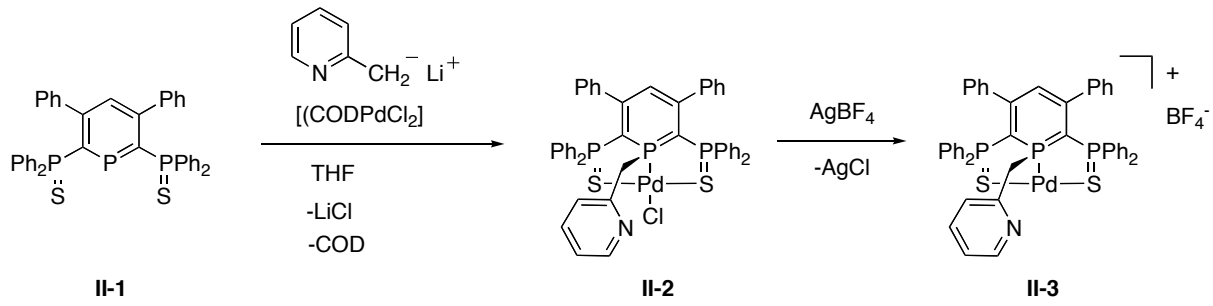
II-11 **II-13**

Scheme 26: *Possible rearrangement of **II-11** upon heating to 100°C in toluene.*

In contrast, neither a (SPS^{R})Pd(III)PhX species resulting from the addition of ArX to a monomeric Pd(I) nor a (SPS^{R})Pd(II)Ph intermediate resulting from the addition of ArX the dimeric Pd(I) species could be detected.

IV. CONCLUSIONS AND PERSPECTIVES

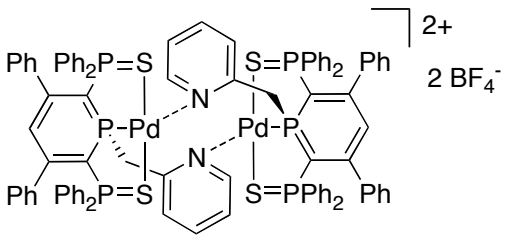
In this chapter we have developed the synthesis of palladium complexes wit the potentially tetradentate SPS^{Pic} ligand. The reaction of complex **II-2** with $AgBF_4$ allowed for the preparation of a stable cationic palladium complex **II-3**.



II-1 **II-2** **II-3**

Scheme 27: *Synthesis of a stable cationic SPS-palladium pincer complex.*

The structure of complex **II-3** could be established by a combination of NMR-spectroscopic and mass-spectrometric studies in combination with DFT calculations to be dimeric.

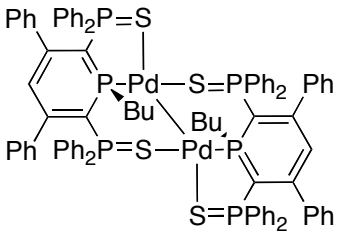


II-3

Scheme 28: *Supposed dimeric structure of **II-3**.*

Furthermore it could be shown, that complex **II-3** can still be used as a catalyst in the allylation of aldehydes with allyltributyltin, in the absence of silver salt, although it is less reactive than the reference catalyst **II-9**.

Mechanistic studies on the reduction of complex **II-9** which is an active catalyst in the Heck reaction and the borylation of iodoarenes reveal the formation of a dimeric Pd(I) species **II-11** upon treatment of **II-9** with lithium triethylborohydride, a so far unprecedented coordination mode of the SPS^{R}-ligand (Scheme 29).

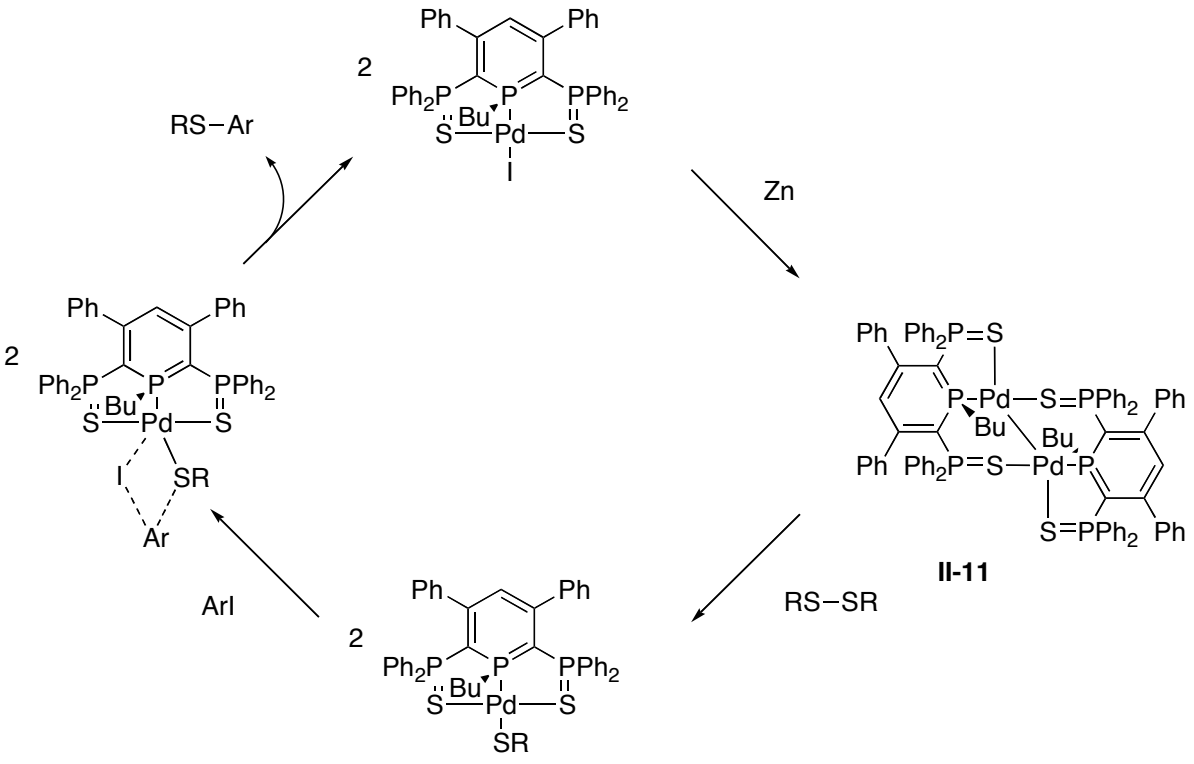


II-11

Scheme 29: *Dimeric SPS^{Bu} palladium(I) complex* ***II-11***.

This complex might be an interesting catalyst precursor for the synthesis of thioethers from disulfides and iodoarenes, as nickel pincer complexes have been reported to be potent catalysts for this transformation in the presence of zinc powder, and reduced nickel(I) species were supposed to be intermediates in this process.[60]

The very stable complex **II-11** might be a good starting point for a mechanistic study of this reaction allowing to test the addition of disulfides.



Scheme 30: *Supposed application of complex* ***II-11*** *in the synthesis of thioethers.*

Furthermore it will be interesting to study the behavior of the analogous SPS^{Bu} nickel complexes starting from the readily accessible [(SPS^{Bu})NiCl] complex, as we have observed in preliminary studies, that these complexes show a paramagnetic behavior after the reduction with lithium triethylborohydride and are much more reactive than complex **II-11**.

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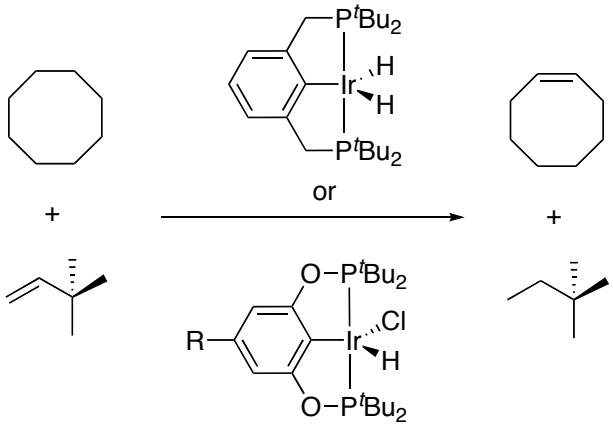
CHAPTER 2: RHODIUM AND IRIDIUM COMPLEXES OF THE SPS^{ME}-LIGAND

I. INTRODUCTION

The [IrHCl(C_6H_3-2,6-($CH_2P^tBu_2$)$_2$)] complex, whose first synthesis was reported by Moulton and Shaw[1] in 1976 can for example be sublimed without decomposition at temperatures as high as 180 °C. This extraordinary thermal stability of pincer complexes makes them an interesting class of compounds for the activation of very strong bonds such as terminal C-H bonds in alkanes, which is one of the most challenging organic transformation as it opens the way to the transformation of poorly reactive alkanes to terminal olefins that are one of the major organic feedstocks for the chemical industry.

The first catalytic transfer dehydrogenation reactions catalyzed by Iridium pincer complexes were reported by Kaska, Jensen and coworkers in 1996.[2, 3] Their studies clearly point out the higher efficiency of pincer complexes compared to other homogeneous catalysts in transfer hydrogention reactions, due to their long term stability (5 days) even under drastic conditions (up to 200 °C).

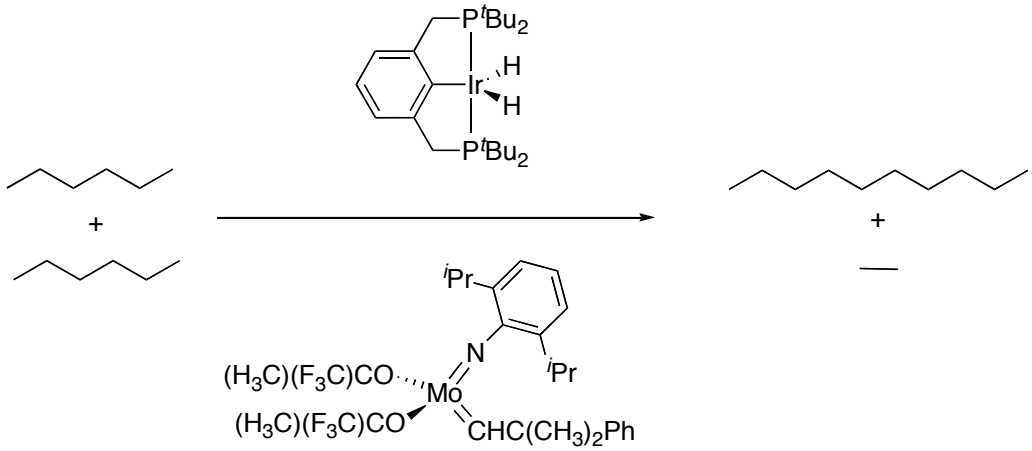
In 2004 Morales-Morales et coll. as well as Brookhart et coll. reported that the related phosphinite iridium pincer complexes showed superior activity in transfer dehydrogenation as well as in acceptor less dehydrogenation, where molecular hydrogen is produced.[4-6]



Scheme 1: *Catalytic trasfer hydrogenation of alkanes with PCP-iridium pincer complexes.*

A very elegant application of these catalysts was reported by Brookhart, Goldman and coworkers in 2006 by the combination of an iridium pincer complex and a Schrock-type metathesis catalyst.[7]

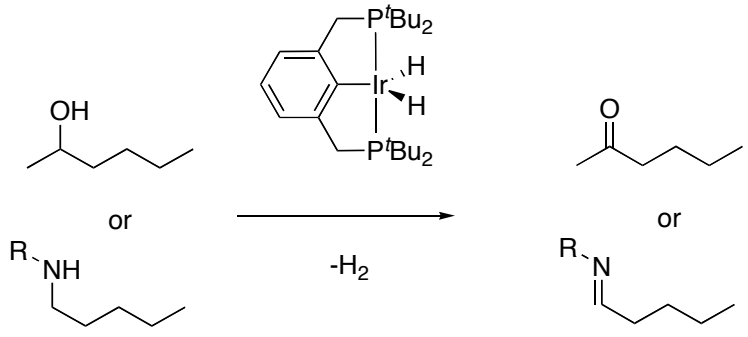
The combination of these two catalysts allowed them to formally perform an overall alkane metathesis. In this way the authors achieved to produce n-decane and ethylene as major products from two molecules of n-hexane (Scheme 2).



Scheme 2: *"Alkane methathesis" by the combination of an iridium pincer complex with a Schrock-type metathesis catalyst.*

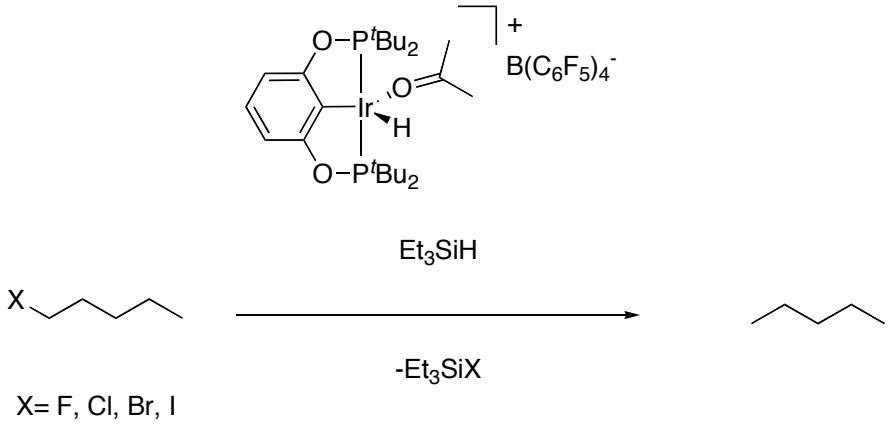
The mechanism of this reaction includes the dehydrogenation of n-hexane to hex-1-ene by the iridium pincer complex as the initial step. In the second step, two consecutive olefine metathesis steps catalysed by the Schrock-type carbene lead to the formation of dec-5-ene, which is then hydrogenated by the iridium pincer complex to yield decane.

The application of iridium pincer complexes in the dehydrogenation of alcohols[8] and amines[9] yielding ketones and imines was reported by Morales-Morales and coworkers (Scheme 3).



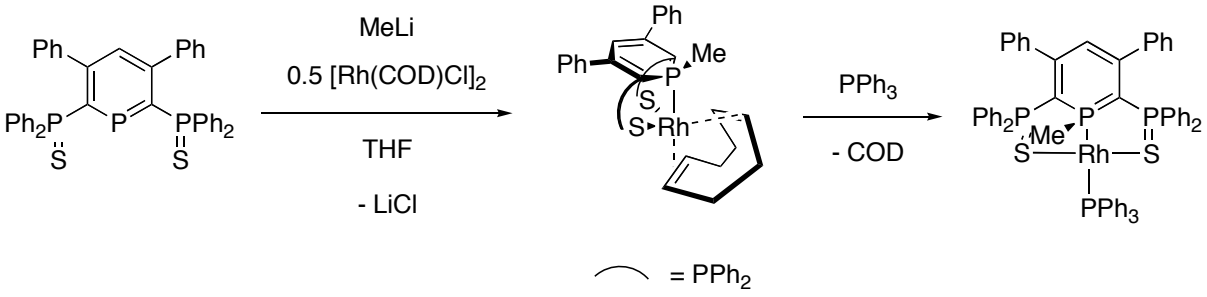
Scheme 3: *Dehydrogenation of alcohols and amines by an iridium pincer complex.*

Another catalytic application of PCP-iridium pincer complexes was reported by Brookhart and Yang in 2007.[10] The authors used in their study a cationic complex for the reduction of alkylhalides with triethylsilane (Scheme 4).



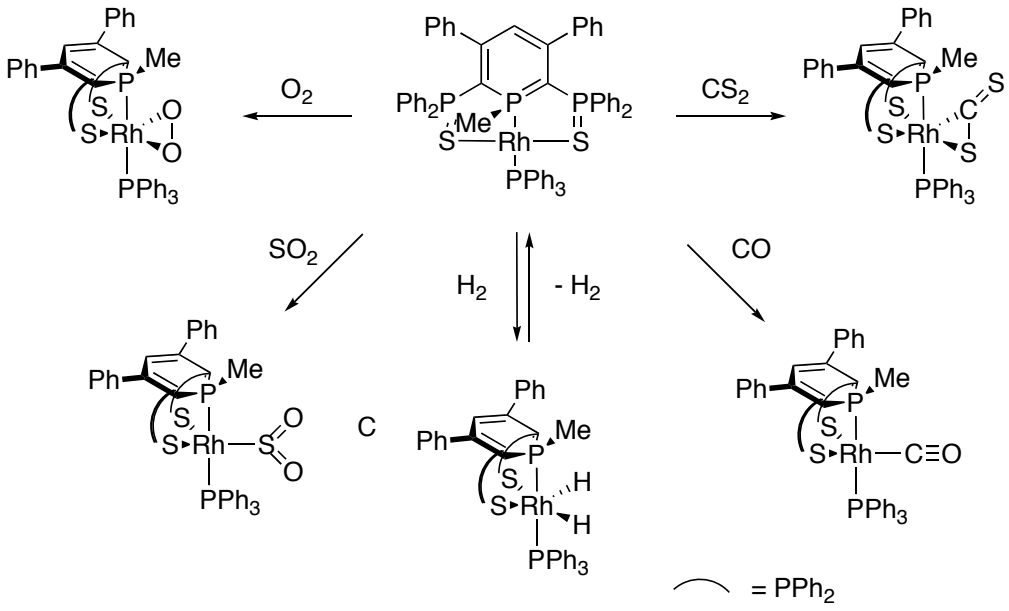
Scheme 4: *Reduction of alkylhalides with triethylsilane catalyzed by a cationic PCP-iridium pincer complex.*

The synthesis and reactivity of SPS^{Me}-rhodium pincer complexes was first described by our group in 2003.[11] The synthesis of these complexes could be readily achieved in analogy to the palladium complexes after addition of methyl lithium to SPS followed by the addition of $[Rh(COD)Cl]_2$, to yield the extremely stable trigonal bipyramidal [(SPS^{Me})Rh(COD)] complex. Upon addition of one equivalent of PPh_3 to the reaction mixture, the COD ligand is readily replaced by the phosphine ligand and the square planar [(SPS^{Me})Rh(PPh_3)]-complex is formed.



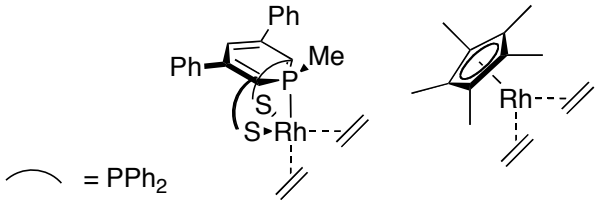
Scheme 5: *Synthesis of [(SPS^{Me})Rh(COD)] and [(SPS^{Me})Rh(PPh_3)] complexes.*

The [(SPS^{Me})Rh(PPh_3)]-complex is highly reactive and readily fixes and activates small molecules such as O_2, CS_2, , SO_2, CO and H_2. Interestingly, the addition of these molecules proceeds selectively from one side of the complex, in *syn*-fashion to the methyl substituent on the phosphorus atom. Interestingly this reaction is reversible in the case of H_2, which could be important for their application in catalysis, such as the dehydrogenation of alkanes (Scheme 6).



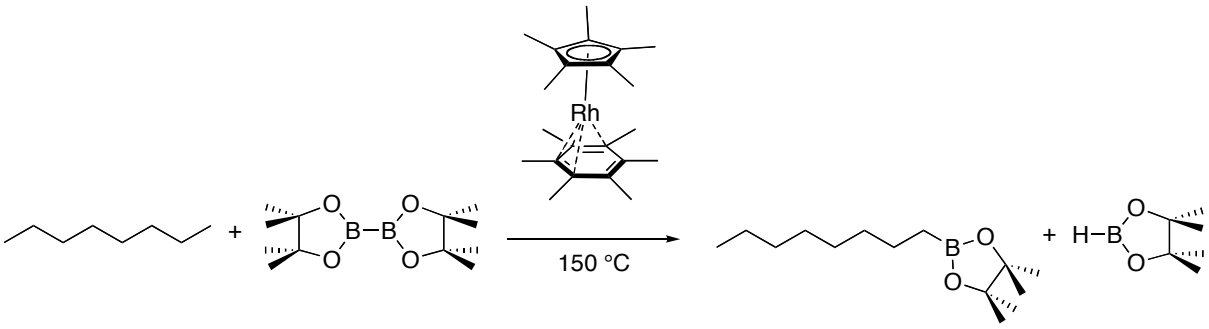
Scheme 6: *Fixation of small molecules by the [(SPS^{Me})Rh(PPh$_3$)]-complex.*

The SPS^{Me}-ligand is an anionic six-electron donor ligand that is capable of occupying one face of a metal center, therefore it was supposed, that the SPS^{Me}-ligand might be compared to cyclopentadienyl ligands (Scheme 7).[12]



Scheme 7: *[(SPS^{Me})Rh(C$_2$H$_4$)$_2$] and [Cp*Rh(C$_2$H$_4$)].*

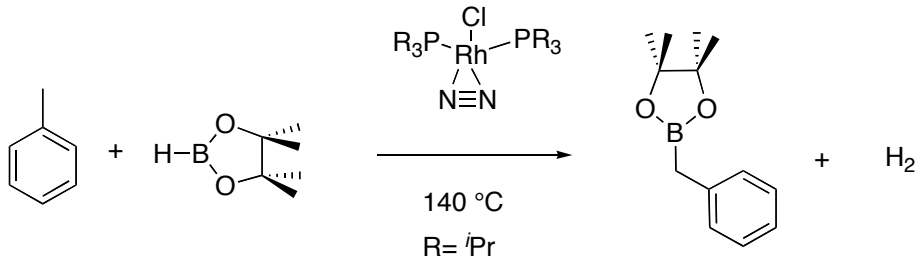
Furthermore it could be shown, by electrochemistry on Ru complexes, that the SPS^{Me} is a more electron donating ligand than the Cp* ligand. Cp* rhodium complexes were recently employed by Hartwig and coworkers for the borylation of alkanes and arenes.[13, 14]



Scheme 8: *Rhodium catalyzed borylation of alkanes.*

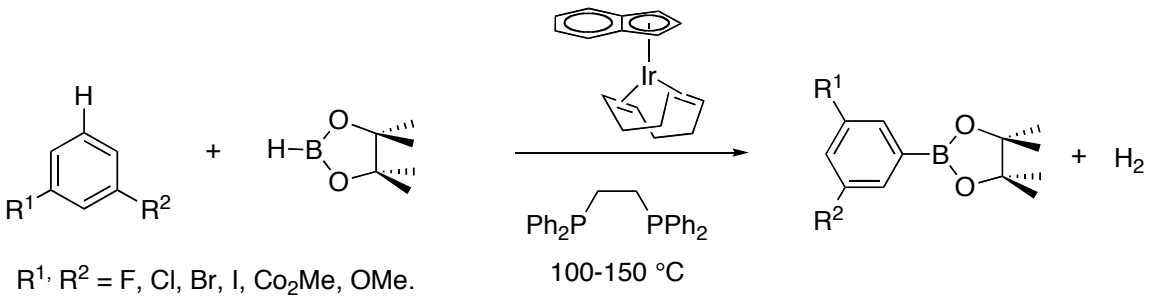
This reaction is of great academic and industrial interest, as it allows functionalizing selectively the most stable bond in alkanes.[15] Additionally the products of this reactions, boronic esters have become one of the most important starting materials due to the development of palladium catalyzed Suzuki-Miyaura coupling reaction that has become one of the most important reactions for the formation of C-C bonds in organic molecules.[16]

Marder and coworkers reported that $[(P^iPr_3)_2Rh(Cl)(N_2)]$ is an active catalyst for the borylation of benzene with pinacolborane.[17] Interestingly, the benzylboronate esters were obtained as the a major product when methyl substituted arene derivatives were used as substrates (Scheme 9).



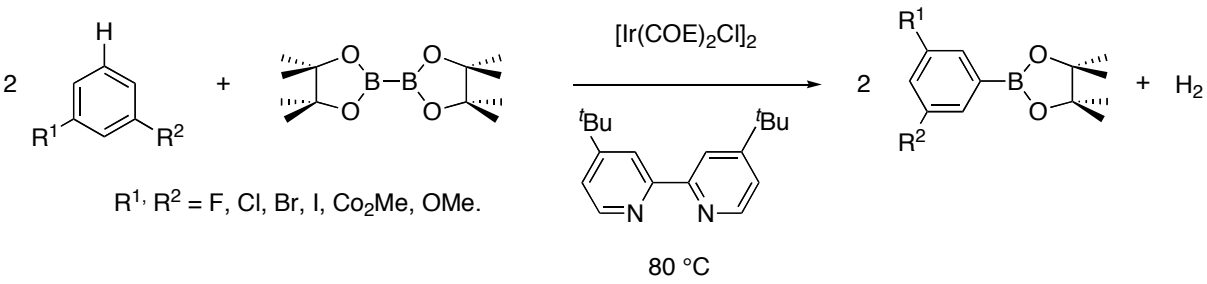
Scheme 9: *Rhodium catalyzed borylation of the benzylic position of toluene.*

Smith and coworkers, showed that the borylation of arenes can be performed with iridium complexes with bidentate ligands such as dppe (Scheme 10).[18] Most remarkably, this transformation can be performed in the presence of various functional groups such halides or esters.



Scheme 10: *Iridium catalyzed borylation of haloarenes.*

Hartwig and Miyaura showed, that the combination of a bipyridine complexes of iridium are highly active catalysts for the borylation of arenes wit bispinacolborane under mild conditions.[19] In this case, various functional groups (CF_3, OMe, Me, Br, Cl) were tolerated (Scheme 11).



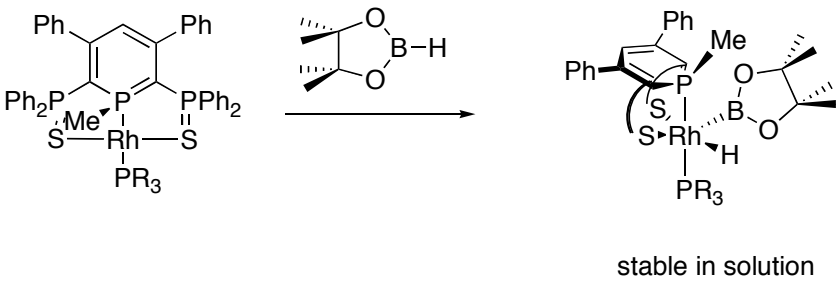
Scheme 11: *Borylation of arenes catalyzed by a bipyridine iridium complex.*

In the first part of this chapter we are going to study iridium and rhodium complexes of the tridentate SPS^{Me} ligand. In the second part of this chapter we will be interested in the application of these precursors to the borylation of alkanes and arenes.

II. SYNTHESIS

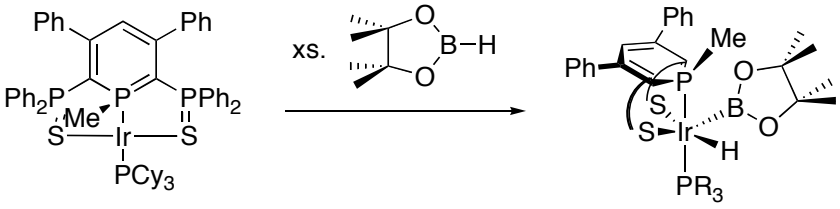
II.1. Rhodium(I) and Iridium(I)-complexes

During the studies concerning the reactivity of the [(SPS^{Me})Rh(PR)$_3$] (R = Me, Ph, Cy) that were carried out in our group[12] it could be observed, that these complexes readily add pinacolborane. Unfortunately these complexes could not be fully characterized, as they decompose upon evaporation of the solvent.



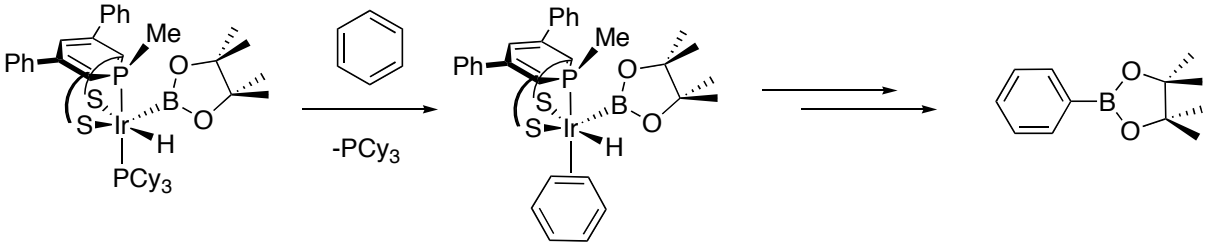
Scheme 12: *Addition of pinacolborane to [(SPS^{Me})Rh(PR$_3$)]-complexes.*

In contrast, the analogous [(SPS^{Me})Ir(PCy)$_3$] is stable in the solid state and could be fully characterized by NMR spectroscopy and microanalysis by M. Doux during her doctoral studies (Scheme 13).[12]



Scheme 13: *Additon of pinacolborane to [(SPS^{Me})Rh(PCy$_3$)].*

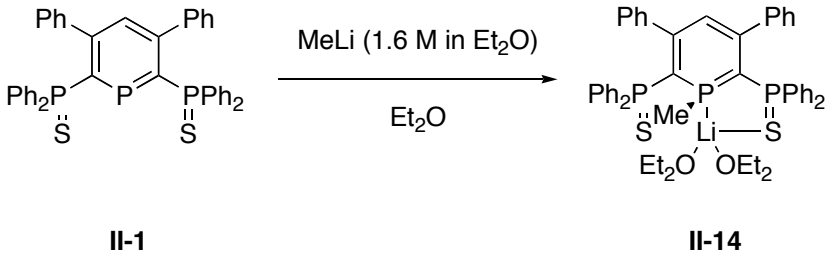
For the use of these complexes in the borylation of arenes and alkanes, a major problem is the generation of an unsaturated species that could react with a substrate. Therefore the use of tertiary phosphines that are tightly coordinated to the metal might be detrimental for the application in catalysis (Scheme 14).



Scheme 14: *Hypothetical reaction pathway.*

Furthermore it was reported by Hartwig and Miyaura that Ir(COE) complexes displayed a high reactivity in borylation reactions, therefore we envisaged to use this metal fragment in our further studies.

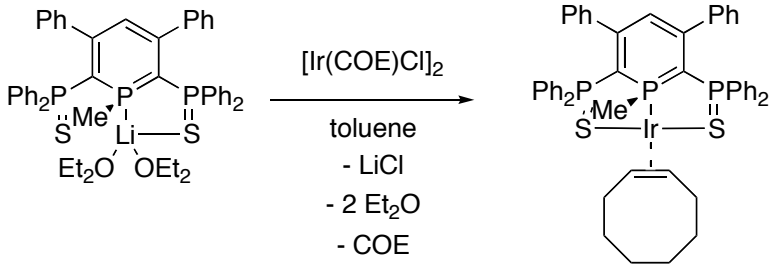
First of all the highly reactive [(SPS^{Me})Ir(COE)] complex **II-15** was prepared. As it was observed before,[12] this complex undergoes fast decomposition in tetrahydrofurane (~5 min.). We postulated, that the decomposition was not due to the intrinsic instability of **II-15** but rather to its reactivity towards THF. Therefore a new synthetic procedure for the synthesis of the anionic SPS^{Me}-ligand was developed, that allows its preparation in the absence of THF. The reaction of a suspension of SPS **II-1** with a slight excess (1.1 equivalents) of a 1.6 M solution of MeLi in diethylether at room temperature in the glove-box led to the immediate quantitative formation of the Li-salt of SPS^{Me-} **II-14** as an orange precipitate. After centrifugation of the resulting suspension, the orange precipitate was dried under vacuum. The ^{31}P NMR of the resulting compound reveals, that by this method, the ligand can be prepared in high purity in the absence of THF. The ^{1}H NMR reveals the presence of 2 equivalents of diethylether per ligand (Scheme 15).



II-1 **II-14**

Scheme 15: *Preparation of the SPS^{Me-}-ligand in the absence of THF.*

The synthesis of the desired iridium complex can be achieved by the addition of $[Ir(COE)_2Cl]_2$ to a solution of the ligand in toluene (Scheme 16).



II-14 **II-15**

Scheme 16: *Synthesis of [(SPSMe)Ir(COE)]* ***II-15****.*

Complex **II-15** was obtained in quantitative yield as judged by ^{31}P NMR immediately (Figure II.8), with its characteristic chemical shifts of 32.8 ppm (*pseudo*-d, $^{2}J_{PP}$=112.5 Hz, PPh_2S) and 13.4 ppm (dd, $^{2}J_{PP}$= 110.3 Hz; $^{2}J_{PP}$= 114.7 Hz). Due to the absence of THF complex **II-15** is now stable for about 30 min. in solution, making it possible to study its reactivity.

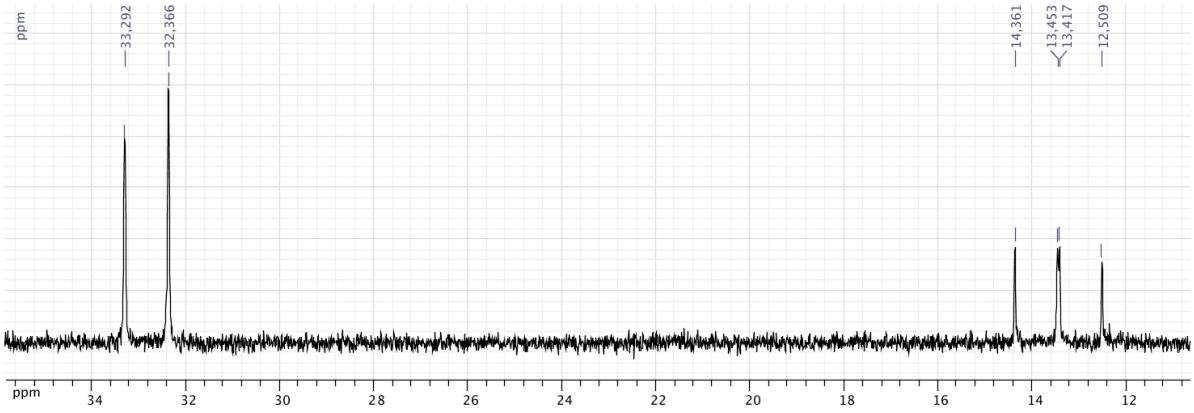
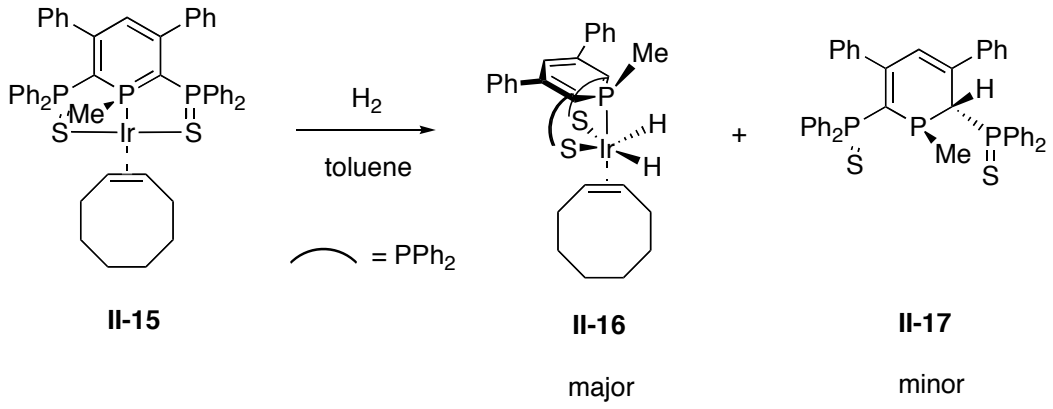


Figure 1: *$^{31}P\{^{1}H\}$ NMR spectrum of complex **II-15** in C_6D_6 after 5 min. at room temperature.*

The ability of **II-15** to undergo oxidative addition was tested with different reactives. For example when hydrogen was bubbled through a freshly prepared solution of **II-15**, the formation of a new major product **II-16** could be observed immediately. The complex shows characteristic chemical shifts of 52.5 ppm (*pseudo*-d, $^{2}J_{PP}$=100.4 Hz, PPh_2S) and 9.2 ppm (t, $^{2}J_{PP}$= 100.4 Hz). Additionally this product shows a characteristic signal in the ^{1}H NMR at a chemical shift of -19.5 ppm (d, $^{2}J_{PH}$= 17 Hz), which is in good agreement with the formation of a symmetric iridium dihydride species (Scheme 17).

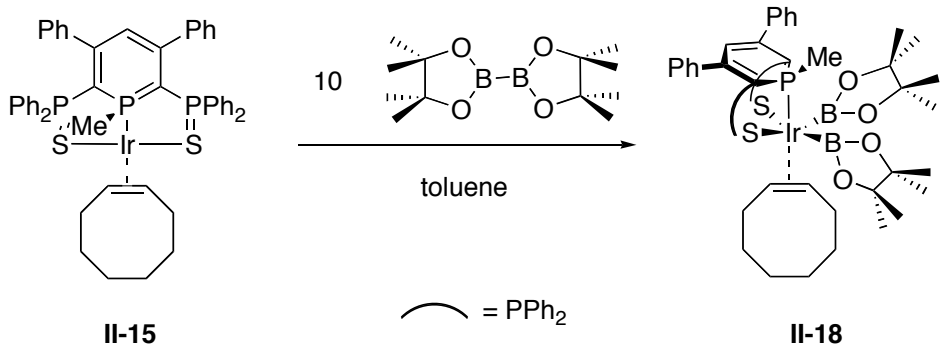


Scheme 17: *Reaction of **II-15** with hydrogen.*

The formation of a minor product could be observed during this reaction, whose quantity depends on the time during which the hydrogen was bubbled through the reaction mixture. Due to its characteristic $^{31}P\{^{1}H\}$ NMR spectrum with chemical shifts of -58.4 ppm and 42.5 ppm this species could be readily be identified as the product of hydrolysis **II-17** of the anionic SPS^{Me}-ligand.[12] Despite many efforts it was not possible to obtain a pure sample of **II-16** or to obtain single crystals of **II-16**.

Additional studies were carried out to check the reactivity of **II-15** towards bispinacolborane. Preliminary studies showed, that the reaction of **II-15** with bispinacolborane was quite slow and therefore, the degradation of the starting material was faster than the reaction with bispinacolborane when the reaction was carried out with one equivalent of bispinacolborane.

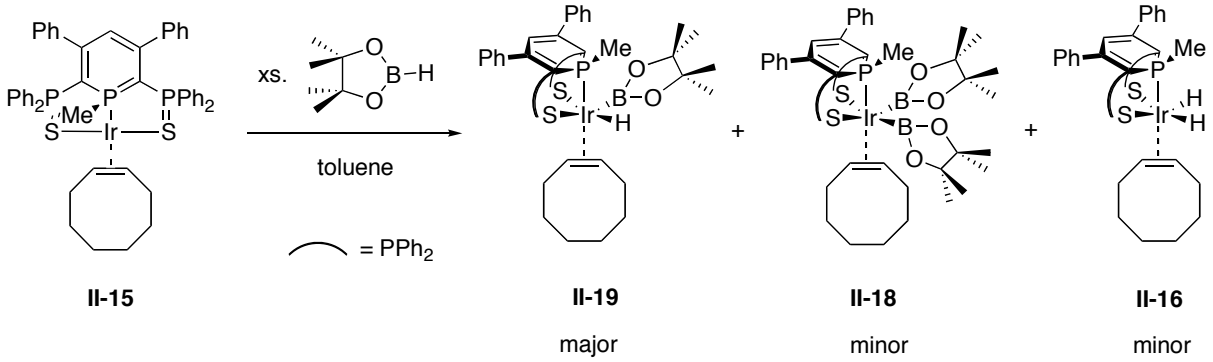
This problem could be circumvented by the addition of a large excess of bispinacolborane (10 equivalents) to a freshly prepared solution of **II-15** (Scheme 18).



Scheme 18: *Reaction of **II-15** with an excess of bispinacolborane.*

The $^{31}P\{^{1}H\}$ NMR spectrum of this shows signals at a chemical shift of 22.7 ppm (t, $^{2}J_{PP}$ = 90.0 Hz) and 43.3 ppm (d, $^{2}J_{PP}$ = 90.0 Hz) along with small amounts of impurities. As it can be seen from the coupling pattern, both diphenylphosphine sulfide groups are equivalent, therefore a *syn*-oxidative addition leading to the Ir(III)-cis-diboryl complex **II-18** is postulated in analogy what was reported before on the related [(SPS^{Me})Ir(PCy$_3$)] complexes.[12]

Surprisingly the reaction of complex **II-15** with an excess of pinacolborane led to a mixture of three products.

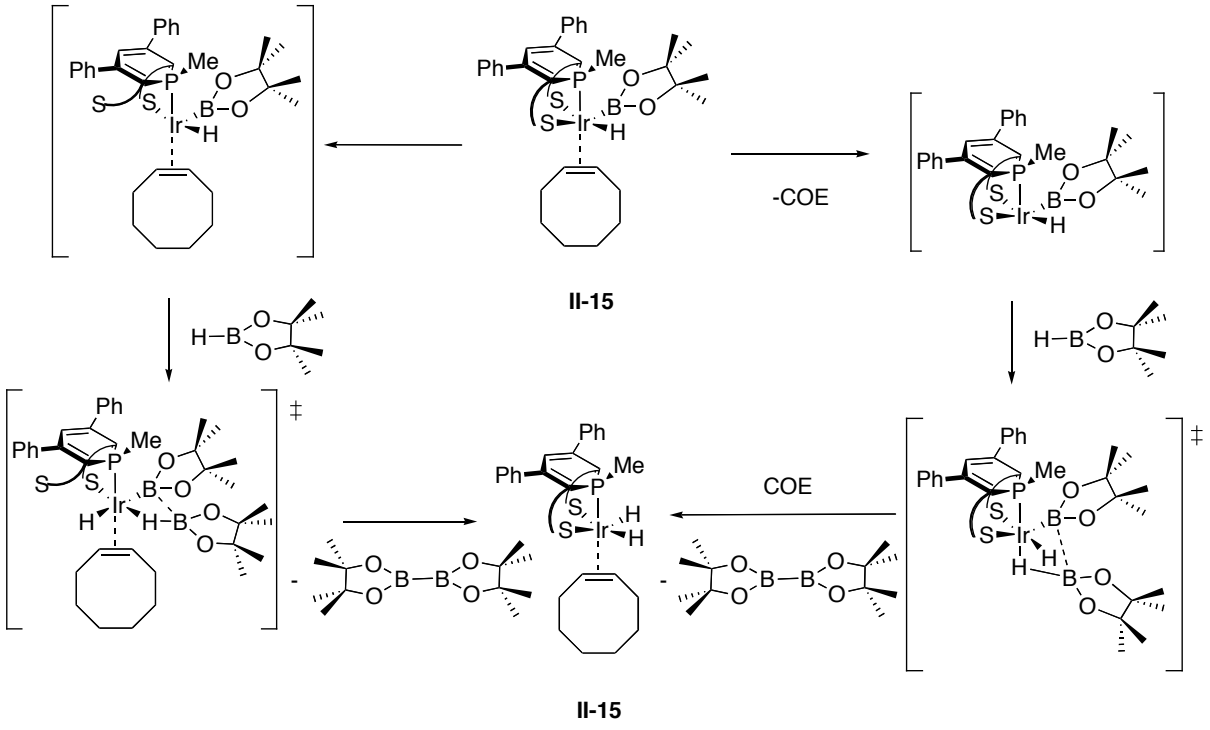


Scheme 19: *Reaction of **II-15** with an excess of pinacolborane.*

The two minor products could readily be identified as **II-16** and **II-18** by the comparison of the signals in the ^{31}P NMR-spectrum of the reaction mixture with those of the reactions with

hydrogen and bispinacolborane. The major product **II-19** shows three signals in the ^{31}P NMR spectrum with chemical shifts of 15.9 ppm (dd, $^{2}J_{PP}$= 80.7 Hz, $^{2}J_{PP}$= 109.6 Hz, PMe), 45.9 ppm (d, $^{2}J_{PP}$= 80.7 Hz, PPh_2S) and 50.5 (d, $^{2}J_{PP}$= 109.6 Hz, PPh_2S). Furthermore a hydride resonance can be observed at a chemical shift of -15.2 ppm (d, $^{2}J_{PH}$= 20.2 Hz). The NMR-data are in excellent agreement with the formation of a dissymmetric boryl hydride complex **II-19**.

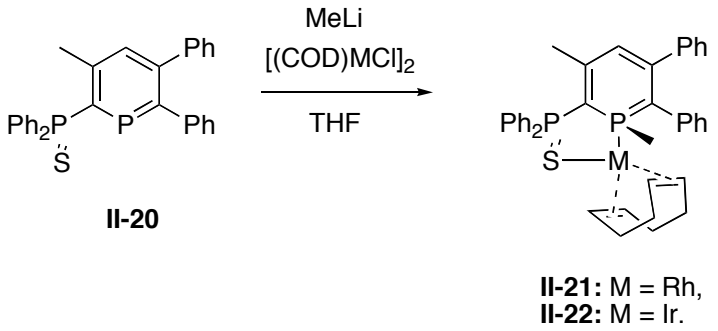
The unexpected formation of products **II-16** and **II-18** is interesting in the perspective of a possible application of **II-15** in the borylation of arenes. A possible explanation for the observed redistribution is the formation of an unsaturated species from **II-19** via the decoordination of the cyclooctene ligand or *via* the decoordination of one of the diphenylphosphinesulfide substituents and the subsequent reaction with a second equivalent of pinacolborane. A sigma bond metathesis with the concomitant formation of bispinacolborane and the subsequent recoordination of cyclooctene or the recoordination of the diphenylphosphinesulfide group would lead to **II-16**



Scheme 20: *Possible mechanism for the formation of* ***II-16*** *from* ***II-19*** *and excess pinacolborane.*

An analogous reaction sequence could be envisaged for the formation of the diboryl complex **II-18**.

As stated before, bidentate diphosphine and bipyridine ligands were successfully used in iridium catalyzed borylation reactions by Hartwig[19] and Smith.[18] Therefore a second type of catalyst precursor was envisaged based on a phosphinine-phosphinesulfide ligand **II-20**. The iridium and rhodium cyclooctadiene complexes of this ligand could be readily obtained according to the procedure reported by M. Doux[12] for the the Rh-complex **II-21** (Scheme 21).



Scheme 21: *Synthesis of rhodium and iridium complexes* ***II-21*** *and* ***II-22***.

The NMR data for both complexes are essentially identical with that reported by Doux for complex **II-21**. Single crystals suitable for X-Ray crystal structure analysis could be obtained from the diffusion hexanes into concentrated solutions of **II-21** and **II-22**. The molecular structures of **II-21** and **II-22** are presented in Figure 2.

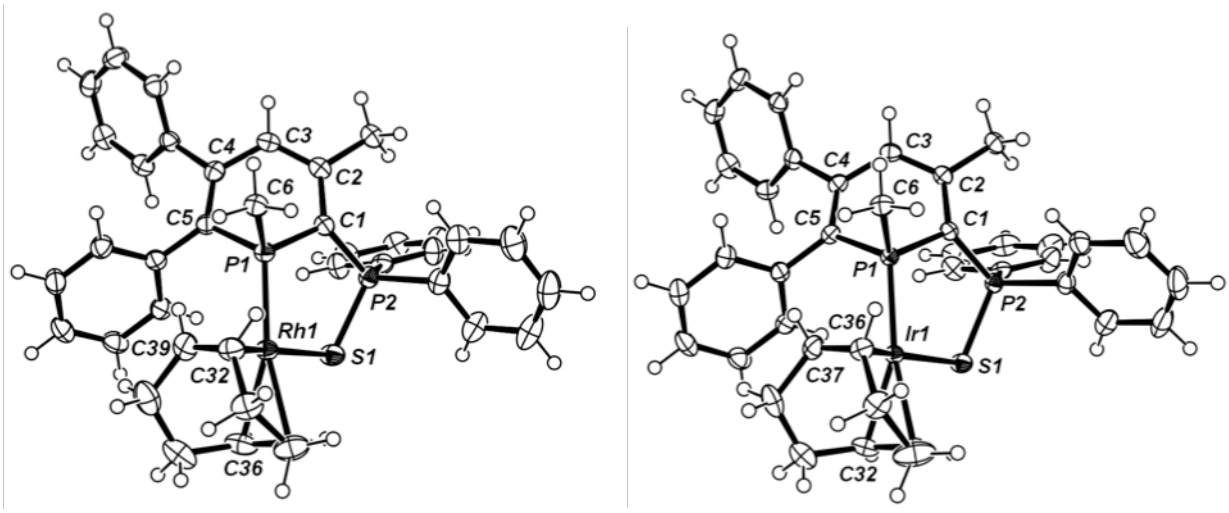
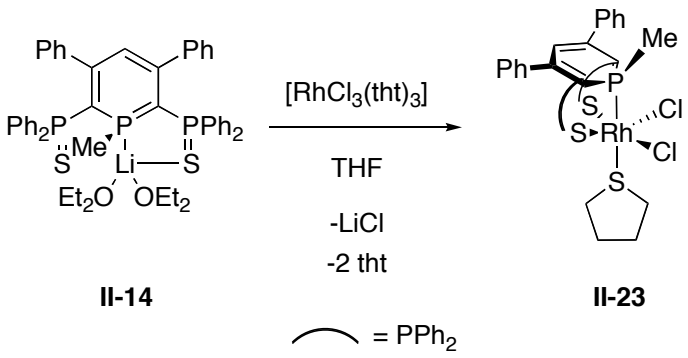


Figure 2: *Molecular structure of complex* ***II-21*** *(left) and* ***II-22*** *(right) (ORTEP-Plot, thermal ellipsoids with 50 % probability, phenyl groups and hydrogen atoms were omitted for clarity, The products crystallized as racemic mixtures, only one enantiomer is presented) Selected bond lengths[Å] and angles[°] for* ***II-21****: Rh1-P1: 2.2778(5), Rh1-S1: 2.3431(5), P1-Rh1-S1: 87.86(2). Selected bond lengths[Å] and angles[°] for* ***II-22****: Ir1-P1: 2.2808(6), Ir1-S1: 2.3301(6), P1-Ir1-S1: 89.15(2).*

As expected for d^8 ML_4 complexes, the metal atoms in both complexes adopt a square planar coordination mode. Both complexes are obtained as racemic mixtures and both enantiomers are present in the unit cell.

II.2. Rhodium(III) and Iridium(III)-complexes

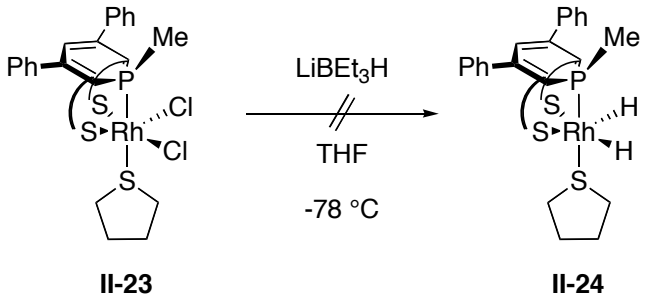
We have previously presented results showing that Ir(I) and Rh(I) complexes of the SPSMe-ligand are extremely reactive species that are hardly isolable. We postulated, that the corresponding Ir(III) or Rh(III) complexes would also be synthetically accessible and much more stable. We imagined, that these complexes could serve as catalyst precursors. The synthesis of a rhodium(III) complex could be readily achieve by the reaction of **II-14** with one equivalent of $[RhCl_3(tht)]$. This reaction leads to the formation of an orange precipitate that is poorly soluble in all organic solvents, yet sufficiently soluble to obtain a ^{31}P NMR spectrum after a long acquisition time. The ^{31}P NMR spectrum shows the formation of a single product with highly coupled characteristic signals at 49.7 ppm (m) and 58.8-61.0 ppm (m). This product is different than the homoleptic complex that was obtained by Doux by the reaction of $[RhCl_3(tht)_3]$ with two equivalents of **II-14**. Therefore it was assumed that the desired product **II-23** was formed (Scheme 22).



Scheme 22: *Synthesis of complex II-23.*

The formation of product **II-23** could be proved by electrospray mass spectrometry by the presence of the $[M\text{-}Cl]^+$ signal at a m/z of 921 with the expected isotopic pattern.

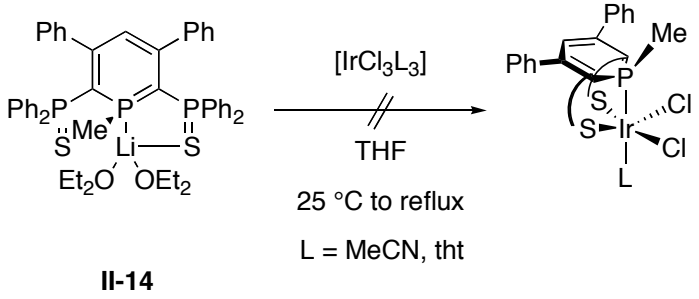
It was tried to transform **II-23** to a dihydride complex **II-24** by the reaction with lithium triethylborohydride in THF at -78 °C (Scheme 23). Unfortunately no product could be isolated from these reactions and only a very complex mixture of products (very broad signals around 35 ppm) could be observed in $^{31}P\{^1H\}$ NMR.



II-23 **II-24**

Scheme 23: *Attempted synthesis of a dihydride complex* ***II-24***.

The synthesis of iridium(III) complexes was attempted by the reaction of **II-14** with $[IrCl_3L_3]$ (L = tht, MeCN). In both cases no reaction could be observed in THF at 25 °C or at reflux after 24 h (Scheme 24).

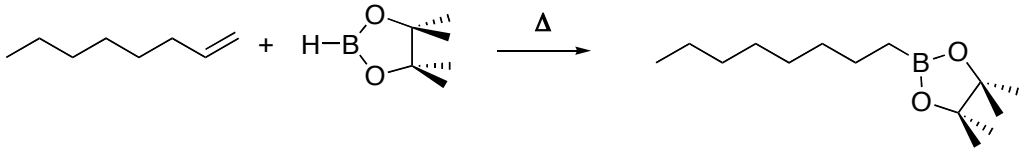


II-14

Scheme 24: *Attempted synthesis of iridium(III) complexes.*

III. CATALYTIC TESTS

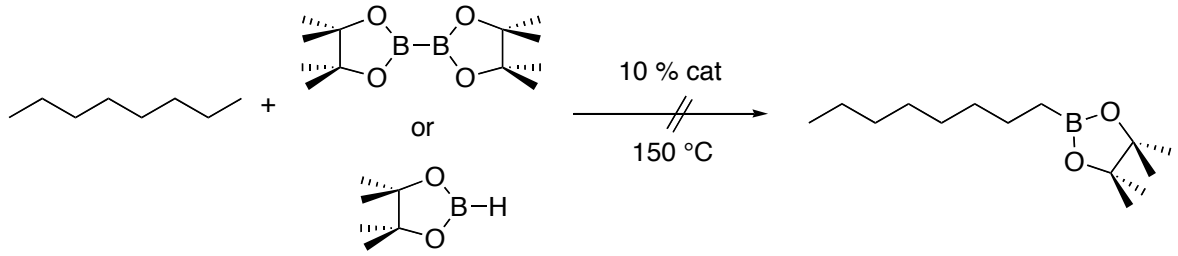
Having in hand several potential catalyst precursors **II-15**, **II-21**, **II-22** and **II-23** (Scheme 25) we decided, to investigate their catalytic activity for the borylation of toluene and *n*-octane. The analysis of the reaction mixture was performed via GC analysis. A standard sample of octyl pinacolboronic ester was obtained by the thermal hydroboration of oct-1-ene with pinacolborane, as reported by Hartwig and coworkers.[13]



Scheme 25: *Thermal hydroboration of oct-1-ene.*

The test reactions for the borylation of octane were carried out in the presence of 10 % of the catalyst precursors **II-15**, **II-21**, **II-22** and **II-23** and 0.5 mmol of Pinacolborane or bispinacol

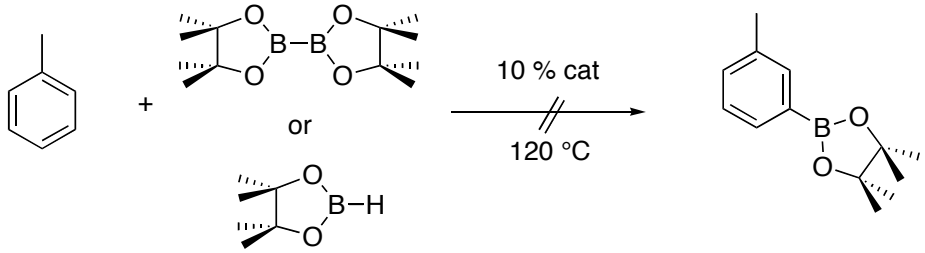
borane in 500 mL of n-octane. As it was not possible to isolate compound **II-15**, the compound was prepared as described above and the borane was added. The mixture was taken to dryness and *n*-octane was added. The other catalyst precursors were isolated and added as solids to a mixture of the corresponding borane and *n*-octane. The reaction mixture was heated to 150 °C in a sealed Schlenk tube (Scheme 26).



Scheme 26: *Attempted borylation of n-octane catalyzed by complexes* ***II-15****,* ***II-21****,* ***II-22*** *and* ***II-23****.*

In all cases not even trace amounts of the desired products could be observed. In contrast, the GC analysis of the reaction mixture revealed the formation of the cyclooctyl pinacolboronic ester in the case of **II-15** and cyclooctenylboronic ester in the case of **II-21** and **II-22** from the hydroboration of the olefin ligands of the catalyst precursors.

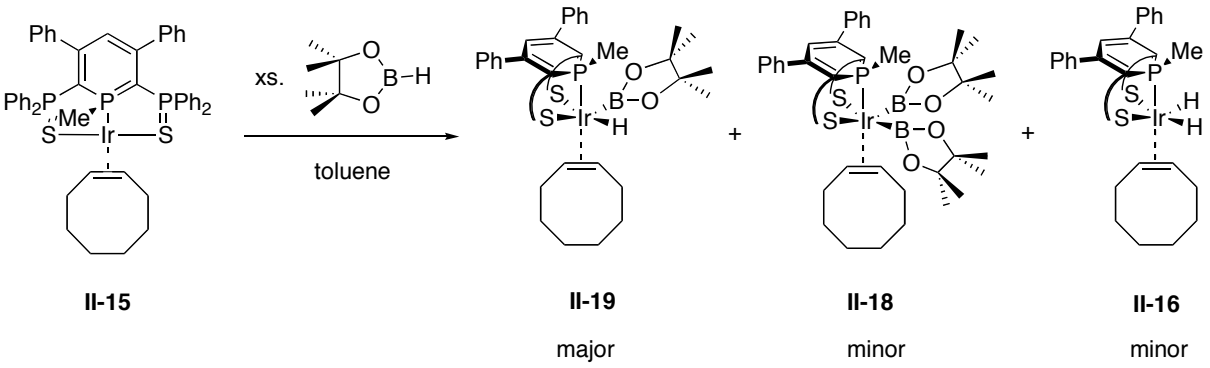
The same reactions were carried out with catalyst precursors **II-15**, **II-21** and **II-22** in the presence of toluene but again no sign of the desire product could be observed (Scheme 27).



Scheme 27: *Attempted borylation of n-octane catalyzed by complexes* ***II-15****,* ***II-21*** *and* ***II-22****.*

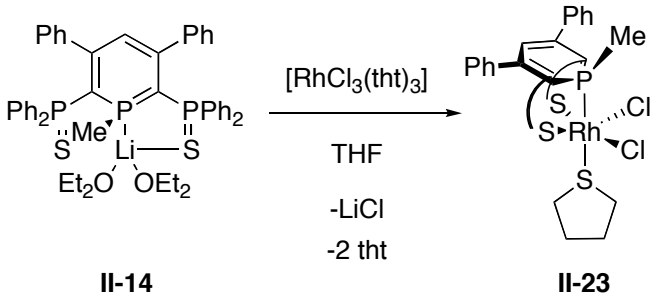
IV. CONCLUSIONS AND PERSPECTIVES

In this chapter the synthesis and reactivity of rhodium and iridium complexes of the tridenate SPS^{Me-} ligand was described. The reactivity of complex **II-15** towards hydrogen, pinacolborane and bispinacolborane was tested. This revealed the formation of a mixture of three products upon reaction with an excess of pinacolborane (Scheme 28).



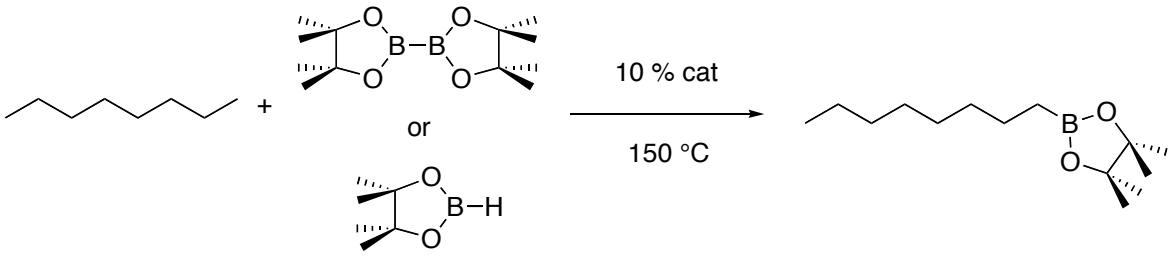
Scheme 28: *Reaction of* ***II-15*** *with an excess of pinacolborane.*

Furthermore a rhodium(III) complex could be isolated from the reaction of **II-14** with [$RhCl_3$(tht)]. This product showed to be very insoluble in all organic solvents and even the acquisition of an $^{31}P\{^1H\}$ was hardly possible. Finally we were able to confirm its formation via ESI-MS.



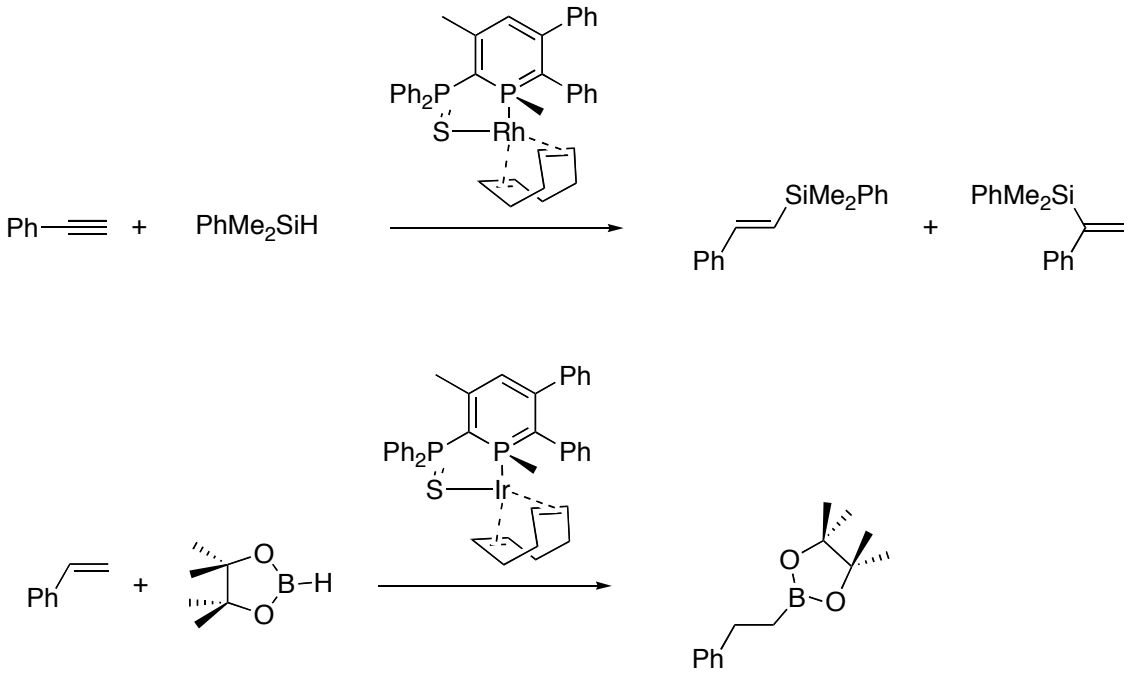
Scheme 29: *Synthesis of a [(SPS^{Me})$RhCl_2$(tht)]* ***II-23****.*

The complexes **II-15**, **II-21**, **II-22** and **II-23** were tested in the borylation of n-octane and toluene but no activity could be observed.



Scheme 30: *Attempted borylation of n-octane catalyzed by complexes* ***II-15****,* ***II-21****,* ***II-22*** *and* ***II-23****.*

However the formation of cyclooctylboryl derivatives could be observed by GC-analysis. Preliminary results indicate that the rhodium complex **II-21** might be a good catalyst for the hydrosilylation of alkynes and the iridium complex **II-22** could be applied to the iridium catalyzed hydroboration of alkynes and olefins.



Scheme 31: *Use of* ***II-21*** *in the hydrosilylation of alkynes and of* ***II-22*** *in the hydroboration of olefins.*

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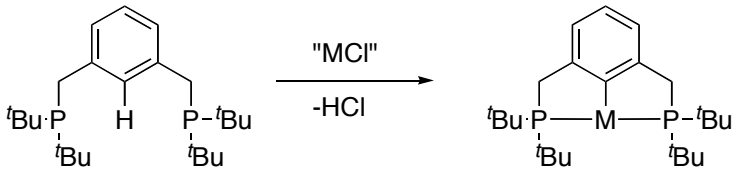
CHAPTER 3: A STRAINED SCS IR PINCER COMPLEX: INTRAMOLECULAR C-H ACTIVATION OF AN AROMATIC RING

I. INTRODUCTION

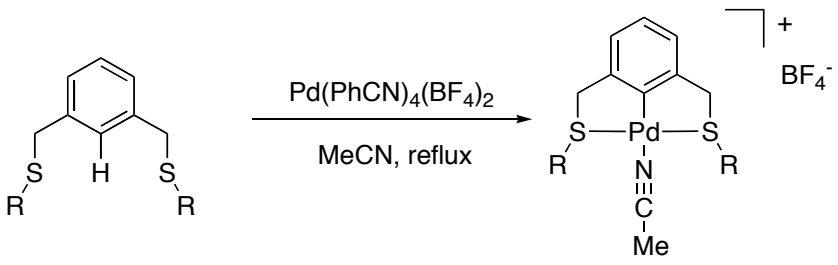
Heteroditopic pincer ligands XCX (X = heteroatom) featuring a carbon atom as central binding site play a crucial role in modern coordination and organometallic chemistry as well as in catalysis.[1] Indeed, it is now well established that subtle structural or electronic changes at the central carbon atom and/or at the ancillary ligands provide a wealth of opportunities to control the reactivity of their complexes. Various systems featuring P, N, O or S as ancillary ligands and anionic aromatic or alkyl binding sites have thus been successfully developed since the pioneering work of Shaw in the 1970s (Scheme 1).[2]



Scheme 1: *First pincer ligand studied by Shaw.*

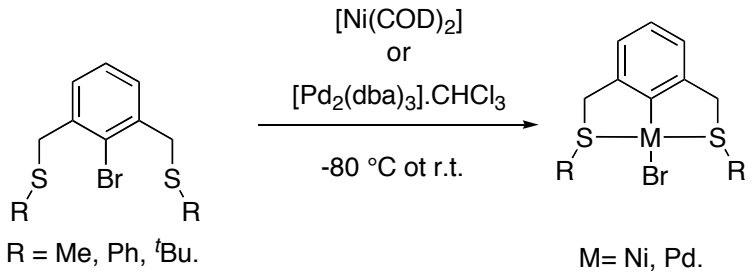
In chapters 1 and 2 the chemistry of palladium, rhodium and iridium complexes of an anionic SPS^R pincer ligand incorporating a central phosphine moiety, was presented. Despite of that it should be noted that systems incorporating sulfur atoms as pendant arms have probably been the less studied so far.[3]

The reported metalation procedures for SCS-pincer arene ligands mainly rely on C-H activation reactions of the arene ligand with cationic metal complexes. For the synthesis of SCS-pincer palladium complexes, mainly $[Pd(PhCN)_4](BF_4)_2]$ has been used as palladium source.



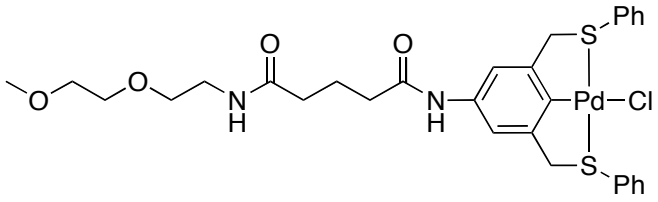
Scheme 2: *Synthesis of SCS-palladium pincer complexes.*

Van Koten and coworker recently reported a strategy relying on the use of the oxidative addition of bromoarene ligands to zerovalent metal precursors such as $[Ni(COD)_2]$ or $[Pd_2(dba)_3].CHCl_3$, allowing for the synthesis of SCS-palladium and nickel complexes under very mild conditions (Scheme 3).[4]



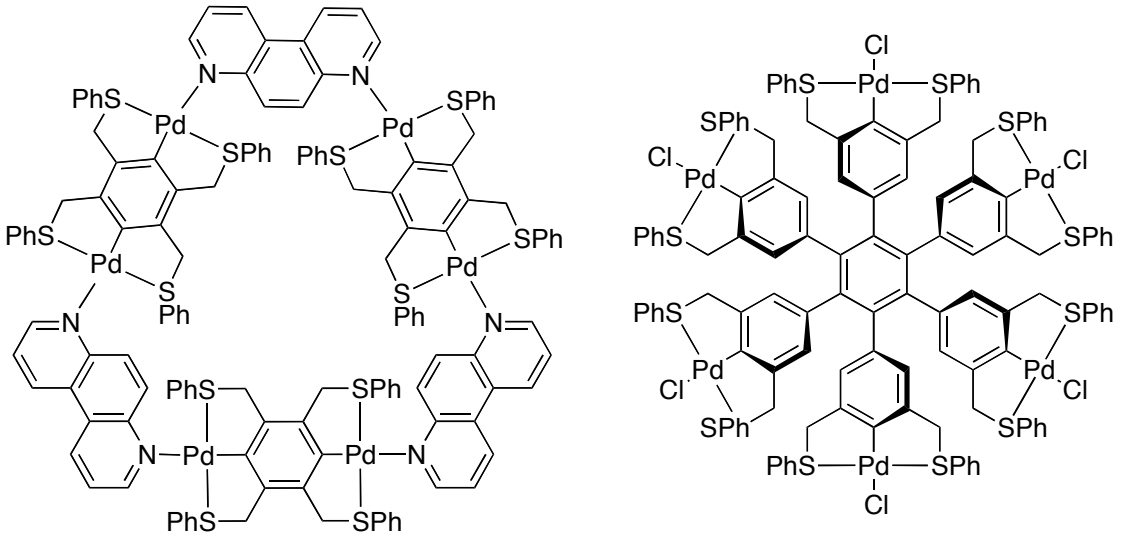
Scheme 3: *Synthesis of SCS-palladium and nickel pincer complexes from zerovalent metal precursors.*

The most prominent application of SCS-palladium complexes is the Heck reaction. The ligand backbone, can be readily functinalized allowing for the introduction of e.g. polyether groups that allow for the easy recovering and recycling of the catalyst by precipitation with diethyl ether (Scheme 4).[5]



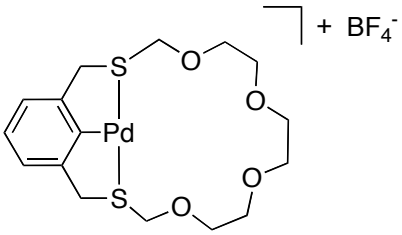
Scheme 4: *Recyclable SCS-palladium catalyst for the Heck reaction.*

Furthermore, SCS-pincer complexes were used as building blocks in supramolecular chemistry and for the synthesis of metallodendrimers (Scheme 5).



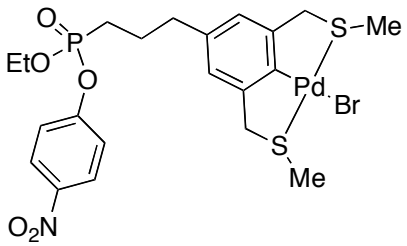
Scheme 5: *Application of pincer complexes in supramolecular and dendrimer chemistry.*

Loeb and coworkers developed metalloreceptors by the combination of SCS-palladium complexes and macrocyclic polyether chains that allow for the molecular recognition of nucleobases specific guest molecules.[6-9] For this purpose, the sulfur donors were functionalized with bridging polyether or calixarene substituents that were to act as receptors for secondary host - guest interactions. As a result, Pd - coordination of a guest molecule is assisted by secondary hydrogen bonding of guest protons to crown ether oxygen atoms or π-stacking interactions with calixarenes (Scheme 6). Modification of the ring size and oxygen distribution in the dithiamacrocycle allowed for the optimization of the binding pockets of these metalloreceptors. Various host - guest complexes have been prepared with amines, imines, and water.



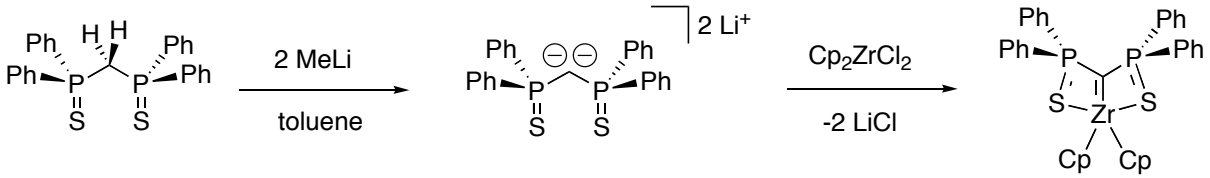
Scheme 6: *SCS-palladium based metalloreceptors.*

Van Koten and coworkers reported the incorporation of SCS-palladium catalyst into the active site of Lipase allowing for the elaboration of transition metal/enzyme hybrid catalysts (Scheme 7).[10]



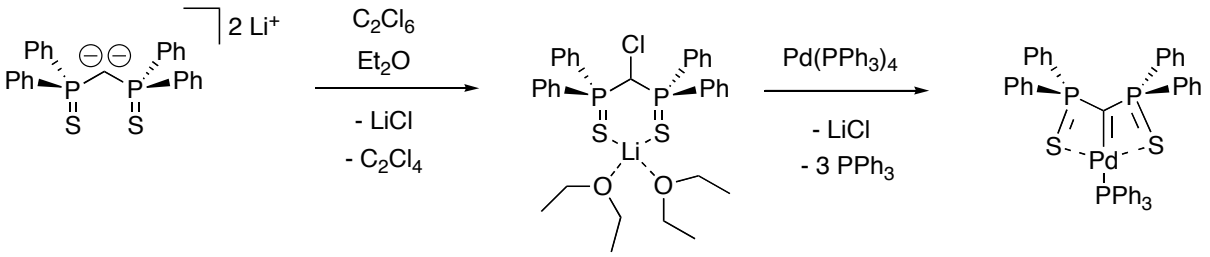
Scheme 7: *SCS-pincer complex with a p-nitrophenol phosphonate moiety allowing for the anchoring in the active site of Lipase.*

Throughout the last years the chemistry of dianionic SCS pincer ligands featuring two phosphino sulfide ancillary groups has been investigated in our group. The dianion of $dppmS_2$ that can be obtained by the reaction of $dppmS_2$ with MeLi in toluene can serves as a carbene precursor, and by the reaction with Cp_2ZrCl_2, pincer carbene complexes were obtained (Scheme 8).[11]



Scheme 8: *Synthesis of a SCS-Zr-carbene complex.*

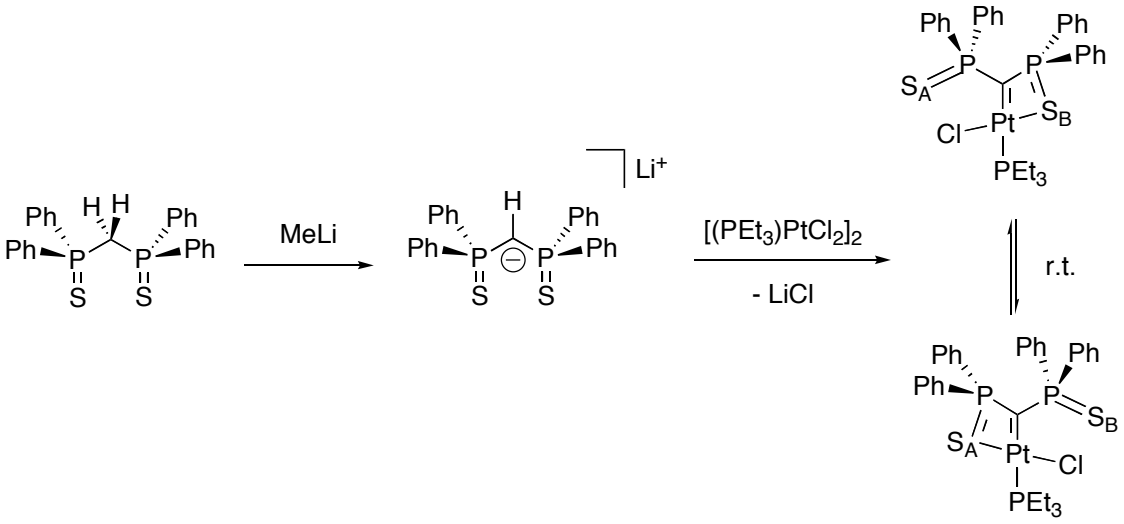
Interestingly the $dppmS_2Li_2$ can be reacted with hexachloroethane to give the carbenoide $dppmS_2LiCl$, which is stable at room temperature and that reacts with e.g. with $Pd(PPh_3)_4$ to give a palladium carbene complex (Scheme 9).[12]



Scheme 9: *Synthesis of a room temperature stable carbenoide and its reaction with $Pd(PPh_3)_4$.*

The use of $dppmS_2Li_2$ and $dppmS_2LiCl$ has allowed for the synthesis of various transition metal, lanthanide and even actinide carbene complexes throughout the last 5 years.[11-19]

In contrast, only one example for the use of the monoanionic $dppmS_2^-$ ligand has been reported so far. Pidcock and coworkers reported the synthesis of $dppmS_2Li$ by deprotonation of $dppmS_2$ with methyl lithium.[20] The reaction of this anion with $[(PEt_3)PtCl_2]_2$ led to the formation of a platinum complex in which only one of the pendant phosphinesulfide ligands is coordinated. The authors could show *via* NMR spectroscopy that the PPh_2S groups are in rapid exchange at room temperature (Scheme 10).[20]



Scheme 10: *Synthesis of [(dppmS$_2$)Pt(PEt$_3$)Cl].*

In this chapter we are going to study the reactivity of the Bis(diphenylphosphinosulfide) methanide anion towards the $[Ir(COE)_2Cl]_2$ precursor (COE = cyclooctene).

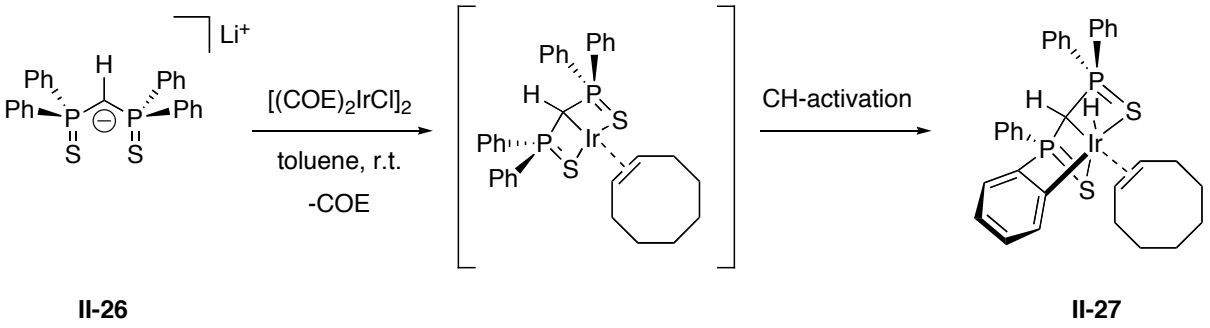
II. SYNTHESIS

Ligand **II-26** was prepared according to a reported procedure that involves the reaction of Bis(diphenyl)phosphinosulfide methane **II-25** with methyllithium in toluene at low temperature (Scheme 11).[20]

II-25 **II-26**

Scheme 11: *Synthesis of ligand **II-26**.*

The reaction of **II-26** with half an equivalent of $[Ir(COE)_2Cl]_2$ in toluene at low temperature led to the quantitative formation of the air stable compound **II-27** whose formulation did not correspond to the expected symmetrical complex (Scheme 12).



Scheme 12: *Reaction of* ***II-26*** *with 0.5* $[Ir(COE)_2Cl]_2$.

Indeed, the ^{31}P NMR spectrum only indicates that complex **II-27** features two magnetically inequivalent phosphorus atoms (AB spin system pattern) at δ = - 0.3 and 60.4 ppm with a $^2J_{PP}$ = 2.9 Hz. The second important information is given by the ^1H NMR spectrum which reveals that complex **II-27** is an hydrido species (doublet, δ -18.10 ppm, J_{PH}= 4.4 Hz) and that one molecule of cyclooctene is still coordinated.

Definitive evidence on the structure of **II-27** was given by an X-ray crystal structure analysis which was carried out on single crystals obtained by the slow diffusion of hexanes into a dichloromethane solution of the complex. A view of one molecule of complex **II-27** is presented in Figure 1.

Complex **II-27** is a tricyclic species which indeed features an Ir-H bond resulting from the insertion of iridium into C-H bond of a phenyl ring of the SCS ligand.[21, 22] This accounts for the non equivalency of the two phosphorus atoms observed in the ^{31}P NMR spectrum. To complete the coordination sphere the two sulfur atoms are coordinated onto the metal in a *cis*-fashion and the central atom of ligand **II-26** is located *trans* to the olefinic ligand. Not surprisingly, **II-27** adopts a nearly octahedral geometry as expected for a complex having a d^6 electronic configuration. The Ir(1)-C(1) alkyl and Ir(1)-C(3) aryl bond distances at 2.169(3) Å and 2.030(3) Å respectively fall in the usual range according to literature data as well as the Ir-H bond (1.46(4) Å).[23-27] Another important structural feature concerns the significant angular constraint put on the phosphorus atom in the five-membered metallacyclic ring (P(1)-C(2)-C(3) angle of 106.8(2)° compared to 120° in other P-Ph groups). This geometric constraint probably accounts for the important upfield shift observed in ^{31}P NMR spectroscopy.

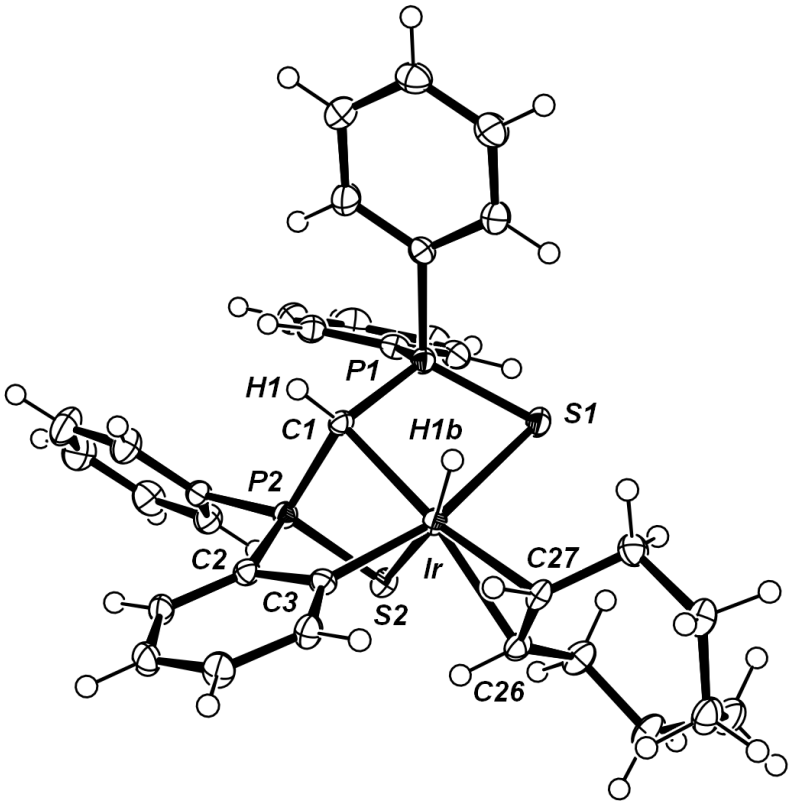
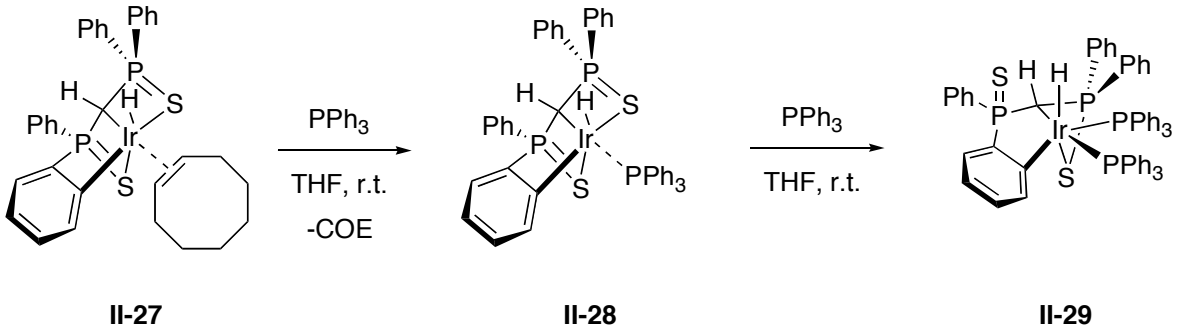


Figure 1: *Molecular structure of* ***II-27****. (ORTEP-plot, thermal ellipsoids, at a 50% probability level.) Selected bond distances (Å) and angles (°): Ir(1)-S(1) 2.587(1); Ir(1)-S(2) 2.564(1); Ir(1)-C(3) 2.030(3); Ir(1)-C(1) 2.169(3); Ir(1)-H(1b) 1.46(4); Ir(1)-C(27) 2.209(4); Ir(1)-C(26) 2.210(3); S(1)-P(1) 1.996(1); S(2)-P(2) 2.002(1); P(1)-C(1) 1.785(3); P(1)-C(2) 1.794(4). P(1)-C(2)-C(3) 106.8(2); P(2)-C(1)-P(1) 124.7(2); P(1)-S(1)-Ir(1) 71.01(4); P(2)-S(2)-Ir(1) 78.62(4); C(1)-P(1)-S(1) 101.9(1); C(1)-P(2)-S(2) 106.8(1); C(3)-Ir(1)-C(1) 85.2(1); S(2)-Ir(1)-S(1) 86.34(3); S(2)-Ir(1)-H(1B) 87(2); S(1)-Ir(1)-H(1B) 163(2).*

In terms of reactivity, complex **II-27** underwent selectively and successively two displacements of ligands with triphenylphosphine (Scheme 13).



Scheme 13: *Reaction of* ***II-27*** *with* PPh_3.

Thus, reaction of **II-27** in THF at room temperature with one equivalent of PPh_3 cleanly led to the displacement of the cyclooctene ligand to afford a single new complex **II-28,** which was fully characterized by NMR spectroscopy and elemental analysis. The spectral data revealed analogous pattern for the SCS ligand in **II-27** and **II-28,** in terms of ^{31}P and ^{1}H chemical shifts, suggesting a similar configuration around the metal center. An X-ray crystal structure analysis was carried out on single crystals of **II-28** to verify that no isomerization occurred during the exchange process. Single crystals of **II-28** were obtained by slowly evaporation of a concentrated solution of **II-28** in dichloromethane and confirmed that the incoming PPh_3 ligand is coordinated *trans* to the alkyl ligand, as is COE in complex **II-27** (see Figure 2).

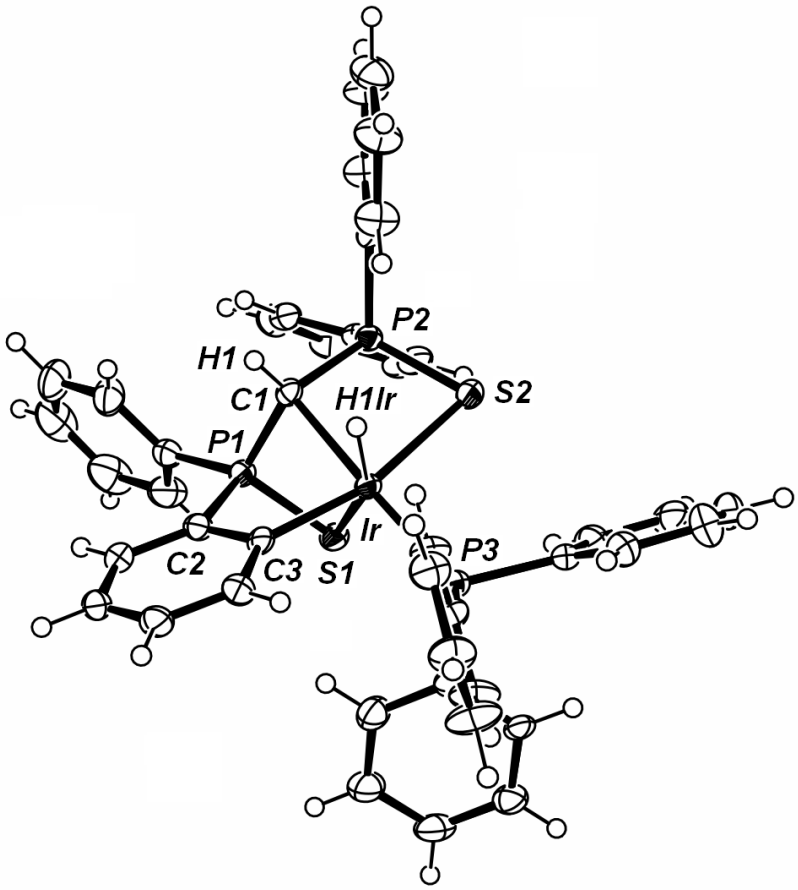


Figure 2: *Molecular structure of one molecule of* ***II-28****. (ORTEP-plot, thermal ellipsoids are drawn at the 50% probability level.) Selected bond distances (Å) and angles (°): Ir(1)-S(1) 2.599(2); Ir(1)-S(2) 2.520(2); Ir(1)-C(3) 2.047(6); Ir(1)-C(1) 2.206(6); Ir(1)-H(1Ir) 1.70(1); Ir(1)-P(3) 2.259(2); S(1)-P(1) 2.004(2) S(2)-P (2) 2.005(2); P(1)-C(1) 1.759(7); P(1)-C(2) 1.797(7). P(1)-C(2)-C(3) 107.5(5); P(2)-C(1)-P(1) 122.4(4); P(1)-S(1)-Ir(1) 70.52(7); P(2)-S(2)-Ir(1) 80.96(7); C(1)-P(1)-S(1) 102.8(2); C(1)-P(2)-S(2) 104.9(2); C(3)-Ir(1)-C(1) 85.7(2); S(2)-Ir(1)-S(1) 87.65(6); S(2)-Ir(1)-H(1Ir) 95(3); S(1)-Ir(1)-H(1B) 156(3).*

Addition of a second equivalent of PPh_3 led to the formation of a second complex **II-29** which, as indicated by ^{31}P NMR spectroscopy, features four magnetically different phosphorus atoms. Interestingly this data also revealed that the most shielded signal assigned to the "strained" phosphinosulfide group is now significantly downfield shifted (from δ = - 0.3 ppm in **II-27** and - 1.1 ppm in **II-28** to + 76.7 ppm in **II-29**). Alternatively, complex **II-29** could be synthesized by reacting two equivalents of PPh_3 with **II-27** in a single step in THF at room temperature. This complex was fully characterized by NMR spectroscopy and elemental analysis, as well as by an X-ray crystal structure analysis. A view of one molecule of complex **II-29** is presented in Figure 3.

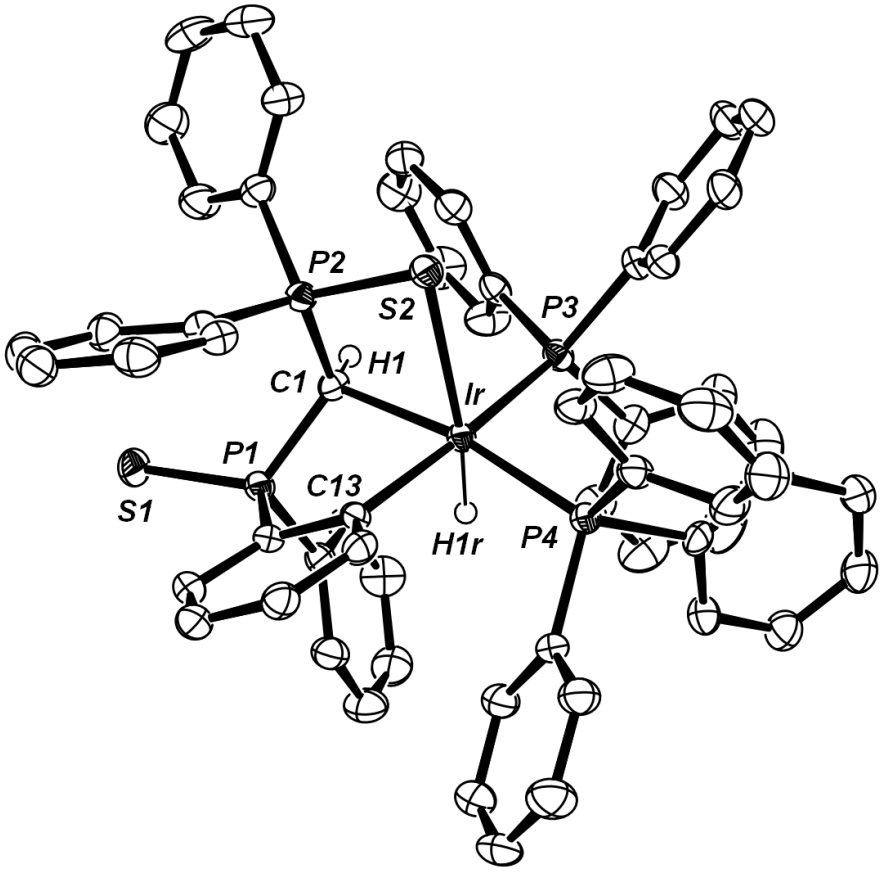


Figure 3: *Molecular structure of one molecule of* ***II-29****. (ORTEP-plot, thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Ir(1)-S(1) 2.587(1); Ir(1)-S(2) 2.564(1); Ir(1)-C(3) 2.030(3); Ir(1)-C(1) 2.169(3); Ir(1)-H(1b) 1.46(4); Ir(1)-C(27) 2.209(4); Ir(1)-C(26) 2.210(3); S(1)-P(1) 1.996(1); S(2)-P(2) 2.002(1); P(1)-C(1) 1.785(3); P(1)-C(2) 1.794(4). P(1)-C(2)-C(3) 106.8(2); P(2)-C(1)-P(1) 124.7(2); P(1)-S(1)-Ir(1) 71.01(4); P(2)-S(2)-Ir(1) 78.62(4); C(1)-P(1)-S(1) 101.9(1); C(1)-P(2)-S(2) 106.8(1); C(3)-Ir(1)-C(1) 85.2(1); S(2)-Ir(1)-S(1) 86.34(3); S(2)-Ir(1)-H(1B) 87(2); S(1)-Ir(1)-H(1B) 163(2).*

As expected from the ^{31}P NMR data and confirmed by crystallography, the "strained" phosphinosulfide ligand has been displaced from the metal. As can be seen in the following

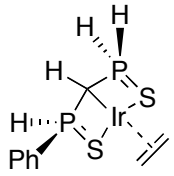
scheme a rearrangement took place and the second phosphinosulfide group is now located *trans* to the hydrido ligand, the two PPh_3 ligands being *trans* to the alkyl and aryl ligands.

III. THEORETICAL STUDY

A DFT theoretical study was carried out to get further insights on the formation of complex **II-27** as well as on its reactivity.

III.1 Computational model

All calculations were carried out using the Gaussian 03 set of programs[28] with the B3PW91 functional[29, 30] in combination with the 6-31+G* basis set for all non-metal-bound atoms (C, H, P), the 6-311+G* for all metal-bound-atoms (C, H, P, S) and the LANL2DZ basis set[31] for iridium with an additional f-polarization function.[32] A model, in which the three innocent phenyl groups and the cyclooctene ligand were replaced by H atoms and one molecule of C_2H_4 respectively, was used (Scheme 14).



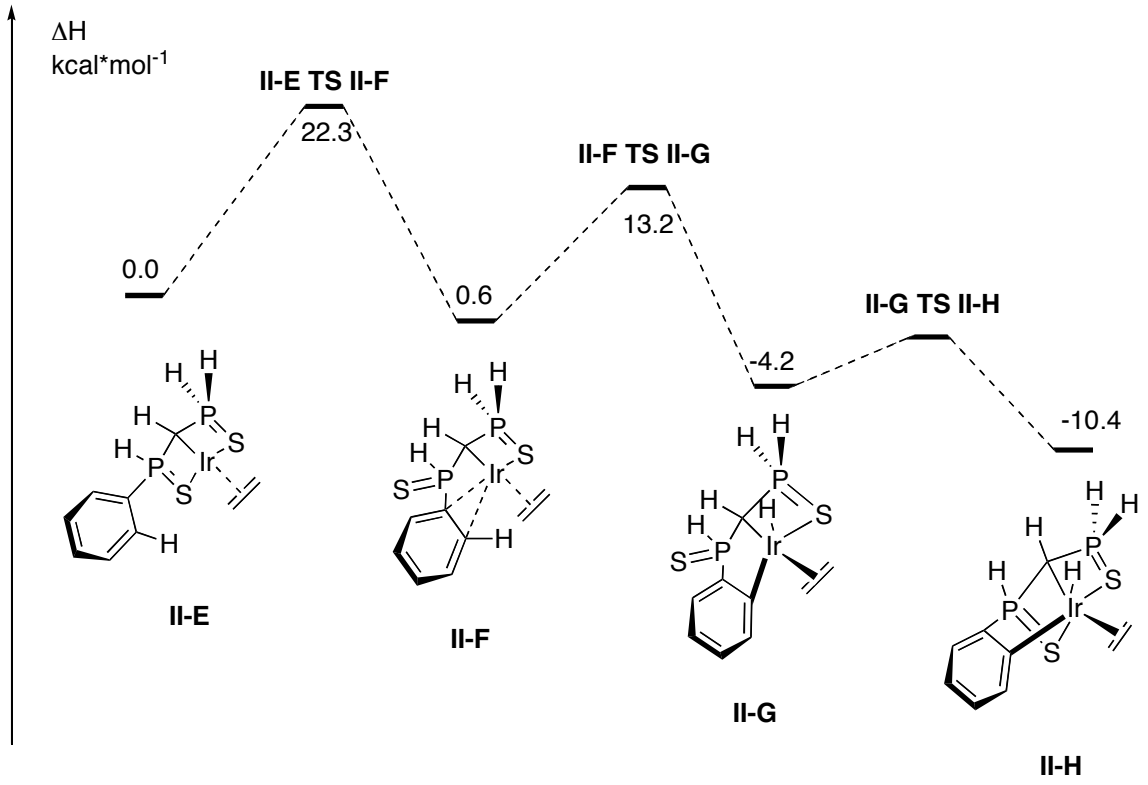
II-E

Scheme 14: *Model compound II-E used as a starting point for the theoretical study.*

III.2 Computational study

We first assumed that reaction of **II-26** with the Ir precursor affords in a first step the square planar Ir(I) complex **II-E** featuring the ligand (coordinated through the central carbon atom and the two ancillary sulphur ligands) and only one molecule of olefin. The calculated mechanism of the whole transformation from **II-E** leading to the Ir(III) hydrido complex **II-H** is presented in Scheme 3. The first step, which involves the decoordination of one phosphinosulfide ligand, is a prerequisite for the oxidative addition of the C-H bond, as the direct insertion is not geometrically feasible. (**Note:** It has recently been reported, that pincer complexes bearing hemilabile donor atoms show interesting reactivity and a superior activity in several catalytic processes, see for example[33-36]) Optimisation of a three coordinated 14 VE complex in which one phosphinosulfide has been deliberately moved away from the metal, yielded structure **II-F** in which one C=C bond of the aromatic ring is η^2-coordinated onto the Ir

center. As can be seen this step is the rate-limiting step and requires an activation energy of $\Delta H^{\neq}$ = +22.3 kcal/mol (**II-E TS II-F**). This electron rich (Ir(I)), coordinatively unsaturated intermediate logically inserts into the most accessible C-H bond (intramolecularly), to afford the pentacoordinated 16 VE hydrido complex **II-G**. This process was found to be slightly exothermic (ΔH = -4.8 kcal/mol) and requires a low activation energy ($\Delta H^{\neq}$ = +12.6 kcal/mol for **II-F TS II-G**). A view of the transition state **II-F TS II-G** is presented in Figure 4. Finally, the last step which involves the coordination of the pendant phosphinosulfide ligand affords the hexacoordinated 18VE complex **IV**. This step was also found to be slightly exothermic (ΔH = -6.2 kcal/mol) and requires a very low activation energy ($\Delta H^{\neq}$ = +1.1 kcal/mol). The overall energetic pathway is consistent with the experimental conditions used (the reaction proceeds at room temperature) and the fact that the whole process is exothermic with the first step controlling the kinetics explains why intermediate complexes **II-E**, **II-F** and **II-G** are never observed in solution.



Scheme 15: *Computed energetic pathway for the conversion of II-E into II-H.*

Finally, this reaction pathway also rationalizes the facile reactivity of complex **II-27** (model **II-H**) towards ligand displacement. Indeed, both coordinatively unsaturated complexes **II-F** and **II-G** are found at 7.3 kcal/mol and 23.5 kcal/mol higher respectively. The substitution of COE in **II-27** from either **II-F** or **II-G** (more likely from **II-G**) occurring rapidly at room temperature is consistent with the DFT calculations.

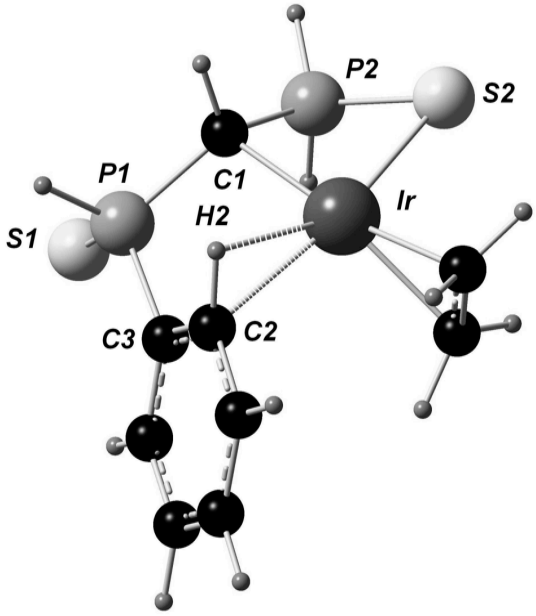
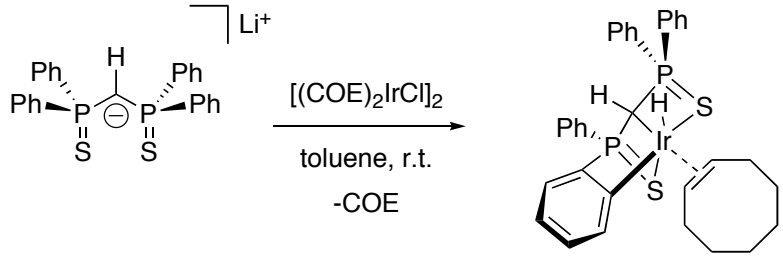


Figure 4: *View of the optimized structure of* ***II-F TS II-G****. Significant bond distances (Å) and bond angles (°). Ir-S(2) 2.355; Ir-C(1) 2.125; P(1)-(S1) 1.964; P(2)-S(2) 2.036; P(1)-C(1) 1.799; P(2)-C(1) 1.777; C(2)-C(3) 1.408; Ir-C(2) 2.379; Ir-H(2) 2.166; C(2)-H(2) 1.109; P(1)-C(1)-P(2) 119.622; P(2)-S(2)-Ir 77.263; S(2)-Ir-C(1) 80.564; P(1)-C(3)-C(2) 119.756; C(3); C(2)-H(2) 120.510; C(2)-(H2)-Ir 86.848; H(2)-Ir-C(2) 27.733; P(1)-C(3)-C(2)-H(2) 6.203*

IV. CONCLUSIONS AND PERSPECTIVES

In conclusion we have shown that monoanion **II-26** behaves as a strained pincer ligand and provides an interesting entry to a new class of highly reactive 16 VE Ir(I) complexes (Scheme 16).

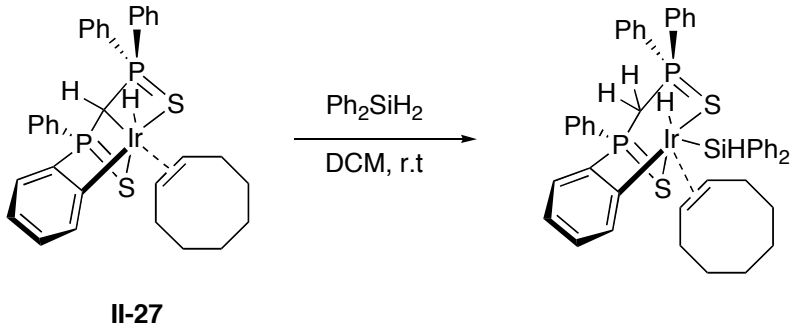


II-26 **II-27**

Scheme 16: *Formation of complex* ***II-27****.*

Furthermore, DFT calculations suggest that only a very weak activation energy is needed to promote the formation of the Ir(III)-H hydrido complex through intramolecular oxidative addition of a C-H bond of one pendant aromatic ring.

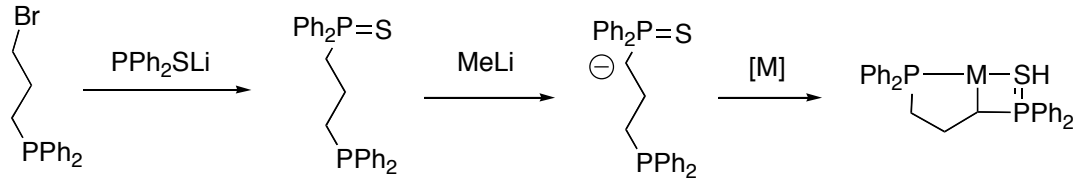
Preliminary studies on the reactivity of complex **II-27** with diphenylsilane showed the formation of iridium silyl complexes (Scheme 17). The isolation of this product is on the way together with mechanistic studies.



II-27

Scheme 17: *Reaction of complex II-27 with diphenylsilane.*

During this study it could be observed, that the geometry of the ligand **II-26** is relatively constraint in the transition metal complexes. This hemilabile character of the phosphinesulfide ligand is very interesting but can also be a problem in mechanistic studies where it might be interesting to isolate reactive intermediates. Therefore it could be envisaged to synthesize phosphine-phosphinesulfide complexes with more than one CH_2 spacer group allowing for the better stabilization of transition metal centers *via* the phosphine and the deprotonation in the α-position of the phosphinesulfide group (Scheme 18).



Scheme 18: *Synthesis of a new anionic SCP pincer ligand.*

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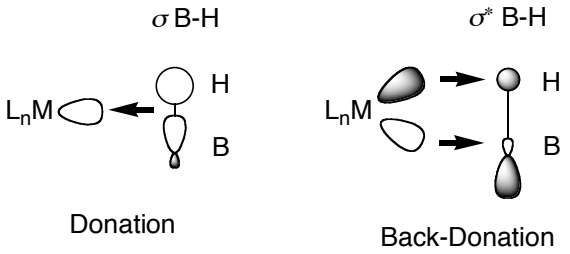
CHAPTER 4: BONDING MODE OF A NEW BIS PHOSPHINE-BORANE ALKYL LIGAND TO A RH(I) SPECIES.

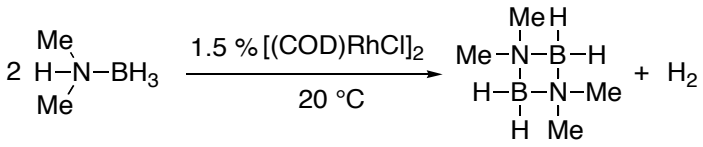
I. INTRODUCTION

The study of B-H bond interactions with transition metal centers is of high significance.[1-6] They are believed to be of primary importance in metal-catalyzed hydroboration and borylation processes involving neutral trivalent boranes and *true* σ-borane complexes (Scheme 1).



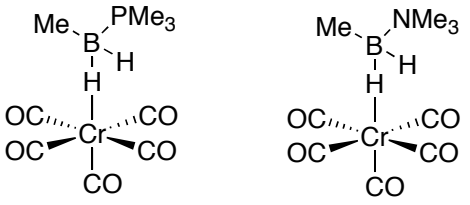
Scheme 1: *Classical Chatt, Dewar, Duncanson model for the σ-B-H coordination to a metal center.*

After the recognition of NH_3-BH_3 and related borane-Lewis base adducts as potential hydrogen storage materials, very recent studies have focused on metal-mediated dehydrocoupling and dehydrogenation reactions (Scheme 2).[7-14]



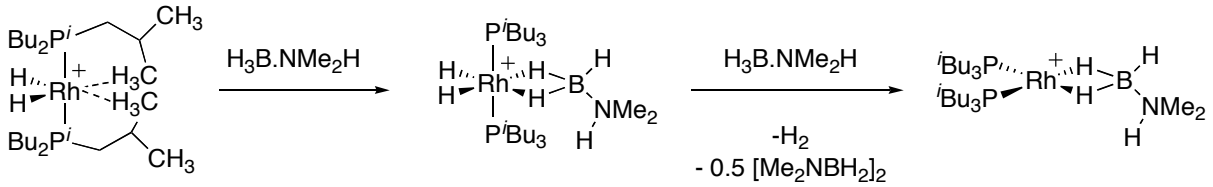
Scheme 2: *Dehydrocoupling of dimethylamineborane catalyzed by rhodium.*

Often invoked or computed as η^1-B–H intermediates in these catalytic systems,[15-17] a number of stable neutral or cationic M(η^1-BH_2R.L) (M = Cr, W, Mn, Ru; L = phosphine or amine) end-on complexes have been isolated affording a better understanding of the M-H-B linkage (Scheme 3).[18, 19]



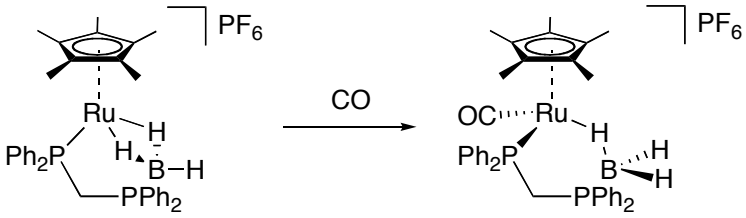
Scheme 3: *Stable σ-BH Cr complexes reported by Shimoi and coworkers..*

Interestingly, complexes displaying a κ^2 H,H coordination of $BH_2R.L$ are scarce[14] and mainly limited to late transition metal (Ru, Rh) that incorporate bidentate chelating ligands displaying only one $BH_2R.L$ moiety(Scheme 4).[20-22]



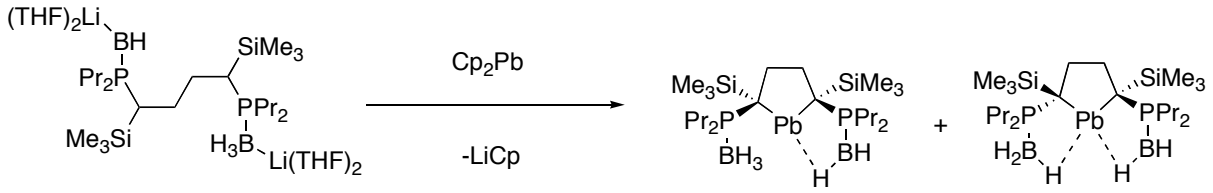
Scheme 4: *Reaction of BH_3NMe_2H with a cationic rhodium complex.*

Weller and co-workers showed that upon addition of a two-electron ligand (such as CO) a change from a κ^2bonding mode to a η^1 end-on coordination mode can be observed (Scheme 5).[21, 22]



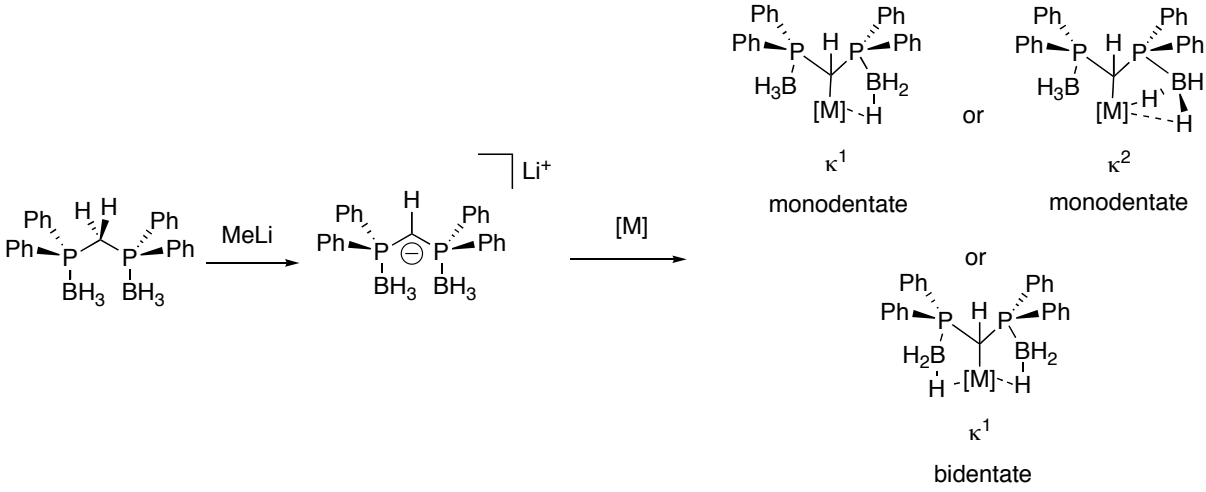
Scheme 5: *Change of the bonding mode upon addition of CO.*

Izod and coworkers recently reported the stabilization of monomeric dialkylstanylenes and plumbylenes with dianionic phosphineborane ligands. In this case, the monomeric form of these highly reactive metallacycles that usually rapidly dimerize is stabilized via agostic B-H interactions to the metal center (Scheme 6).



Scheme 6: *Synthesis of dialkylplumbylenes by Izod and coworkers.*

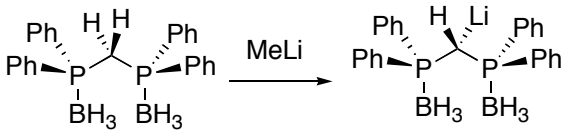
In chapter 3, we have studied the synthesis of iridium complexes of an anionic SCS pincer ligand based on dppm. The bis-borane adduct of dppm is known and the deprotonation of $dmpm(BH_3)_2$ was already studied by Schmidbaur in 1979. Therefore it could be imagined that $dppm(BH_3)_2$ would equally allow for the synthesis of an anionic ligand, although no transition metal complex of this type of ligand has been reported to date. We were interested in the reactivity of highly reactive transition metal precursors such as $[Rh(COD)Cl]_2$ that are usually used in the dehydrogenation of phosphineboranes.



Scheme 7: *Envisaged use of the anionic ligand $dppm(BH_3)_2$ as a ligand in coordination chemistry.*

II. SYNTHESIS

The reaction of compound **II-30** with one equivalent of MeLi (Et_2O solution) in toluene at -78°C followed by warming to room temperature was quantitative as shown by ^{31}P and ^{11}B NMR (new broad singlet at 9 ppm for **II-31** *vs* 15 ppm for **II-30** in ^{31}P and a broad doublet at -33.2 ppm in ^{11}B with J_{PB}= 64 Hz for **II-31** vs 36.6 ppm for **II-30**).



II-30 **II-31**

Scheme 8: *Synthesis of ligand* ***II-31***.

The anion **II-31** was isolated by simple evaporation to dryness of the crude mixture. The signal for the methanide proton is seen in **II-31** as a triplet at 1.37 ppm ($^2J_{HP}$=11Hz), at much higher field than the methylene signal in **II-30** (3.18 ppm). Despite extensive drying under vacuum, the presence of *ca.* 3/4 equivalent of Et_2O per anion **II-31** was seen in the ^{1}H NMR spectrum.

Crystals suitable for X-Ray analysis were obtained from a toluene/hexanes diffusion. The structure is quite surprising (Figure 1), with two monoanionic fragments having very different geometries, but confirms the existence of anion **II-31**.

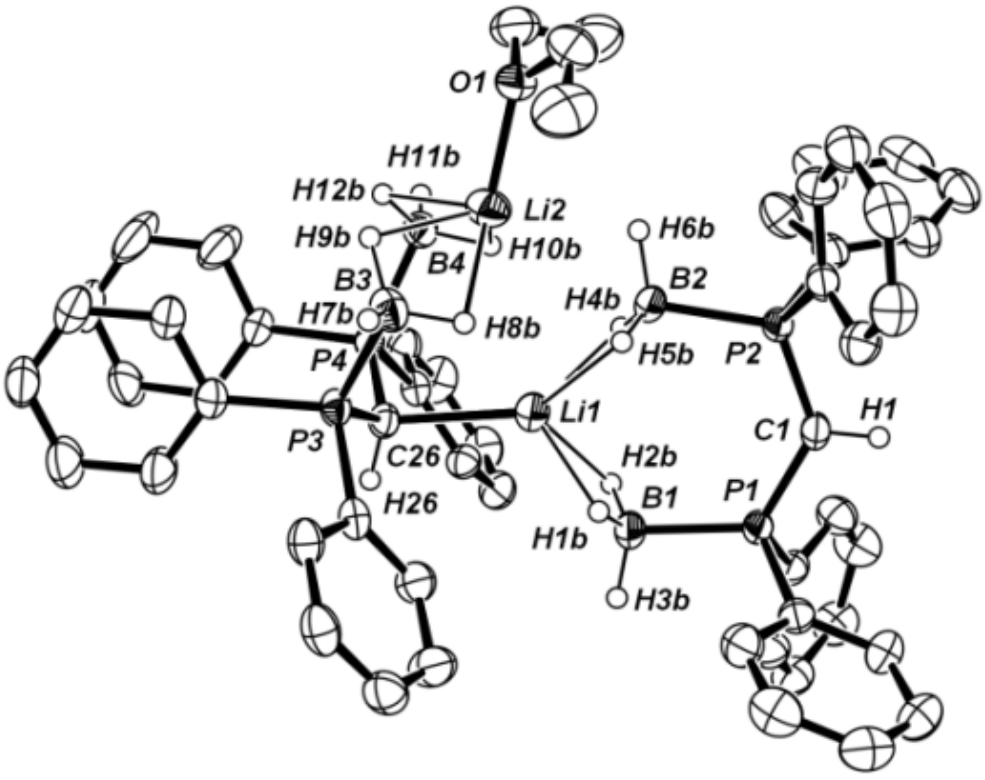
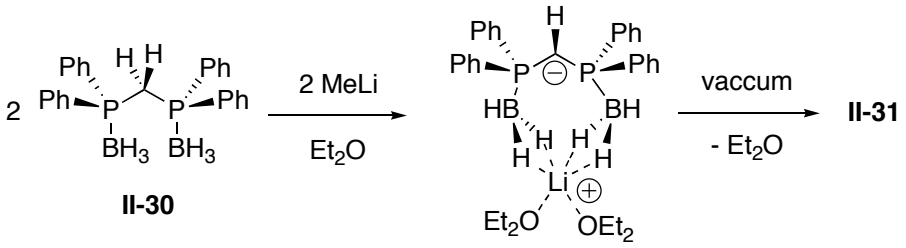


Figure 1: *Molecular structure of compound* ***II-31*** *(ORTEP-Plot (50 % Thermal ellipsoids, selected hydrogen atoms were omitted for clarity). Selected bond distances (A) and angles (°): P1-C1:1.719(2), B1-H1b: 1.1208, B1-H3b: 1.0831, Li1-C26: 2.295(4), P1-C1-P2: 130.7(1), P3-C26-P4:120.9(1), Li2-O1:1.905(4).*

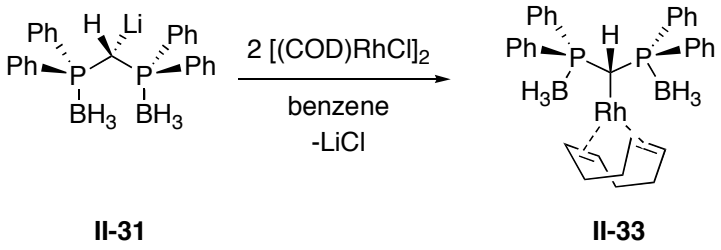
The structure of **II-31** is rather surprising and we would have expected the formation of a solvated monomeric lithium complex **II-32**. It can be imagined that **II-31** is formed from such a species upon extensive drying of the reaction mixture under vacuum.



Scheme 9: *Formation of* ***II-31*** *upon extensive drying of* ***II-32*** *under vacuum.*

The molecular structure of **II-32** has recently been reported by Westerhausen and coworkers.[23]

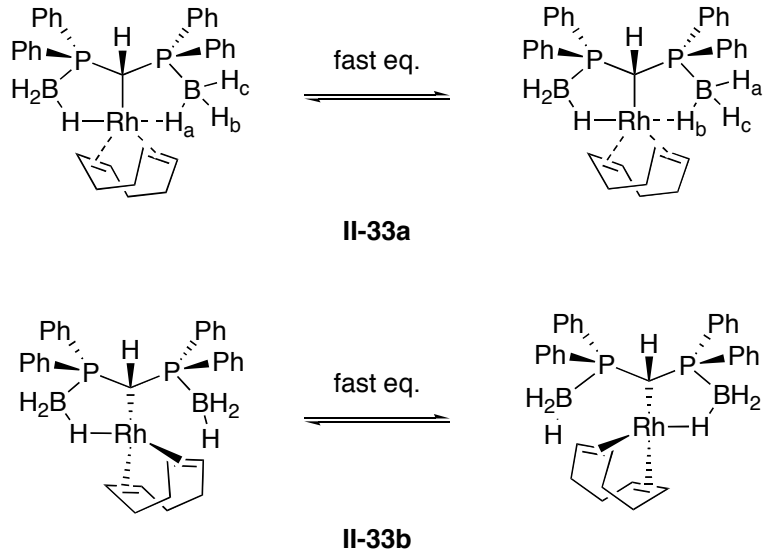
Addition of a benzene solution of anion **II-31** to a benzene solution of ½ equiv. of $[Rh(COD)Cl]_2$ led to the formation of a brown solution and precipitation of LiCl. $^{31}P\{^1H\}$ NMR spectroscopy of the crude reaction mixture showed the appearance of a single new complex **II-33**, characterized by a broad singlet at 5 ppm (Scheme 10).



Scheme 10: *Reaction of* ***II-31*** *with [(COD)RhCl]₂.*

After isolation, this complex was fully characterized by NMR, elemental analysis and X-ray diffraction. In the ^1H NMR spectrum, a very weak broad signal for the BH_3 moieties is observed, as expected because of the potential coupling with three other NMR active nuclei (^{11}B, ^{31}P and ^{105}Rh) in addition to the quadrupolar nature of the ^{11}B nucleus. Selective decoupling experiments were therefore carried out. The $^1H\{^{11}B,^{31}P\}$ spectrum (353 K, C_7D_8) shows a well resolved doublet at 0.81 ppm, allowing to extract the H-Rh coupling constant of 3.4 Hz. The $^1H\{^{11}B\}$ spectrum presents a poorly resolved doublet of doublet, which allows the measurement of the J_{PH} coupling constant ($^2J_{PH}$ = 8.9 Hz). Interestingly, only one signal is found for the two BH_3 moieties suggesting either the coordination of both BH_3 on the Rh center (**II-33a**, Scheme 11, pentacoordinated Rh species, with fast equilibration process for each BH_3) or a fast dynamic

process equilibrating a coordinated and non coordinated BH_3 moieties (**II-33b**, Scheme 11, tetracoordinated Rh species, and fast equilibration process for each BH_3 once decoordinated) as well as fast rotation of the two BH_3 groups. Finally, the alkyl proton is only slightly upfield shifted (1.11 ppm, t, $^2J_{HP}$ = 11.07 Hz) in **II-33** compared to the methanide proton in **II-31**.



Scheme 11: *Envisaged dynamic processes in* ***II-33*****.**

The equivalence of the BH_3 moities and the absence of any hydride resonance in the ^1H NMR spectrum confirm that the complex has not undergone any oxidative addition of a B-H bond. Variable temperature experiments were carried out, but lowering the temperature down to 190 K (in solution) did not lead to any appreciable modification of the $^1H\{^{11}B,^{31}P\}$ spectrum of the BH_3 signal. This is in agreement with a low energy barrier for the B-H interconversion process (lower than 5 kcal/mol) (*vide infra*). Suitable crystals for X-ray analysis were obtained from a slow diffusion of hexanes into a benzene solution of the complex. The structure is presented in Fig. 2. It shows a distorted square planar geometry around the Rh center, as depicted for **II-33b** in Scheme 10. The C1 carbon is coordinated to the metal with a Rh-C1 distance of 2.157(2)Å (typical of Rh-C single bond)[24, 25] and *trans* to one double bond of the COD ligand (angle C1 atom mid C26-C33 bond: 161.8°). The metrical parameters in the BPCPB ligand do not appear to have been significantly modified upon coordination to the Rh(I) center. The most interesting feature of this complex in the solid state is the coordination of the B(1)-H(1bc) to the Rh center. It can be described as an agostic interaction with the $RhX(L)_2$ unsaturated center. Despite the intrinsic low precision on hydrogen location by X-ray crystal analysis, the B(1)-H(1bc) bond distance of 1.32(3) Å is significantly longer than the other B-H bond distances (average 1.17(3) Å), indicating donation of electron density to the Rh center. The Rh(1)-H(1bc) bond distance of 1.83(3) Å is in the range found for agostic interactions.[14,26] The Rh(1)-H(2bc) distance to the non bonded BH_3 fragment is also rather short at 2.37(3) Å. All the parameters

point to a weak interaction of the hydrogen with the Rh center, consistent with a fast equilibration between all hydrogens in the solution ^{1}H NMR spectrum.

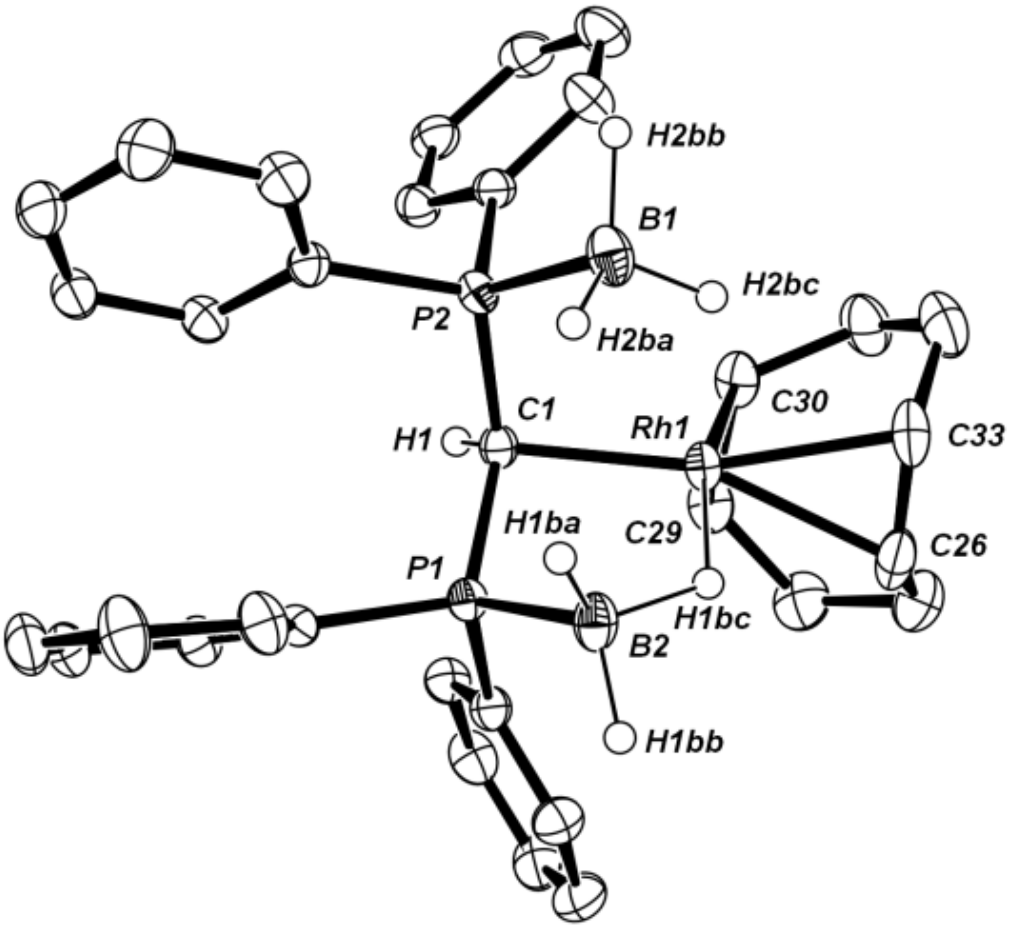
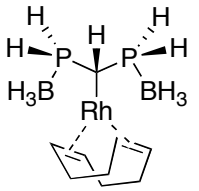


Figure 2: *Molecular structure of* ***II-33*** *(ORTEP-Plot, 50 % thermal ellipsoids, selected hydrogen atoms were omitted for clarity). Selected bond distances (A) and angles (°): Rh1-C1: 2.157(2), Rh1-H1bc: 1.83(3), Rh1-H2bc: 2.37, B1-H1bc: 1.32(3), P1-B1: 1.917(3), P1-C1: 1.786(2), C1-H1: 1.07(3). P1-C1-P2: 123.7(1), P1-C1-Rh1 92.6(1).*

III. THEORETICAL STUDY

III.1. Computational Model

For the optimization of the possible structures a model complex was used, replacing the phenyl groups of dppm with protons (Scheme12).

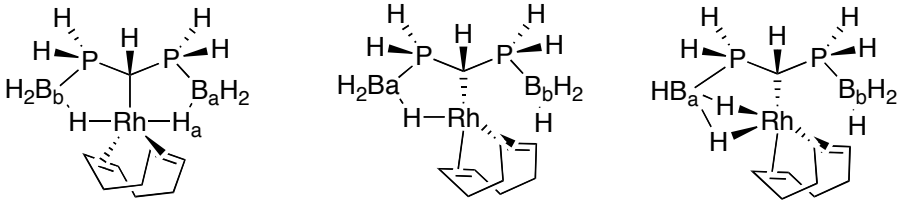


Scheme 12: *Model complex used for structure optimization.*

Calculations were performed with the GAUSSIAN 03 series of programs.[27] The B3PW91 functional [28, 29] was used in combination with the 6-31+G* basis set for all non-metal-bound atoms (C, H, P), the 6-311+G* for all metal-bound-atoms (C, H, P, S) and the LANL2DZ basis[30] for iridium with an additional f-polarization function (exponent = 1.350).[31] The stationary points were characterized as minima by full vibration frequencies calculations (no imaginary frequency).

III.2. Computational Study

DFT calculations not only can support hydrogen location from X-ray, but also gain insight into the mechanisms rendering the BH_3 fragments equivalent in the ^1H NMR spectra.[32] Three species were optimized as minima (scheme 13) with phenyl groups replaced by hydrogen atoms: **II-I** corresponds to the postulated BPT structure **II-33a**, **II-J** to a SP structure close to **II-33b**, and a third species **II-K** bearing a κ^2 BH_2 interaction with the Rh center.



II-I	**II-J**	**II-K**
0.0	-0.5	1.1

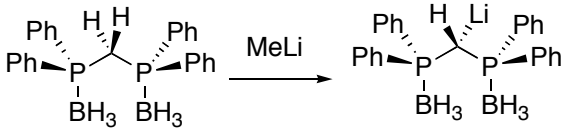
Scheme 13: *Relative free energies of calculated structures II-I - II-K in kcal mol[1]*

The first obvious result from these calculations is the relative energies of the three species **II-I**-**II-K**. They are all found within 1.7 kcal/mol. The tetracoordinated species **II-J** appears to be only marginally more stable than the pentacoordinated **I-I**. Apart from the coordination of the BH bonds, the main difference between **II-I** and **II-K** resides in the coordination of the COD ligand. Indeed, in **II-I**, the two CC double bonds of the COD ligand occupy the equatorial plane of the BPT, and the two H-Rh interactions are perpendicular to this plane. On the other hand, in **II-J**, one double bond is *trans* to the CH bond and the other *trans* to the BH bond as it was found in the crystal structure **3**. The metrical parameters found in **II-J** are in very good agreement with

those measured in the X-ray structure of **3**. In particular, the Rh-H and B-H bond distances are very well reproduced: 1.812 Å (calc) *vs* 1.83(3) Å in **II-33**, and 1.280 Å (calc)*vs* 1.32(3) Å in **II-33**, respectively. The other B-H bonds are calculated at 1.20 Å, very close to the average B-H bonds observed (1.17 Å). The main difference between **II-J** and **II-33** is the distance from the Rh center to the closest non bonded B-H bond 3.59 Å and 2.37 Å, respectively. This difference in distance results from a rotation of the *non* bonded BH_3, with an insignificant associated energy. In order to obtain **II-I** from **II-J**, two independent movements are required: bringing the non bonded BH_3 closer and a rotation of the COD ligand. The optimized geometry of **II-I** is not perfectly symmetrical in terms of BH bond distances to the Rh center: 1.94 Å and 2.07 Å. As expected, these longer bond distances are correlated to slightly shorter B-H bond distances than in **II-J**: 1.25 Å. **II-I** and **II-J** are involved in the fast process rendering the two BH_3 fragments equivalent by ^{1}H NMR spectroscopy. The activation energy associated with this process is likely to be very small. A TS between two structures **II-J** allowing the interconversion of the position of the B-H bonds in a single BH_3 fragment was searched. This only led to **II-K**, a minimum on the potential energy surface and not a TS, in which a κ^2 BH_2 interaction is observed. In terms of bond distances, BH bonds are shorter and Rh-H bonds are longer (1.25 Å and 2.017-2.033 Å respectively) in perfect agreement with a κ^2 coordination. The energy of **II-K** is only 1.6 kcal/mol above **II-J**. Overall, the DFT calculations show the potential energy surface to be very flat, and are therefore in full agreement with the observed fluxional behavior.

IV. CONCLUSIONS AND PERSPECTIVES

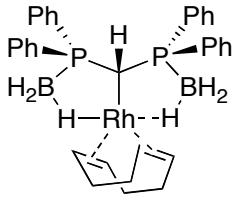
In this chapter we have shown that the $dppm(BH_3)_2$ adduct can be readily deprotonated to form a methanide compound **II-31** (Scheme 14).



II-30 **II-31**

Scheme 14: *Deprotonation of dppm(BH$_3$)$_2$.*

Upon coordination to a Rh center, **II-31** acts as a weak "pincer" ligand through the formation of a Rh−CH bond and weak B−H agostic bonds as demonstrated by NMR, X-ray and DFT studies (Scheme 14).



Scheme 15: Pincer-type coordination in complex **II-33**.

Further work is in progress involving the full electronic description of **II-33** as well as reactivity studies.

The coordination of this new potentially tridentate ligand **II-31** to other transition metals or lanthanides could be give valuable information for the interaction of phosphineboranes with metal centers.

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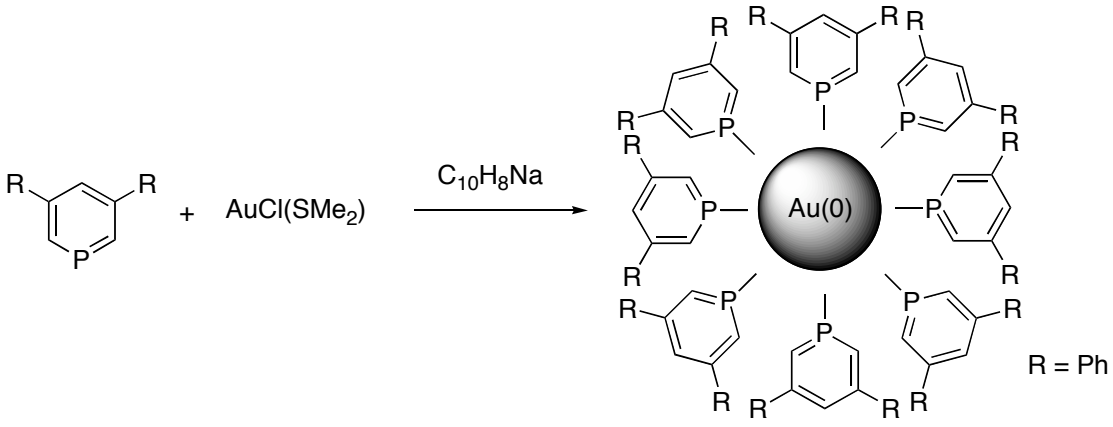
PART III:

Phosphinines and Nanoparticles

CHAPTER 1: PROTODESILYLATION OF 2,6-DISUBSTITUTED SILYLPHOSPHININES. A JOINT EXPERIMENTAL AND THEORETICAL STUDY

I. INTRODUCTION

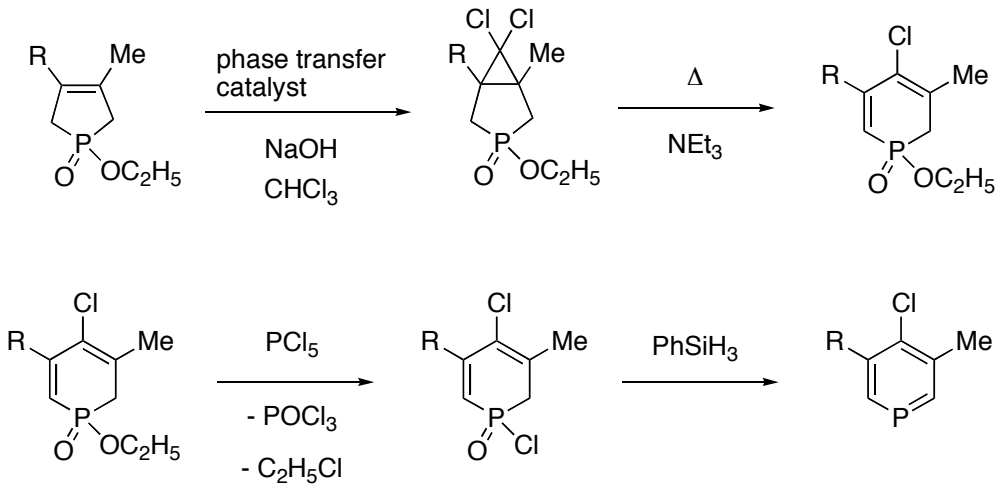
Phosphinines[1-3] are one of the most important classes of phosphorus aromatic heterocycles with phospholes[4] and their anionic derivatives. Due to their very specific electronic properties that strongly differ from that of classical phosphines and related nitrogen heterocycles, they have found applications in coordination chemistry for the stabilization of highly reduced complexes[5, 6] and in homogeneous catalysis such as the hydroformylation of olefins. [7-12] More recently they also proved to be well adapted for the growing and stabilization of metallic nanoparticles[13, 14] (Scheme 1).



Scheme 1: *Synthesis of gold nanoparticles stabilized by phosphinines.*

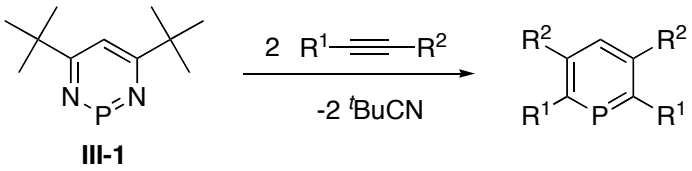
However, it appeared from these last studies that the substitution pattern of the ring plays a crucial role on the coordinating ability of the ligand as well as on the solubility of the resulting nano materials. The most interesting performances in terms of particle size and shape were obtained with 3,5-disubstituted phosphinine derivatives. Though many synthetic approaches toward functional phosphinines have been devised, most of these studies focused on the elaboration of 2,6-disubstituted derivatives and methods providing a convenient access toward 3,5-disubstituted phosphinines have been much less studied.

In most cases, these approaches rely on multistep procedures that are specific from the nature of the functional groups grafted at the 3 and 5 positions. [15] An example for the synthesis of a 2,6-unsubstituted phosphinines is the method reported by Keglevich and co-workers in 1992 (Scheme 2).[15-23] Starting from a dihydrophosphole-oxyde upon cyclopropanation with dichlorocarbene and a subsequent deprotonation, this sequence leads to a dihydrophosphinine oxyde that can be reduced to the corresponding 3,4,5-trisubstituted phosphinine in two steps.



Scheme 2: *Synthesis of 3,4,5-tisubstituted phosphinines by Keglevich and co-workers.*

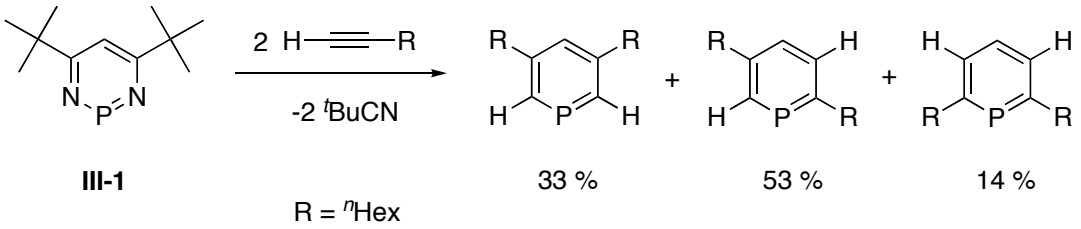
Several years ago Le Floch and co-workers reported a synthetic strategy that allows the synthesis of tetrafunctional derivatives. Polyfunctional compounds,[24-27] polydentate ligands, [28, 29] and phosphorus macrocycles [30-33] could be easily prepared from disubstituted alkynes and 1,3,2 diazaphosphinine **III-1** through a cycloaddition/cycloreversion sequence (Scheme 3).



III-1

Scheme 3: *Synthesis of tetrafunctional phosphinines.*

However this process could not be successfully extended toward the synthesis of disubstituted derivatives with terminal alkynes since in most cases cycloadditions did not proceed regioselectively. Thus for example, reaction of **III-1** with 1-octyne yields a mixture of three possible isomers, the 2,5-disubstituted derivative being predominant.

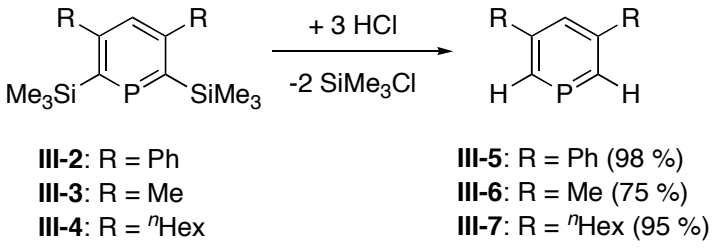


Scheme 4: *Mixture of phosphinines upon reaction of* ***III-1*** *with oct-1-yne.*

In order to devise a convenient route toward 3,5-disubstituted phosphinines, we decided to investigate the protodesilylation of 2,6-disilylphosphinines, which are produced regiospecifically when silylalkynes are employed as partners in these cycloaddition/cycloreversion sequences. In this chapter these results will be presented in combination with a theoretical study, which sheds some light on this protodesilylation process.

II. EXPERIMENTAL STUDY

The synthesis of 3,5-disubstituted phosphinines bearing alkyl or phenyl substituents **III-5 – III-7** was achieved by a highly regioselective method, employing a two-step strategy. In the first step the trimethylsilyl group was used as a directing group in the cycloaddition/cycloreversion reaction sequence leading selectively to 2,6-di-(trimethylsilyl)-substituted phosphinines **III-2 – III-4**. Then we found that the protodesilylation of these compounds could be simply driven to completion upon reaction with a slight excess (1.5 equiv. per $SiMe_3$) of 2 M HCl in ethereal solution (Scheme 5).



Scheme 5: *Protodesilylation of 2,6-di-(trimethylsilyl)-phosphinines with HCl.*

Monitoring the reaction by ^{31}P NMR spectroscopy allowed two interesting observations. During the synthesis of **III-7**, formation of a monosilyl compound was evidenced by the appearance of a signal at δ = 238 ppm showing a characteristic coupling constant $^2J_{PH}$ of 62.9 Hz. A second intermediate, which does not exhibit a measureable coupling constant with the phosphorus nucleus, was also detected in the crude reaction mixture at δ = 86 ppm. This chemical shift, which is not in the usual range for the phosphorus atom of phosphinines

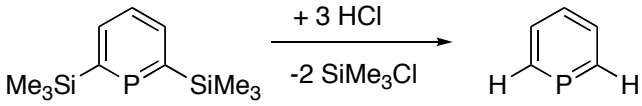
(phosphinines usually appear at low field between 180 and 250 ppm depending on the substitution scheme), indicates that during the process the aromaticity of the ring is disrupted. More specifically, this chemical shift is in the usual range of a chloro-phosphine that might result from the nucleophilic attack of chloride to the phosphorus atom.

Compounds **III-5 – III-7** were isolated by evaporation of the solvent, excess HCl and Me_3SiCl and were characterized by means of NMR spectroscopy and high-resolution mass spectrometry. The ^1H NMR spectra of the 2,6-unsubstituted compounds show a very characteristic triplet because of the coupling of the phosphorus atom with the protons in the 2 and 6 position with a large $^2J_{PH}$ coupling constant of about 40 Hz. Note that the chemical shift of the H4 hydrogen atom was also found to be strongly dependent on the substitution scheme (between 7.9 ppm for R = Ph and 6.8 ppm for R = Me), as usually observed in other substituted phosphinines.

III. THEORETICAL STUDY

III.1 Computational model

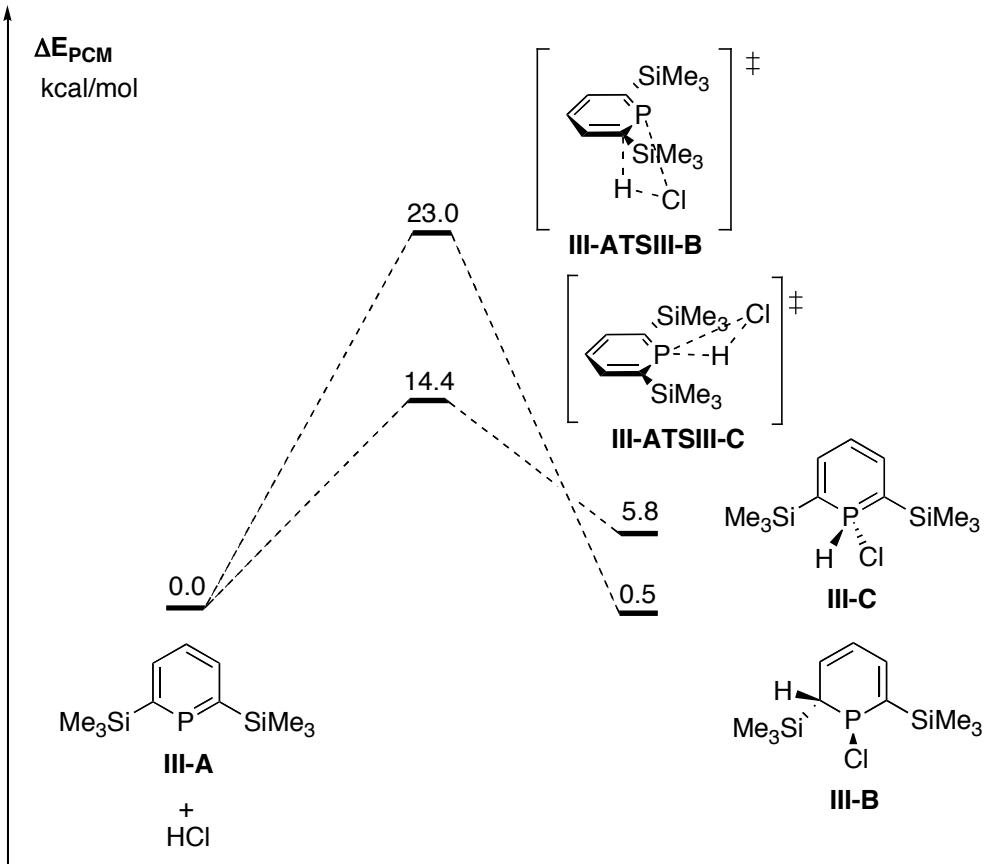
All calculations were performed using the B3LYP-functional.[34-36] Geometry optimizations were made at the 6-31+G(d) level of theory for all atoms. Single point calculations using the PCM method [37-40] were used to take into account the solvent effects, considering diethyl ether as the solvent with the larger 6-311+G(d,p) basis set. The GIAO method[41] was used to calculate phosphorus chemical shifts. The protodesilylation of 2,6-di-(trimethylsilyl)-phosphinine was regarded as a model reaction for the computational study.



Scheme 6: *Model reaction studied by means of DFT-calculations.*

III.2 Addition of HCl on 2,6-di-(trimethylsilyl)-phosphinine III-A

As a first step in the desilylation reaction the addition of HCl on the phosphinine **III-A** was studied. There are two different pathways that had to be considered: a) the 1,2-addition of HCl to the phosphorus-carbon double bond which leads to a 1-P-chloro-1,2-dihydrophosphinine **III-B** or b) an oxidative addition of HCl to the phosphorus atom leading to a λ^5-phosphinine **III-C** (Scheme 7).



Scheme 7: *Energetic profile of the addition of HCl on phosphinine* ***I****.*

In both transition states, the hydrogen-phosphorus or hydrogen-carbon bonds are rather short and quite close to their final distances, while the phosphorus-chloride bonds are still pretty long (Figure 1).

Thus the energy of these transition states should be directly related to the protonation energy at the phosphorus atom or at the α-position. Accordingly, the transition state leading to the λ^5-phosphinine **III-C** is lower in energy than the transition state leading to the chlorophosphine **III-B** ($\Delta E^{\ddagger}_{\text{III-ATSIII-B}}$ = 14.4 kcal/mol vs. $\Delta E^{\ddagger}_{\text{III-ATSIII-C}}$ = 23.0 kcal/mol) that corresponds to a higher proton affinity at the phosphorus atom than at the α-carbon atom (211.1 kcal/mol vs. 207.5 kcal/mol).[42]

It should also be noted that the addition of HCl leading to the λ^5-phosphinine **III-C** does not adopt C_{2v} symmetry, as was previously observed in the case of the addition of H_2 to the parent phosphinine C_5H_5P.[43] Since **III-B** and **III-C** are both close in energy and kinetically accessible, the elimination process of Me_3SiCl from each species had to be calculated. In order to allow for the elimination of Me_3SiCl from **III-B** to form the monosilylated phosphine $C_5H_4PSiMe_3$, the trimethylsilyl and the chlorine substituent have to adopt a *cis* stereochemistry.

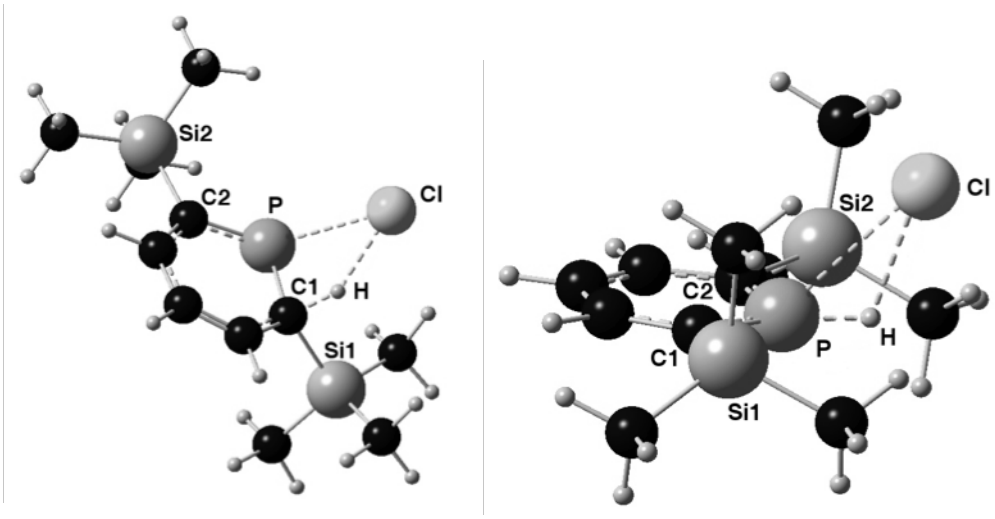


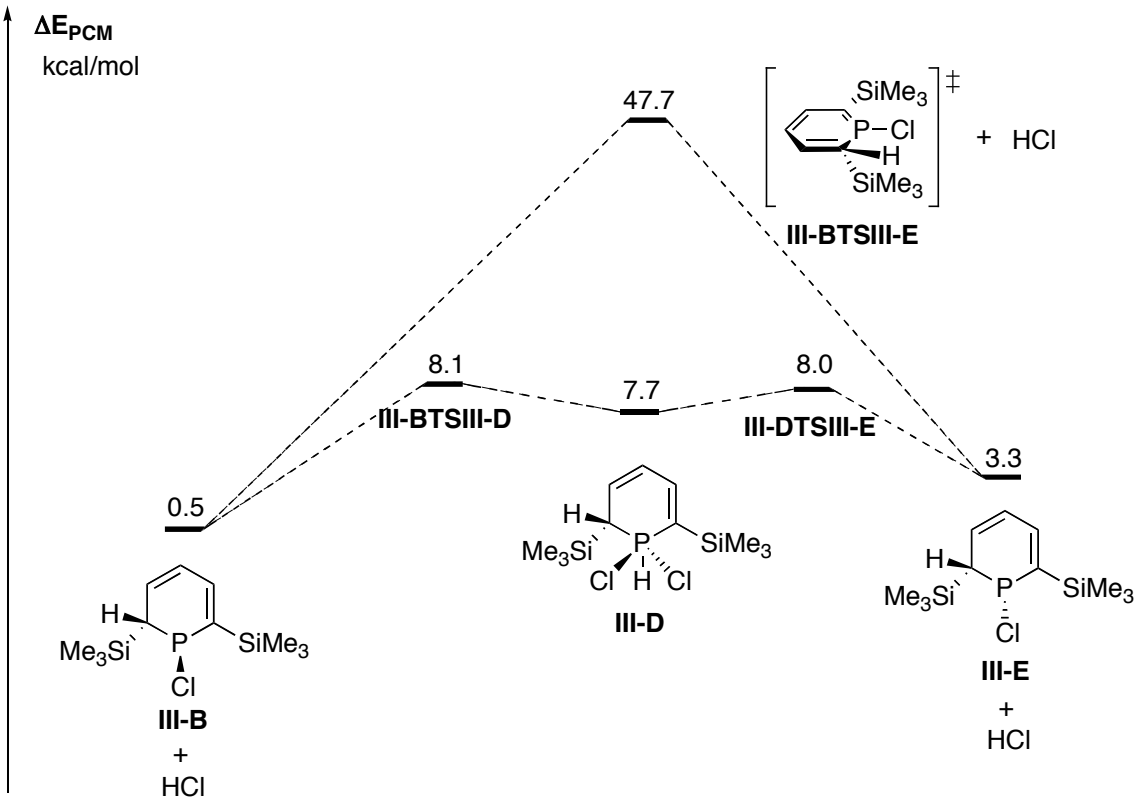
Figure 1: *View of* ***III-ATSIII-B*** *(left). Significant bond lengths in Å, angles in °: C1-P: 1.812, C2-P: 1.754, C1-H: 1.187, P-Cl: 3.032 H-Cl: 1.941, C1-P-C2: 103.4. View of* ***III-ATSIII-C*** *(right). Significant bond lengths in Å, angles in °: C1-P: 1.712, C2-P: 1.712, P-H: 1.410, P-Cl: 2.984, H-Cl: 2.168, C1-P-C2: 114.4.*

III.3. Isomerisation of intermediates III-B and III-C

III.3.a. Isomerisation of chlorophosphine III-B

The inversion of the phosphorus atom in **III-B** to form its diastereomer **III-E** was thus investigated, prior to the elimination process. As can be seen in Scheme 8, the direct isomerization requires a significant activation energy ($\Delta E^{\ddagger}_{\mathbf{III\text{-}BTSIII\text{-}E}}$ = 47.2 kcal/mol) not accessible under the experimental conditions. A second pathway, which relies on the addition of a second molecule of HCl onto chlorophosphine **III-B** was considered. This addition was found to be endothermic ($\Delta E_{\mathbf{III\text{-}B_III\text{-}D}}$ = 7.2 kcal/mol) and requires a rather low activation energy ($\Delta E^{\ddagger}_{\mathbf{III\text{-}BTSIII\text{-}D}}$ = 7.6 kcal/mol).

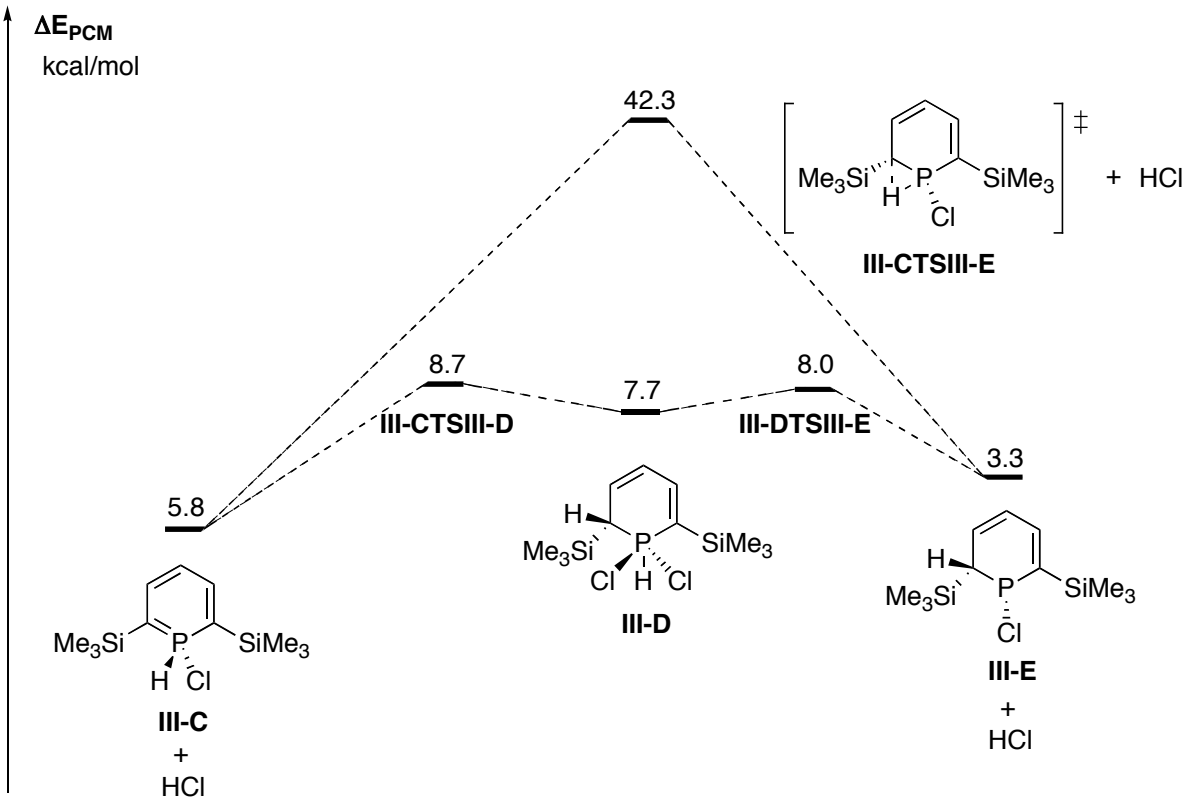
As expected, the energetic profile of the subsequent elimination step from **III-D** to form **III-E** is very comparable to the energetic profile of the addition step ($\Delta E_{\mathbf{III\text{-}D_III\text{-}E}}$=-4.4 kcal.mol^{-1}, $\Delta E^{\ddagger}_{\mathbf{III\text{-}DTSIII\text{-}E}}$ = 0.3 kcal.mol^{-1}).



Scheme 8: *Energetic profile for the isomerisation of phosphine **III-B** to phosphine **III-E**.*

III.3.b. Isomerisation of the λ⁵-phosphinine III-C

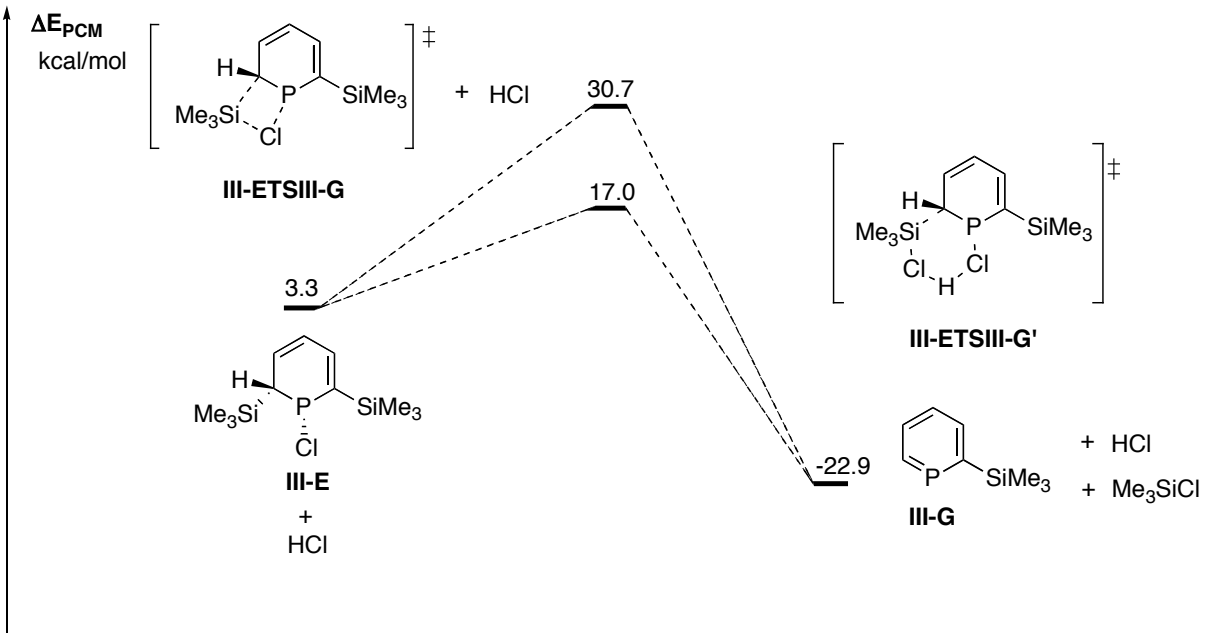
Again two mechanisms for the isomerisation of the λ⁵-phosphinine had to be taken into account. The first one consists in the direct conversion of **III-C** into **III-E** via a 1,2-sigmatropic hydrogen shift. As reported for the parent λ⁵-phosphinine C_5H_5P-H_2, this rearrangement requires a very important activation energy ($\Delta E^{\ddagger}_{\text{III-C_TS_III-E}}$ = 36.5 kcal.mol^{-1}) and may not occur under the experimental conditions used (see Scheme 9). Interestingly, we found that compound **III-D** can also be obtained from the reaction of a second molecule of HCl onto the λ⁵-phosphinine **III-C**. As can be seen in Scheme 9, this reaction is slightly endothermic ($\Delta E_{\text{III-CTSIII-E}}$ = 1.9 kcal.mol^{-1}) and requires a lower activation energy ($\Delta E^{\ddagger}_{\text{III-CTSIII-E}}$ = 3.0 kcal.mol^{-1}). The elimination of HCl, which yields chlorophosphine **III-E**, has been discussed above.



Scheme 9: *Isomerisation of λ^5-phosphinine III-C to phosphine III-E.*

III.4. Desilylation

Having rationalized the formation of compound **III-E** we then turned our attention to the elimination of Me_3SiCl, which provides the monosilylated phosphinine **III-G**, an observable intermediate in the reaction.



Scheme 10: *Desilylation of chlorophosphine III-E.*

The direct *syn*-elimination of trimethylsilyl chloride was computed but the corresponding four-centered transition state was found to be relatively high in energy ($\Delta E^{\ddagger}_{\text{III-ETSIII-G}}$ = 27.4 kcal/mol). A more convincing alternative was found by considering the involvement of a molecule of HCl.

A more accessible 6-centered transition state was located ($\Delta E^{\ddagger}_{\text{III-ETSIII-G'}}$ = 13.7 kcal.mol^{-1}). This last step is highly exothermic ($\Delta E_{\text{III-E_III-G}}$ = -19.4 kcal.mol^{-1}) and yields **III-G** (see Scheme 10).

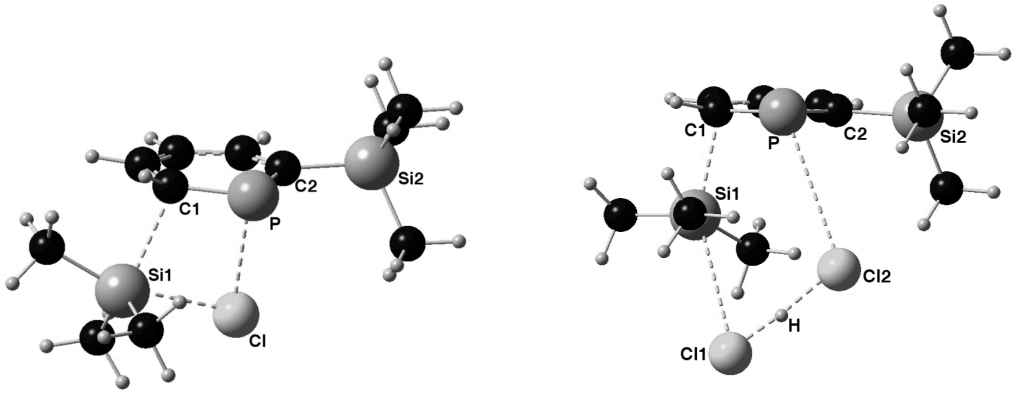
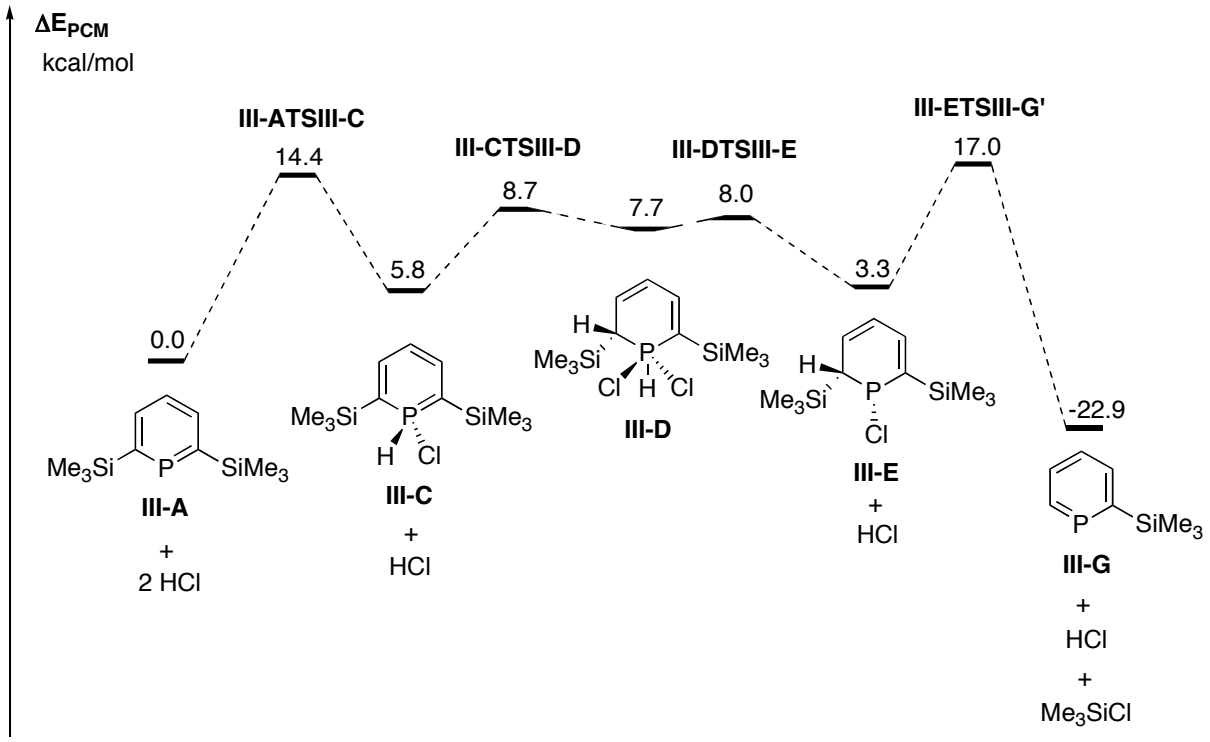


Figure 2: *View of III-ETSIII-G (left). Significant bond distances in Å, angles in °: C1-H: 1.089, C1-Si1: 2.475, C1-P: 1.784, C2-P: 1.763, P-Cl: 2.698, Si1-Cl: 2.596; C1-Si1-Cl: 76.8. View of III-ETSIII-G' (right): C1-H: 1.091, C1-Si1: 2.453, C1-P: 1.775, C2-P: 1.751, P-Cl2: 4.015; Si1-Cl1: 3.507; C1-Si1-Cl1: 151.4.*

III.5. Summary of the first desilylation step

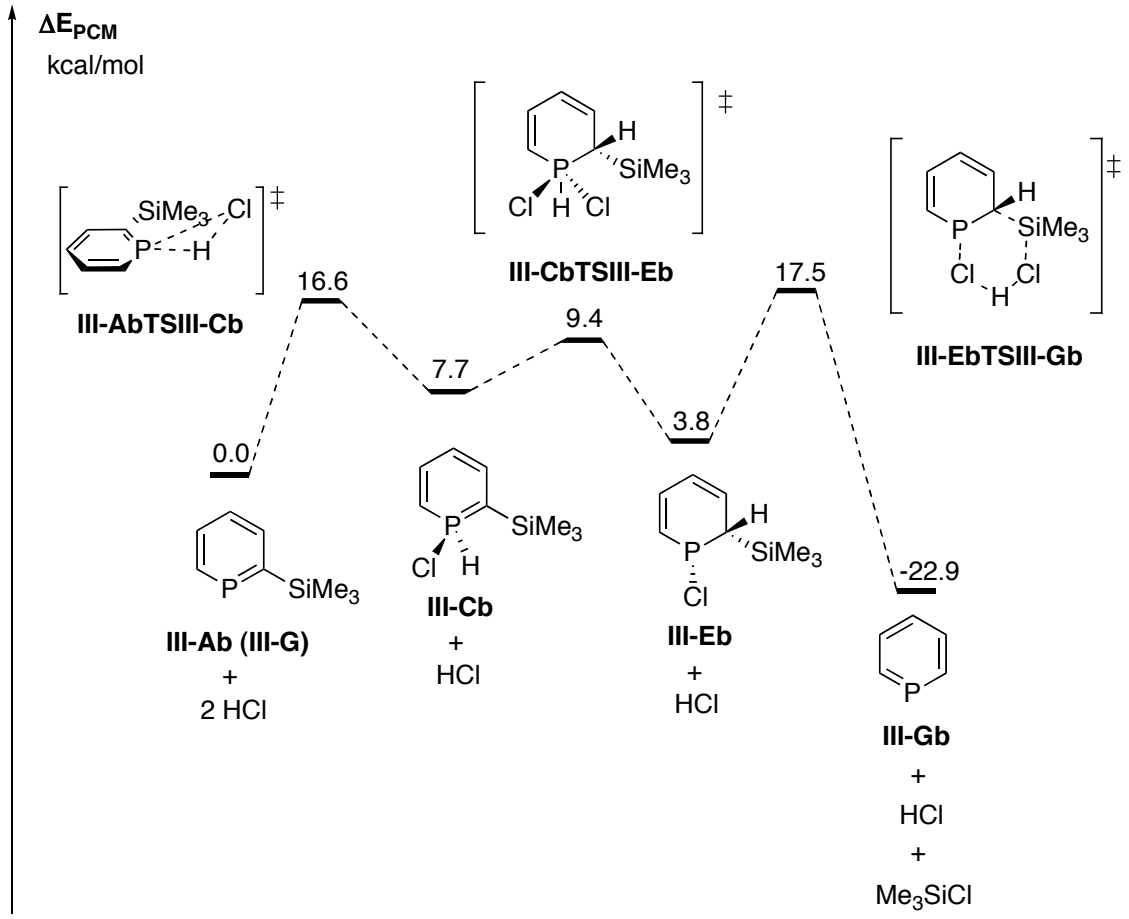
The calculated pathway is fully consistent with the fact that an intermediate at 86 ppm in ^{31}P NMR is observed. DFT calculations of the ^{31}P NMR shift for **III-B** and **III-E** show chemical shifts of 100 and 106 ppm respectively, which are in the usual range of chemical shifts of chlorophosphine derivatives.



Scheme 11: *Summary of the first protodesilylation step.*

III.6. Second desilylation step

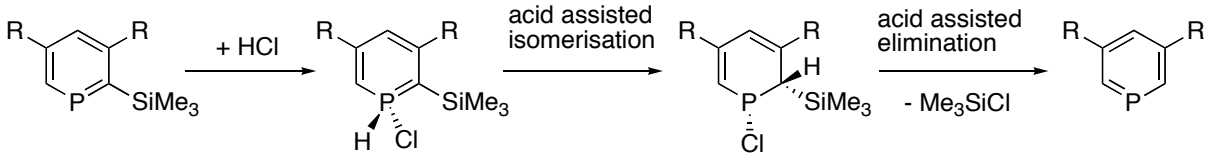
An analogous reaction scheme was computed for the formation of the bis-desilylated compound. As expected, the energetic pathway is similar. The main difference with the elimination of the first trimethylsilyl moiety lies in the fact that we observe, for the second elimination, the simultaneous addition-elimination of HCl for the isomerization of **III-Bb** into **III-Eb** (Scheme 12).[44]



Scheme 12: *Mechanism of the second desilylation step.*

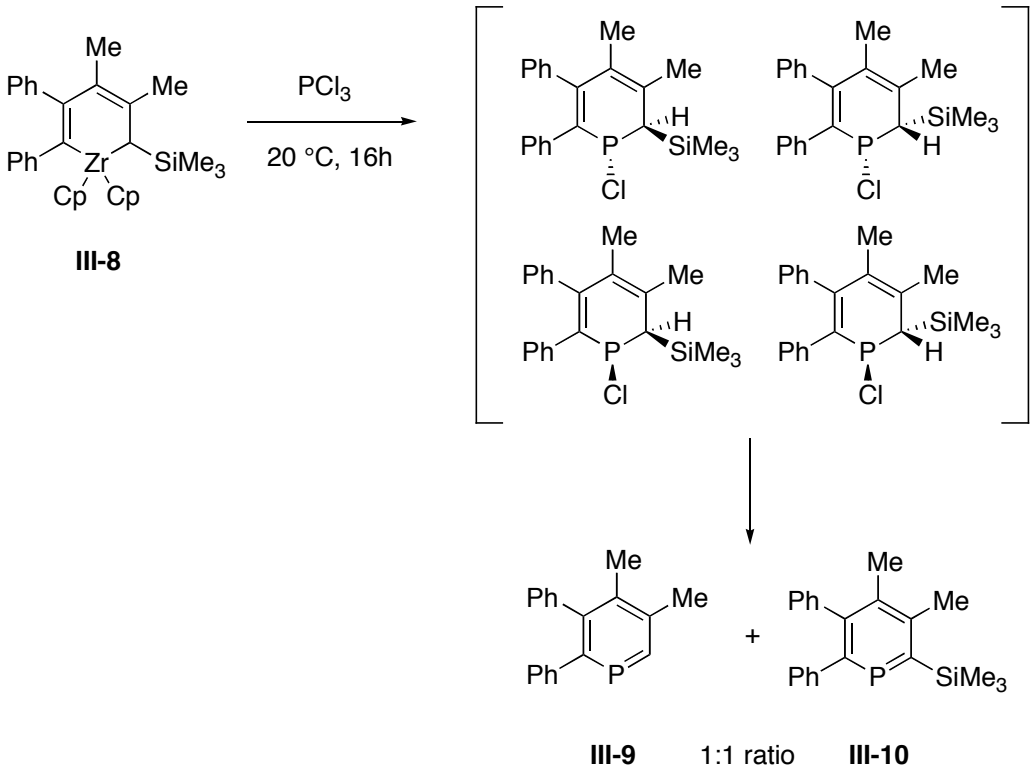
IV. CONCLUSION AND PERSPECTIVES

In conclusion, it has been shown in this chapter, that 2,6-unsubstitued phosphinines can be easily produced in high yields from the simple reaction of HCl with readily available 2,6-di(trimethylsilyl)phosphinine derivatives. This straightforward route yields access to various 3,5-difunctionalized derivatives whose synthesis was somewhat tedious. Contrary to what could be expected, the mechanism of this protodesilylation process does not rely on a simple addition elimination sequence. Rather, as shown by DFT calculations, it involves the formation of intermediates bearing a hypervalent phosphorus center, such as in **III-D**. The readily accessible hypervalent state of the P center allows a low energetic reaction path for this transformation, from either compound **III-B** or **III-C**. This mechanism, involving dihalogeno-λ^5-phosphinines, is reminiscent of the one proposed for the α-bromination of 2-halogeno-phosphinines by our group.[45]



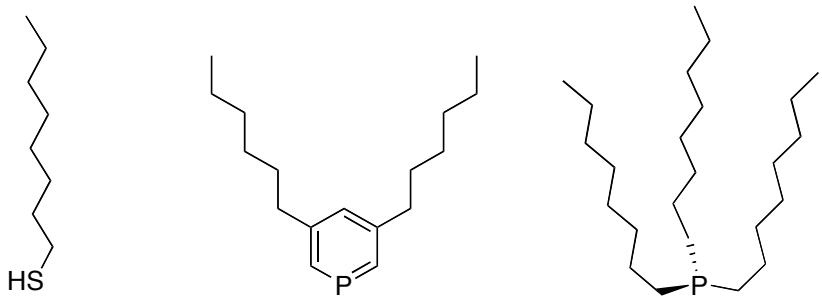
Scheme 13: *Proposed reaction mechanism for the protodesilylation of silylphosphinines on the basis of DFT calculations.*

Note that the mechanism suggested by our calculations is consistent with the experiments conducted by Hunter et al.[46] on the formation of the 2,3-diphenyl-4,5-dimethylphosphinine **III-9** and the 2-trimethylsilyl-3,4-dimethyl-5,6-diphenylphosphinine **III-10**, in a 1:1 ratio, from the reaction of the zirconacycle **8** with PCl_3. This ratio might be explained by the fact that the reaction of the zirconium complex yields the four possible diastereomers of 1-*P*-chloro-1,2-dehydrophoshinine in a statistical ratio. These diastereoisomers might then undergo either the elimination of HCl (which corresponds to **III-BTSIII-A** in our model) or an elimination of Me_3SiCl (**III-ETSIII-G'**) according to their stereochemistry leading to two phosphinine in a 1:1 ratio (Scheme 14).



Scheme 14: *Phosphinine synthesis by Hunter et al.*

The development of this method of synthesis of 3,5 disubstituted-phosphinines with various substituents allows to study the influence of the substitution pattern of the phosphinines on the properties (monodispersity, stability) of phosphinine stabilized nanoparticles.



Scheme 15: *Ligands for the stabilization of transition metal nanoparticles.*

Furthermore it will be possible to compare the properties of nanoparticles stabilized by phosphinines with large alkyl chains, with those stabilized by common ligands like octanethiol and tri-n-octylphosphine (Scheme 15).

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CHAPTER 2: PHOSPHININE-STABILIZED TRANSITION METAL NANOPARTICLES

I. INTRODUCTION

I.1. Historical Background

Soluble gold nanoparticles have been known for more than two thousand years and were used as pigments for esthetic and curative purposes. Their use to make ruby glass and for coloring ceramics was known in these ancient times as exemplified by the famous Lycurgus cup (dated 4th century AD, British Museum).[1]

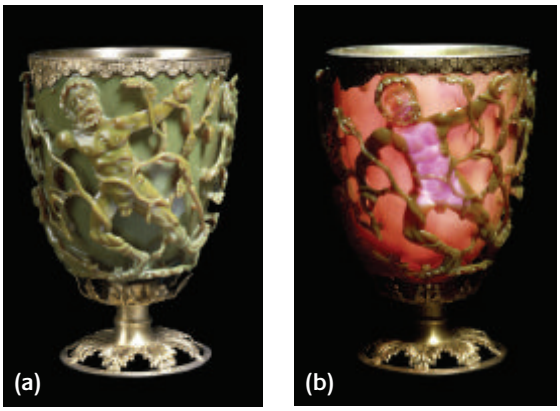
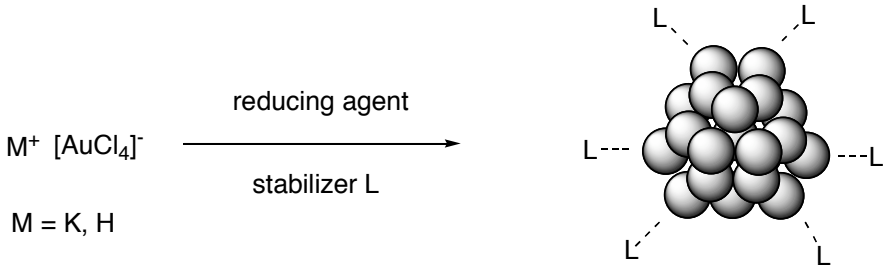


Figure 1: *Picture of the Lycurgus cup in (a) ambient light (b) lighted from the back*[2]

The synthetic strategy for the synthesis of colloidal solutions of gold that was developed by Faraday in 1857, that consists in the reduction of tetrachloroaurate $[AuCl_4]^-$ with a reducing agent (phosphorus in CS_2 as a reducing agent, in the original version), is still one of the most popular methods that is used nowadays for the preparation of gold nanoparticles (NPs).

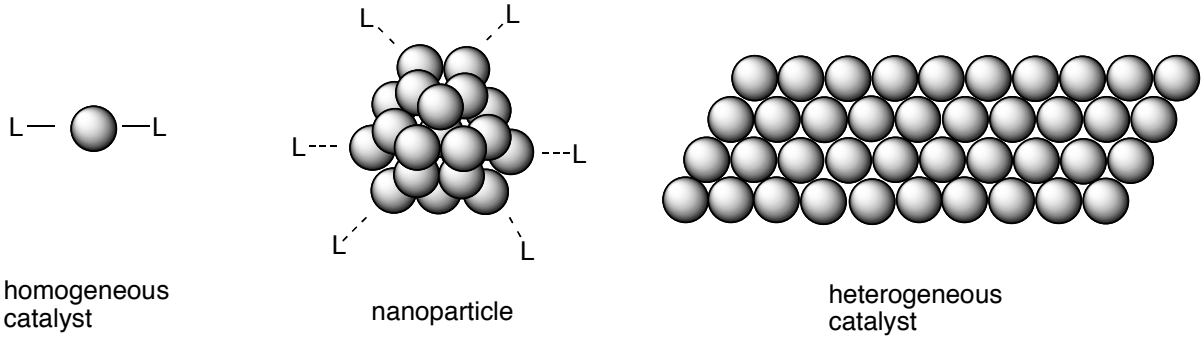


Scheme 1: *Synthesis of colloidal gold by reduction.*

Although it was already proposed by Kunckels in the 17th century that the special properties of colloidal gold solutions were due to the fact that the gold particles were "to small to be seen" it was only in the 1920's that Zsigmondy made the final demonstration of the heterogenous nature of colloid solutions for which he obtained the Nobel prize in 1925.[3]

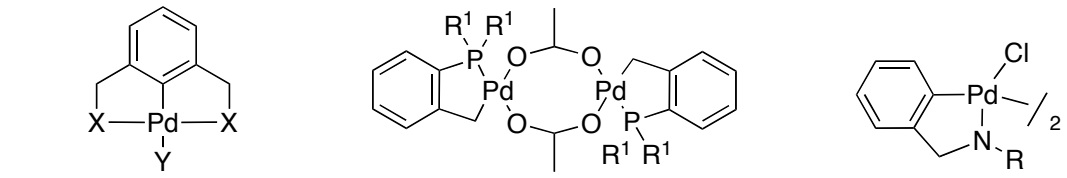
I.2. Synthesis and applications

The field of NPs catalysis has recently attracted high interest because NPs are supposed to combine the advantages of homogeneous (selectivity, activity) and heterogeneous (recyclability) catalysts and therefore meet the demand for modern green catalysis. Due to their particular matter state, between homogeneous and heterogeneous, these frontier species are sometimes called "semi-heterogeneous" catalysts.



Scheme 2: *Bridging the gap between homogeneous and heterogeneous catalysis.*

Although the distinction between homogeneous and heterogeneous catalysts seems to be well-defined, in many cases it is not easy draw a final conclusion whether a catalytic process involves a homogeneous or a heterogeneous active species. In this regard the role of nanoparticles becomes even more important. For example the use of palladium(II)-pincer and palladacycle complexes in the Heck-reaction has been intensely studied throughout the last years (Scheme 3).



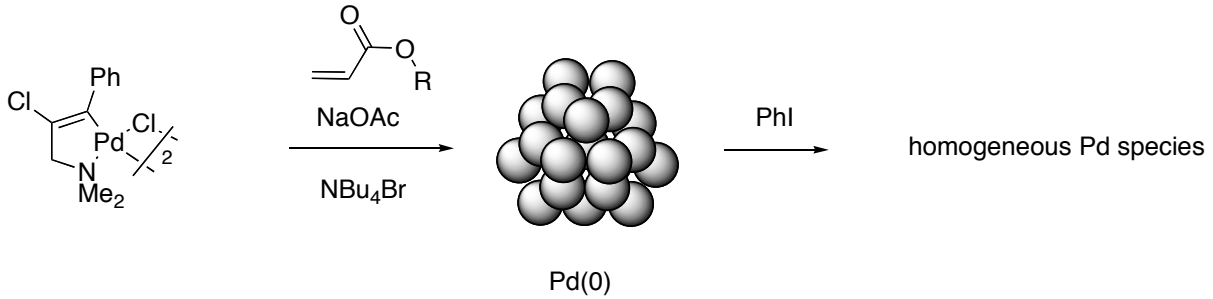
X = NR_2, PR_2, $OP(OR)_2$, SR
R = alkyl, aryl
Y = Cl, Br, I, OTf, OAc

Herrmann-Beller palladacycle

R^1= *o*-tolyl

Scheme 3: *Palladacycles and pincer complexes used as pre-catalysts in the Heck reaction.*

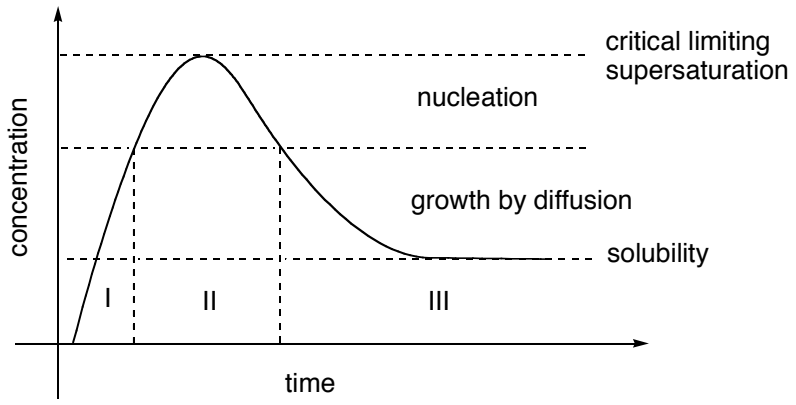
One characteristic feature of this type of catalyst is the presence of an induction period during which the palladium(II)-complex is reduced to a highly active catalyst species. It could be shown by Beletskaya and coworkers,[4] that this induction period could be shortened by the addition of $NaBH_4$ to the reaction mixture. Furthermore Gladysz and coworkers were able to prove the formation of Pd colloids from these catalyst precursors under the conditions of the Heck reaction.[5] Although the formation of Pd colloids had thus been proven there was no evidence that the active species in the catalytic cycle is of colloidal nature. Dupont and coworkers investigated the fate of nanoparticles formed by the decomposition of a palladacycle precatalyst throughout the catalytic cycle and could observe the immediate disappearance of palladium colloids after the addition of iodobenzene, showing that the oxidative addition of iodobenzene to the colloids is a very fast reaction. Reactions of this solution with acrylate esters gave the expected Heck reaction products. Together with kinetic measurements this proves the non-heterogeneous nature of the catalyst in the Heck reaction. [6]



Scheme 4: *Studies by Dupont et al. on the nature of the active species in the Heck reaction.*

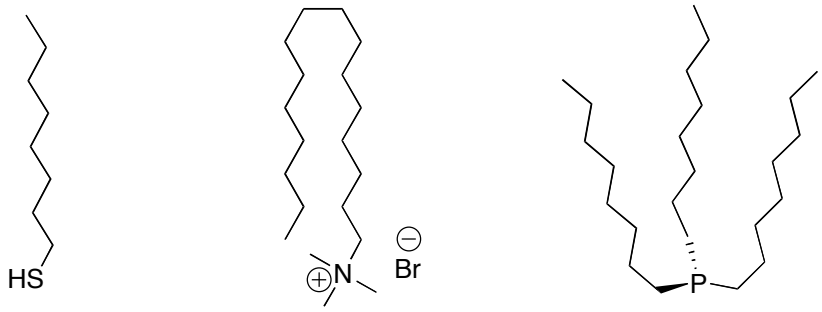
Whereas in the former case the intermediate formation of the nanoparticles is more an "accidental" observation, substantial effort has been made during the last 30 years to develop the synthesis and application of preformed transition metal nanoparticles in catalysts.[7] The preparation of zerovalent nanocatalysts can be performed by various methods in different media. The choice of the reaction parameters (metal precursor, reducing agents, stabilizer, solvent, temperature, atmosphere) allows to control the size and shape of the NPs formed.

As a first approximation the model of LaMer[8] can be used to describe the formation of NPs (Scheme 5). According to this model the formation of nanoparticles involves two steps: nucleation of an initial "seed" and growth. In the nucleation step precursors are decomposed (thermal decomposition, chemical reduction) (I) to form a supersaturated solution of monomers followed by a burst of nucleation of NPs (II). When the monomer concentration falls below a critical concentration, nucleation stops but the nuclei continue to grow by incorporating additional monomers present in the reaction medium (III) or by other more complex mechanisms. If steps I and III are well separated in time then monodisperse nanoparticles can be obtained.



Scheme 5: *LaMer diagram.*

The role of the capping agents used for the stabilization of NPs is to first of all sterically protect the NPs from agglomeration, and secondly allow the redispersion of the isolated NPs in non-polar solvents. Therefore the capping agents often posses large alkyl chains (Scheme 6).

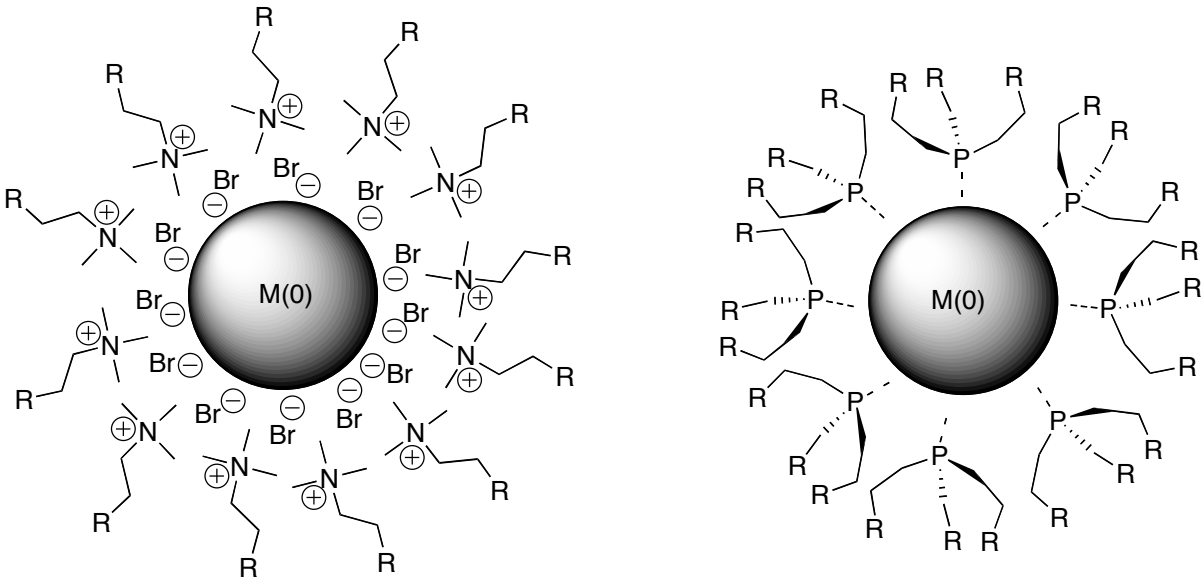


Scheme 6: *Commonly used stabilizers in the synthesis of zerovalent transition metal NPs.*

Additionally the preferential adsorption of ligands to different crystalline phases can lead to the formation of shape controlled nanocrystals such as cubes, bars, triangles, etc.. [9-11]

In contrast to phosphines, that are considered to interact with the metal surface through coordination of the phosphorus lone pair, surfactants like cetyltrimethylammonium bromide (CTAB) stabilize NPs by electrosteric interactions, a combination of electrostatic and steric interactions.

For example in the case of Pd(0)-NPs formed in the presence of tetra-n-butyl ammonium bromide it could be shown by Deng[12] and Finke,[13] that the adsorption of the ammonium cations on the surface of the NP is mediated by halide anions that form a mono layer on the surface of the NP (Scheme 7).



Scheme 7: *Stabilization of NPs through a) electrosteric interactions and b) coordination.*

Having in mind the application of nanoparticles as quasi-homogeneous catalysts "in solution" the stabilizing effects of ligands are ambivalent. Ligands are needed to keep the nanoparticles in solution and protect them from agglomeration. On the other hand, the ligands are in competition with substrate molecules for the coordination of the active sites of the transition metal colloids and might therefore hamper the catalyst activity if the ligands are too tightly bound to the metal surface.

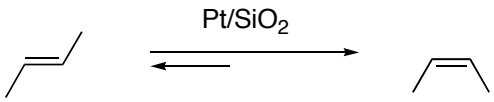
As in the case of the *in-situ* prepared nanoparticles it should be noted that the preformed nanoparticles can serve in some instances as a source for highly active zerovalent molecular catalysts. Therefore extreme care has to be taken in qualifying the active species in catalysis when using nanoparticles precursors. Indeed results reported by Chaudret in 2000 concerning enantioselective allylic alkylation using nanoparticles with chiral stabilizing phosphines ligands have recently been reevaluated by van Leeuwen and coworkers.[14] These authors showed the active catalyst to be a molecular palladium (0) species.

Apart from the use of nanoparticles as catalysts in solution, they can also be deposited on classical heterogeneous supports like silica gel, carbon or nano and mesoporus materials. Haruta and coworkers reported, for example, that gold nanoparticles on solid support are extremely active catalysts for the oxidation of CO to CO_2.[15] Furthermore they were able to show that there is a direct relation between the catalyst activity and the particle diameter. [16-18]

Different methods have been studied for the synthesis of these materials. They can be obtained for example by the impregnation of the solid support with a transition metal salt and the subsequent reduction or by the incorporation of preformed nanoparticles during the synthesis of the material.

Considering the large effort that has been made during the last decades on the synthesis of size and shape controlled NPs only relatively few catalytic processes based on these materials were reported so far compared to classical heterogeneous catalysts that are used in the chemical industry for more than 40 years: "Thus, the question arises as to the true practical value of size- and shape-selective methods of metal NPs preparation beyond their academic interesting basic research. There is reason to be optimistic." (M. T. Reetz)[7]

An example, displaying the interest of size and shape controlled NP preparation was presented by Lee et al recently. In their report the authors showed that the activity of platinum NPs supported on silica for the isomerisation of 2-Butene depends on the shape of the NPs[19] (Scheme 8). Therefore *trans*-2-butene can be selectively isomerized to the *cis*-2-butene, due to the favorable interaction of *cis*-2-butene with the Pt(111) surface of their tetrahedral platinum nanocrystals.



Scheme 8: *Cis-trans-Isomerisation of Olefines catalyzed by Pt-NPs.*

Apart from the application in catalysis, transition metal NPs have attracted high interest due to their special magnetic properties that are dominated by finite size and surface effects.[20] In large magnetic particles it is well-known that there is a multidomain-structure where regions of uniform magnetization are separated by domain walls. In the case where the NPs are smaller than a critical size, it costs more energy to create a domain wall between two domains than to support the external magnetostatic energy of the single-domain state. The critical diameter (for spherical particles) is typically in the range of 10 - 100 nm (Fe = 15 nm, Ni = 55 nm) and depends on the material. A single-domain particle is uniformly magnetized, with all spins in the same direction. The magnetization can only be reversed by spin rotation, therefore these materials posses a very high coercivity[21] and are of high interest e.g. for the construction of high-density data-storage devices.[22]

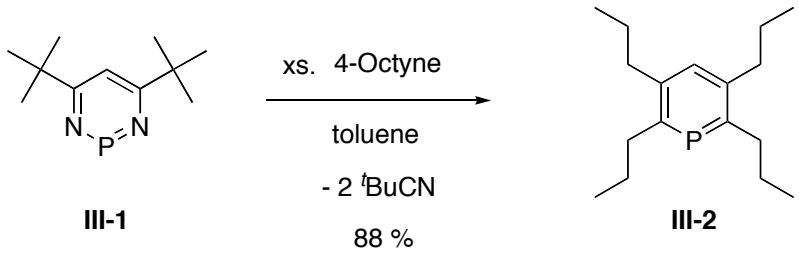
Several years ago it was demonstrated by Le Floch,[23-28] Elschenbroich[29-33] and others that phosphinines, due to their special electronic properties, are well suited for the stabilization of low-valent transition metal complexes. Moores *et al.* recently showed, that phosphinines can efficiently stabilize gold NPs.[34] The phosphinine capped NPs could be incorporated into silica

and the resulting materials were successfully used as optical sensors for molecules like PMe_3 or Thiols, due to influence of the capping agent on the plasmon band of the gold NPs.[35]

In this chapter we will be focusing on the synthesis and characterization of NPs obtained from chemical reduction or thermal decomposition of zerovalent transition metal complexes stabilized by phosphinines.

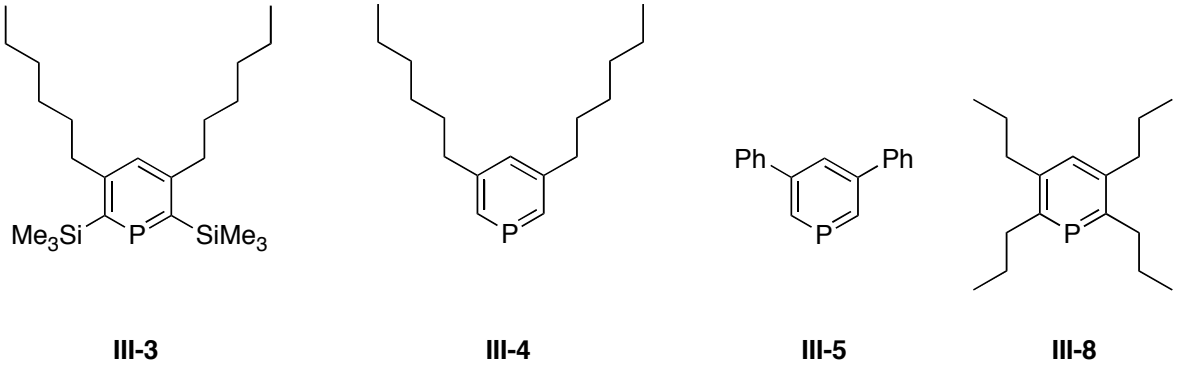
II. LIGANDS

The 3,5-disubstituted phosphinines that were used in the following studies were produced by the procedures that are described in Part 3, Chapter I. The synthesis of 2,3,5,6-tetrapropylphosphinine was achieved by the reaction of 1,3,2-diazaphosphinine with an excess of 4-Octyne in toluene (Scheme 7). The reaction mixture was heated to reflux for 7 days. After evaporation of the solvent, the pure phosphinine could be obtained in 88% yield after flash-column chromatography (hexanes/SiO_2).



Scheme 9: *Synthesis of 2,3,5,6-Tetrapropylphosphinine.*

The four ligands depicted in Scheme 10 were chosen to study the synthesis of transition metal NPs. The 3,5-diphenylphosphinine **III-5** was already used by Moores *et al.* to study the synthesis of gold-NPs.

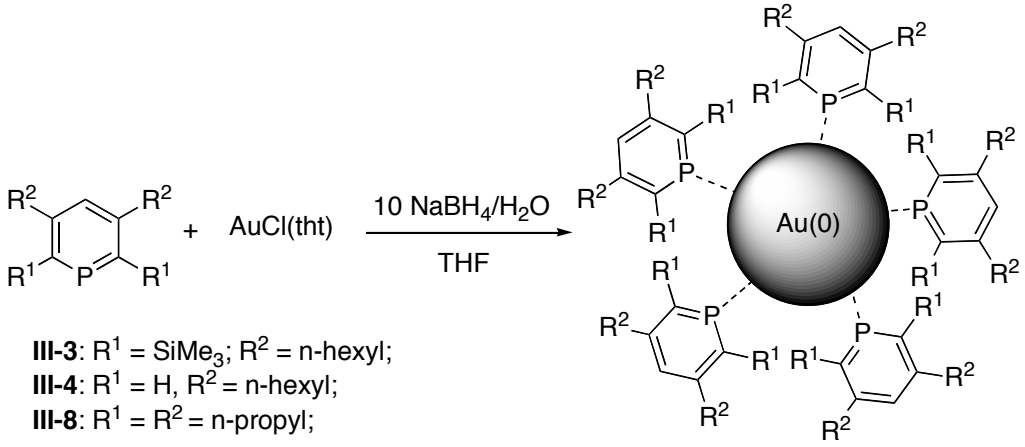


Scheme 10: *Ligands used for further studies.*

III. SYNTHESIS OF NANOPARTICLES

III.1. Influence of steric-hindrance

To probe the influence of the steric bulk in the 2,6-position of the phosphinine on the monodispersity and size of the NPs stabilized by phosphinines, gold NPs were synthesized with ligands **III-3, III-4** and **III-8** and compared to the results obtained by Moores and coworkers with 3,5-diphenylphosphinine **III-5**. The gold NPs were obtained by the reduction of a mixture of 1 equivalent of [AuCl(tht)] and 1 equivalent of the corresponding phosphinine ligand in THF (2mL) with a solution of 10 equivalents of sodium borohydride in water (Scheme 9). In preliminary tests, it was observed that the best results in terms of monodispersity were obtained with a gold/ligand ratio of 1 under these conditions and when the solution of sodium borohydride was added rapidly in a single portion. Therefore the following studies were carried out in this way.



Scheme 11: *Synthesis of gold nanoparticles stabilized by phosphinines* ***III-3, III-4*** *and* ***III-8***.

After 30 min the reaction mixture was diluted with water and the NPs were isolated by extraction of the aqueos phase with dichloromethane. TEM-images of the NPs prepared by this method in comparison to the NPs prepared by Moores et al. are shown in Figure 2.

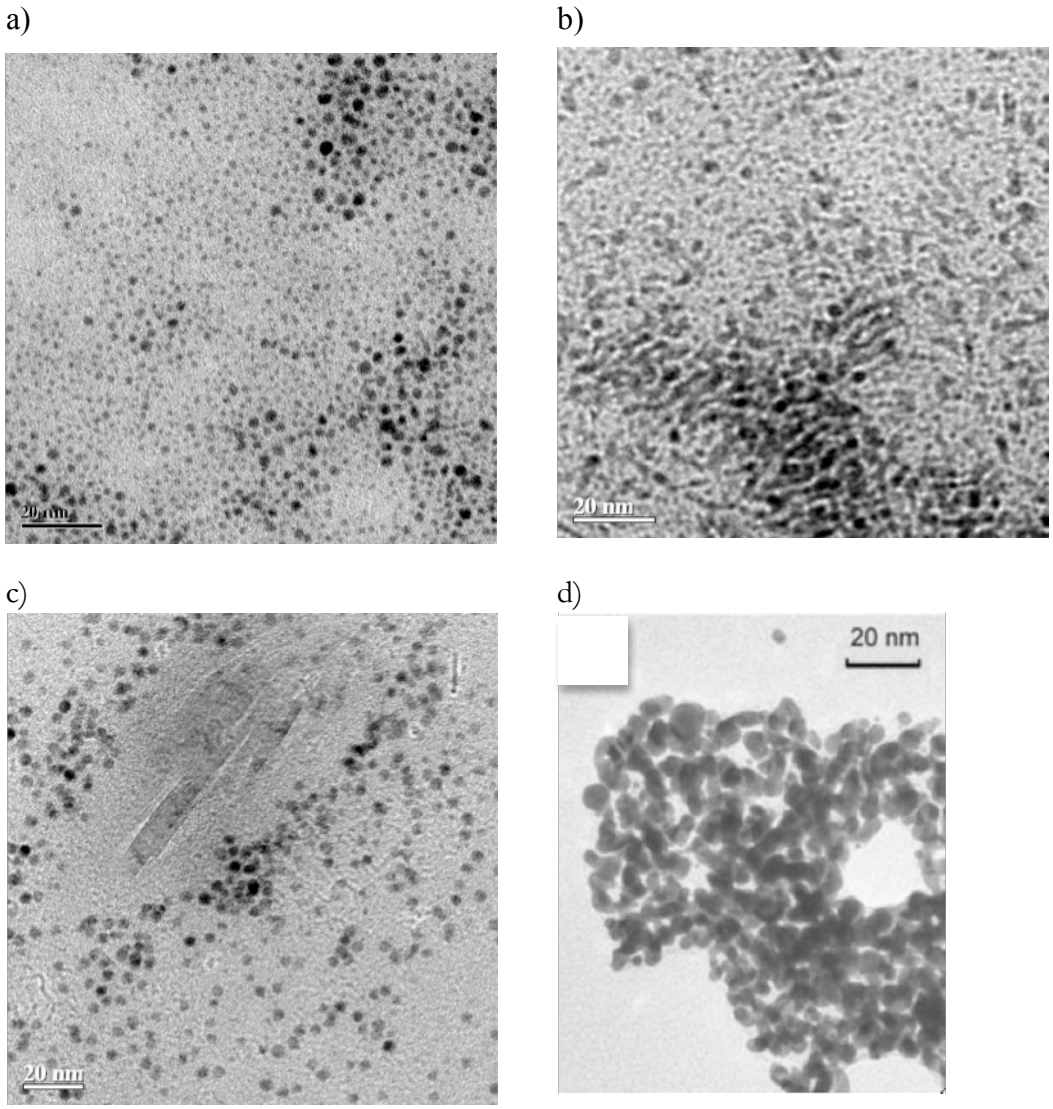


Figure 2: *TEM-images of gold nanoparticles stabilized with a) 2,3,5,6-Tetrapropylphosphinine, b) 2,6-Di(trimethylsilyl)-3,5-di(hexyl)-hosphinine, c) 3,5-Di(hexyl)-phosphinine, d) 3,5-Di(phenyl)phosphinine.*[36]

The presence of the phosphinine ligands on the surface of the NPs was proved by infrared-spectroscopy. The IR-spectrum of a sample of NPs stabilized with ligand **III-8** is shown in Figure 3 compared to the spectrum of the free ligand. The IR-spectrum of the NPs stabilized with ligand **III-8** (Figure 3b) clearly shows the presence of the characteristic bands of Ligand **III-8** between 1200 cm^{-1} and 1800 cm^{-1}, that were attributed to the vibrations of the phosphinine by Moores,[36] as well as the some bands in the region of 2900 – 3000 cm^{-1}, that are characteristic for the vibration of C-H-Bonds in alkyl groups.

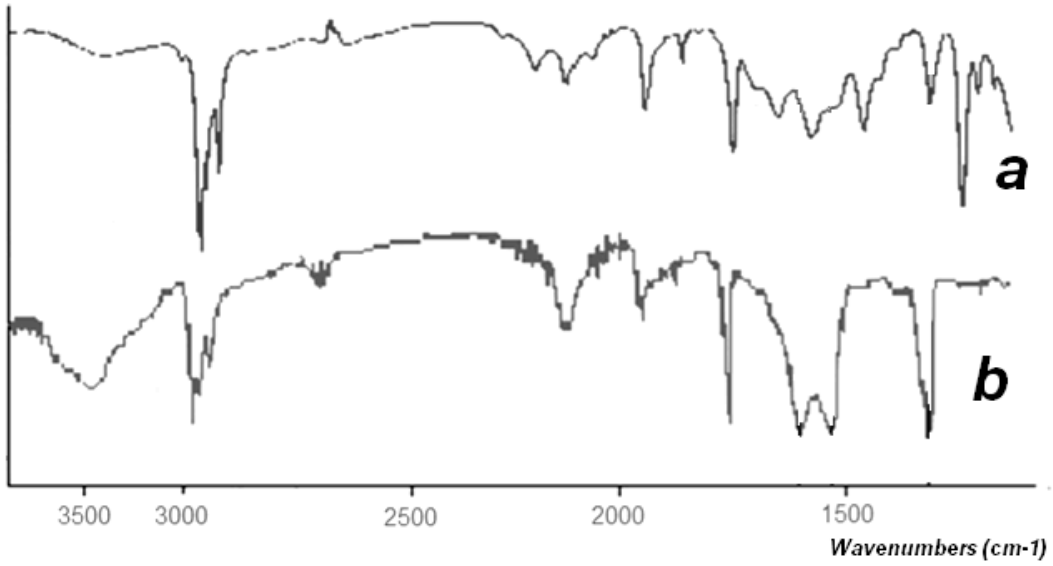
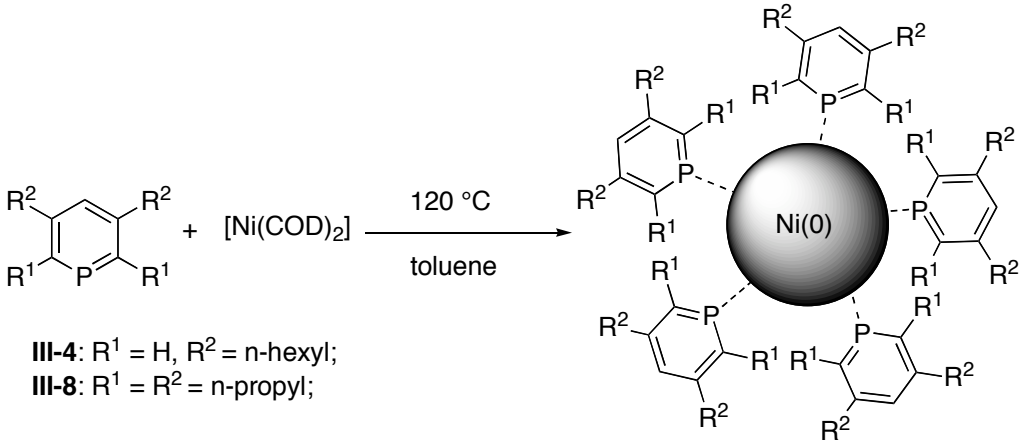


Figure 3: *Infrared spectra (KBr-pellet) of a) Ligand **III-8**; b) gold nanoparticles stabilized with Ligand **III-8**.*

III.2. Synthesis of nickel nanoparticles

As nickel(0)-tetrakisphosphinine complexes are well known and relatively stable it was to be expected that the reduction of a nickel(II)-precursor in the presence of phosphinines might lead to complex mixtures of different complexes and colloids. Therefore a different synthetic strategy was envisaged. The thermal decomposition of a zerovalent transition-metal precursor is another well-known route to produce NPs. In a first series of experiments, $[Ni(COD)_2]$ was heated to 120 °C in toluene in the presence of ligand **III-8** (0.5 or 1 equivalent) (Scheme 10). The initially pale yellow solution of $[Ni(COD)_2]$ turned dark red upon addition of the phosphinine ligand. After 2 h at 120 °C the color of the solution had changed from red to black.



Scheme 12: *Synthesis of phosphinine stabilized nickel-nanoparticles.*

The formation of NPs could be verified by transition electron microscopy (Figure 3). To prevent the nickel NPs from oxidation, the microscopy grids were prepared by depositing a drop of the reaction mixture on a microscopy grid in a glove box under argon atmosphere.

a) b)

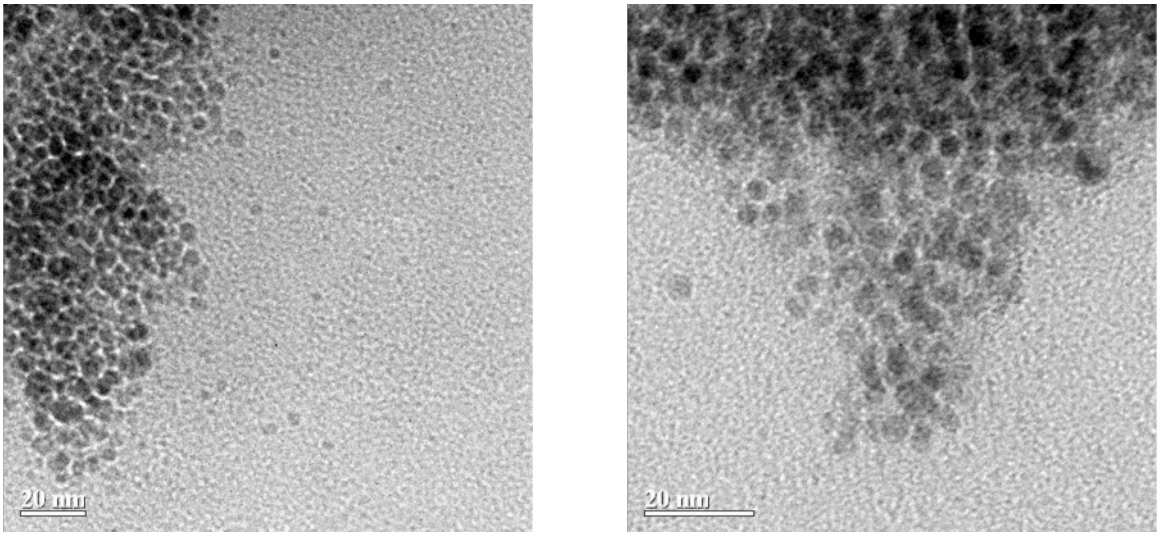


Figure 3: *TEM-images of nickel-nanoparticles stabilized with a) 0.5 equiv. of Ligand* ***III-8****, b) 1 equiv. of Ligand* ***III-8****.*

As can been seen by electron microscopy, the ratio of metal precursor to ligand does not seem to have an influence on the size and monodispersity of the obtained NPs (a)5 nm ± 0.7 nm and b) 5nm ± 0.6 nm respectively) in the case of Ligand **III-8**.

Whereas the NPs are stable for several weeks in the absence of oxygen, an immediate change in their magnetic properties can be observed when exposed to air. After the exposure to air, the nanoparticles show a very pronounced ferromagnetic behavior. Despite that a TEM image of the NPs exposed to air shows that this change in the magnetic properties does not result from the agglomeration of the NPs. Therefore it seems most likely, that the change in the magnetic properties results from the oxidation of the nickel NPs (**Note:** The rapid oxidation of nickel-nanoparticles stabilized by phosphines has been reported before by Park *et al.*[37]).

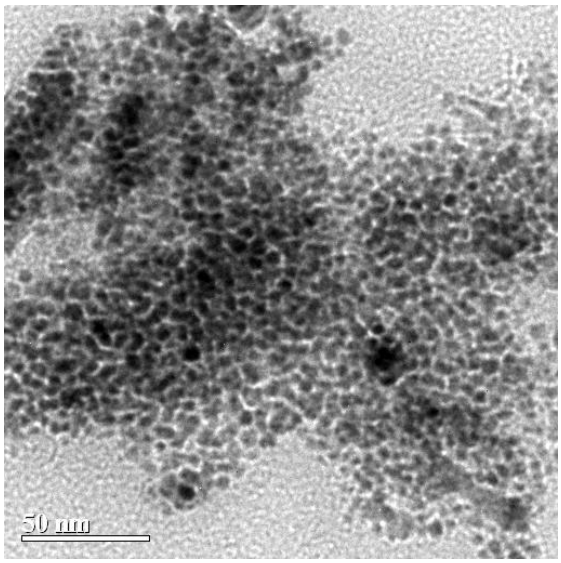


Figure 4: *TEM-image of a sample of nickel NPs stabilized with 1 equiv. of Ligand after exposure to air.*

Furthermore it could be observed *via* IR-spectroscopy, that even after exposure of the NPs to air, the Ligand **III-8** could still be detected on the surface of the NPs. The infrared spectrum of nickel NPs exposed to air (KBr-pellet) compared to the spectrum of Ligand **III-8** is shown in Figure 5.

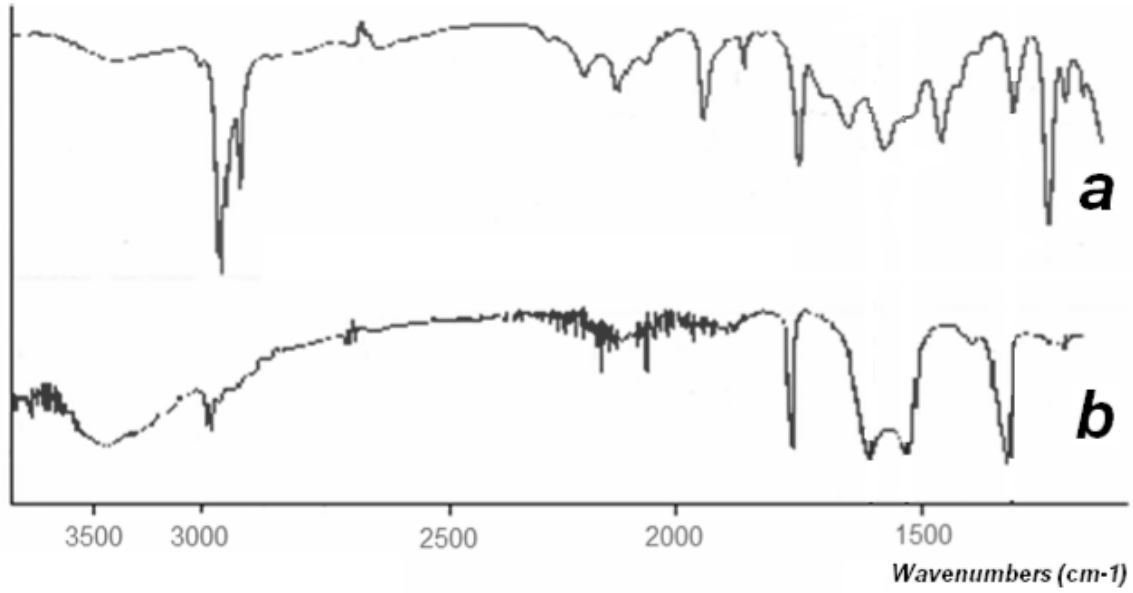
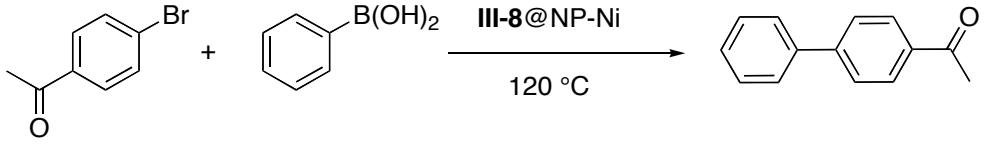


Figure 5: *IR-spectra (KBr-pellet) of a) ligand **III-2** and nickel NPs stabilized with ligand **III-2** after exposure to air.*

As in the case of the gold nanoparticles characteristic bands in the range of 1200 cm^{-1} to 1800 cm^{-1} allow for the detection of ligand **III-8**.

The use of the NPs stabilized with ligand **III-8** in Suzuki-Miyaura reactions was tested before and after exposure to air under the conditions reported by Park et al..[37] No conversion of 4-bromoacetophenone to the corresponding biaryl could be observed under these conditions even at catalyst loadings as high as 5 % of nickel (Scheme 13).



Scheme 13: *Catalytic test reactions with nickel NPs stabilized with ligand **III-2**.*

Different reasons might explain the absence of catalytic activity for nickel NPs stabilized by phosphinines. In analogy to Pd NPs, that serve as a reservoir for Pd(0)-phosphine complexes it might be possible that Ni(0)-phosphine complexes are leached from nickel NPs. Nickel(0)-phosphine-complexes are known to be potent catalysts for Suzuki-Miyaura coupling reactions with poorly reactive chloroarenes even at room-temperature.[38] In contrast, nickel complexes with phosphinines are very unlikely to be good catalysts for cross coupling reactions.

Surprisingly when ligand **III-4** was used with the same protocol as for ligand **III-8**, no NPs could be isolated. The reaction mixture changed its color from deep-red to dark brown upon heating to 120 °C but only the formation of amorphous material could be observed by electron microscopy (Figure 6a). Additionally, when the reaction mixture was exposed to air, its color immediately changed from dark brown to off-white and an insoluble precipitate was formed. A possible explanation of these observations would be the formation of very small sub-nano nickel clusters under these conditions that cannot be detected by transition electron microscopy. As it is not possible to heat the reaction mixture to a much higher temperature in toluene to allow for the formation of nanoparticles, it was tried to perform the thermal decomposition of $[Ni(COD)_2]$ in 1-octadecene (ODE). Due to its higher boiling point (352 °C at ambient pressure) it is possible to study the formation of nanoparticles at higher temperatures.

The reaction mixture was heated stepwise starting from 120 °C in steps of 20°C. After 1h at each temperature, a sample for electron microscopy was prepared.

At 220 °C the formation of small nanoparticles could be observed. The nanoparticles could be isolated by precipitation with ethanol. The nanoparticles obtained under these conditions are relatively small (2 nm) and polydisperse (Figure 6b) compared to those obtained with ligand **III-8** in toluene. Furthermore they can be redispersed in non-polar solvents after the isolation and seem to be less sensitive toward oxidation.

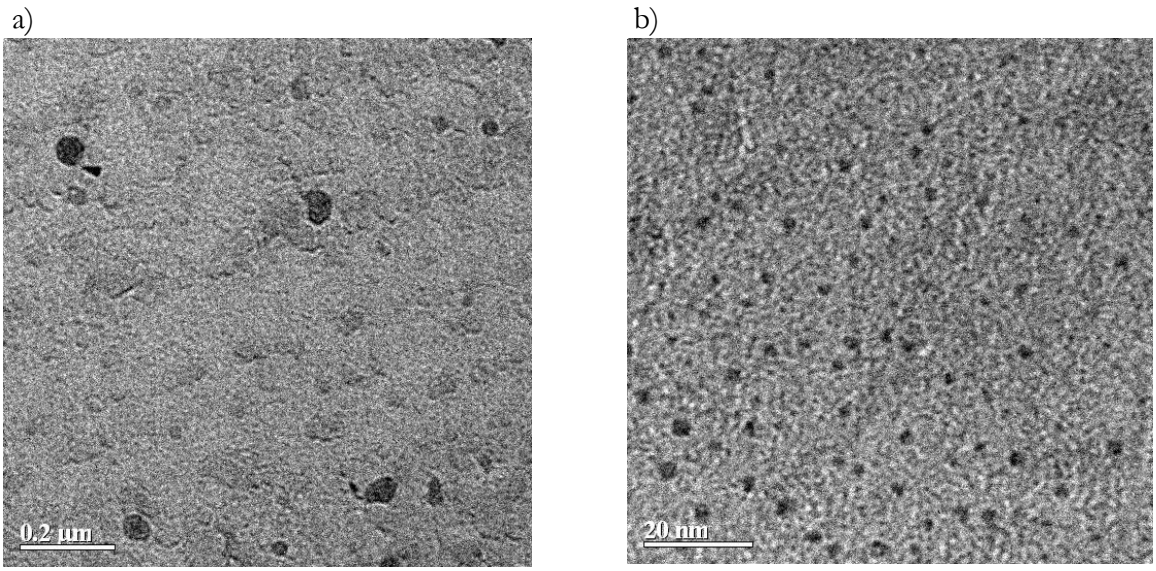


Figure 6: *TEM image of the reaction mixture of the thermal decomposition of [Ni(COD)$_2$] in the presence of a) ligand* ***III-4*** *in toluene at 120 °C, b) Ligand* ***III-4*** *in 1-octadecene at 220°C.*

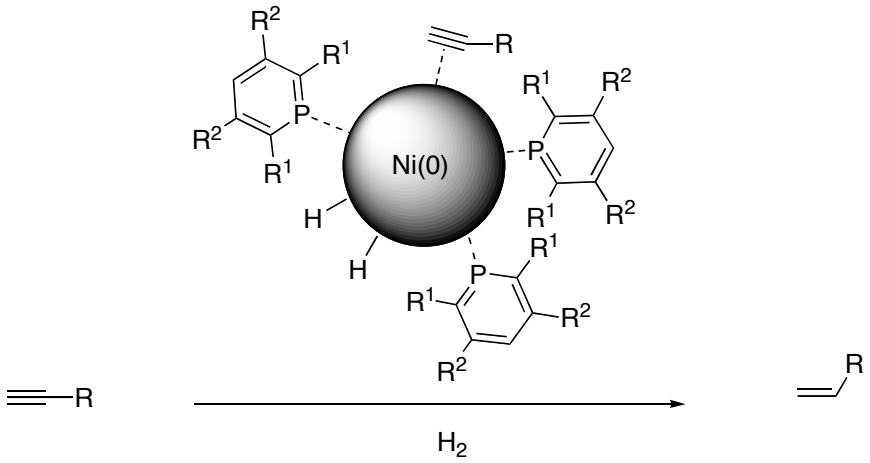
IV. CONCLUSION AND PERSPECTIVES

In this chapter we have shown the influence of the substitution pattern of the phosphinine ring on the size and distribution of gold nanoparticles.

These materials can be readily synthesized by reduction and are stable on a long term without any sign of agglomeration or decomposition of the phosphinine ligand. Furthermore it was shown that phosphinines are suitable for the stabilization of nickel nanoparticles formed by a thermal decomposition of [Ni(COD)$_2$]. No catalytic activity could be detected for nanoparticles stabilized with ligand **III-8** in the Suzuki-Miyaura cross coupling.

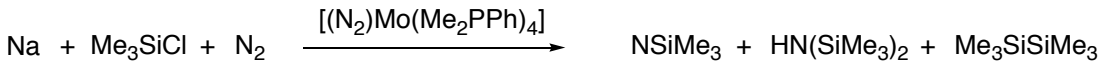
The characterization of the nickel nanoparticles with more elaborate analytic methods like XPS spectroscopy would allow for the characterization of the oxidation state of the surface nickel atoms. Furthermore the magnetic properties could be studied via SQUID-measurements.

The application of phosphinine stabilized nickel NPs might be more promising in selective hydrogenation reactions, as for example the hydrogenation of alkynes to alkenes.[39]



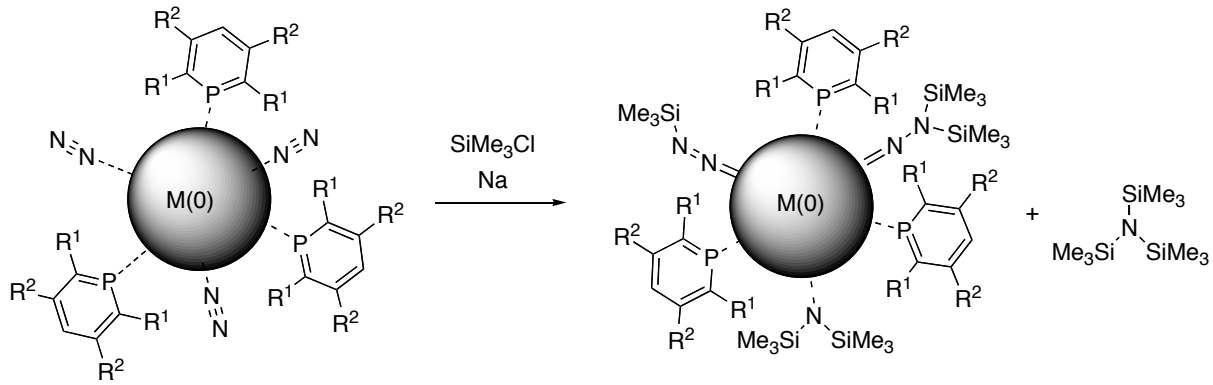
Scheme 14: *Selective hydrogenation of alkynes.*

An important property of phosphinines is their stability towards reducing agents such as alkaline metals compared to tertiary phosphines with aryl substituents. Early transition metal complexes of phosphinines were reported for example by Elschenbroich[30] and our group.[28] These studies prove that phosphinines are able to stabilize these complexes under reductive conditions. This could be beneficial if the use of this complexes in catalytic process under reductive conditions is envisaged. For example Hidai and coworkers reported in 1989 that molecular nitrogen can be functionalized by molybdenum phosphine complexes(Scheme 15).[40, 41]



Scheme 15: *Synthesis of $N(SiMe_3)_3$ from N_2, $SiMe_3Cl$ and Na catalyzed by a molybdenum phosphine complex.*

One of the drawbacks of the catalyst used by Hidai is the intrinsic instability of arylphosphine under reductive conditions. Therefore it could be beneficial to use phosphinines to stabilize molecular or nano-sized catalysts for this interesting transformation (Scheme 16).



Scheme 16: *Fixation and fucntionalisation of dinitrogen by phosphinine stabilized molybdenum nanoparticles.*

V. REFERENCES

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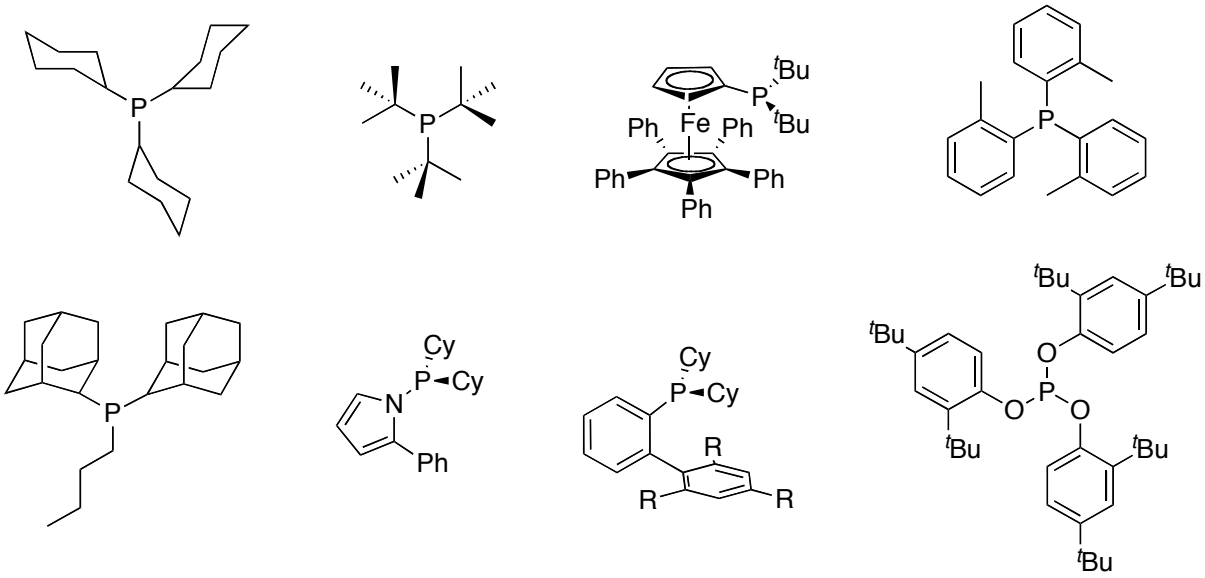
PART IV:

1-Phosphabarrelenes

CHAPTER 1: SYNTHESIS OF STERICALLY HINDERED 1-PHOSPHABARRELENE LIGANDS

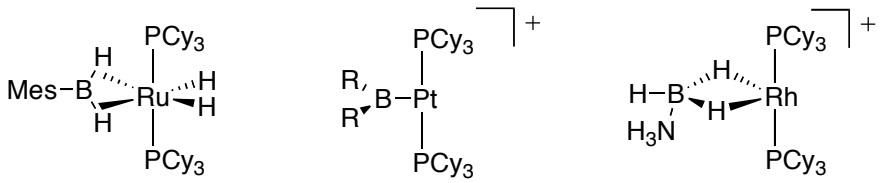
I. INTRODUCTION

Sterically crowded monodentate tertiary phosphines have found important applications in the kinetic stabilization of unsaturated low-valent transition metal complexes.[1-9] Some of these complexes proved to be among the most active catalysts in organic transformations of synthetic relevance, such as the very well documented Pd catalyzed cross coupling reactions. [8, 10-14]



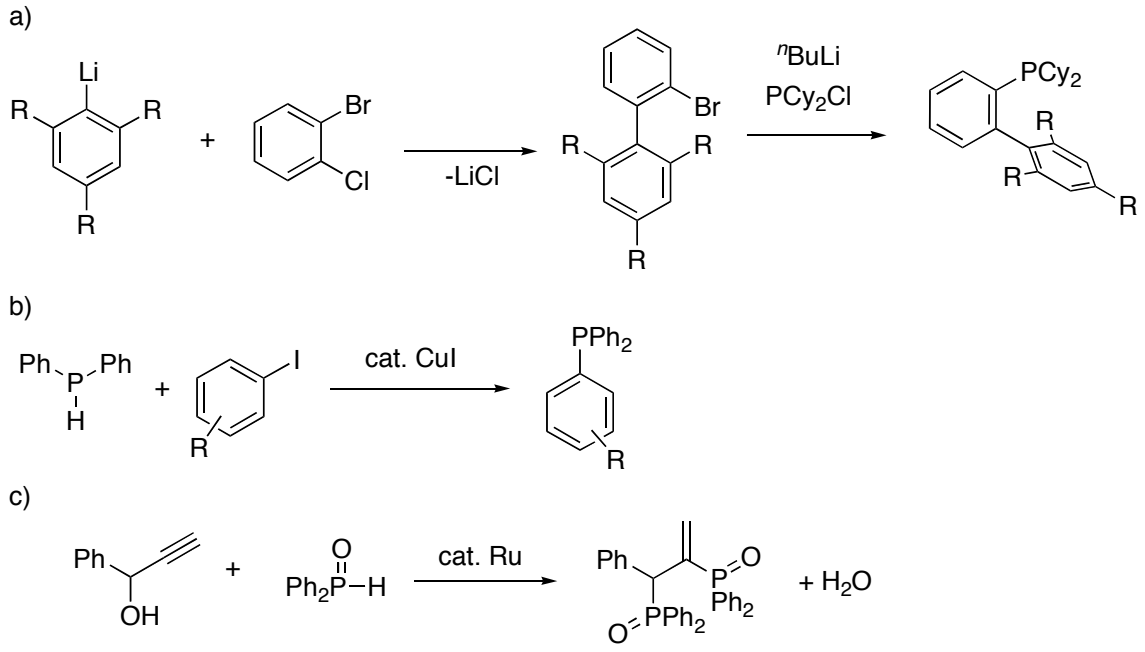
Scheme 1: *Monodentate phosphine and phosphite ligands with sterically demanding substituents.*

In some instances, the unsaturation of the metal coordination sphere could be used for the stabilization of highly reactive species.[15-20] Controlling the steric environment and the electronic properties of tertiary phosphines thus allows to finely tune the degree of coordinative unsaturation of a metal center, and in turn its reactive behavior. Yet this remains an important challenge, since highly unsaturated species may activate even the most unreactive bonds. It is therefore a highly delicate task to stabilize these unsaturated compounds.



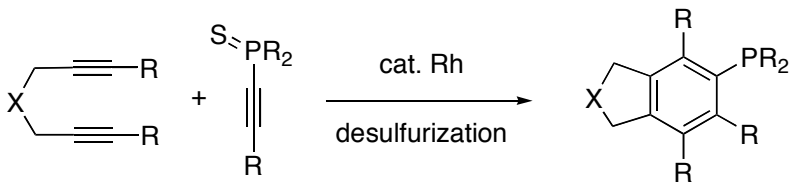
Scheme 2: *Stabilization of highly reactive species by sterically hindered trialkylphosphine ligands.*

In most cases, bulky phosphines are available through multistep synthesis from halogenated derivatives[8,12] or through metal catalyzed phosphination[12, 21-24] or phosphinylation[25] processes (Scheme 3).



Scheme 3: a) *Synthesis of Buchwald-type phosphines b) Synthesis of unsymmetrical triarylphosphines by copper-catalyzed phosphination c) Synthesis of bidentate phosphines by ruthenium catalyzed phosphinylation.*

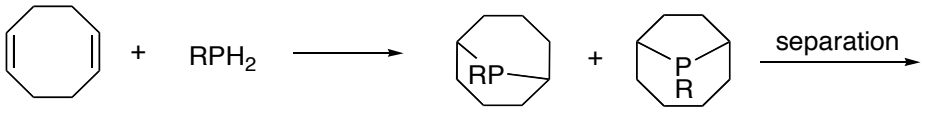
Another very elegant method for the synthesis of bulky phosphines, that consists in the formally [2+2+2]-cycloaddition of a tethered diyne with a 1-alkynylphosphine sulfide catalyzed by rhodium, was reported by Oshima and coworkers in 2007 - 2008 [26, 27] (Scheme 4).



Scheme 4: *Synthesis of sterically hindered phosphines via [2+2+2]-cycloaddition.*

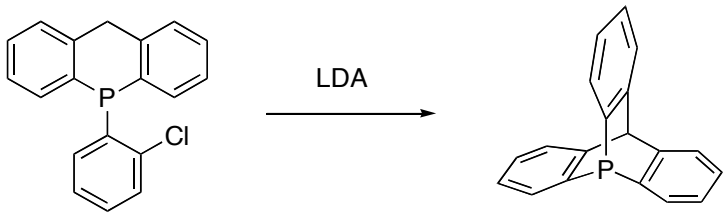
Bicyclic phosphines have shown to be very promising class of ligands in homogenous catalysis. Despite the encouraging results in hydroformylation reactions, the application of these ligands remains still relatively rare.

For example phosphabicyclononanes (Phoban) can be readily obtained from the reaction of primary phosphines with 1,5-cyclooctadiene, providing the two regioisomers 9-*R*-9-phosphabicyclo[3.3.1]nonane and 9-*R*-9-phosphabicyclo[4.2.1]nonane, that need to be separated before they can be used in catalysis.[28] (Scheme 5).



Scheme 5: *Synthesis of Phoban-ligands.*

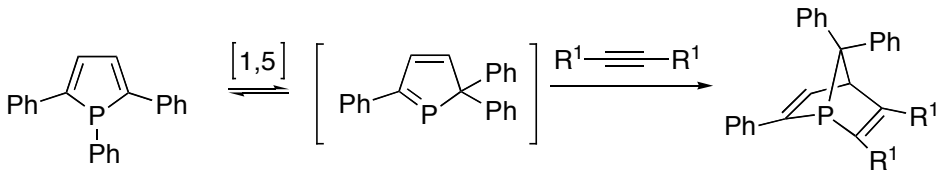
The synthesis of 9-phosphatriptycene was first reported in 1974 by Bickelhaupt and coworkers.[29] The key step in the synthesis of 9-phosphatriptycene is the intra-molecular attack of the carbanion on the chloride atom formed upon deprotonation with LDA. However it is difficult to apply this method to the preparation of functionalized 9-phosphatriptycenes, because of tedious preparation of the dibenzo-dihydrophosphinines.



Scheme 6: *Synthesis of 9-phosphatriptycene by Bickelhaupt and coworkers.*

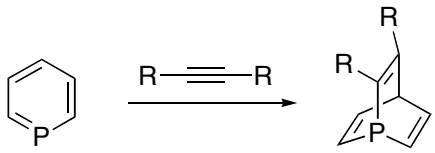
In this perspective, low coordinated phosphorus species featuring either C≡P or C=P bonds, which exhibit a close reactivity to their carbon counterparts, were shown to behave as efficient precursors of cyclic phosphines and phosphorus containing cage-compounds.

For example, 1-phosphanorbornadienes can be readily obtained by the reaction of phospholes with alkynes (Scheme 7). The first step of this reaction sequence is the [1,5]-sigmatropic phenyl shift leading to a λ^3-phosphole, that reacts as a diene in a [4+2] hetero Diels Alder reaction with various alkynes to give the corresponding 1-phosphanorbornadienes.



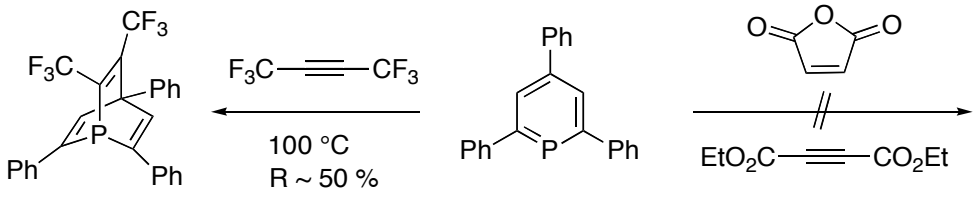
Scheme 7: *Synthesis of phospha-norbornadienes from phospholes.*

1-phosphabarrelenes, can be prepared by a similar approach through a [4+2] Diels Alder reactions between phosphinines and alkynes (Scheme 8). In this case, the phosphinine acts as the heterodiene moiety.



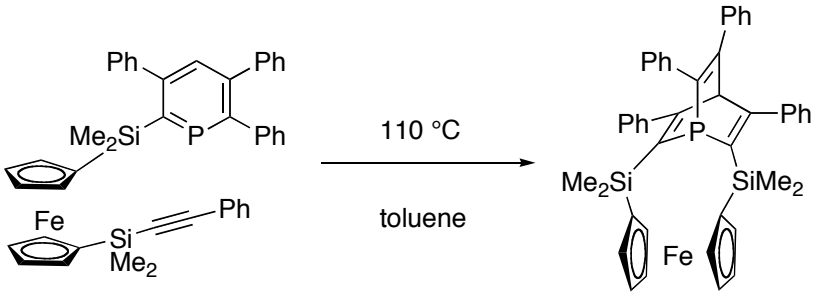
Scheme 8: *Preparation of 1-phosphabarrelenes via a Dials-Alder reactions.*

However , in many cases the reaction is not favorable and highly reactive alkynes have to be employed. For example in the case of 2,4,6-triphenylphosphinine no reaction can be observed between the phosphinine and maleic anhydride or diethyl-butyne-1,4-diaote. In contrast, if the more reactive hexafluoro-but-2-yne is employed, the corresponding 1-phosphabarrelene can be obtained in modest yield (Scheme 9). [30, 31]



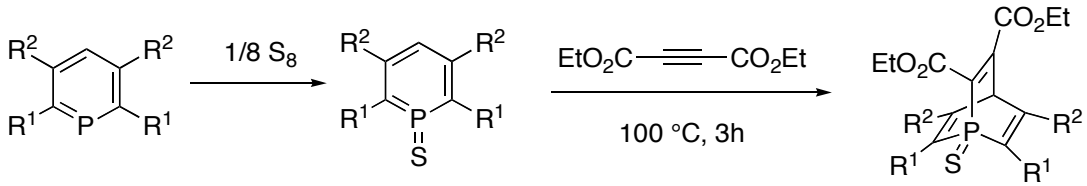
Scheme 9: *Reaction of 2,4,6-triphenylphosphinine with activated alkynes and maleic anhydride.*

An intramolecular Diels-Alder reaction of a non-activated alkyne was reported by our group in the case of a ferrocenyl-phosphinine substituted with an alkyne on the second cp-ring (Scheme 10).[32]



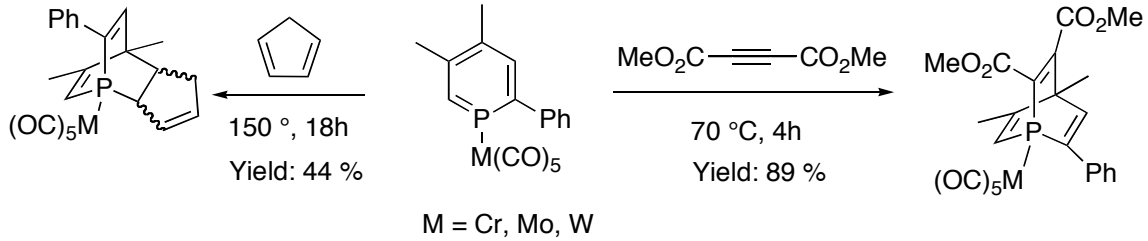
Scheme 10: *Intramolecular Diels-Alder reaction of a phosphinine with a non-activated alkyne.*

Two methods are known that enable activation of phosphinines toward the [4+2] cycloaddition. The first one is the oxidation of the phosphorus atom with sulfur to obtain the corresponding phosphinine sulfides, that are much more reactive than the phosphinines (Scheme 11).



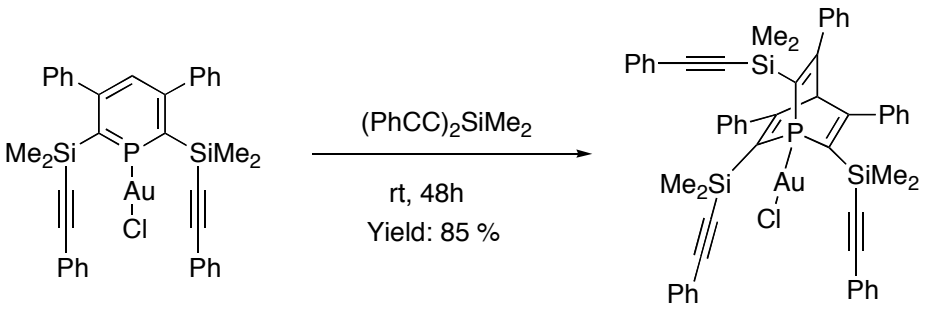
Scheme 11: *Activation of phosphinines by sulfurization of the phosphorus atom.*

The second method consists in the coordination of the phosphinine to a group 6 transition metal. Upon reaction of these complexes with dienophile, 1-phosphabarellenes can be obtained in high yield even when non-activated alkynes or alkenes, like cyclopentadiene or maleic amides are used as a dienophile (Scheme 12).[33, 34]



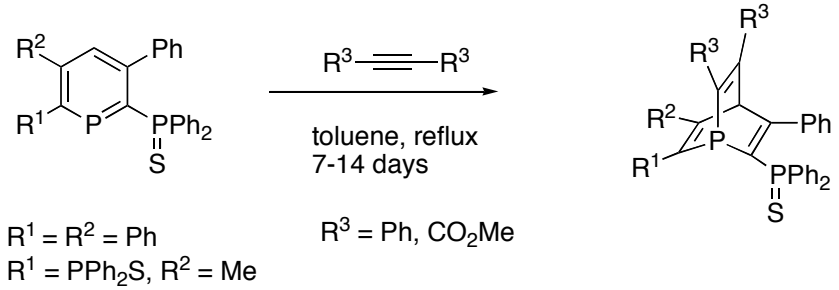
Scheme 12: *Activation of phosphinines by coordination of group 6 transition metals.*

This activation is even more favorable in the case of gold(I)-complexes of phosphinines (Scheme 13).[35]



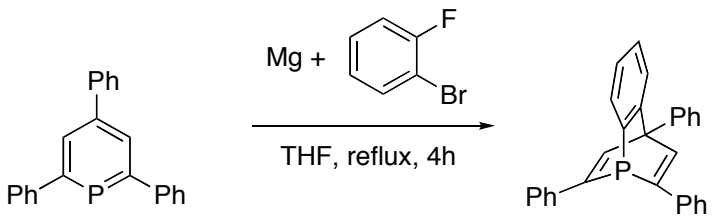
Scheme 13: *Diels-Alder reaction of a phosphinine activated by the coordination to Au(I).*

Recently it was found in our group,[36] that in the case of phosphinines, that are substituted with an electron withdrawing diphenylphosphinesulfide substituent in the 2 (and 6) position, that the Diels-Alder reaction with moderately activated alkynes such as diphenylacetylene or dimethyl-butyne-1,4-dioate the corresponding 1-phosphabarrelenes could be obtained in high yield, even after the very long heating periods required for complete conversion of the starting materials (Scheme 14).



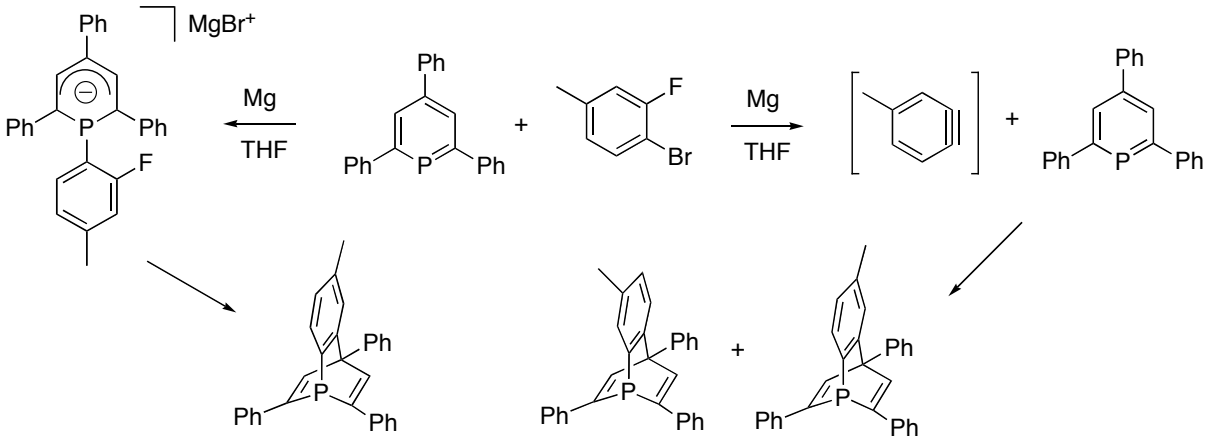
Scheme 14: *Diels Alder reaction of diphenylphosphine sulfide substituted phosphininies.*

Märkl and Breit reported on the addition of in-situ generated benzyne to phosphinines. In this case, benzyne was generated from bromofluorobenzene with magnesium in the presence of the phosphinine. In general, low to moderate yields were obtained by this method and isolation of the phosphabarrelene is complicated by the formation of by-products (Scheme 15). [37-39]



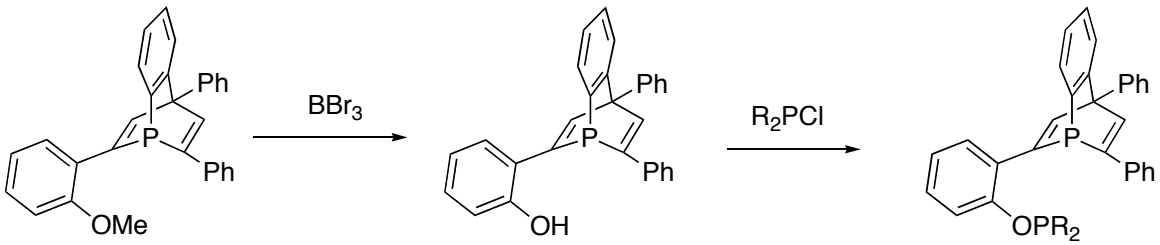
Scheme 15: *Synthesis of Benzo-1-phosphabarrelene according to Märkl and Breit.*

Breit and coworkers proved the formation of benzyne under the reaction conditions by employing methyl-substituted bromofluorobenzene, leading to two different regio-isomers that can only be obtained if benzyne is involved in the formation of the phosphabarrelene. In contrast a reaction involving an anionic intermediate resulting from the nucleophilic attack of a Grignard reagent to the phosphinine would lead to only one single product (Scheme 16). [38]

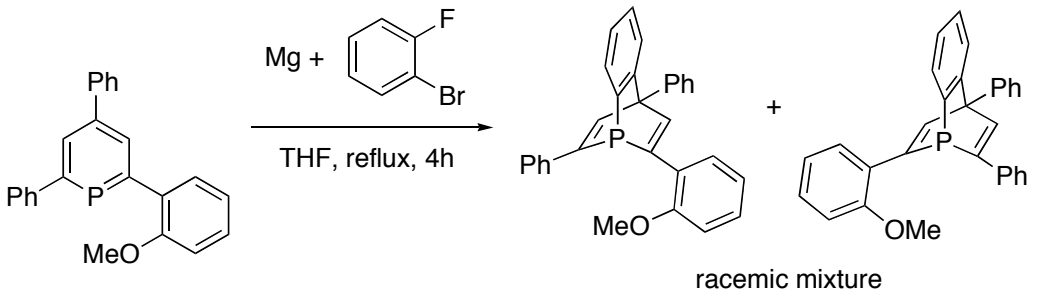


Scheme 16: *Comparison of two possible mechanisms for the formation of Benzo-1-phosphabarrelene with bromofluorobenzene and magnesium.*

In further studies, Breit and coworkers developed the synthesis of chiral and bidentate 1-phosphabarrelene ligands.[40] The chiral phosphabarrelenes were obtained by the reaction of benzyne with asymmetric phosphinines as a racemic mixture and the pure enantiomers could be separated by chiral preparative HPLC (Scheme 17). The methoxy-substituted 1-phosphabarrelenes that were obtained by this method were then treated with BBr_3 to give the hydroxy-substituted derivatives that can be transformed into the corresponding bidentate phosphabarrelene-phosphite by reaction with a chlorophosphine (Scheme 18).

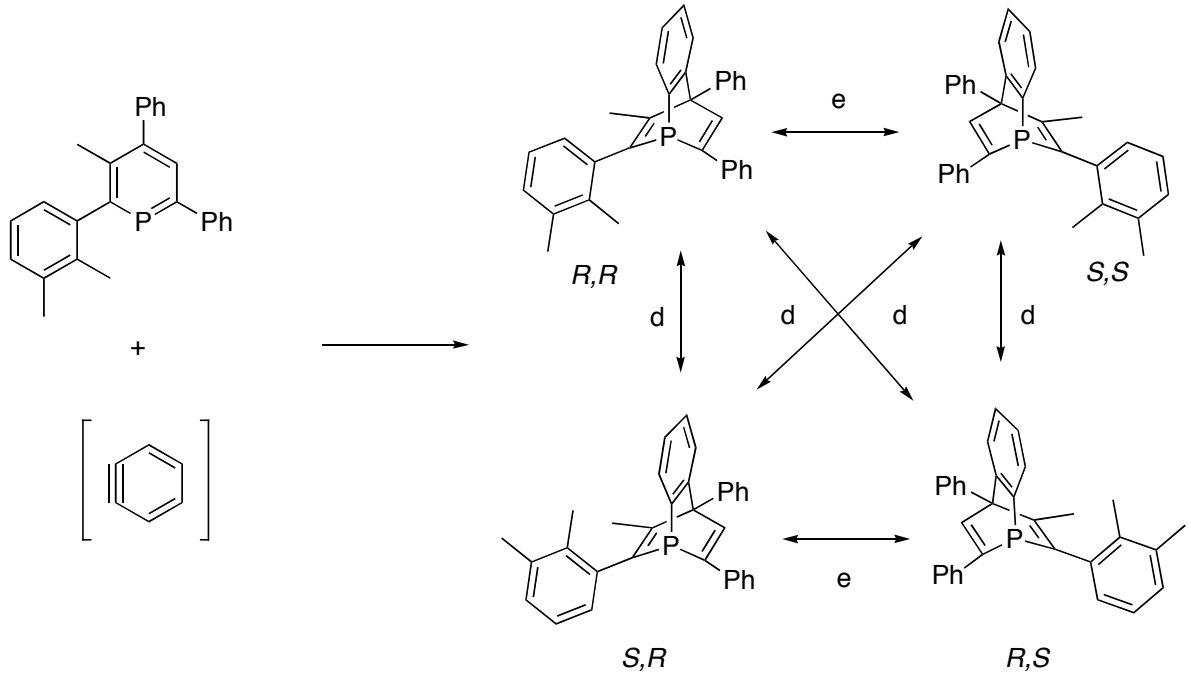


Scheme 17: *Synthesis of chiral 1-phosphabarrelene by Breit.*



Scheme 18: *Synthesis of bidentate 1-phosphabarrelene-phosphite ligands.*

Recently Müller and coworkers reported the synthesis of chiral 1-phosphabarrelenes starting from an atropoisomeric-phosphinine leading to pairs of diastereoisomers (Scheme19).[41, 42]



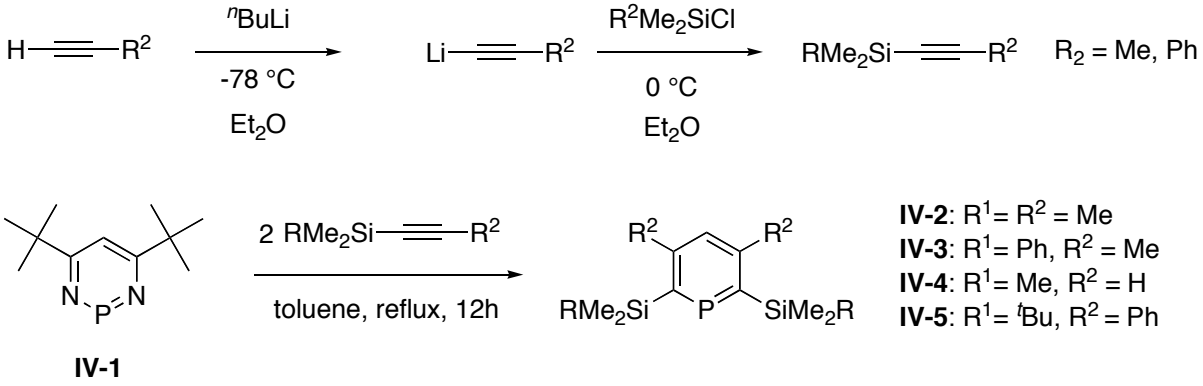
Scheme 19: *Synthesis of chiral phosphabarrelenes starting from an atropisomeric phosphinine (e: enantiomers; d: diasterioisomers).*

In this chapter we will focus on the synthesis of sterically hindered phosphabarrelene derivatives substituted with bulky silyl-substituents as well as on the analysis of their electronic properties by means of NMR-spectroscopy, X-Ray-crystallography and DFT-calculations.

II. SYNTHESIS

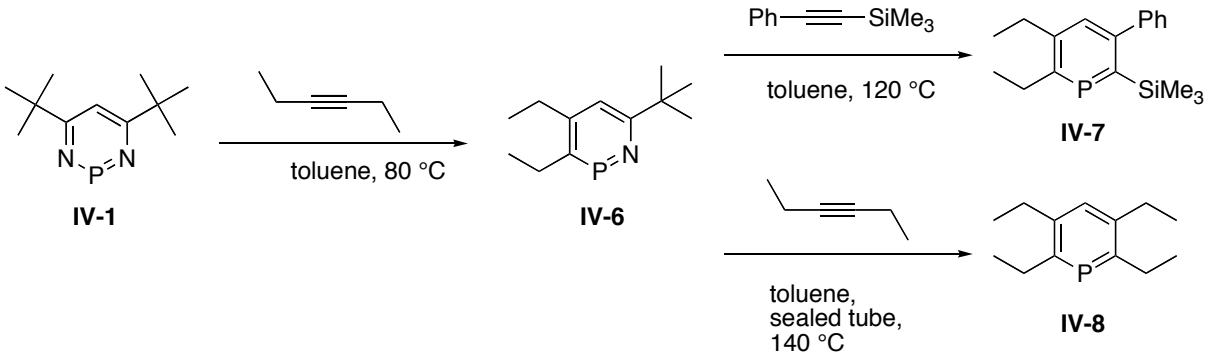
II.1. Phosphinines

The phosphinines that were used in this study were prepared from 1,3,2-diazaphosphinine,[43] by the reaction with the corresponding alkynes. The 1-silylalkynes, that were used could be readily obtained by deprotonation of the terminal alkynes with *n*-BuLi in diethylether and subsequent addition of the desired chlorosilane (Scheme 20). The phosphinines could be isolated as white crystalline solids in good yield (63-80 %) after column chromatography (hexanes/SiO_2).



Scheme 20: *Synthesis of 2,6-disilyl-substituted phosphinines* ***IV-2*** *-* ***IV-5****.*

Additionally 2-trimethylsilyl-3-phenyl-5,6-diethylphosphinine **IV-7**, was prepared by a stepwise reaction (Scheme 21).



Scheme 21: *Preparation of 2-trimethylsilyl-3-phenyl-5,6-diethylphosphinine* ***IV-7*** *and 2,3,5,6-(tetraethyl)-phosphinine* ***IV-8****.*

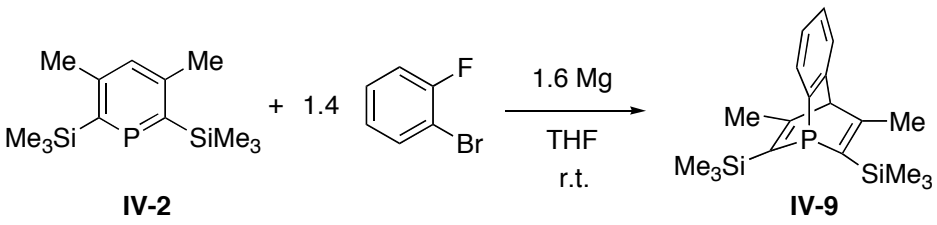
If the reaction of 3-hexyne with diazaphosphinine **IV-1** is carried out at 80 °C, only one equivalent of pivalonitrile is exchanged. The consumption of **IV-1** was followed by ^{31}P NMR

(appearance of a new signal for the monoaza-intermediate **IV-6** at δ = 270.5 ppm). The second cycloadditon/cycloreversion sequence was carried out at 120 °C with an excess of 1-trimethylsilyl-2-phenyl-acetylene. Monitoring the reaction by ^{31}P NMR spectroscopy shows that all the monoaza-intermediate **IV-6** was consumed after 12 h. The phosphinine was isolated as an off-white crystalline solid after column chromatography in good yield.

The monoazaphosphinine could equally be reacted with a second equivalent of 3-hexyne to give 2,3,5,6-tetraethylphosphinine **IV-8**. It should be noted that this reaction does not occur at 120 °C, therefore the reaction had to be carried out in a sealed tube in an oil bath at 140 °C. The product was obtained as a colorless oil after column chromatography.

II.2. Synthesis of 1-Phosphabarrelenes

For the synthesis of the silyl-substituted benzo-1-phosphabarrelenes the method of Märkl was used.[39] The reaction conditions were optimized for the reaction of phosphinine **IV-2** with the *in-situ* generated benzyne. When the reaction was followed by ^{31}P NMR spectroscopy, it could be observed, the formation of a single new product at a chemical shift of δ = -60.1 ppm, in the usual range for 1-phosphabarrelens was formed. Full conversion of phosphinine **IV-2** (δ = 273.5 ppm) was reached at room-temperature, when 1.4 equivalents of bromofluorobenzene and 1.6 equivalents of magnesium turnings were used. 1-phosphabarrelene **IV-9** could be isolated in good yield (75 %) as an off-white crystaline solid after recrystalization from methanol.



IV-2 **IV-9**

Scheme 22: *Synthesis of 1-phosphabarrelene IV-9.*

The product was characterized by NMR spectroscopy and HR-MS-spectrometry. Single crystals suitable for X-Ray crystal structure analysis were grown from a saturated solution of **IV-9** in methanol at -18 °C. The X-Ray crystal structure of phosphabarrelene **IV-9** is presented in Figure 2.

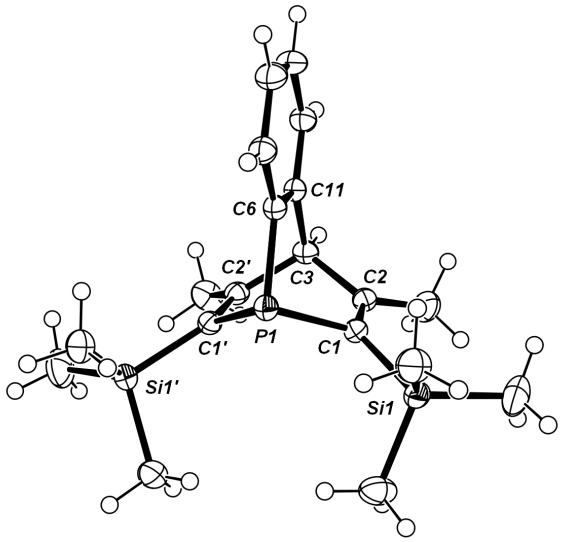
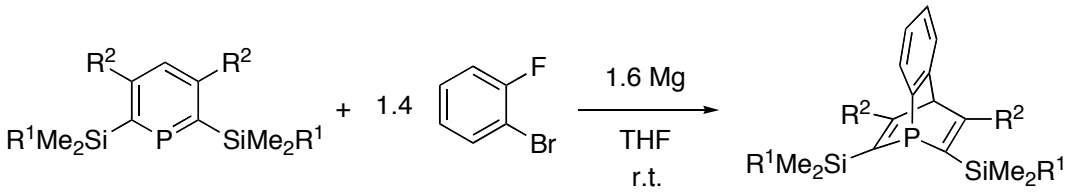


Figure 1: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of phosphabarrelenes* ***IV-9****. Selected bond lengths [Å] and angles [°] for: P1-C1: 1.863(2), P1-C6: 1.835(2), C1-C2: 1.342(2), C2-C3: 1.540(2), C3-C11: 1.520(3), C6-C11: 1.400(3), C1-P1-C1': 97.5(1), C1-P1-C6: 95.12(7), P1-C1-Si1: 113.56(8).*

The synthesis of the 1-phosphabarrelenes **IV-10** – **IV-12** could be achieved in good yield (63-80 %) by the same procedure. (Scheme 23). All products were characterized by NMR-spectroscopy. Single crystals suitable for X-Ray crystal structure analysis could be obtained by recrystallization of **IV-12** from methanol. The X-Ray crystal structure of ligand **IV-12** is presented in Figure 3.



IV-3: R^1 = Ph, R^2 = Me,
IV-4: R^1 = Me, R^2 = H,
IV-5: R^1 = tBu, R^2 = Ph.

IV-10: R^1 = Ph, R^2 = Me,
IV-11: R^1 = Me, R^2 = H,
IV-12: R^1 = tBu, R^2 = Ph.

Scheme 23: *Synthesis of ligands* ***IV-10 - IV-12****.*

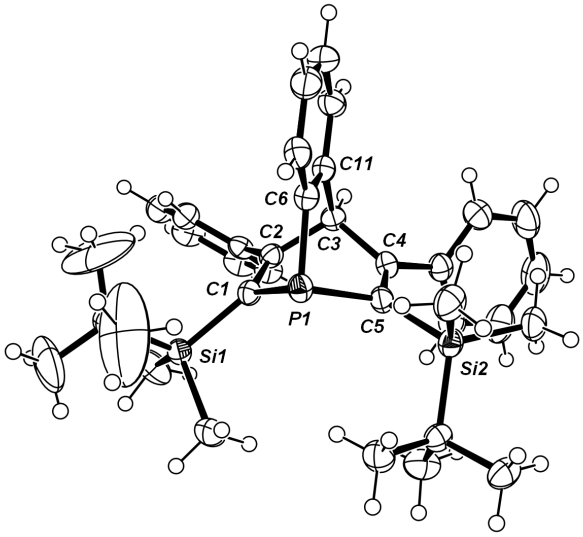
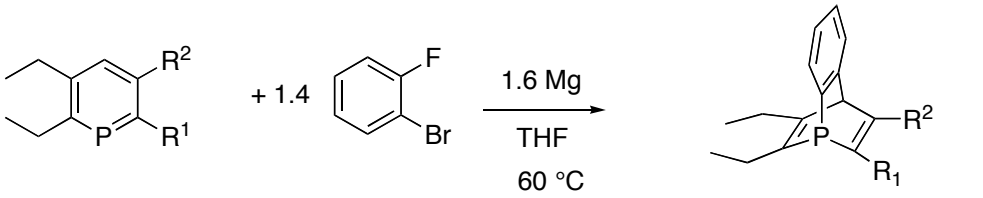


Figure 3: *Molecular structure of ligand* ***IV-12*** *(ORTEP-representation, thermal ellipsoids at a 50 % probability). Selected bond lengths [Å] and angles [°]: P1-C1: 1.858(3), P1-C5: 1.863(3), P1-C6: 1.831(3), C1-C2: 1.349(4), C2-C3: 1.537(4), C3-C4: 1.533(4), C4-C5: 1.341(4), C3-C11: 1.526(4), C6-C11: 1.409(4), C1-P1-C5: 97.5(1), C1-P1-C6: 96.3(1), P1-C1-Si1: 117.8(2).*

In the case of phosphinines **IV-7** and **IV-8**, no reaction could be observed at room temperature but the reaction, readily occurred at 60 °C to yield phosphabarrelenes **IV-13** or **IV-14**.



IV-7: $R^1 = SiMe_3$, $R^2 = Ph$
IV-8: $R^1 = R^2 = Et$

IV-13: $R^1 = SiMe_3$, $R^2 = Ph$
IV-14: $R^1 = R^2 = Et$

Scheme 24: *Synthesis of phosphabarrelenes* ***IV-13*** *and* ***IV-14****.*

Monitoring the reaction by ^{31}P NMR spectroscopy, the formation of the phosphabarrelenes **IV-13** and **IV-14** could be observed, due to the appearance of a characteristic signal at $\delta \approx -59$ ppm. The phosphabarrelenes could be isolated as off-white crystalline solids after precipitation of the magnesium salts with hexanes and filtration over celite. The ^{31}P NMR shifts of phosphabarrelenes **IV-9** – **IV-14** are summarized in Table 1.

Table 1: *^{31}P NMR shifts for ligands phosphabarrelenes* ***IV-9 – IV-14*** *in $CDCl_3$.*

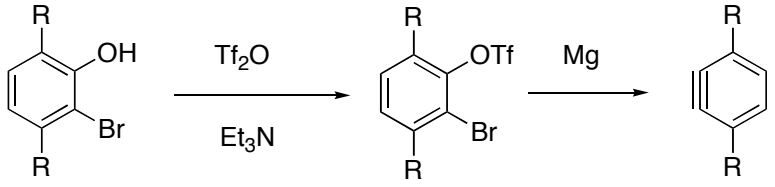
Ligand	δ(ppm)
IV-9	-59.9
IV-10	-59.3
IV-11	-78.8
IV-12	-54.8
IV-13	-58.9
IV-14	59.1

II.3. Use of *o*-bromo phenyltriflates as benzyne precursors.

Despite the fact that phosphabarrelenes have shown to be a promising class of ligands,[36, 37, 38, 40] and many efforts have been taken to functionalize the phosphinines[41, 42] that were used for the synthesis, no systematic study of the substitution of the benzyne precursors used in the synthesis of phosphabarrelenes has been carried out to date.

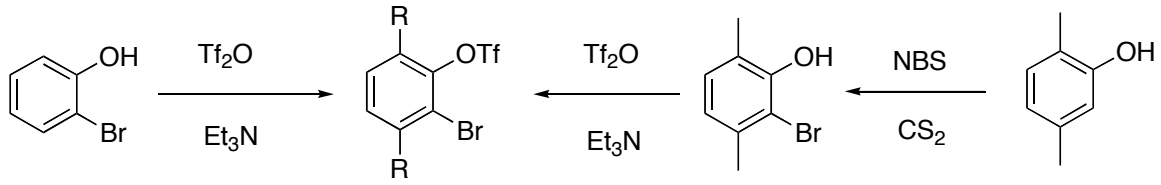
A major problem in this perspective might be the availability and price of substituted *o*-bromofluorobenzenes that are relatively rare and costly. Therefore we decided to investigate a different precursor that should allow to generate benzyne under the reaction conditions.

A class of compounds that is structurally related to *o*-bromofluorobenzenes are *o*-bromophenyltriflates, which can be readily obtained from *o*-bromophenols and are supposed to readily generate benzyne derivatives upon reaction with magnesium.



Scheme 25: *Envisaged use of o-bromophenyltriflates as benzyne precursors.*

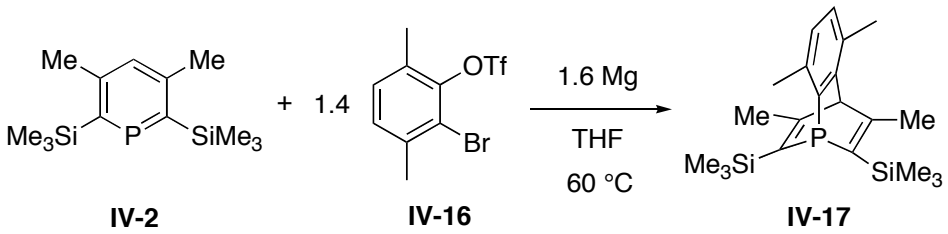
To test the ability of *o*-bromophenyltriflates to serve as a benzyne precursor in the synthesis of 1-phosphabarrelenes compounds *o*-bromophenyltriflate **IV-15** and 2-bromo-3,5-dimethyl-phenyl-triflate **IV-16** were prepared from *o*-bromophenol and xylenol according to literature procedures. (Scheme 26).[44]



IV-15: R = H
IV-16: R = Me

Scheme 26: *Synthesis of benzyne precursors* ***IV-15*** *and* ***IV-16***.

The synthesis of phosphabarrelene **IV-9** could be achieved with benzyne generated from *o*-bromophenyltriflate **IV-15**. In this case, no reaction can be observed at room temperature, but ligand **IV-9** is formed as a single product as judged by ^{31}P NMR spectroscopy, when the reaction is carried out at 60 °C. In the same way phosphabarrelene **IV-17** could be obtained from the reaction of **IV-2** and **IV-16**. The product was obtained as an off white powder after recrystallization from methanol in good yield (75 %) and was characterized by NMR spectroscopy and high resolution mass spectrometry.

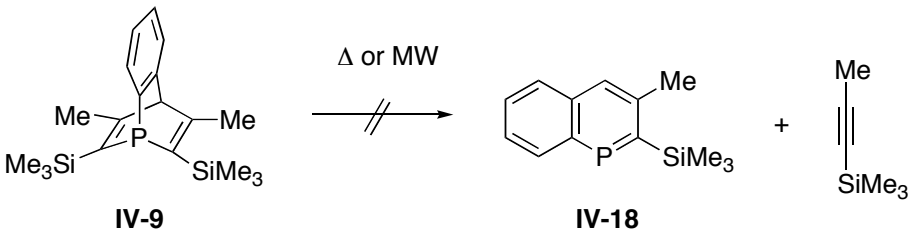


IV-2 **IV-16** **IV-17**

Scheme 27: *Synthesis of phosphabarrelene* ***IV-17***.

II.4. Reactivity

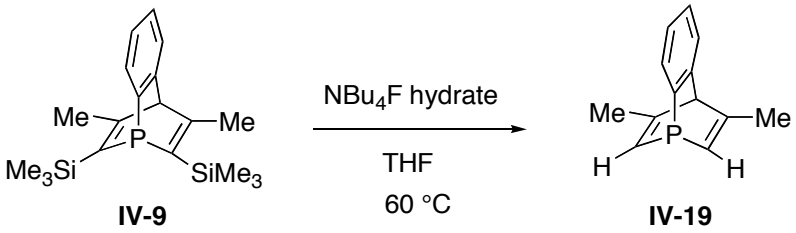
The thermolysis of phosphabarrelene **IV-9** was studied by heating in an oil bath and under microwave irradiation. In both cases, under harsh conditions (up to 280 °C in toluene) no signs of a cycloreversion reaction leading to phosphanaphthalene **IV-18** could be observed **.**



IV-9 **IV-18**

Scheme 28: *Attempted thermolysis of phosphabarrelene* ***IV-9***.

In contrast the reaction of phosphabarrelene **IV-9** with tetra-n-butylammonium fluoride hydrate readily led to the formation of desilylated phosphabarrelene **IV-19** (Scheme 29). In the ^{31}P NMR a characteristic signal at a chemical shift of δ = -79.7 ppm with a large $^{2}J_{PH}$ coupling constant (62.0 Hz) is observed for **IV-19**. The product could be characterized by NMR spectroscopy and high-resolution mass spectrometry.



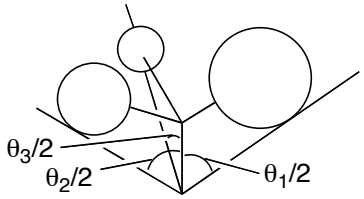
Scheme 29: *Hydrodesilylation of phosphabarrelene IV-9.*

A sample of 2,4,6-triphenylphosphabarrelene **IV-20**, that was used as reference compound in further studies could be obtained as described by Märkl and Breit from 2,4,6-triphenylphosphinine.[37, 39]

III. STERIC AND ELECTRONIC PROPERTIES

III.1. Steric properties

A method to classify the steric demand of phosphine ligands was introduced by Tolman in 1977.[45] He suggested, that a geometrical cone angle could be used to describe the steric demand of phosphine ligands. The cone angle of a tertiary phosphine ligand is defined as the vertex of a cylindrical cone, situated at 2.28 Å from the centre of the phosphorus atom, which diverges outwards toward the R groups and borders the van der Waals radii of the peripheral atoms. This model can equally be used to estimate cone angles for unsymmetrical phosphines (Scheme 30). In this case the cone angle is obtained by the use of Equation 1.



$$\Theta = (2/3)(\theta_1/2 + \theta_2/2 + \theta_3/2)$$

Equation 1

Scheme 30: *Method of measuring cone angles for unsymmetrical ligands.*

The crystallographic cone angles of ligands **IV-9** was determined by the method of Mingos *et al.*[46] from the X-Ray crystal structure, considering a van der Waals radius of 1.00 Å for hydrogen atoms and compared with those of other common tertiary phosphines (Table 2).

Table 2: *Crystallographic cone angles of tertiary phosphines.*

Ligand	Cone angle [°]
PMe_3	118
PPh_3	145
IV-9	154
PCy_3	170
P^tBu_3	182
$P(o\text{-tol})_3$	195

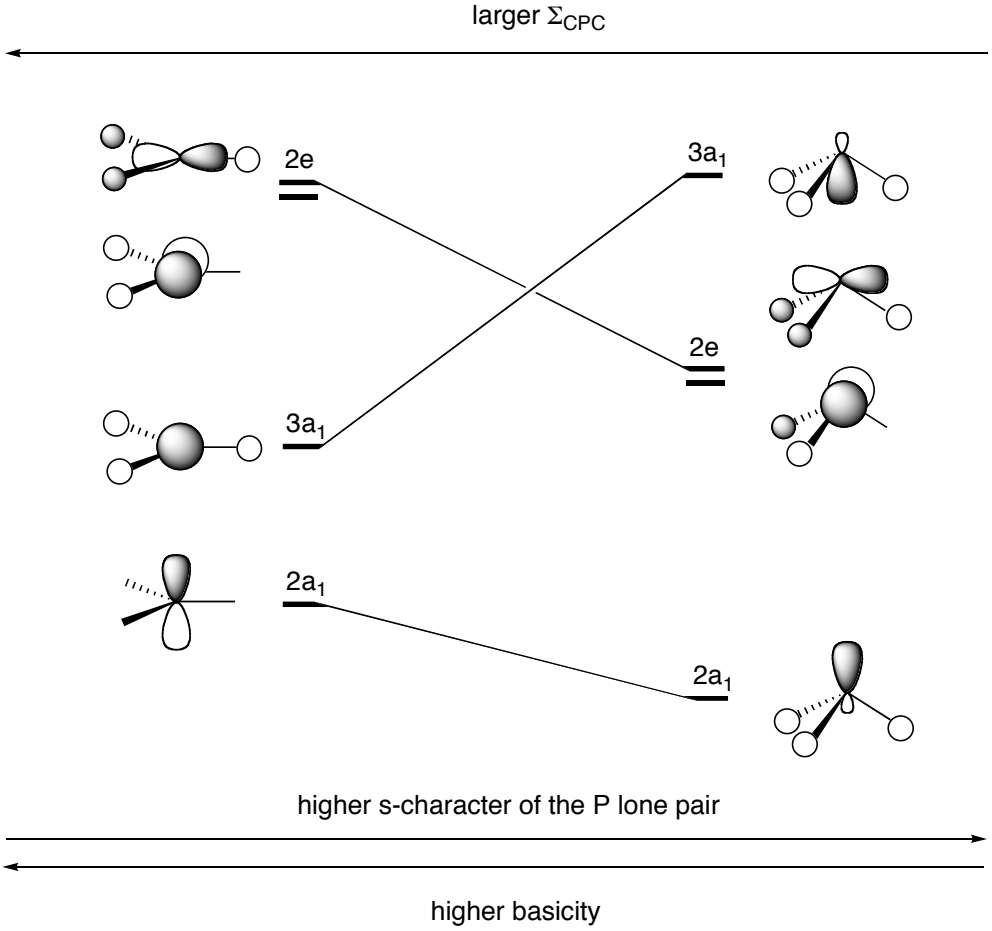
The comparison of the cone angle of ligand **IV-9** with those of bulky, acyclic phosphines shows that the cone angle of ligand **IV-9** is rather low compared to acyclic phosphine ligands. Nevertheless it should be expected, that the phosphabarrelenes behave as bulky ligands, as they posses a much more rigid structure than acyclic phosphine ligands and therefore should not change their cone angle to a high extent upon coordination to a transition metal.

III.2. Electronic properties

Generally in the description of transition metal-phosphine (M-P) bonding, the electronic interaction is regarded as having σ and π components.[47] The σ component involves donation of electrons from the ligand lone pair to an empty orbital, of σ symmetry, on the metal. The π component involves back-donation, from filled metal orbitals of π symmetry to empty orbitals of the appropriate symmetry on the phosphine ligands.

Scheme 31 shows a partial Walsh diagram for the deformation of PA_3 molecule from a planar to a pyramidal geometry. Pyramidalization at phosphorus is accompanied by a significant decrease in energy of the HOMO ($2a_1$). This orbital is the phosphine lone pair, and its fall in energy is a consequence of mixing phosphorus 3s character (from the $3a_1$ MO) into the phosphorus 3p, (of $2a_1$). The amount of mixing and hence the degree of pyramidality is dependent on the electronegativity of the substituents A. The more electronegative the substituents A, the greater the mixing and the more pyramidal the equilibrium PA_3 geometry (i.e.,

the smaller the A-P-A angle (in acyclic phosphines)) that results. For highly pyramidal geometries the LUMOs are the 2e set of P-A σ^* orbitals.



Scheme 31: *Partial Walsh diagram for the pyramidal distortion of a PA_3 molecule and the relation between Σ_{CPC}, s-character of the phosphorus lone pair and basicity of tertiary phosphines.*

In this description, in accord with ab initio calculations,[48, 49] these are antibonding combinations of P 3px, and 3py with A σ orbitals, in addition, they could have some P 3d character.[47] The energy of the LUMOs falls rapidly as the phosphine becomes more pyramidal, as a consequence of reduced overlap between the P 3and A σ orbitals as the A atoms move out of the xy plane. For the same reason the P-A σ orbitals are destabilized as A-P-A angles are reduced. Therefore this simplified picture of the electronic structure of phosphines is consistent with the ab initio calculations described above. In this description the geometric consequences of coordinating a phosphine to a metal will mainly derive from depopulation of the HOMO, through P to M σ donation, and from population of the LUMOs, as a result of M to P π-back-bonding. The result of partially populating the 2e LUMOs will be to increase the P-A bond lengths and to increase the driving force for PA pyramidalization. On reducing the amount of M-

P back bonding we should therefore expect a shortening of P-A distances and increased A-P-A bond angles.

III.2.a. Sum of the CPC angles

A very rough method to estimate the basicity of a tertiary phosphine is to measure the sum of the CPC-angles. The sum of the CPC-angles (Σ_{CPC}) reflects the hybridization of the phosphorus atom (Scheme 31).[50]

In Table 3 the sums of the CPC angles of common phosphine ligands are compared to those of phosphabarrelenes **IV-9**, **IV-12** and **IV-20**.

Table 3: *Σ_{CPC} for phosphabarrelenes IV-9, IV-12, IV-20 and selected tertiary phosphines.*

Ligand	Σ(<CPC) [°]	Reference
IV-20	282.7	Breit[38]
IV-9	287.7	this work
IV-12	290.1	this work
PMe_3	297.4	CCDC
PPh_3	307.2	CCDC
$P(o\text{-tol})_3$	308.4	CCDC
PCy_3	311.4	CCDC
P^tBu_3	322.3	CCDC

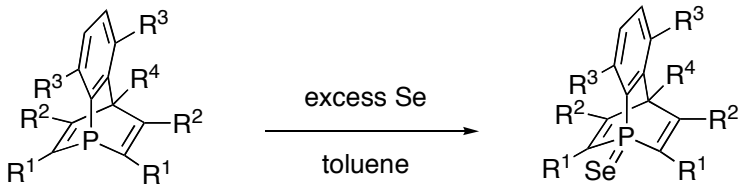
As can be seen from Table 3, the Σ_{CPC} in the phosphabarrelenes are by far smaller than in common acyclic phosphines. Yet it can be noticed, that increasing the steric demand of the substituents in the α-position of the phosphorus atom Ph < $SiMe_3$ < $SiMe_2tBu$ results in an increase of the sum of the angles in the phosphabarrelenes **IV-9**, **IV-12** and **IV-20**, although this increase is much less pronounced than in the case of the acyclic phosphines.

As the Σ_{CPC} of the phosphine reflects the hybridization of the phosphorus atom, it should be expected, that the lone pairs of the phosphabarrelenes show a much higher s-character than common phosphines and should therefore be less σ-donating ligands.

III.2.b. ^{31}P-^{77}Se coupling constants

The reaction of tertiary phosphines with selenium in toluene at reflux leads to the corresponding phosphine selenides. The $^{1}J_{31P\text{-}77Se}$ coupling constant in these compounds allows for the evaluation of the s-character of the lone pair of the phosphorus atom.[51] In general it could be observed that electron-withdrawing substituents lead to a decrease in the $^{1}J_{PSe}$ coupling constant whereas electron-donating substituents lead to an increase of the coupling constant, what is correlated to a decrease of the s-character of the phosphorus lone pair. As it was stated before the s-character of the phosphorus lone pair also depends on the size of the CPC-angles.

The phosphabarrelene selenides **IV-21 - IV-26** could be obtained by heating the phosphabarrelenes with an excess of selenium after 7-10 days. The reaction was followed by ^{31}P NMR spectroscopy and after consumption of the starting material the excess selenium was filtered off and phosphabarrelene selenides were obtained as colorless crystalline solids in quantitative yield (Scheme 32).



IV-9: $R^1 = SiMe_3$, $R^2 = Me$, $R^3 = R^4 = H$;
IV-10: $R^1 = SiMe_2Ph$, $R^2 = Me$, $R^3 = R^4 = H$;
IV-11: $R^1 = SiMe_3$, $R^2 = R^3 = R^4 = H$;
IV-12: $R^1 = SiMe_2{}^tBu$, $R^2 = Me$, $R^3 = R^4 = H$;
IV-17: $R^1 = SiMe_3$, $R^2 = R^3 = Me$, $R^4 = H$;
IV-20: $R^1 = Ph$, $R^2 = R^3 = H$, $R^4 = Ph$;

IV-21: $R^1 = SiMe_3$, $R^2 = Me$, $R^3 = R^4 = H$;
IV-22: $R^1 = SiMe_2Ph$, $R^2 = Me$, $R^3 = R^4 = H$;
IV-23: $R^1 = SiMe_3$, $R^2 = H$, $R^3 = R^4 = H$;
IV-24: $R^1 = SiMe_2{}^tBu$, $R^2 = Me$, $R^3 = R^4 = H$;
IV-25: $R^1 = SiMe_3$, $R^2 = R^3 = Me$, $R^4 = H$;
IV-26: $R^1 = Ph$, $R^2 = R^3 = H$, $R^4 = Ph$;

Scheme 32: *Synthesis of phosphabarrelene selenides IV-21 – IV-26.*

Phosphabarrelene selenides **IV-21 – IV-26** were characterized by NMR spectroscopy and HRMS-spectroscopy. In the case of phosphabarrelene selenides, single crystal suitable for X-Ray crystal structure analysis could be obtained by slow evaporation of a solution in toluene. The molecular structures of **IV-21** and **IV-24** are presented in Figure 4.

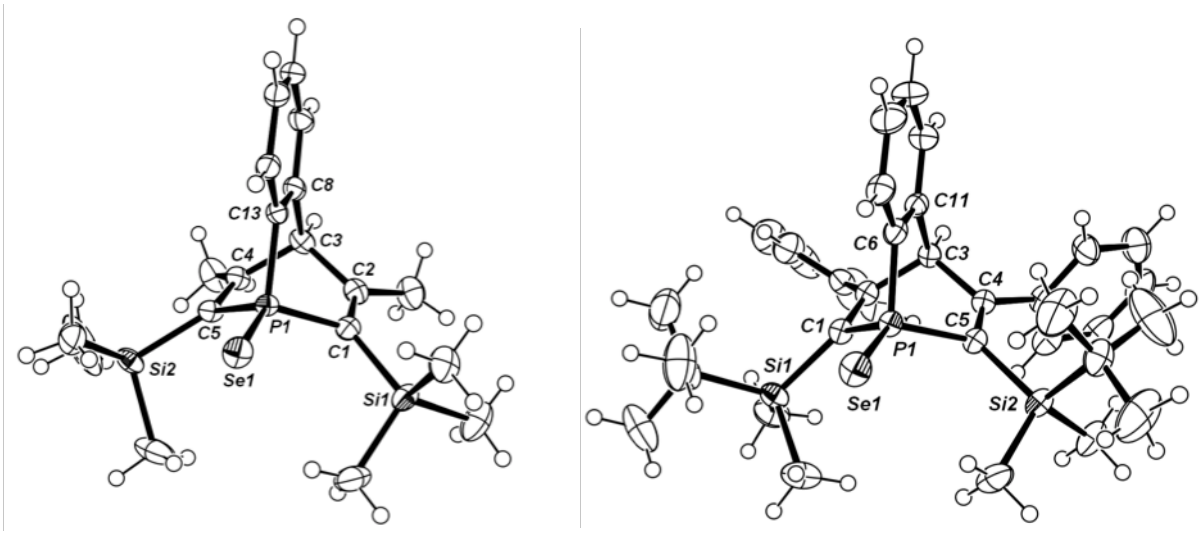
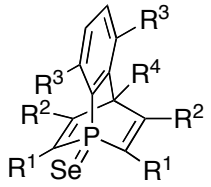


Figure 4: *Molecular structure of phosphabarrelene selenides* ***IV-21*** *and* ***IV-24*** *(ORTEP-representation, thermal ellipsoids at a 50 % probability). Selected bond lengths [Å] and angles [°] for* ***IV-21****: P1-Se1: 2.1041(5), P1-C1: 1.834(2), P1-C5: 1.828(2), P1-C13: 1.804(2), C1-P1-C5: 101.3(1), C1-P1-C13: 99.4(1), C5-P1-C13: 99.3(1). Selected bond lengths [Å] and angles [°] for* ***IV-24****: P1-Se1: 2.0918(5), P1-C1: 1.841(2), P1-C5: 1.848(2), P1-C6: 1.816(2), C1-P1-C5: 100.34(8), C1-P1-C6: 99.51(8), C5-P1-C6: 99.08(8).*

The molecular structures of **IV-21** and **IV-24** show a shortening of the P-C bonds upon oxidation of phosphorus atom from P^{III} to P^{V}. Furthermore a significant widening of 12.3 ° of the CPC angles can be observed in the case of **IV-21** which is less pronounced in the case of **IV-24** with 8.8 °.

The $^{1}J_{PSe}$ coupling constants of phosphabarrelenes are presented in Table 4 in comparison to those of selenides of common phosphine ligands.

Table 4: *^{31}P-^{77}Se Coupling constants.*

	R^1	R^2	R^3	R^4	$\delta(^{31}P)$ ppm	$^1J_{PSe}$ Hz
IV-26	Ph	H	H	Ph	6.6	840
$SeP(2\text{-furyl})_3$					-22.1	793
IV-24	$SiMe_2{}^tBu$	Ph	H	H	9.2	791
IV-23	$SiMe_3$	H	H	H	-2.7	787
IV-22	$SiMe_2Ph$	Me	H	H	4.8	776
IV-21	$SiMe_3$	Me	H	H	4.3	772
IV-25	$SiMe_3$	Me	Me	H	1.0	756
$SePPh_3$					35.9	732
$SePCy_3$						703
$SeP(^tBu)_3$						690

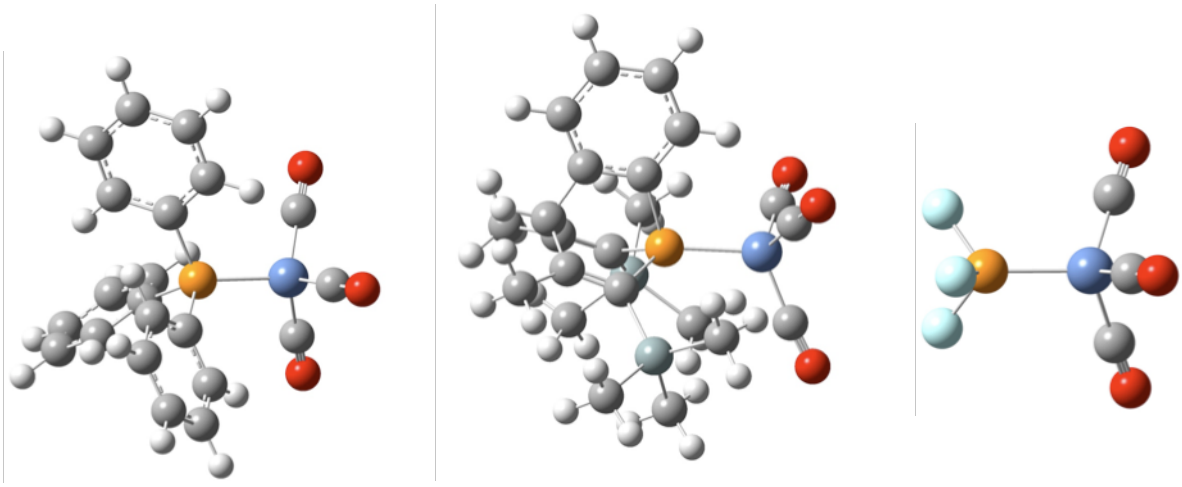
First of all, this study shows that phosphabarrelenes show relatively high $^1J_{PSe}$ coupling constants compared to common phosphine ligands like PPh_3, reflecting the higher s-character of the phosphorus atom in phosphabarrelenes.

Secondly the influence of the substitution pattern on the J_{PSe} coupling constants was studied. As it had to be expected, the change of the substituents on the silyl groups of the phosphabarrelene has only a minor influence on the phosphorus selenium coupling constant. In contrast the substitution of the double bonds of the phosphinine with electron withdrawing or electron donating has a major influence. It can be observed, that the triphenyl-substituted barrelene **IV-26** shows by far the largest coupling constant. Interestingly the J_{PSe} coupling constant shows to be relatively sensitive towards the substitution of the benzo-bridge of the phosphabarrelene, showing the interest on an access on further functionalized benzyne precursors, that could allow for the tuning of phosphabarrelene not only sterically but also electronically.

III.2.c. DFT-calculations and Charge Decomposition Analysis

Finally still another method that is frequently used to evaluate the electronic properties of phosphine ligands, the analysis of the infrared vibrational frequencies of $LNi(CO)_3$ complexes, was employed to study the donor capacities of phosphabarrelene ligands. Because of the high toxicity of $Ni(CO)_4$ it was decided not to synthesize and measure the infrared spectra of these complexes but rather conduct a DFT study on the corresponding model complexes.

In the CDA method the canonical, natural, or Kohn-Sham molecular orbitals of the complex are expressed in terms of MOs of appropriately chosen fragments. In the cases studied, the Kohn-Sham orbitals of the complexes are formed in the CDA procedure as a linear combination of the MOs of the ligand and those of the remaining [$Ni(CO)_3$] fragment. In all cases, the ligands and the metal fragments were computed in the geometry of the complex. The optimized model structures of complexes **IV-A - IV-C** are presented in Figure 5. Unfortunately the X-Ray crystal of compounds **IV-A** and **IV-C** are unknown, so that it was not possible to validate the calculated model structures (**Note:** The only monophosphine $Ni(CO)_3$-complex that was structurally characterized is [(^{t}Bu_3P)$Ni(CO)_3$][52]).



IV-A **IV-B** **IV-C**

Figure 5: *Optimized model structures **IV-A – IV-C**. Selected bond lengths [Å] and angles [°] for **IV-A**: Ni1-P1: 2.25, Ni1-CO: 1.79, C-O: 1.15. Selected bond lengths [Å] and angles [°] for **IV-B**: Ni1-P1: 2.28, Ni1-CO: 1.80, C-O: 1.15. Selected bond lengths [Å] and angles [°] for **IV-C**: Ni1-P1: 2.12, Ni1-CO: 1.81, C-O: 1.15.*

The orbital contributions are divided in four parts: (i) the mixing of the occupied MOs of the ligand and the unoccupied MOs of the metal fragment. This value (noted d) represents the L→M donation; (ii) the mixing of the unoccupied MOs of the ligand and the occupied MOs of the metal fragment. This value (noted b) accounts for the M→L back donation; (iii) the mixing of the occupied MOs of the ligand and the occupied MOs of the metal fragment. This term (noted r), which describes the repulsive polarization between the ligand and metal fragment, is negative because electronic charge is removed from the overlapping area of the occupied orbitals; (iv) the residual term (Δ) which results from the mixing of the unoccupied MOs of the two respective fragments. This term is very close to zero for closed-shell interactions. This value constitutes an important probe to determine whether the bonding studied can be really classified as a donor-

acceptor interaction following the Dewar-Chatt-Duncanson model. An important deviation from $\Delta = 0$ implies that the bond studied is more appropriately described as a normal covalent bond between two open shell fragments.

Table 5: *Results of the CDA-calculations.*

Complex	d	b	d/b	b/(d+b)	r	Δ
IV-A	0.643	0.073	8.81	10.20	-0.142	-0.026
IV-B	0.810	0.135	6.00	14.29	-0.141	-0.041
IV-C	0.721	0.136	5.30	15.87	-0.081	-0.051

Structure optimization: Gaussian03,[53] B3PW91[54, 55]/6-31G* (P, C, H, F, O) Ni: Hay Wadt-ECP[56] with an additional f-polarization function[57]

The small values of the residual terms (Δ) show that the analysis according to the Dewar – Chat –Duncanson model is pertinent. From the b/(d+b), which describes the contribution of the backdonation to the bonding interaction between the metal fragment and the ligand. From this value it becomes clearly visible that the phosphabarrelene in complex **IV-B** is a more electron accepting ligand than PPh_3, but less electron accepting than PF_3.

The CDA analysis additionally allows for the decomposition of the molecular orbitals into the fragment orbitals of the ligand and the resting metal fragment. In a first step, the energies of the frontier orbitals that were suspected to be involved in the metal ligand bonding were compared.

The interaction between a metal fragment and a ligand in a first approximation can be divided into two parts: donation of electron density from the ligand to the metal and backdonation from the metal to the ligand.

In phosphine ligands the lone pair of the phosphorus atom (HOFO or HOFO-1) is responsible for the donation to a metal center by the interaction with the LUFO of the metal fragment. The magnitude of this interaction is mainly dependent on the energy difference between those orbitals. The energy of the fragment orbitals of the $Ni(CO)_3$ remain almost constant, as can be seen in Table 6. This reflects the similar geometry of the metal containing fragment in all three cases. In contrast the fragments orbitals of the ligands show important energy differences. Consequently, PPh_3, the ligand with highest σ-donating ability shows the highest energy of the lone pair of the phosphorus atom. As expected ligand the energy of the lone pair of ligand **IV-9** is slightly lower than in the case of PPh_3 and the lowest energy is observed for PF_3.

Table 6: *Frontier orbital energies in [LNi(CO)$_3$] complexes.*

	Orbital	**IV-A** (PPh_3)	**IV-B** (IV-9)	**IV-C** (PF_3)
Ligand	LP	-5.70	-6.05	-8.75
	π^*		-0.62	
	π^*		-0.54	
	π^*		0.79	
	σ^*	1.92	1.89	0.03
	σ^*	1.98	2.13	0.03
Ni(CO)$_3$	*HOFO*	-6.87	-6.81	-6.70
	LUFO	-2.78	-2.75	-2.68

The π-back donation which is the donation of electron density from the occupied orbitals of the metal center to unoccupied ligand orbitals. In the case of tertiary phosphines it could be shown, that the degenerate σ^* P-C orbitals interact with the HOMO of the metal center to accept electron density. The magnitude of this interaction depends on the energy of the participating orbitals. As the ligand orbitals are much higher in energy than those of the metal fragment, the interaction is more important the lower the energy of the accepting orbitals. Due to the C_S symmetry of the ligand **IV-9** the σ^* orbitals are not degenerate unlike in the case of $C3_V$ symmetric PPh_3 and PF_3 ligands. One of these orbitals is slightly lower in energy in **IV-9** than in PPh_3. Most importantly, in the case of the phosphabarrelene **IV-9** the σ^* orbitals are not the lowest unoccupied frontier orbitals of the ligand fragment. Low-lying orbitals (LUFO, LUFO+1 and LUFO+3) resulting from the mixing of the π^* orbitals of the double bonds of the ligand with low-lying 3p-orbitals of e symmetry of the phosphorus atom are observed that are lower in energy than the σ^* P-C orbitals.

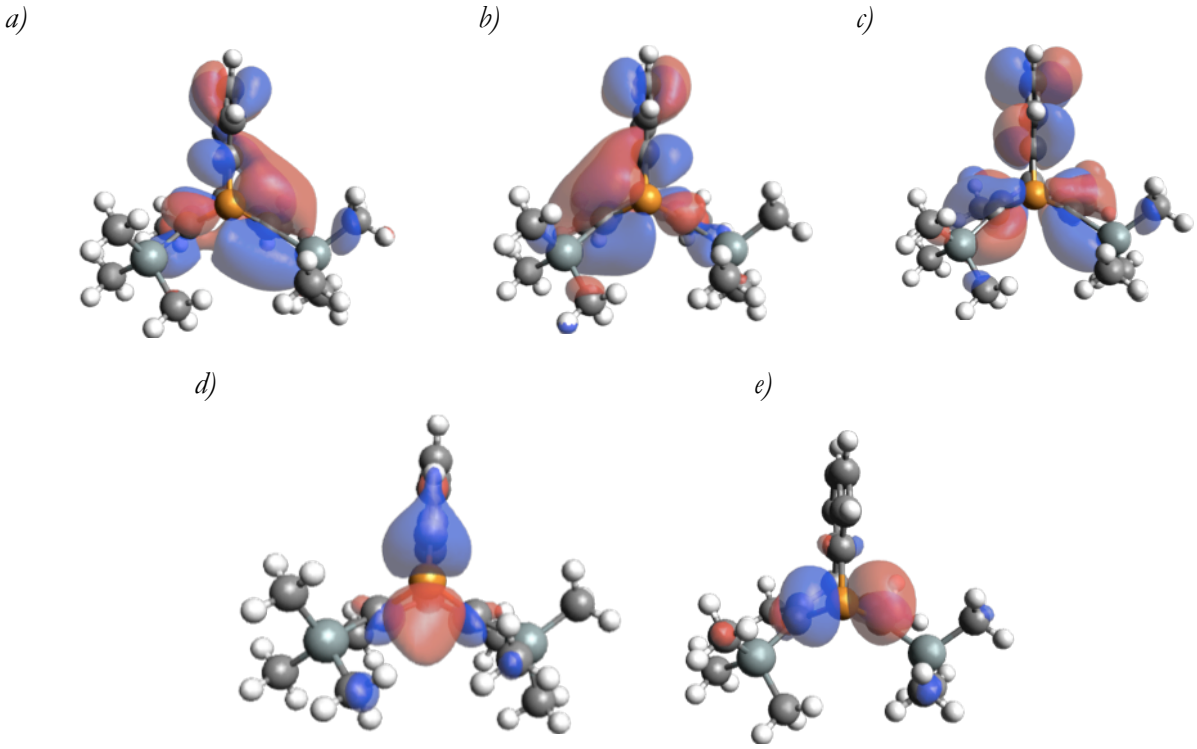
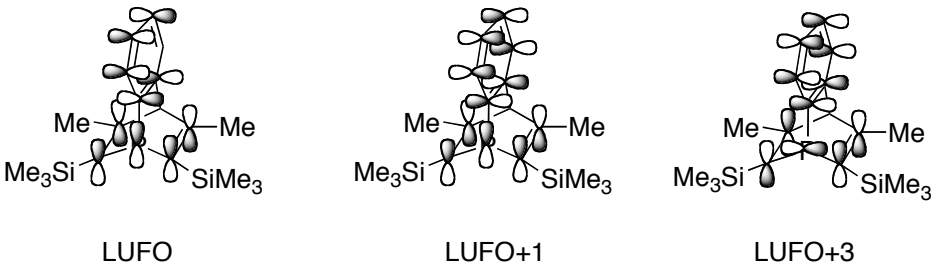


Figure 6: *(a) LUFO, (b) LUFO+1, (c) LUFO+3 (d) LUFO+4 and (e) LUFO+6 orbitals of ligand* ***IV-9*** *in complex* ***IV-B****.*

The analysis of the π-backdonation in complex **IV-B** shows a small contribution of these LUFO, LUFO+1 and LUFO+3.

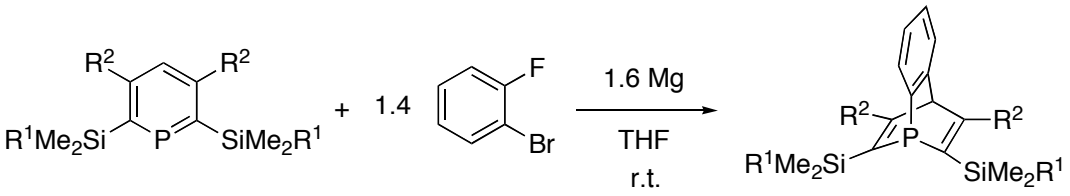


Scheme 31a: *Contribution of π*-Orbitals to LUFO, LUFO+1 and LUFO+3.*

In conclusion, it must be assumed that ligand **IV-9** is a weakly basic phosphine ligand, due to the important s-character of the phosphorus lone pair. Finally, the π-backdonation into the σ* P-C orbitals does not appear to play an important role. Rather, the CDA calculations reveal the existence of lower lying orbitals with π-symmetry available for backdonation from metal centers. These result from the mixing of the π* orbitals of the double bonds of the phosphabarrelene with 3p orbitals of the phosphorus atom.

IV. CONCLUSIONS AND PERSPECTIVES

In this chapter we were able to show that phosphabarrelenes with sterically demanding silyl substituents in the α-positions of the phosphorus atoms can be readily obtained from the corresponding 2,6-disilylsubstituted phosphinines via a [4+2]-cycloaddition with in-situ generated benzyne. This method allows for the synthesis of phosphabarrelenes with silyl groups of tunable size (Me, Ph, ^{t}Bu).



IV-2: R^1 = Me, R^2 = Me,
IV-3: R^1 = Ph, R^2 = Me,
IV-4: R^1 = Me, R^2 = H,
IV-5: R^1 = tBu, R^2 = Ph.

IV-9 : R^1 = Me, R^2 = Me,
IV-10: R^1 = Ph, R^2 = Me,
IV-11: R^1 = Me, R^2 = H,
IV-12: R^1 = tBu, R^2 = Ph.

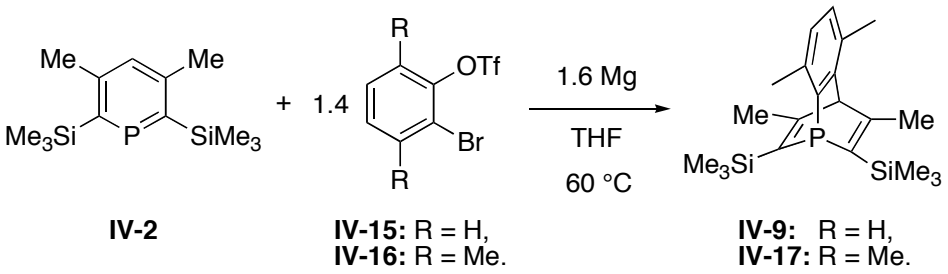
Scheme 33: *Synthesis of silyl substituted phosphabarrelenes*

The analysis of the X-Ray crystal structures shows that the silyl substituted phosphabarrelenes are more sterically demanding than triphenylphosphine. Their cone angle is smaller than the cone angle of bulky acyclic phosphines. Yet it can be expected that the phosphabarrelenes might have similar steric properties due to the rigidity of the bicyclic core of the phosphabarrelene.

The analysis of the electronic properties has shown that phosphabarrelenes behave as poor σ-donor ligands due to the important s-character of the phosphorus lone pair.

The CDA calculations confirm this observation and show that the phosphorus lone pair is significantly lower in energy in ligand **IV-9** than in PPh_3. No significant difference can be observed in the energies of the σ^* P-C orbitals in ligand **IV-9** and PPh_3, but lower lying orbitals with π-symmetry available for backdonation from metal centers could be observed in ligand **IV-9**. Overall, ligand **IV-9** might be described as a bulky, poorly electron donating phosphine ligand.

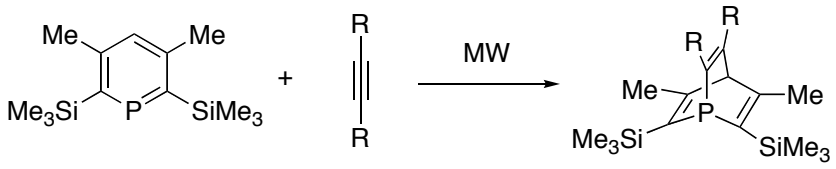
Interestingly it could be shown that the use of *o*-bromophenyltriflates, that are readily accessible and relatively cheap compared to *o*-bromofluorobenzenes, is a possibility for the *in situ* generation benzyne for the Diels-Alder reaction. This method has allowed for the introduction of methyl groups on the benzo-bridge of the phosphabarrelene (Scheme 34).



IV-2 **IV-15:** R = H, **IV-16:** R = Me. **IV-9:** R = H, **IV-17:** R = Me.

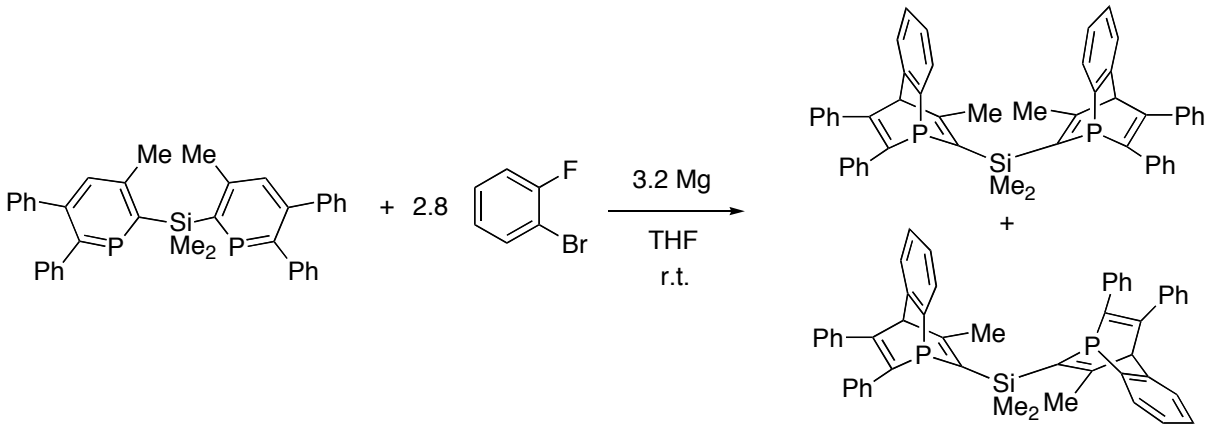
Scheme 34: *Use of o-bromophenyltriflates as benzyne-precursors.*

A thorough study of the coordination chemistry and the application of ligand **IV-9** in palladium and platinum catalyzed cross-coupling and hydrosilylation reactions will be presented in the following chapters. A way to use less activated alkynes for the synthesis of phosphabarrelenes could be the use of microwave reactor. It has been described, that microwave irradiation can be beneficial for the outcome of classical [4+2] Diels-Alder reactions.[58]



Scheme 35: *Envisaged synthesis of phosphabarrelenes with non-activated alkynes under microwave heating.*

The synthesis of a bidentate bis-phosphabarrelene ligand could possibly be achieved from bis-phosphinines (Scheme 36).[59]



Scheme 36: *Synthesis of a hypothetical bis-phosphabarrelene ligand from a bis-phosphinine.*

In this case the formation of two diastereoisomers must be expected, as the second cycloaddition reaction can take place from the same or the opposite side as the first addition. The

presence of the chiral environment directly on the phosphorus atom might be beneficial in catalytic processes.

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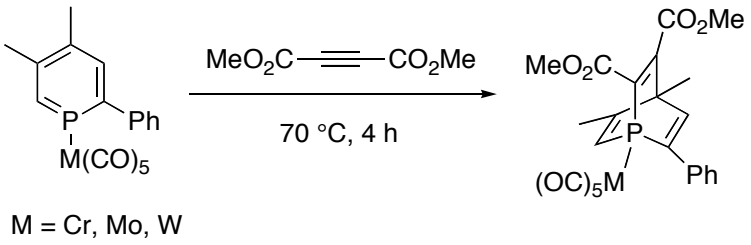
CHAPTER 2: COORDINATION CHEMISTRY OF 1-PHOSPHABARRELENES

I. INTRODUCTION

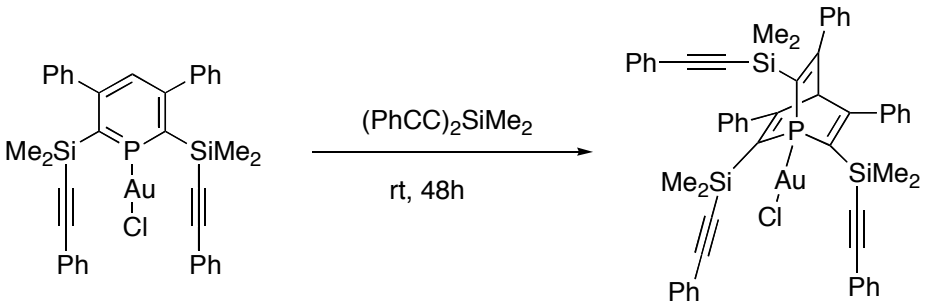
Although the first synthesis of phosphabarrelenes by Märkl[1] dates back to 1971, their use as ligands in coordination chemistry is quite recent and only very few transition metal complexes have been reported so far, and will be presented here exhaustively.

In their reports Mathey[2] and Märkl[3] described the first preparation of group 6 transiton metal coordinated phosphabarrelenes. It should be noted that in this case, the coordination of the transition metal fragment was used for the activiation of the phosphinine starting material for the [4+2]-cycloadditon reaction with alkynes as was mentioned before in Chapter 1 (Scheme 1). These complexes were characterized by NMR and IR spectroscopy but not structural data was reported.



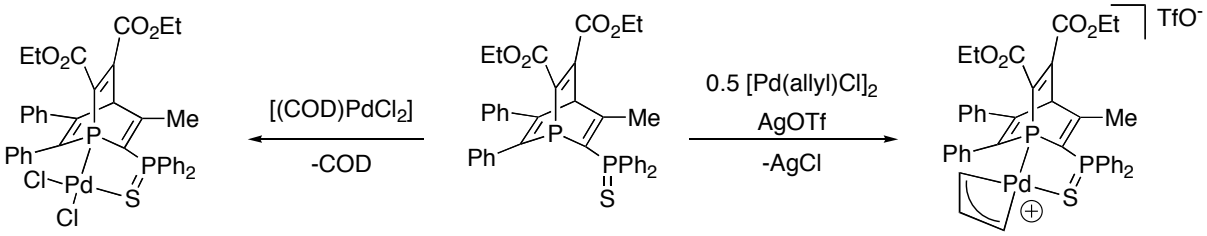
Scheme 1: *Synthesis of group 6 complexes of phosphabarrelenes by Mathey and Märkl.*

The first transition metal complexes incorporating phosphabarrelenes that were fully structurally characterized was reported by our group in 1999.[4] The coordination of gold chloride to the phosphinine was used, as in the case of Mathey and Märkl, to increase the reactivity of the phosphinine for the Diels-Alder reaction with non-activated alkynes (Scheme 2).



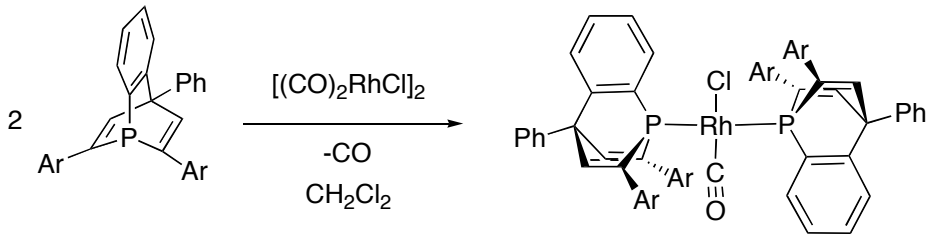
Scheme 2: *Isolation of the first structurally characterized phosphabarrelene gold(I) complex.*

In 2005, our group[5] reported the synthesis of palladium complexes with a bidentate phosphabarrelene ligand (Scheme 3). These cationic π-allyl complexes showing interesting activity in the allylation of amines and the Suzuki-Miyaura coupling. Additionally the synthesis of several complexes of late transition metal complexes (Rh, Pt, Au) were reported with the same ligand.[6]



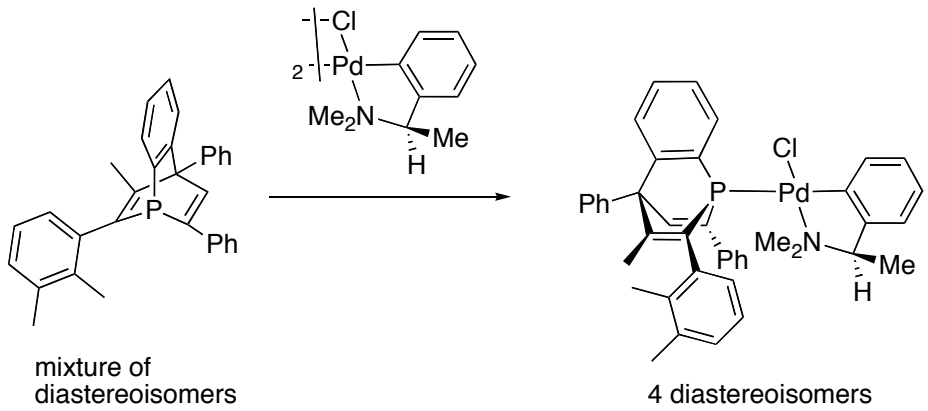
Scheme 3: *Synthesis of palladium complexes with a bidentate phosphabarrelene ligand.*

In 2006, Breit and coworkers reported the isolation of rhodium complexes with triaryl phosphabarrelenes and 2,6-diisopropyl-4-phenyl phosphabarrelene (Scheme 4).[7] In their study, the authors compared the characteristic vibrational frequencies of the carbonyl ligand of these complexes with those of the corresponding triphenylphosphine and 2,4,6-triphenylphosphinine rhodium complexes. The authors concluded on the basis of this data, that the π-acceptor properties of phosphabarrelenes are in between of those of PPh_3 and 2,4,6-triphenylphosphinine. Furthermore these results show that the electronic properties of phosphabarrelenes can be influenced by the variation of the substituents.[7, 8]



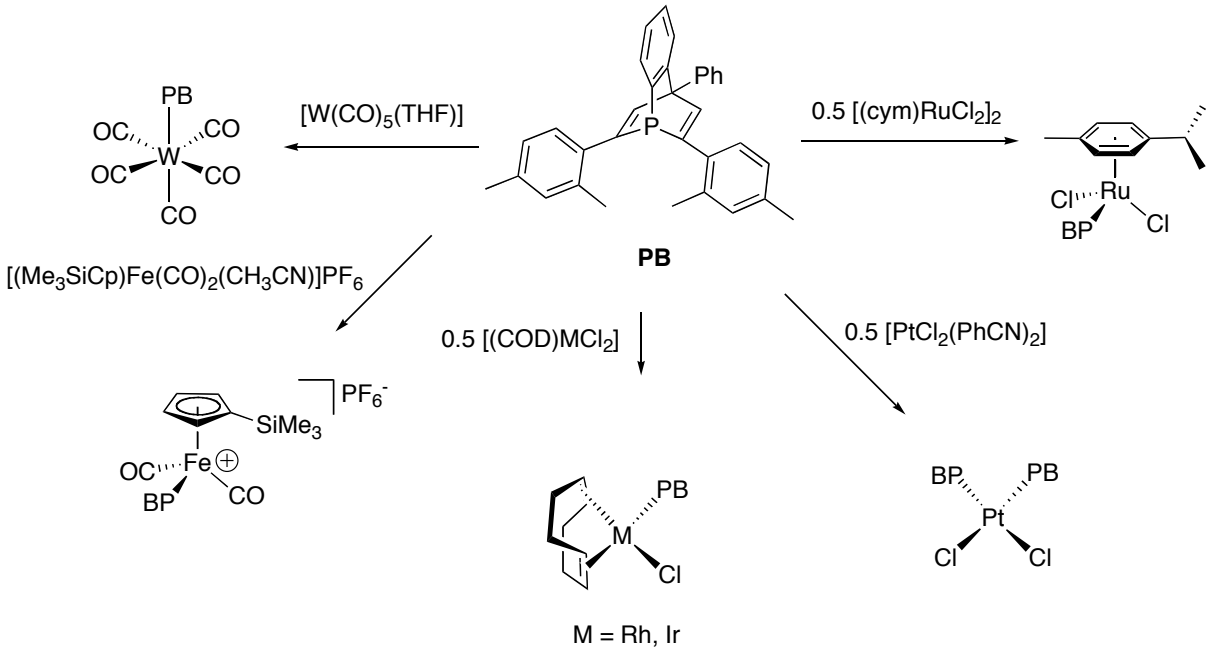
Scheme 4: *Synthesis of rhodium complexes by Breit and coworkers.*

The coordination of the chiral atropoisomeric phosphabarrelenes to a chiral palladium complex reported by Müller *et. al.* in 2007 proved the formation of 4 diastereoisomers by ^{31}P NMR spectroscopy and therefore the existence of a rotational barrier between the atroposiomeric complexes (Scheme 5).[9]



Scheme 5: *Determination of diastereomeric ratio of atropoisomeric phosphabarrelenes with a chiral palladium complex.*

Early in 2009, Tooze and coworkers reported the synthesis of several transition metal complexes of 2,4-dixylyl-4-phenyl phosphabarrelene (Scheme 6).[10] In this case only the iron and the ruthenium complex were fully structurally characterized.



Scheme 6: *Phosphabarrelene complexes reported by Tooze.*

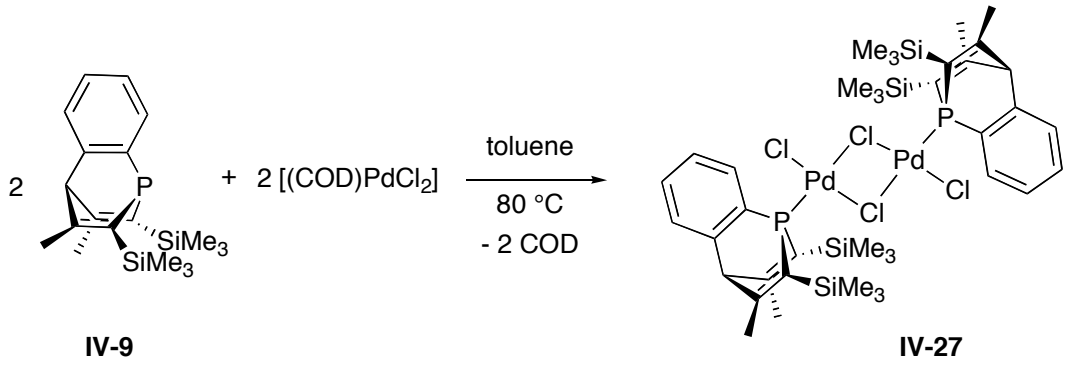
In conclusion, 1-phosphabarrelenes have only been used scarcely in coordination chemistry and catalysis. Most examples were reported with late transition metals. As it could be shown in Chapter 1, 2,6-silyl substituted 1-phosphabarrelene **IV-9** is a relatively bulky monodentate phosphine ligand. Interestingly, its electronic properties are substantially different from bulky

alkylphosphines. Therefore it seemed promising to thoroughly study the coordination chemistry of this ligand to evaluate its capability of stabilizing transition metal complexes with group 9-11 metals.

II. COMPLEXES OF GROUP 10

II.1. Palladium

In the first place, the coordination of phosphabarrelene **IV-9** was investigated with the $PdCl_2$-fragment. A mixture of **IV-9** with [(COD)$PdCl_2$] was heated in toluene at 80 °C. The color of the reaction mixture changed from bright yellow to orange and the formation of a red microcrystalline solid could be observed upon cooling to room temperature. The product was poorly soluble in common organic solvents at room temperature, yet enough to be characterized by NMR spectroscopy. Due to the initial stoichiometry of Pd/**IV-9** = 1:1 and the lack of free starting material the product was proposed to be the corresponding chloro-bridged dimer **IV-27** (Scheme 7).



IV-9 **IV-27**

Scheme 7: *Synthesis of the chloro-bridged dimer palladium phosphabarrelene complex IV-27.*

In the ^{31}P NMR, the characteristic signal of **IV-9** (δ = -60.1 ppm) disappeared in favor of a new signal at a chemical shift of δ = 2.1 ppm. The ^{1}H NMR shows an important deshielding of the H-8 proton in **IV-27** of $\Delta\delta$ = 0.9 ppm (from δ = 7.6 ppm in **IV-9** to δ = 8.5 ppm in **IV-27**) which is located in the β-position of the phosphorus atom on the benzo bridge of the phosphabarrelene.

Single crystals suitable for X-Ray crystal structure analysis were obtained by the slow evaporation of a solution of **IV-27** in THF. The molecular structure of complex **IV-27** is presented in Figure 1 and confirmed our first assignment.

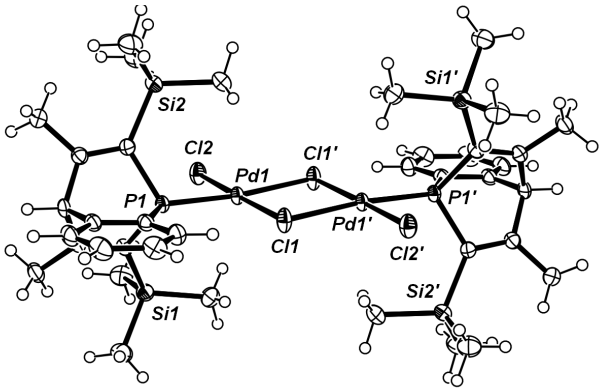
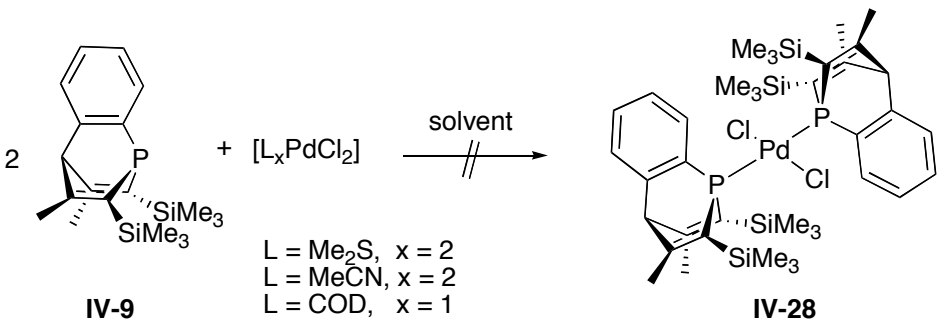


Figure 1: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability, a THF molecule was omitted for clarity) of phosphabarrelene palladium complex* ***IV-27****. Selected bond lengths [Å] and angles [°]: Pd1-P1: 2.2190(6), Pd1-Cl1: 2.3256(6), Pd1-Cl1': 2.4286(6), Pd1-Cl2: 2.2894(7), P1-Pd1-Cl1': 173.46(2), Cl1-Pd1-Cl2: 176.10(2), P1-C1-Si1: 127.2(1), P1-C5-Si2: 125.8(1).*

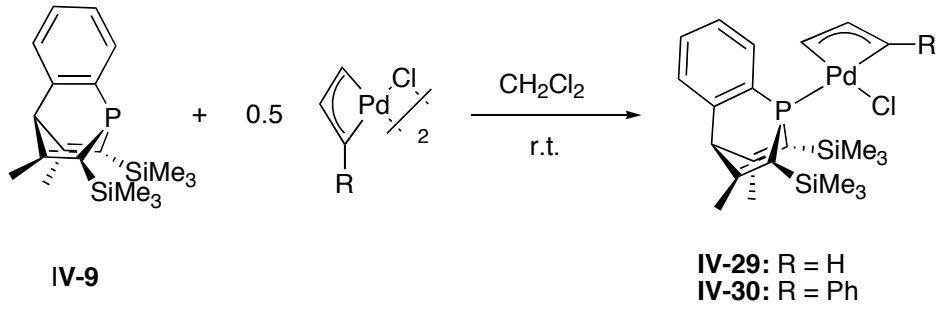
The palladium atom adopts a square planar coordination as should be expected for a palladium(II)-center with d^8 electron configuration. The angles P1-Pd1-Cl1' and Cl1-Pd1-Cl2 with 173.5 ° and 176.1 ° show only slight deviation from the theoretical value of 180 °. The widening of the P1-C1-Si1 angle from 113.6 ° in ligand **IV-9** to 127.2 ° can be observed in complex **IV-27** upon coordination of **IV-9** to palladium. The Pd1-Cl2 distance of 2.2894(7) Å is significantly shorter than the distance of the Pd1 atom with the bridging chloride atoms Cl1 and Cl1'. It should be noted that the distances of bridging chloride atoms to the Pd1 atom are not equal, with the Pd1-Cl1' distance being slightly longer with 2.4286(6) Å compared to 2.3256(6) Å for Pd1-Cl1, due to the higher *trans*-effect of the phosphabarrelene compared to the chloride atom.

Despite many efforts it was not possible to synthesize diphosphabarrelenedichloropalladium complex **IV-28** (Scheme 8). Even with a large excess of **IV-9** or with different palladium precursors, the only product that can be observed in ^{31}P NMR is complex **IV-27**.



Scheme 8: *Attempted synthesis of complex* ***IV-28****.*

In contrast, the synthesis of allylpalladium complexes **IV-29** and **IV-30** was achieved in quantitative yields by mixing **IV-9** with the corresponding allylpalladium precursors in dichloromethane at room temperature (Scheme 9). The quantitative formation of complex **IV-29** could be observed by the appearance of a signal at a chemical shift of δ = -6.1 ppm (δ = -9.0 ppm for **IV-30**). The NMR spectra of **IV-29** and **IV-30** are essentially equal, therefore only the NMR spectra of **IV-29** will be discussed here. The signals of the ligand **IV-9** are only slightly different in **IV-29**. The $^{3}J_{HH}$ coupling constants of these methylene protons reflects their orientation (*cis*: $^{3}J_{HH}$= 10.5 Hz vs. *trans:* $^{3}J_{HH}$= 5.3 Hz) towards the central CH. Similarly in the ^{13}C NMR a large $^{2}J_{PC}$= 32.4 Hz is observed for the carbon atom in the *trans* position to phosphorus and a small coupling constant $^{2}J_{PC}$= 2.5 Hz for the carbon atom in the *trans* position to the chlorine atom.



IV-9

IV-29: R = H
IV-30: R = Ph

Scheme 9: *Synthesis of allylpalladium complexes IV-29 and IV-30.*

Single crystals of **IV-29** and **IV-30** were obtained by slow evaporation of dichloromethane solutions of both complexes. The molecular structures are presented in Figure 2.

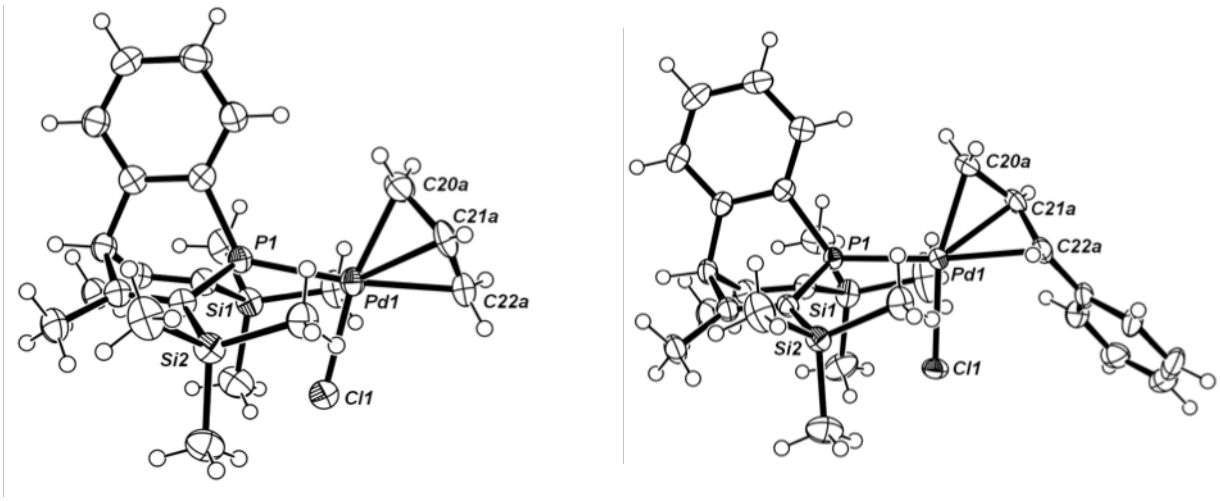
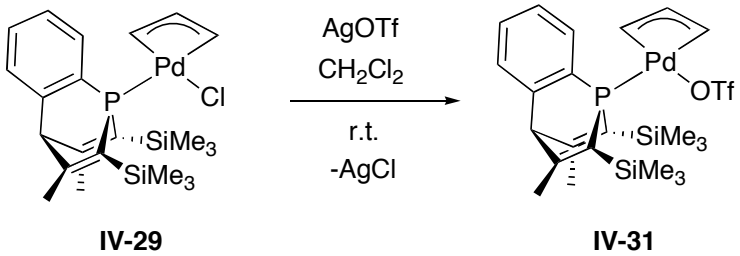


Figure 2: *Molecular structures (ORTEP-representation, thermal ellipsoids at a 50 % probability, one of two independent identical molecules in the asymmetric unit cell, a disorder of the allyl groups has been omitted in both cases) of phosphabarrelene* ***IV-29*** *(left) and* ***IV-30*** *(right). Selected bond lengths [Å] and angles [°] for* ***IV-29****: P1-Pd1: 2.291(1), Pd1-Cl1: 2.374(1), Pd1-C20a: 2.123(5), Pd1-C22a: 2.210(5), P1-Pd1-Cl1: 86.89(4), P1-Pd1-C22a: 172.7(2), C20a-Pd1-Cl1: 168.1(1). Selected bond lengths [Å] and angles [°] for* ***IV-30****: P1-Pd1: 2.2929(4), Pd1-Cl1: 2.394(5), Pd1-C20a: 2.119(2), Pd1-C22a: 2.260(2), P1-Pd1-Cl1: 88.5(1), P1-Pd1-C22a: 172.91(6), C20a-Pd1-Cl1: 164.1(1).*

The structural parameters of complexes **IV-29** and **IV-30** are similar. In both complexes the palladium atom adopts a square planar geometry with the phosphabarrelene and the chlorine atom in *cis* configuration. The Pd1-C22a bond distance is slightly longer in **IV-30** than in **IV-29**, as described for the IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) allyl palladium complexes reported by Nolan and coworkers.[11] In contrast the lengthening of the Pd1-C22a bond distance is less pronounced with only 0.05 Å in the phosphabarrelene complexes compared to the corresponding IPr complexes where the difference is of 0.074 Å.

The abstraction of the chloride atom of complex **IV-29** with silver triflate in dichloromethane leads to the formation of a well-defined product, with a characteristic signal in phosphorus NMR at a chemical shift δ = -12.1 ppm (Scheme 10).



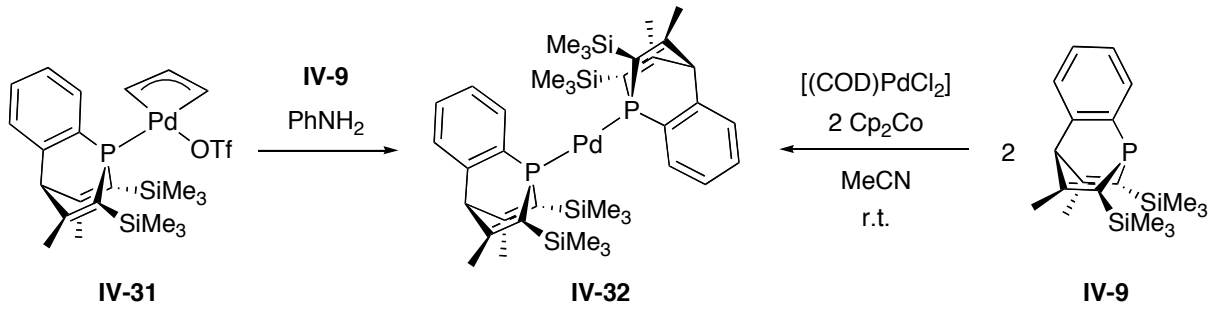
IV-29 **IV-31**

Scheme 10: *Chloride abstraction with silver triflate from* ***IV-29****.*

The product was also characterized by NMR spectroscopy and high resolution mass spectroscopy. The NMR data of **IV-31** are very similar to those of **IV-29**. Therefore it can be supposed that the triflate anion is coordinated to the palladium center.

As we were interested to use ligand **IV-9** in palladium catalyzed cross-coupling reactions, we were wondering whether or not this ligand would be able to stabilize efficiently palladium(0) complexes, as these are proposed intermediates in several palladium catalyzed reactions.

The reaction of complex **IV-31** with aniline in the presence of a second equivalent of **IV-9** led to the formation of a stable 14 VE palladium (0) diphosphabarrelene complex **IV-32** by nucleophilic attack on the allyl ligand (Scheme 11).[12] Only few examples of this type of complexes have been reported to date with bulky alkyl phosphines and NHC ligands. Complex **IV-32** can equally be obtained by the reduction of [(COD)$PdCl_2$] with cobaltocene in the presence of two equivalents of **IV-9**. Best yields were obtained when the reduction was carried out in acetonitrile. The product is air sensitive but can be stored without any signs of decomposition under inert gas atmosphere.



IV-31 **IV-32** **IV-9**

Scheme 11: *Synthesis of diphosphabarrelene palladium(0) complex IV-32.*

In the phosphorus NMR a signal at δ = -31 ppm can be observed for **IV-32**. The signal of proton H-8 in β-position of the phosphorus atom is subjected to an important deshielding and can now be found at δ = 8.9 ppm ($\Delta\delta$ = 1.3 ppm compared to **IV-9**). An evidence for the formation of a palladium complex with two phosphorus ligands in *trans* configuration is the appearance of an AXX' coupling pattern in the ^{13}C NMR for most of the carbon atoms of the ligand, due to the coupling with the two different phosphorus atoms.

Single crystals suitable for X-Ray crystal structure analysis could be obtained by crystalization of **IV-32** from a concentrated solution in hexanes at -18 °C. The molecular structure of **IV-32** is presented in Figure 3.

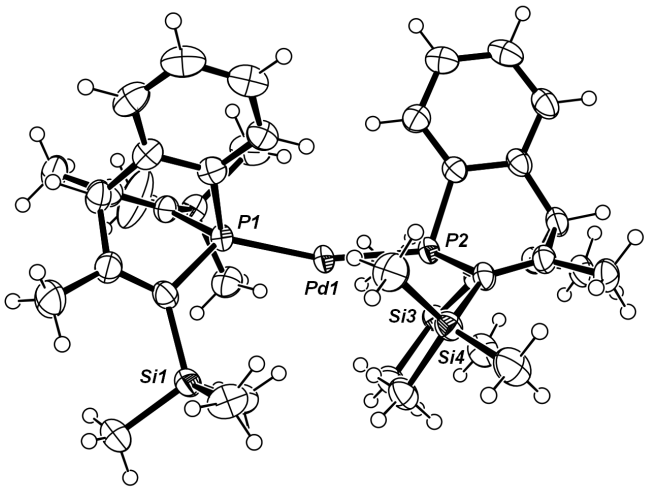
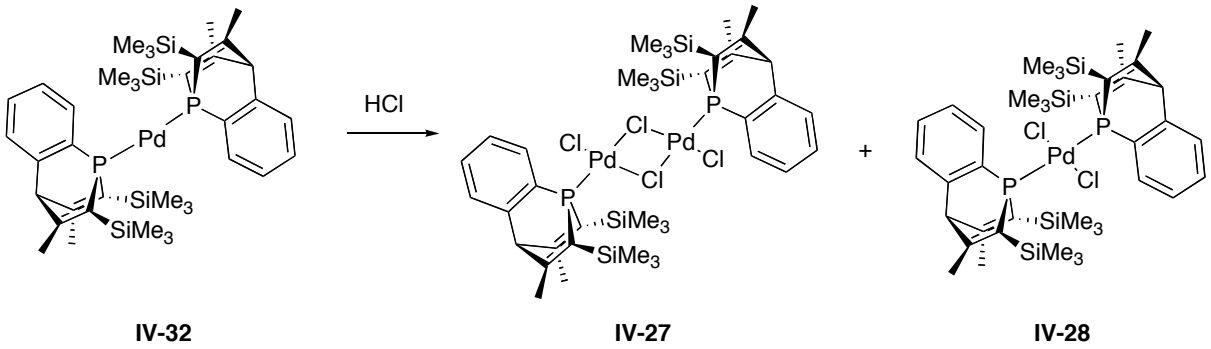


Figure 3: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex* ***IV-32****. Selected bond lengths [Å] and angles [°]: Pd1-P1: 2.274(1), Pd1-P2: 2.268(1), P1-Pd1-P2: 160.65(4), P1-C1-Si1: 119.7(2), P1-C5-Si2: 117.3(2).*

The X-Ray crystal structure of compound **IV-32** reveals an almost linear coordination of the palladium atom. As in the case of $[Pd(PCy_3)_2]$ the P1-Pd1-P2 angle of 160.7 ° deviates significantly from the expected 180 °, that would be expected for a d^{10} transition metal fragment. As in the case of $[Pd(PCy_3)_2]$, no agostic interaction between protons of the ligand and the palladium center could be observed.

The addition of 2 equivalents of a solution of hydrogen chloride in diethylether to complex **IV-32** led to an immediate change of the colour from pale yellow to bright yellow. A complex mixture of products can be observed in phosphorus NMR. The major product that was observed is the poorly soluble compound **IV-27** that appears with the concomitant decoordination of ligand **IV-9**. A minor product **IV-28** could also be identified due to the formation of a small fraction of bright yellow crystals upon slow evaporation of the reaction mixture. (Scheme 12).



IV-32 **IV-27** **IV-28**

Scheme 12: *Reaction of complex* ***IV-32*** *with hydrogen chloride.*

The molecular structure of complex **IV-32** is presented in Figure 4.

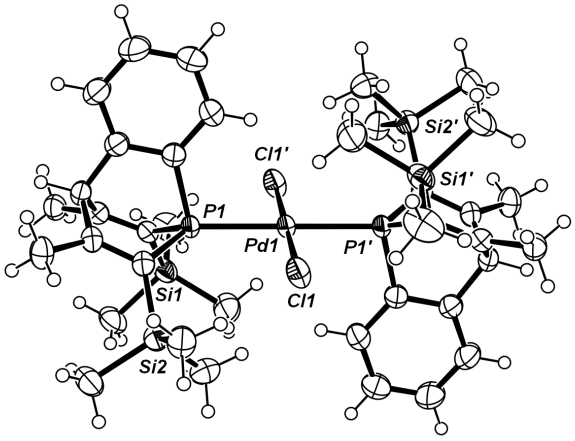
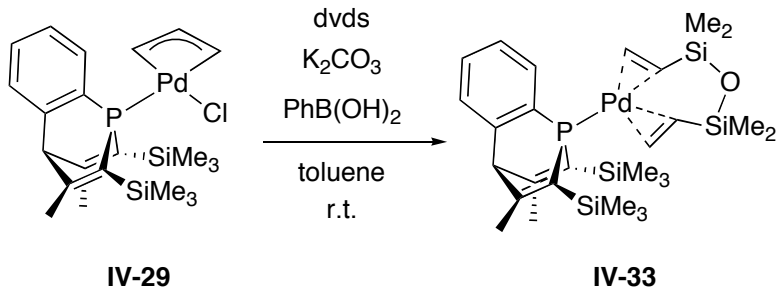


Figure 4: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability, a THF molecule was omitted for clarity) of complex* ***IV-28****. Selected bond lengths [Å] and angles [°]: P1-Pd1: 2.3435(7), Pd1-Cl1: 2.297(1), P1-Pd1-P1': 180.00(4), Cl1-Pd1-Cl1': 180.00(5), P1-Pd1-Cl1: 85.65(3), P1-C1-Si1: 124.5(2).*

The palladium center adopts a square planar geometry with the phosphabarrelene ligands in *trans* stereochemistry and P1-Pd-P1' and Cl1-Pd1-Cl1' angles of 180 ° as expected for a square planar geometry. In contrast, the P1-Pd1-Cl1 angle of 85.65(3) ° shows the slight distortion from the ideal square planar case. The extremely long P1-Pd1 distance of 2.3435(7) Å compared to 2.2190(6) Å in **IV-27** accounts for the important steric demand of ligand **IV-9**. In contrast, the Pd1-Cl1 distance of 2.297(1) Å is in the usual range of Pd-Cl distances.

The long Pd1-P1-distance in **IV-28** shows the weak coordination of ligand **IV-9** to the palladium atom. Therefore one might suppose that **IV-28** is the kinetic product of the reaction of **IV-29** with hydrogen chloride, that evolves by decoordination to give the thermodynamic product **IV-27**. Therefore the synthesis of **IV-28** from palladium(II) precursors might not be possible.

During our studies concerning Suzuki-Miyaura coupling reactions we observed that phosphabarrelene palladium allyl complex **IV-29** shows a higher catalytic activity at room temperature than the palladium (0) complex **IV 32**. Therefore it was supposed that complex **IV-29** is reduced to a palladium (0) complex in the presence of phenylboronic acid and potassium carbonate. To prove this hypothesis, dvds (1,3-divinyldimethyldisiloxane) was added to a mixture of **IV-29**, phenylboronic acid and potassium carbonate (Scheme 13). The quantitative formation of **IV-29** to the tricoordinate monophosphine palladium(0) complex **IV-33**, can be observed by ^{31}P NMR spectroscopy after 2h. Complex **IV-33** exhibits a characteristic signal at a chemical shift of δ = -28.8 ppm.



IV-29 **IV-33**

Scheme 13: *Synthesis of complex* ***IV-33****.*

Single crystals suitable for X-Ray crystal structure analysis could be obtained by slow evaporation of a solution of **IV-33** in diethylether. The molecular structure of **IV-33** is presented in Figure 5.

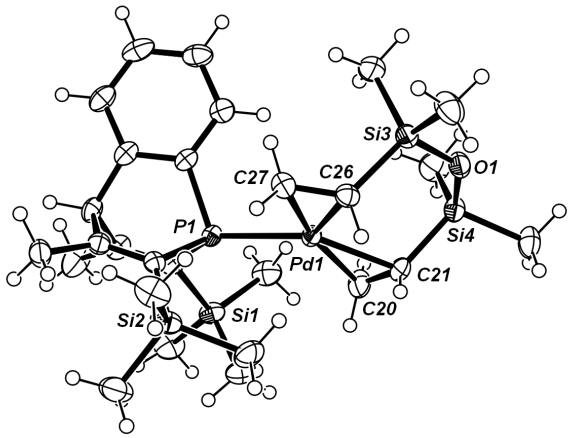
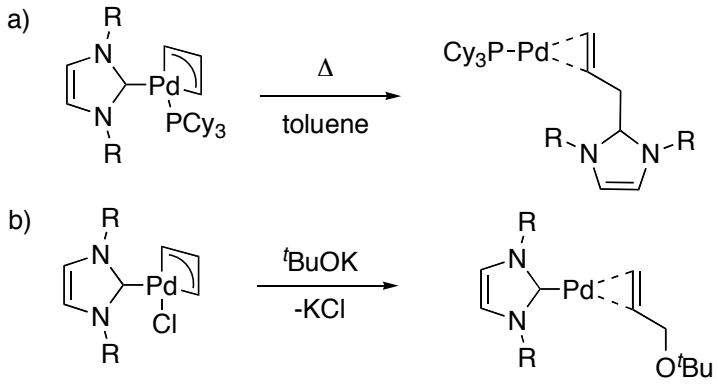


Figure 5: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex* ***IV-33****. Selected bond lengths [Å] and angles [°]: Pd1-P1: 2.3527(5), Pd1-C20: 2.174(2), Pd1-C21: 2.196(2), Pd1-C26: 2.193(2), Pd1-C27: 2.213(2), P1-Pd1-C20: 107.43(6), P1-Pd1-C21: 144.55(5), P1-Pd1-C26: 124.39(5), P1-Pd1-C27: 87.61(5), P1-C1-Si1: 117.8(1), P1-C5-Si2: 124.3(1).*

The difference of the P1-Pd1-olefin angles with 126 ° (P1-Pd1-(C20-C21)) and 106 ° (P1-Pd1-(C26-C27)) reflects the distortion around the planar tricoordinated palladium atom. In spite of the asymmetric structure formed in the solid state, the NMR signals of the trimethylsilyl groups of the ligand as well as the signals of the olefins show the symmetric structure of **IV-33** in solution. The P1-Pd1 distance is significantly longer in compound **IV-33** with 2.3527(5) Å compared to the Pd1-P1 distance in **IV-32** with 2.274(1) Å accounting for the exceedingly important steric crowding around the palladium atom.

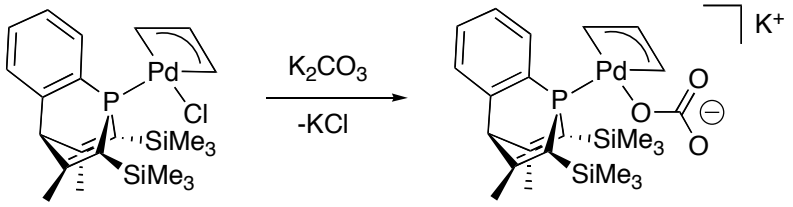
The mechanism of the reduction of allylpalladium complex **IV-29** was the subject of further studies. The formation of highly unsaturated mono-phosphine palladium species is of

high interest, as monophosphine palladium complexes were shown to be intermediates in cross-coupling and amination reactions.[13] It should be noted, that in our case, the generation of the palladium (0) phosphine fragment can be carried out under very mild conditions, as these reductions usually require high temperatures[14] or strong bases[15] as for example in the case of NHC palladium complexes (Scheme 14).



Scheme 14: *Reduction of allylpalladium complexes (a) by reductive elimination, (b) by nucleophilic attack by alkoxides.*

The addition of potassium carbonate to a solution of complex **IV-29** in toluene immediately leads to the formation of a new species with a chemical shift of δ = -11 ppm, slightly upfield shifted ($\Delta\delta$ = -2 ppm) from the starting product. This new species was supposed to be complex **IV-34** (Scheme 15).



IV-29 **IV-34**

Scheme 15: *Reaction of IV-29 with potassium carbonate.*

Unfortunally it has not been possible yet to obtain single crystals of **IV-34**. Nevertheless, the analysis of the reaction mixture in FT-ICR-ESI-MS[a] proved the formation of complex **IV-34** by the appearance of a signal at a molecular mass of 553.09 m/z with the expected isoptopic pattern for **IV-34** (Figure 6).

[a] The ESI-MS and gas-phase IR measurements were performed by the group of Dr. P. Maître at the University of Orsay (Paris 11).

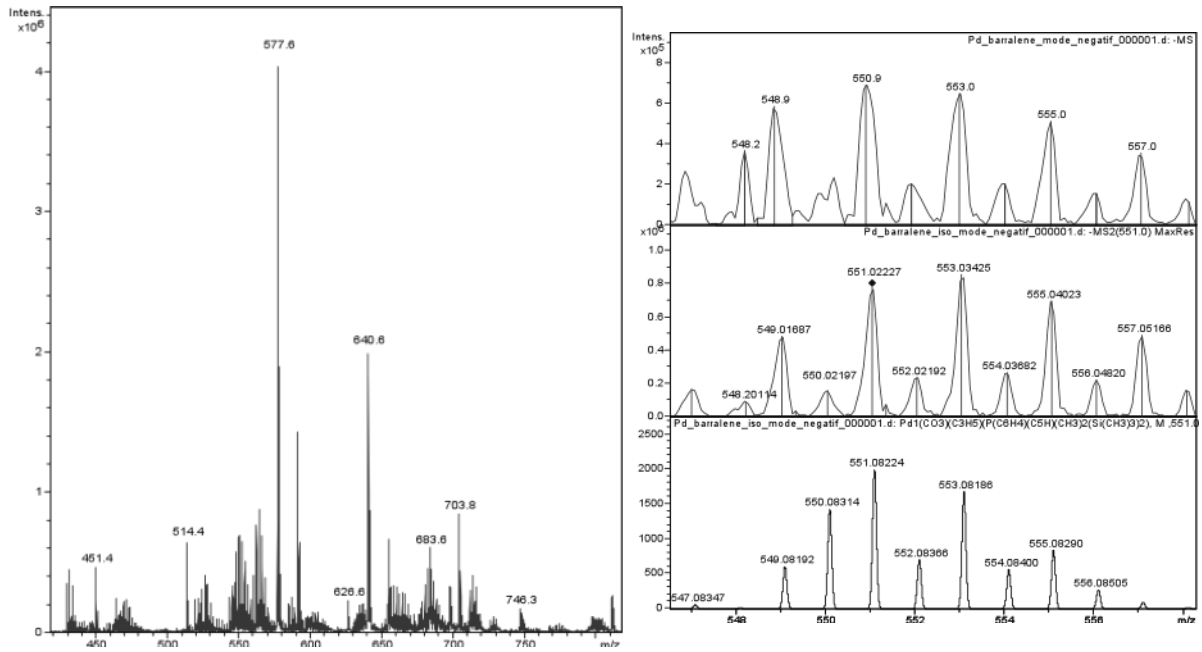


Figure 6: *FT-ICR-ESI-MS spectrum of a mixture of complex* ***IV-29*** *and potassium carbonate: (a) negative ion-mode mass spectrum (b) isotopic pattern of complex* ***IV-34*** *(all fragments)* ***(c)*** *isotopic pattern of* ***IV-34*** *(isolated fragment), (d) simulated isotopic pattern for complex* ***IV-34***.

Additionally an infrared study was performed in the gas phase on the isolated mass fragments at *m/z* of 553.09. In parallel, model complexes **IV-D** and **IV-E** (Figure 7) that correspond to complexes **IV-29** and **IV-34** were optimized by DFT calculations. Structure optimizations were carried out using the Gaussian 03 set of programs[16] with the B3PW91 functional[17, 18] in combination with the 6-31+G* basis set for all non-metal atoms (C, H, P, Cl, O), apart form the $SiMe_3$ groups for which the 3-21G basis set was used, to reduce the calculation time. The LANL2DZ basis set[19] with an additional f-polarization function[20] was used for palladium.

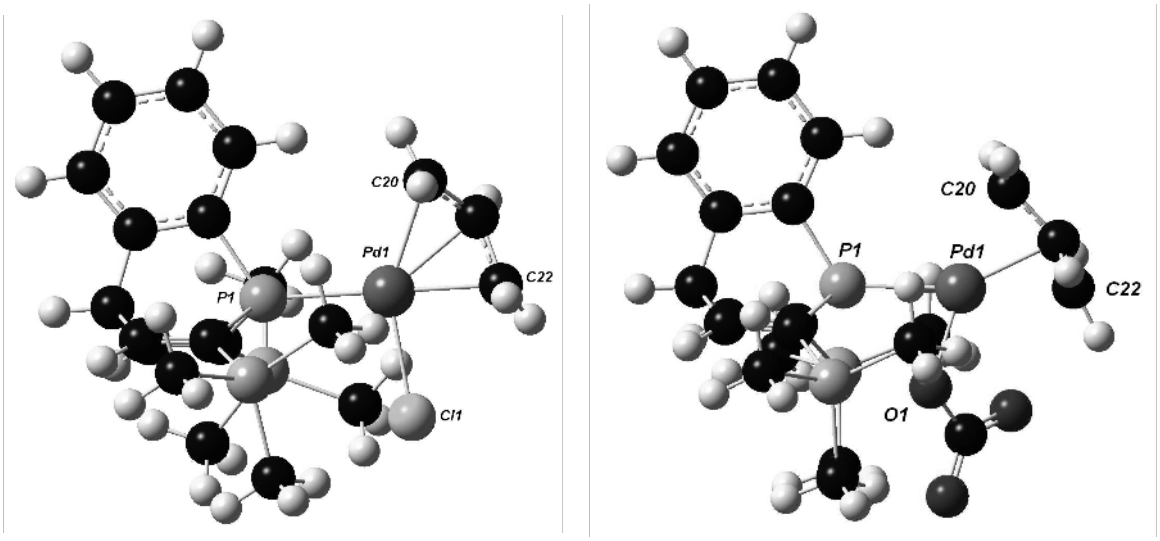


Figure 7: *Optimized structures for model complexes* ***IV-D*** *(left) and* ***IV-E*** *(right). Selected bond lengths and angles for* ***II-A****: Pd1-P1: 2.339, Pd1-Cl1: 2.383, Pd1-C20: 2.158, Pd1-C22: 2.196, P1-Pd1-C22: 172.7, C20-Pd1-Cl1: 161.8. Selected bond lengths and angles for* ***II-B****: Pd1-P1: 2.283, Pd1-O1: 2.047, Pd1-C20: 2.173, Pd1-C22: 2.247, P1-Pd1-O1: 75.7, P1-Pd1-C22: 169.4, C20-Pd1-O1: 170.3.*

Apart from the P1-Pd1-distance (2.339 in **IV-A** vs. 2.291 in **IV-29**), which is overestimated in, the calculated structure fits well with the X-Ray crystal data that was obtained for complex **IV-29**.

The comparison of the IR-spectra of **IV-34** in the gas phase with the calculated IR spectrum of **IV-E** shows a characteristic IR-band at about 1700 cm^{-1} for the asymmetric stretching of the CO groups of the carbonate atoms (1680 cm^{-1} for **IV-34** and 1703 cm^{-1} for **II-B**) in both spectra (Figure 8). The deviation of ~50 cm^{-1} is in the usual range of that was observed for stretching frequencies calculated with DFT-method and the B3PW91 functional.[21] The large intensity for the band at 1325 cm^{-1} results from the coupling of the carbonate stretching with vibrations of the $SiMe_3$ groups.

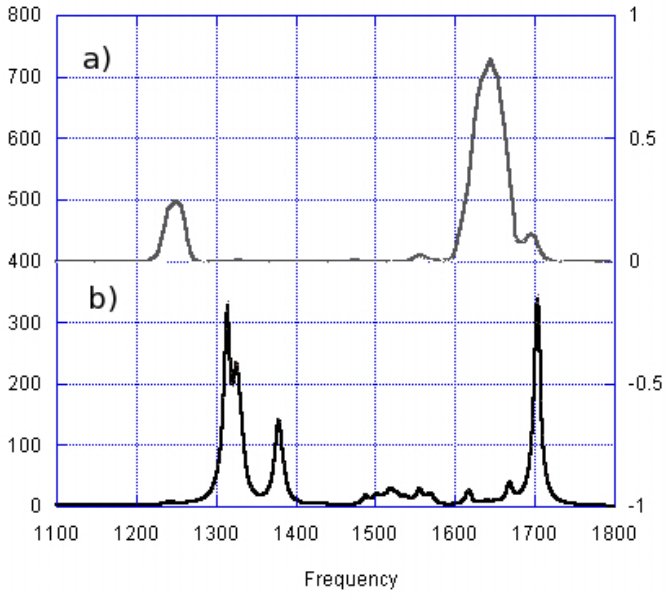


Figure 8: *(a) Gas-phase infrared spectrum of* ***IV-34****, (b) calculated infrared spectrum of* ***II-B****.*

The 1H NMR spectrum of compound **IV-34** shows a significant deshielding of the protons of the CH_2 group of the allyl ligand in the trans position to the carbonate ligand (2.14 ppm in **IV-29** vs. 2.69 ppm in **IV-34** and 3.80 ppm in **IV-29** vs. 4.14 ppm in **IV-34**). This clearly shows the electronic effect of the substitution of the chlorine atom by carbonate.

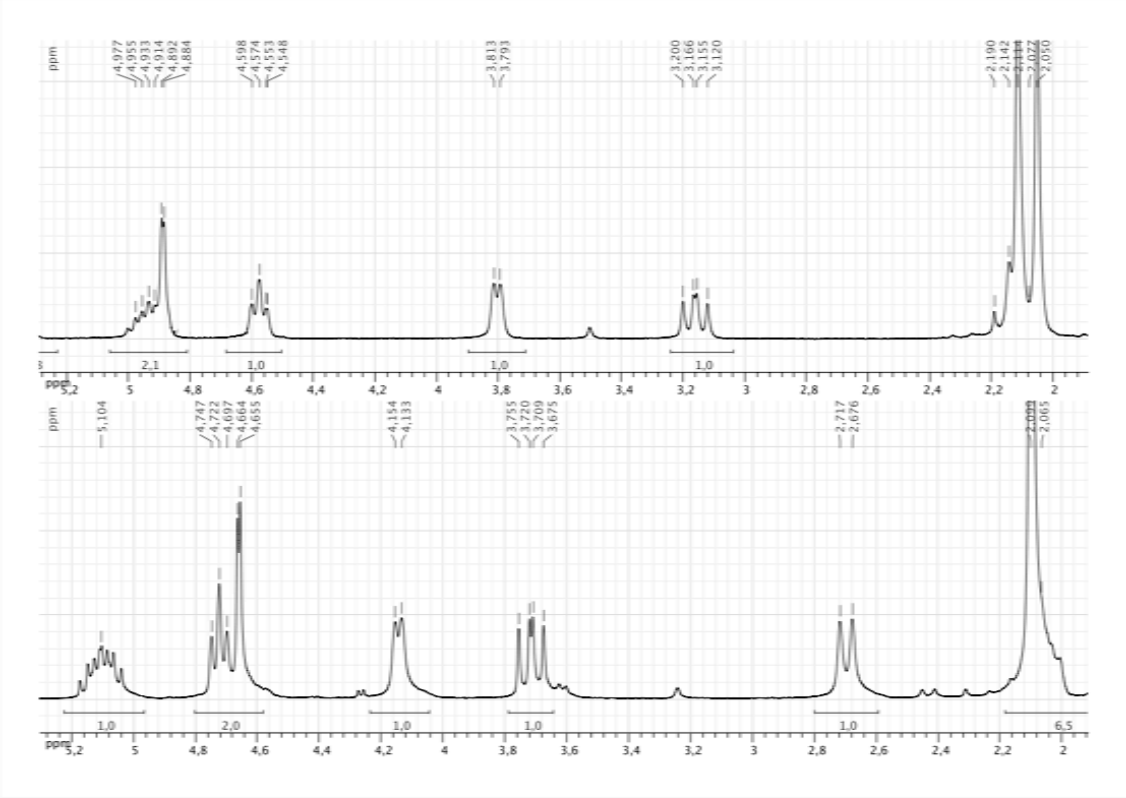
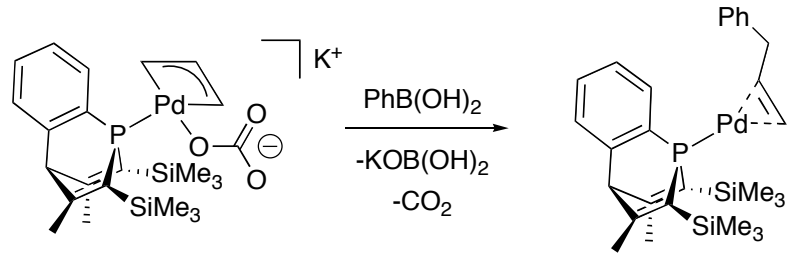


Figure 9: *Comparision of the 1H NMR spectra of complexes* ***IV-29*** *(up) and* ***IV-34*** *(down).*

The addition of one equivalent of phenylboronic acid to complex **IV-34** leads to a change of the color of the reaction mixture from pale to intense yellow (Scheme 16). The appearance of a single peak in ^{31}P NMR can be observed at δ = -22.1 ppm. A small impurity can be observed in the ^{31}P NMR spectrum from the decomposition of complex **IV-35**, giving traces of palladium metal and diphosphabarrelene palladium (0) complex **IV-32** (Figure 10).



IV-34 **IV-35**

Scheme 16: *Reaction of complex* ***IV-34*** *with phenylboronic acid.*

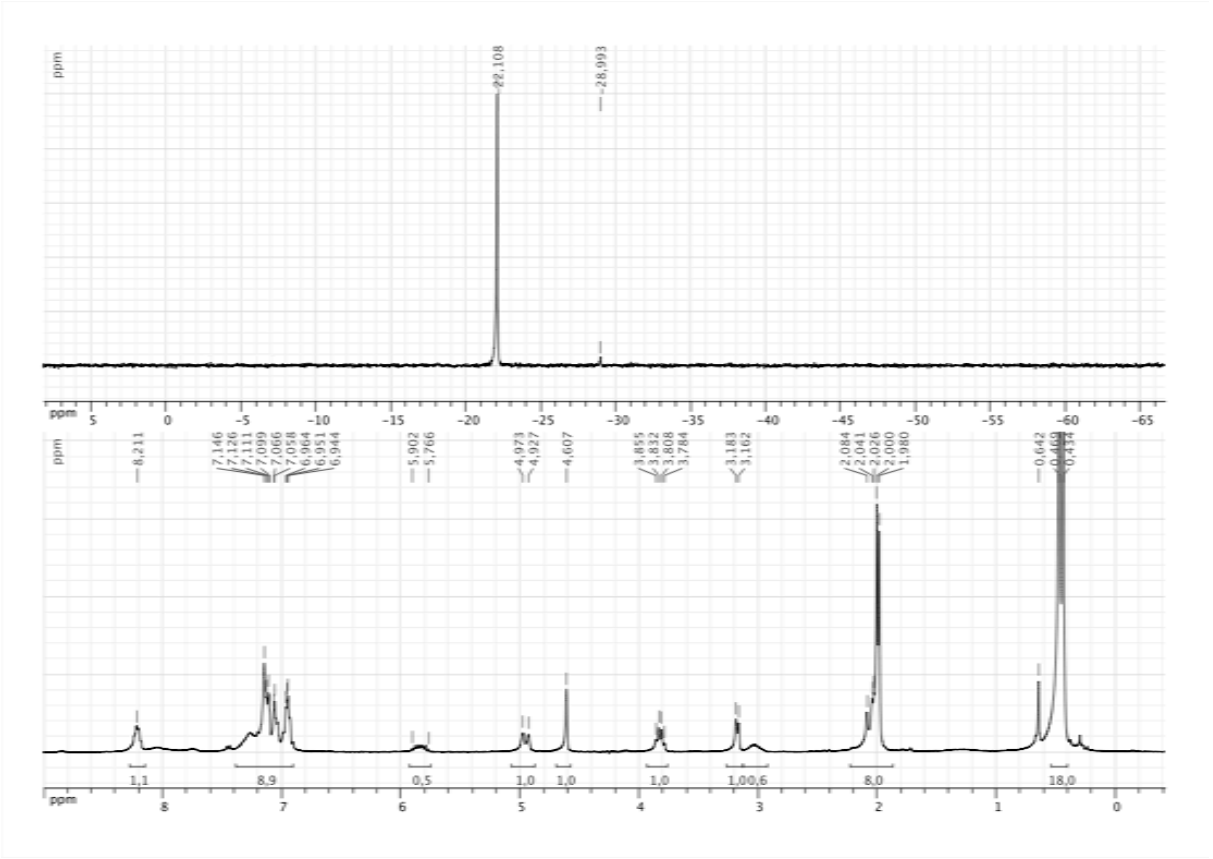
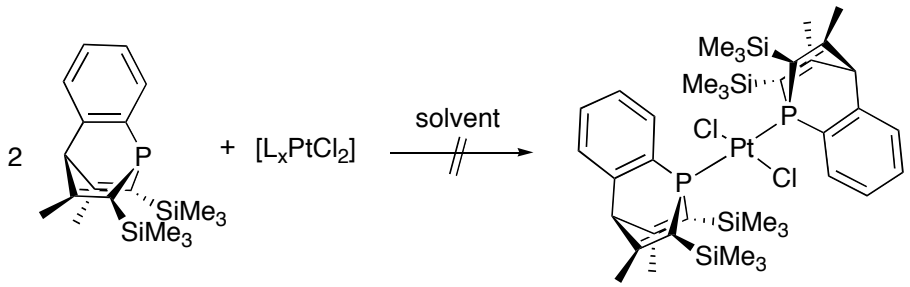


Figure 10: *(up)* $^{31}P\{^{1}H\}$ *and (down)* ^{1}H *NMR spectra of compound* ***IV-35***.

The proton NMR spectrum of **IV-35** (Figure 6) shows three signals for the olefinic protons of the coordinated allylbenzene at δ = 4.95 ppm, δ = 3.82 ppm and δ = 3.17 ppm. The signals are significantly electronically shielded due to the coordination to the palladium (0), as can be seen for the signals of the vinyl groups in **IV-33**. Furthermore a shift of the signal of H-8 to lower field δ = 8.21 ppm (Δδ = 0.5 ppm) is observed in **IV-35**, whereas the signal of H-8 in the all π-allyl-complexes could be observed in the region of δ = 7.8 ppm. Unfortunately it was not possible to further characterize complex **IV-35** due to its relatively fast decomposition at room temperature and the formation of palladium metal and the liberation of ligand **IV-9**. Related (NHC)Pd(0)-allylether have been postulated to be an intermediates in the activation of allylpalladium NHC complexes, but to the best of our knowledge no spectroscopic data have been reported so far. In the case of PPh_3, the analogous reaction is reported to form rapidly $Pd(PPh_3)_4$ and palladium metal.[15]

II.2. Platinum

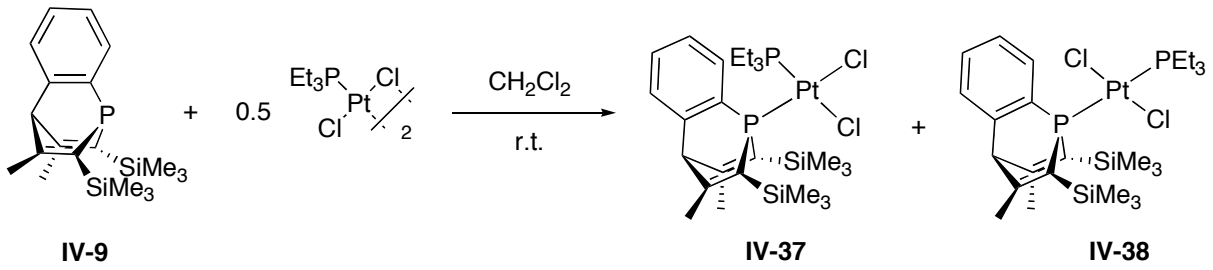
When we started this study in 2008, the reaction of **IV-9** with common $[L_xPtCl_2]$ precursors (L = COD, x=1; L = SMe_2, PhCN, x=2) was attempted (Scheme 17) in order to get some information on the electronic properties of ligand **IV-9** from the $^1J_{PPt}$ coupling constant. As in the case of the analogous palladium precursors, this reaction did not occur. The synthesis of the analogous *cis*-diphosphabarrelene platinum chloride complexes was reported early in 2009 by Tooze and coworkers using the 2,6-dixylyl-4-phenyl-phosphabarrelene.[10]



IV-9 **IV-36**

Scheme 17: *Attempted synthesis of platinum complex* ***IV-36***.

In our case, the synthesis of a mixed phosphabarrelene phosphine platinum chloride complex can be achieved, when $[(PEt_3)PtCl]_2$ is used as a precursor, which is readily cleaved to give a mixture of *cis* **IV-37** and *trans* **IV-38** complexes (Scheme 18). The isomers can be selectively interconverted by recrystallization from different solvent mixtures.



Scheme 18: *Synthesis of complexes IV-37 and IV-38.*

Both isomers display very characteristic pattern in ^{31}P NMR. The *cis*-isomer **IV-37** shows a very small $^{2}J_{PP}$ coupling constant of ca 13.9 Hz. The $^{1}J_{PPt}$ coupling constants in this type of complexes has often been used to evaluate the electronic properties of phosphine ligands. The value of the $^{1}J_{PPt}$ coupling constant of 3837 Hz in **IV-37** is larger than for the PEt_3 with 3536 Hz, due to the poorer donating properties of the phosphabarrelene. $^{1}J_{PPt}$ coupling constants of *cis*-$[(PR_3)(PEt_3)PtCl_2]$ complexes are summarized in Table 1. The comparison of the coupling constants shows that the lone pair in ligand **IV-9** shows a higher s-character than in PPh_3.

Table 1: *$^{1}J_{PPt}$ coupling constants in cis-$[(PR_3)(PEt_3)PtCl_2]$ complexes*

Ligand	$^{1}J_{PPt}$(L) Hz	$^{1}J_{PPt}$(PEt_3) Hz	$^{2}J_{PP}$ Hz	Reference
PF_3	7388	2869	19	Jacobson[22]
$POPh_3$	6249	2977	17	Ahmad[23]
PCl_3	6054	3197	22	Jacobson[22]
$PClPh_2$	4343	3311	17	Jacobson[22]
IV-9	3837	3536	15	this work
PPh_3	3815	3373	17	Jacobson[22]
PEt_3	3520	3520	19	McFarlane[24]

The *trans*-isomer **IV-38** shows a large $^{2}J_{PP}$ coupling constant of 500.6 Hz, characteristic for *trans*-diphosphine complexes. The $^{1}J_{PPt}$ coupling constants in the *trans*-isomer are much smaller with 2525 Hz for the phosphabarrelene and 2585 Hz for the triethylphosphine.

The molecular structures of **IV-37** and **IV-38** are presented in Figure 11.

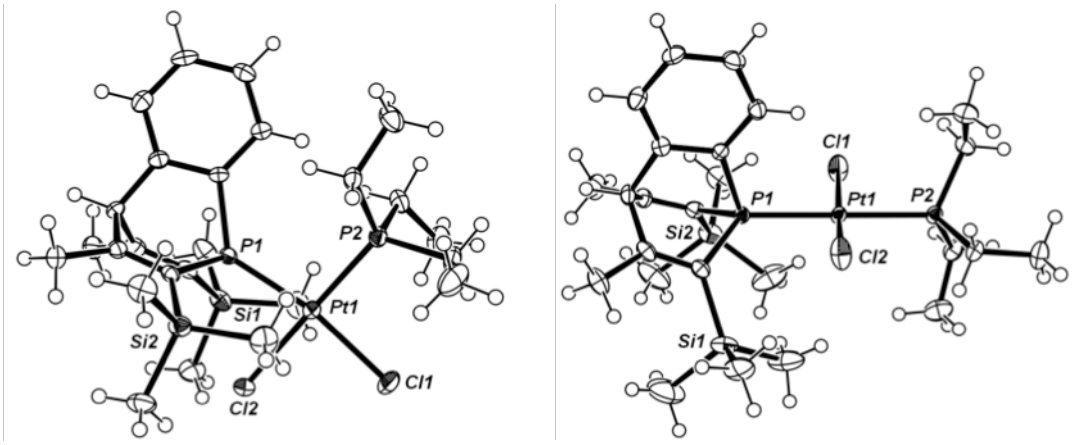
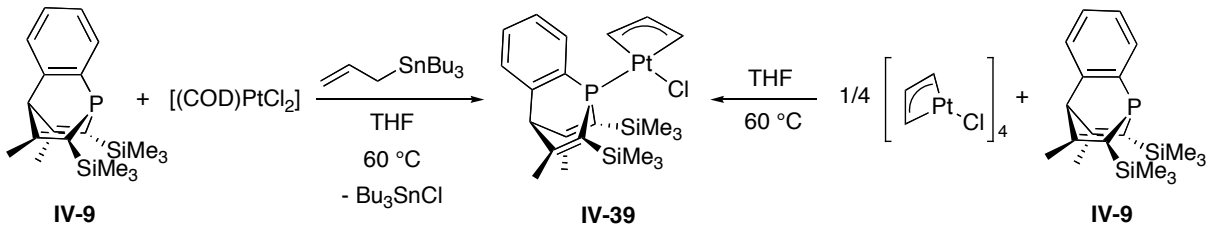


Figure 11: *Molecular structures (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complexes* ***IV-37*** *(left) and* ***IV-38*** *(right). Selected bond lengths [Å] and angles [°] for* ***IV-37****: Pt1-P1: 2.253(1), Pt1-P2: 2.241(1), Pt1-Cl1: 2.361(1), Pt1-Cl2: 2.376(1), P1-Pt1-P2: 100.07(4). Selected bond lengths [Å] and angles [°] for* ***IV-38****: Pt1-P1: 2.3236(8), Pt1-P2: 2.2933(8), Pt1-Cl1: 2.312(1), Pt1-Cl2: 2.301(1), P1-Pt1-P2: 179.48(3), Cl1-Pt1-Cl2: 172.30(4), P1-Pt1-Cl1: 93.06.*

The synthesis of the allylplatinum complex **IV-39** could be achieved by two different methods. First, the reaction the [(COD)$PtCl_2$] with ligand **IV-9** and a slight excess of allytributyltin (1.2 equiv.) gave **IV-39** (Scheme 19). Although a quantitative conversion of the starting material could be observed by ^{31}P NMR (δ = 7 ppm, $^{1}J_{PPt}$ = 4577 Hz), the isolation of the product from the reaction mixture was tedious and the product could only be isolated in a modest 60 % yield.



Scheme 19: *Synthesis of allylplatinum complex* ***IV-39****.*

A more convenient procedure for the synthesis of **IV-39** is the reaction of **IV-9** with the allyl platinum chloride precursor. The quantitative formation of **IV-39** could be observed by ^{31}P NMR after 4 h at 60 °C in THF (Scheme 19). By this method the product can be obtained in nearly quantitative yield by evaporation of the solvent.

Single crystals suitable for X-Ray crystal structure analysis were obtained by cooling a concentrated solution of **IV-39** in THF to -18 °C. The molecular structure of **IV-39** is presented in Figure 12.

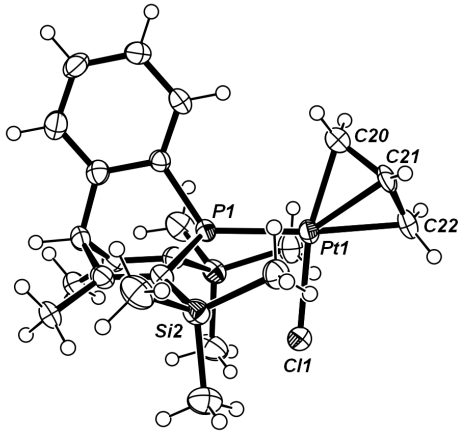
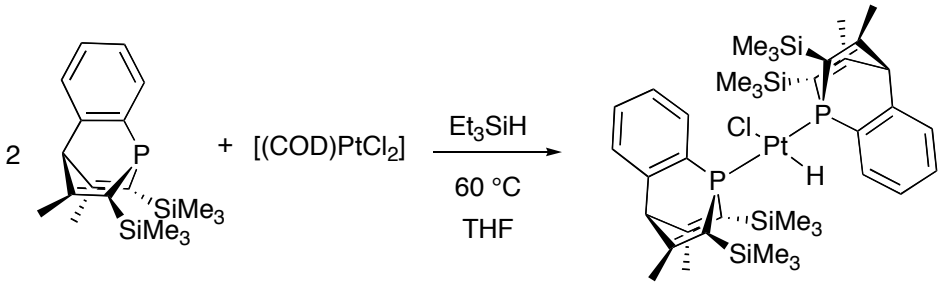


Figure 12: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex* ***IV-39****. Selected bond lengths [Å] and angles [°]: Pt1-P1: 2.261(1), Pt1-Cl1: 2.373(1), Pt1-C20: 2.100(6), Pt1-C22: 2.18(3), P1-Pt1-C22: 171.4(7), P1-Pt1-Cl1: 85.68(5), C20-Pt1-Cl1: 167.6(2).*

The molecular structures shows the expected square planar coordination of the platinum atom. The P1-Pt1-C22 angle of 171.4(7) ° and the P1-Pt1-Cl1 angle of 85.68(5) ° reveal the slight distortion from the ideal square planar case.

In the course of catalytic studies concerning the hydrosilylation of alkynes (*vide infra*) we could observe that the reaction of ligand **IV-9** with [(COD)$PtCl_2$] and triethylsilane at 60 °C in THF led to the formation of a product with a signal at a ^{31}P NMR shift of δ = -13.0 ppm featuring platinum satellites ($^1J_{PPt}$ = 3120 Hz) (Scheme 20).



IV-9 **IV-40**

Scheme 20: *Synthesis of chlorohydride complex IV-40.*

In the ^{1}H NMR spectrum a signal can be observed at a chemical shift of δ = -15.56 ppm. The triplet shows a $^2J_{PH}$ coupling constant of 15.3 Hz, due to the coupling with two equivalent

phosphorus atoms and satellites from the coupling with a platinum atom with a $^{1}J_{PtH}$ coupling constant of 588.4 Hz. On the basis of these data, the formation of *trans*-diphosphabarrelene-chlorohydride complex **IV-40** was assumed.

The structure of **IV-40** could be confirmed by X-Ray crystal structure analysis. The molecular structure of **IV-40** is presented in Figure 13.

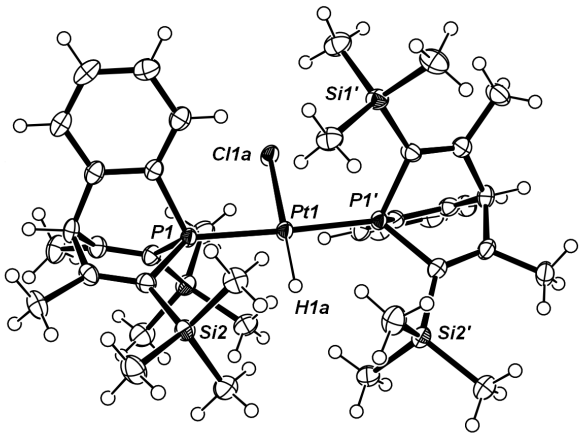
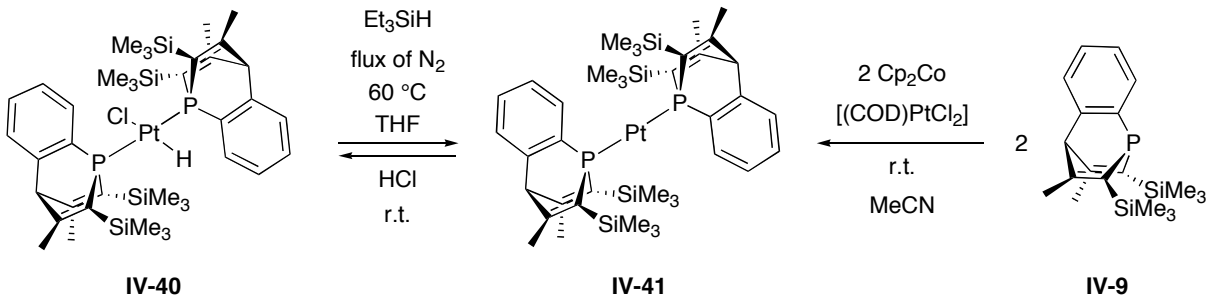


Figure 13: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex* ***IV-40*** *(THF molecules were omitted for clarity). Selected bond lengths [Å] and angles [°]: Pt1-P1: 2.293(1), Pt1-Cl1a: 2.4123(2), Pt1-H1a: 1.68(1), P1-Pt1-P1': 177.03(5), H1a-Pt1-Cl1a: 180.00(2).*

The molecular structure of **IV-40** shows the *trans*-coordination of the two phosphabarrelenes on the square planar platinum atom, which is in agreement with the NMR data.

The efforts to reduce complex **IV-40** by the reaction with an excess of triethylsilane led to a signal of a minor product **IV-41** (< 5%) in the ^{31}P NMR spectrum of the reaction mixture at δ = 5.6 ppm with a large $^{1}J_{PPt}$ coupling constant of 4644 Hz. Further studies showed, that the conversion of **IV-40** to this product could be favored by performing the reaction of **IV-40** with triethylsilane in a flux of nitrogen. Therefore we assumed that during the reduction of **IV-40** with triethylsilane hydrogen chloride was formed that reacted with **IV-41** to give **IV-40** upon return to room temperature. As we supposed that the product was the zerovalent complex **IV-41**, the reduction of [(COD)$PtCl_2$] in the presence of ligand **IV-9** with cobaltocene was investigated. This reaction provided complex **IV-41** as a single product in high yield (95 %) (Scheme 21).



IV-40 **IV-41** **IV-9**

Scheme 21: *Synthesis of platinum (0) diphosphabarrelene complex* ***IV-41****.*

The NMR analysis showed the absence of any hydride resonance. The structure of complex **IV-41** could be confirmed by X-Ray crystal structure analysis. The molecular structure of **IV-41** is presented in Figure 14.

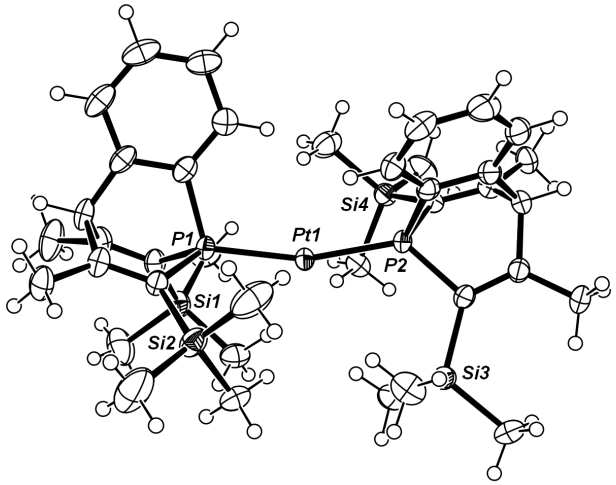
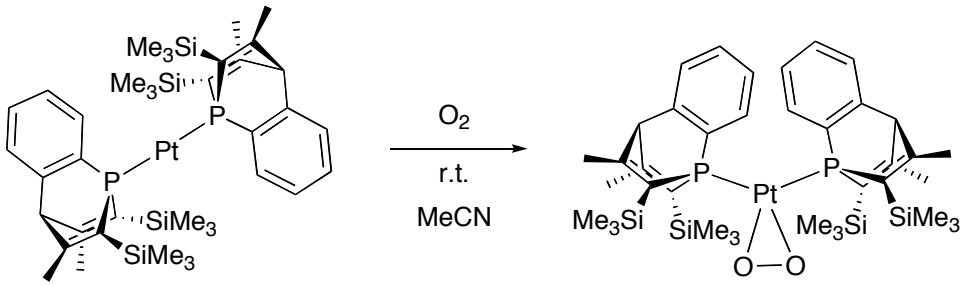


Figure 14: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex* ***IV-41****. Selected bond lengths [Å] and angles [°]: Pt1-P1: 2.239(1), Pt1-P2: 2.243(1), P1-Pt1-P2: 162.62(4).*

It should be noted that complex **IV-41** is a rare example of a 14 VE $Pt(0)L_2$ complex.[12, 25] Interestingly the Pt1-P1 and Pt1-P2 distances with 2.239(1) Å and 2.243(1) Å are close to those of the $[Pt(PCy_3)_2]$ complex[26] (2.231(4) Å), although the two ligands display different electronic properties. Due to the higher π-acceptor properties of the phosphabarrelene compared to tricyclohexylphosphine, a shorter Pt-P distance should be expected for **IV-41**. The P1-Pt1-P2 bite angles are comparable in both complexes (162.62(4) ° in **IV-41** *vs.* 160.0(5) ° in $[Pt(PCy_3)_2]$) and markedly different from that of the $[Pt(P(^tBu)_2Ph)]$ complex,[26] where agostic interactions between the central platinum atom and alkyl C-H groups can be observed.

Complex **IV-41** is sensitive towards air and upon exposure of a solution of **IV-41** to oxygen, the formation of a new species **IV-42**, a relatively rare, stable, oxygen adduct[27, 28] of complex **IV-41** can be observed in ^{31}P NMR at a chemical shift of δ = -25.2 ppm ($^{1}J_{PPt}$ = 4277 Hz) (Scheme 22).



IV-41 **IV-42**

Scheme 22: Formation of an oxygen adduct of platinum(0)-complex **IV-42**.

Single crystals of **IV-42** could be obtained from a concentrated solution of **IV-42** in acetonitrile. The molecular structure of complex **IV-42** is presented in Figure 15.

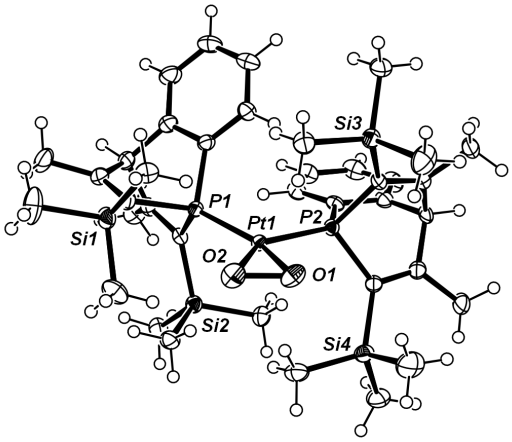
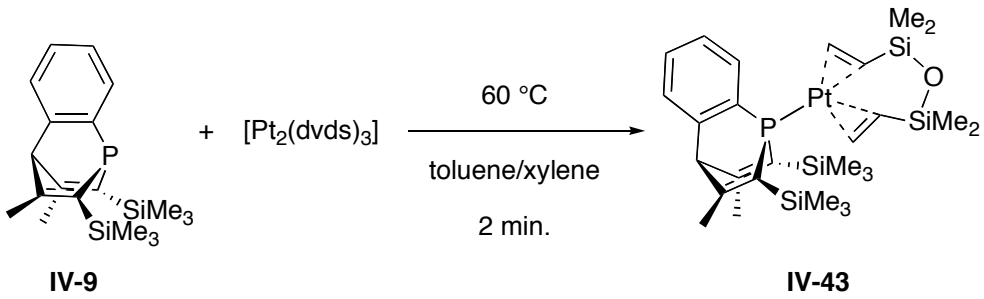


Figure 15: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex* ***IV-42****. Selected bond lengths [Å] and angles [°]: Pt1-P1: 2.2428(7), Pt1-P2: 2.2532(8), Pt1-O1: 2.014(2) Pt1-O2: 2.019(2) O1-O2: 1.473(3), P1-Pt1-P2: 104.69(3) .*

The Pt1-P1 and Pt1-P2 distances of 2.2428(7) Å and 2.2532(8) Å in **IV-42** are identical to the ones found in **IV-41** with 2.239(1) Å and 2.243(1) Å. The O1-O2 distance of 1.473(3) Å is comparable to those of the two other reported oxygen adducts of $[(PPh_3)_2PtO_2]$[27] and $[((^tBu)_2PPh)PtO_2]$[28] (1.432 and 1.520 Å respectively) and significantly longer than in molecular oxygen with 1.207 Å and comparable to the O-O distance in O_2^{2-} with 1.490 Å.[29] Interestingly the

two bulky phosphabarrelenes adopt a *cis*-coordination mode in **IV-42,** with a P1-Pt1-P2 angle of only 104.69(3) °.

The reaction of the Karstedt catalyst $[Pt_2(dvds)_3]$[30] with ligand **IV-9** leads to the formation of the very stable 16 e^- complex **IV-43** (Scheme 23) with a ^{31}P NMR chemical shift of -16.7 ppm and a $^1J_{PtP}$ coupling constant of 3764 Hz.



IV-9 **IV-43**

Scheme 23: *Reaction of ligand IV-9 with Karstedt's catalyst.*

Single crystals of complex **IV-43** could be obtained by the recrystallization from diethylether. The molecular structure of **IV-43** is presented in Figure 13.

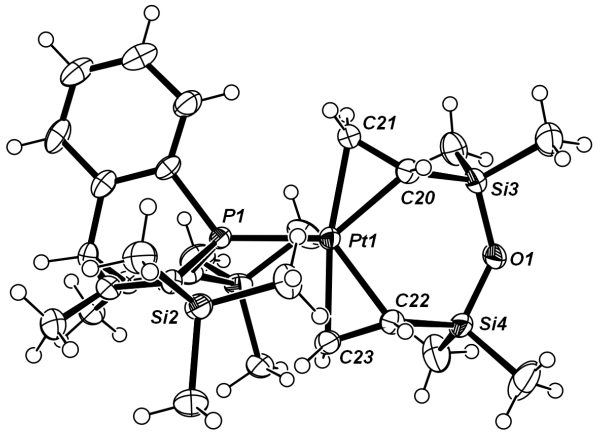


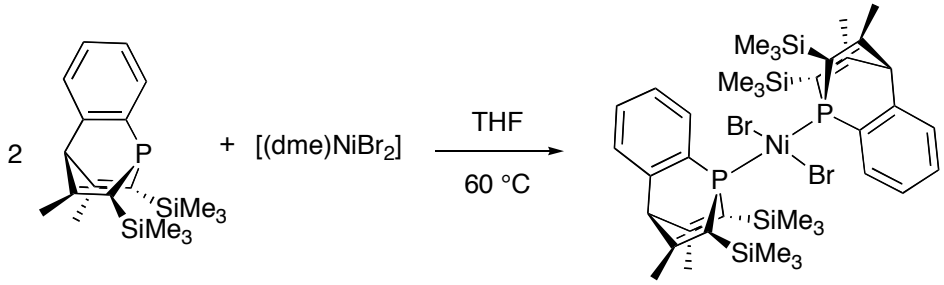
Figure 16: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex IV-43. Selected bond lengths [Å] and angles [°]: Pt1-P1: 2.283(3), Pt1-C20: 2.13(1), Pt-C21: 2.14(1), C20-C21: 1.42(1), C22-C23: 1.43(1).*

The bond distance and the Pt-olefin angles in **IV-43** are similar than those reported by Berthon-Gelloz *et al.* in the case of *N*-Heterocyclic Carbene Pt (dvds) complexes[31] showing the minor influence of the electronic properties of the ligand on these parameters. The P1-Pt1-olefin

angles of 108.2 ° and 120.5° display the slightly distorted planar tricoodination of the platinum atom.

II.3. Nickel

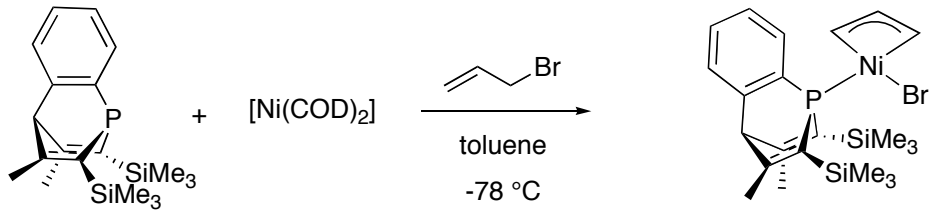
The reaction of ligand **IV-9** with [(dme)$NiBr_2$] in THF led to the formation of an off-white precipitate (Scheme 24). The ^{31}P NMR spectrum of the isolated precipitate in $CDCl_3$ shows a large signal at a chemical shift of δ = 59.3 ppm. The proton NMR did not show any change of the signals compared to the free ligand **IV-9**. Most importantly, no change can be observed for H-8 that usually shows an shift to lower field upon coordination (for example in complex **IV-27** $\Delta\delta$(H-8) = 0.9 ppm). Therefore it can be assumed that complex **IV-44**, if it forms might be very unstable and in equilibrium with the starting material.



IV-9 **IV-44**

Scheme 24: *Reaction of ligand* ***IV-9*** *with [$NiBr_2$(dme)].*

No reaction could be observed between ligand **IV-9** and [$Ni(COD)_2$]. In contrast, the formation of a new orange product with a chemical shift of δ = -10.4 ppm could be observed upon addition of allylbromide to the mixture of ligand **IV-9** and [$Ni(COD)_2$] at -78 °C (Scheme 25). The product readily decomposed at room temperature in solution and only large signals could be observed in ^1H NMR, because of paramagnetic impurities.



IV-9 **IV-45**

Scheme 25: *Formation of complex* ***IV-45***

Nevertheless, single crystals suitable for X-Ray crystal structure analysis could be obtained from a concentrated solution of **IV-45** in toluene at -18 °C. The molecular structure of **IV-45** is presented in Figure 17.

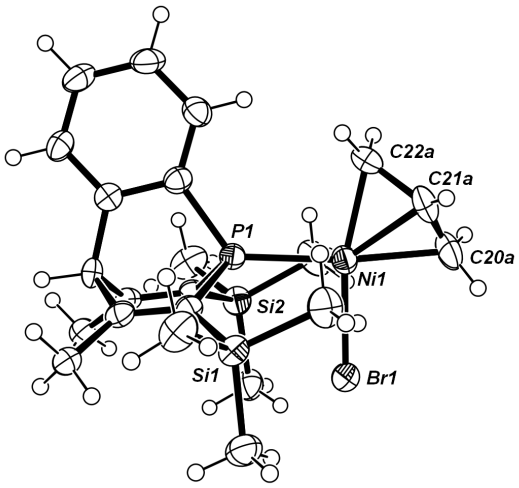
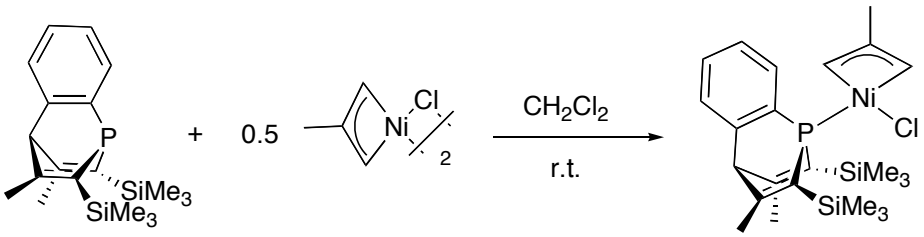


Figure 17: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex* ***IV-43****. Selected bond lengths [Å] and angles [°]: Ni1-P1: 2.198(2), Ni1-Br1: 2.335(1), Ni1-C20a: 2.061(6), Ni1-C22a: 2.000(6), P1-Ni1-C20a: 172.8(2), P1-Ni1-Br1: 92.59(5).*

The structure of **IV-45** is comparable to those of the palladium and platinum allyl complexes **IV-29** and **IV-39**.

A more stable complex can be obtained by the reaction of methallyl nickel chloride-dimer with ligand **IV-9** in dichloromethane (Scheme 26). The ^{31}P NMR chemical shift of **IV-46** of δ = -11.0 ppm is comparable to the one of **IV-45**. Due to its higher stability complex **IV-46** could be completely characterized by NMR spectroscopy.



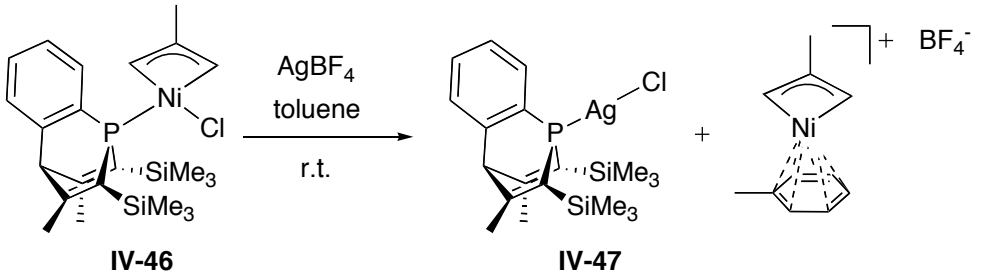
IV-9 **IV-46**

Scheme 26: *Synthesis of methallyl nickel chloride phosphabarrelene complex* ***IV-46****.*

The attempted synthesis of a cationic nickel allyl complex by abstraction of the chloride ion from **IV-46** with silver tetrafluoroborate in toluene did not lead to the expected cationic nickel complex (Scheme 27), but to the formation of a silver complex **IV-47** with a chemical shift of δ

= -37.6 ppm and characteristic $^{1}J_{PAg}$ coupling constants of 522.5 Hz and 603.9 Hz for the silver isotopes ^{109}Ag and ^{107}Ag.

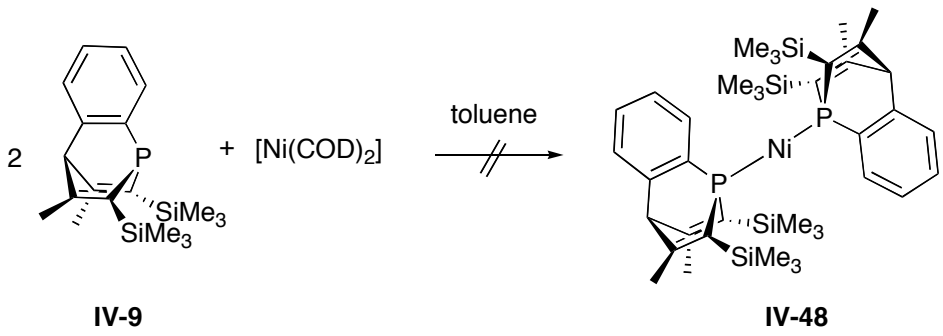
Although no further studies were carried out to investigate the outcome of the allyl nickel fragment the formation of a cationic arene nickel allyl complex should be expected, according to some recent reports of Brookhart and coworkers. [32]



IV-46 **IV-47**

Scheme 27: *Formation of a silver chloride phosphabarrelene complex upon addition of a silver salt to* ***IV-46*****.**

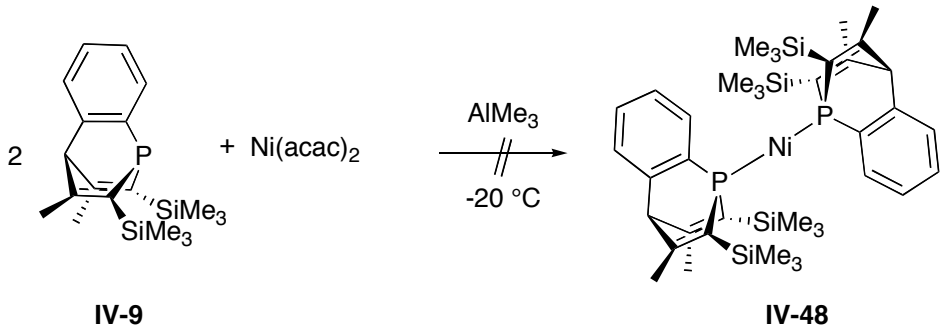
With the aim of developing catalytic processes using nickel complexes of ligand **IV-9**, the synthesis of the nickel analogue of the Pd and PtL_2 14 VE complexes **IV-32** and **IV-41** was attempted, but none met success. For example no reaction could be observed between $[Ni(COD)_2]$ and ligand **IV-9** (Scheme 28).



IV-9 **IV-48**

Scheme 28: *Attempted synthesis of a 14 VE diphosphabarrelene nickel (0) complex.*

It was tried to synthesize a nickel(0) complex via the reduction of $Ni(acac)_2$ with $AlMe_3$ in the presence of ligand **IV-9** in analogy to a procedure reported by Jonas and coworkers[33] for the synthesis of $[((PCy_3)_2Ni)_2N_2]$ but only the formation of a complex mixture of products could be observed (Scheme 29).



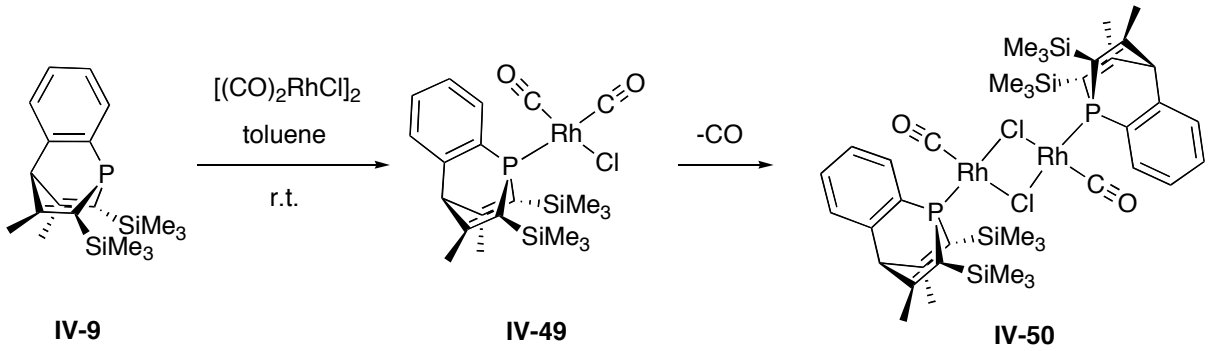
IV-9 **IV-48**

Scheme 29: *Attempted synthesis of complex IV-48.*

III. COMPLEXES OF GROUP 9

III.1. Rhodium

In analogy to the report of Breit and coworkers[7, 8] the reaction of ligand **IV-9** with $[(CO)_2RhCl]_2$ was studied (Scheme 30). If the reaction was carried out in a Rh/**IV-9** ratio of 1:1, complex **IV-49** could be obtained immediately as the only product. Complex **IV-49** was completely characterized by NMR spectroscopy and the infrared spectrum shows three characteristic bands at wavenumbers of 1971, 1998 and 2085 cm^{-1}, that are in agreement with a complex containing two carbonyl ligands. The ^{31}P NMR spectrum shows a signal for **IV-49** at a chemical shift δ = -3.6 ppm and a characteristic $^1J_{PRh}$ coupling constant of 130 Hz.



IV-9 **IV-49** **IV-50**

Scheme 30: *Synthesis of rhodium-complexes IV-49 and IV-59.*

After 48 h of stirring complex **IV-49** in toluene in an open vessel, the complete conversion of **IV-49** to a new product **IV-50** with a ^{31}P chemical shift of δ = 10.5 ppm with a significantly larger $^1J_{PRh}$ coupling constant of 181 Hz can be observed. Furthermore the infrared spectrum shows only one band in the carbonyl region at 1972 cm^{-1}. The formation of a dimeric chloro-bridged complex **IV-50** was expected, resulting from the loss of one CO molecule. The structure

of **IV-50** could be confirmed by X-Ray crystal structure analysis. The molecular structure of **IV-50** is presented in Figure 18.

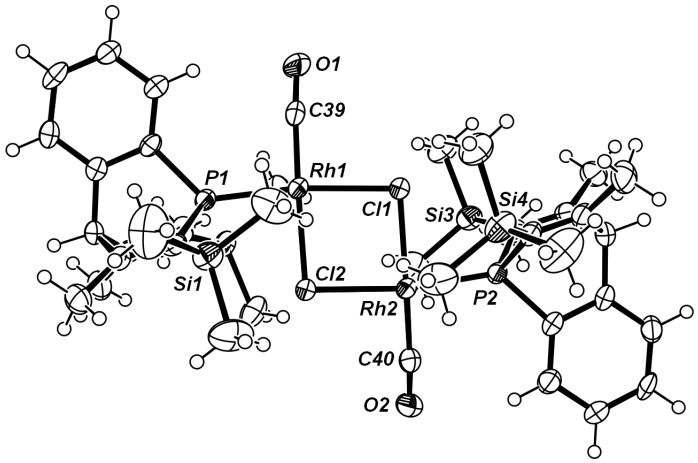
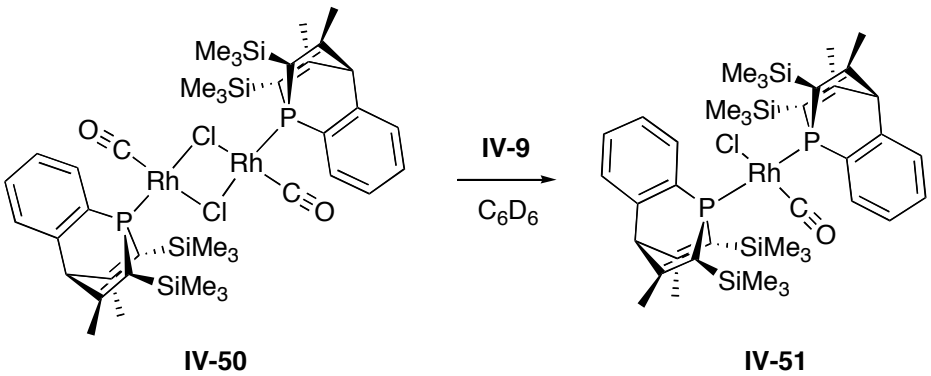


Figure 18: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex* ***IV-50*** *(Benzene molecules were omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1-P1: 2.218(1), Rh1-Cl1: 2.409(1), Rh1-Cl2: 2.415(1), Rh1-C39: 1.783(4), C39-O1: 1.144(4), P1-Rh1-Cl1: 172.62(3), Cl2-Rh1-C39: 176.9(1).*

The rhodium atom shows a slightly distorted square planar coordination. The Rh1-Cl1 and Rh1-Cl2 distances show only minor differences.

The reaction of **IV-50** with a second equivalent of ligand **IV-9** led to the formation of *trans*-diphosphabarrelene complex **IV-51** (Scheme 31) with a ^{31}P chemical shift of δ = -5.5 ppm and a $^{1}J_{PRh}$ coupling constant of 136 Hz.



Scheme 31: *Reaction of complex* ***IV-48*** *with phosphabarrelene* ***IV-9****.*

The structure of complex **IV-51** could be confirmed by X-Ray crystal structure analysis. Its molecular structure is depicted in Figure 19.

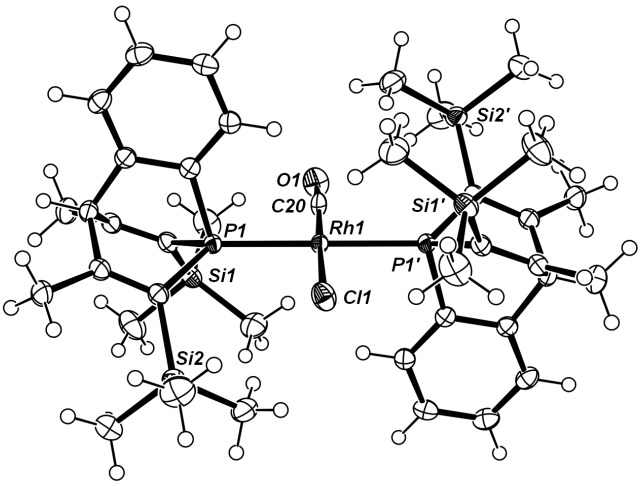


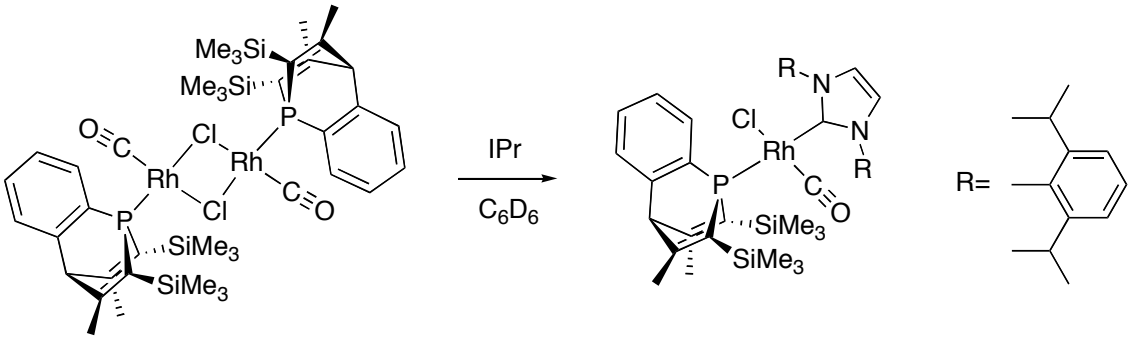
Figure 19: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex* ***IV-51****. Selected bond lengths [Å] and angles [°]: Rh1-P1: 2.3341(5), Rh1-Cl1: 2.343(2), Rh1-C20: 1.82(1), P1-Rh1-P1': 180.0°, C20-Cl1: 178.2(4).*

This type of rhodium complexes have occasionally been used to probe the electronic properties of phosphine ligands.[7, 34] The values of stretching frequencies of the carbonyl ligand in *trans*-diphosphine chloro carbonyl complexes are summarized in Table 2. The carbonyl stretching frequencies show that **IV-9** is more electron donating than 2,4,6 triphenylphosphabarrelene **IV-20** or $P(OPh)_3$ presenting the same electronic properties as the more common PPh_3. This is in agreement with the results, obtained for the $^1J_{PSe}$ coupling constants and confirms the influence of the substitution pattern on the electronic properties of phosphabarrelenes.

Table 2: *Stretching frequencies of the carbonyl ligands of trans-[(L)$_2$Rh(CO)Cl] complexes.*

Ligand	ν(CO) cm^{-1}	Reference
PMe_3	1958	Intille[34]
IV-9	1963	this work
PPh_3	1965	Intille[34]
IV-20	1993	Breit[7]
$P(OPh)_3$	2010	this work

The dimeric complex can equally be used for the synthesis of mixed phosphabarrelene N-heterocyclic carbene complex **IV-52** by the reaction with 1 equivalent of the corresponding IPr ligand (Scheme 32).



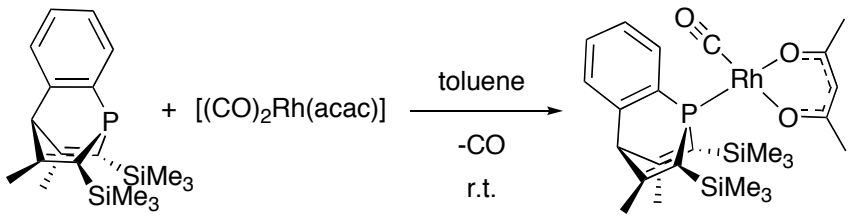
IV-50 **IV-52**

Scheme 32: *Reaction of complex* ***IV-50*** *with IPr.*

A ^{31}P NMR signal can be observed at a chemical shift δ = -4.1 ppm with a $^{1}J_{PRh}$ coupling constant of 122 Hz. The $^{1}J_{PRh}$ coupling constant is smaller in **IV-52** than **IV-51** because of the higher *trans*-effect of the NHC-ligand than that of the phosphabarrelene **IV-9**. Consequently, the carbonyl band of **IV-52** can be found at 1952 cm^{-1} in the infrared spectrum, which is an even lower frequency than in the case of the *trans*-[$(PMe_3)_2$Rh(CO)Cl)] complex.[34]

The reaction of ligand **IV-9** with [(acac)Rh$(CO)_2$] allows for the preparation of a chloride free rhodium complex **IV-53** (Scheme 33). This type of complexes has been used as a precatalyst in rhodium catalyzed hydroformylation reactions as the formal active species can be easily generated from in-situ, without the formation of HCl, which has shown to be detrimental to the performance of the catalyst.[35]

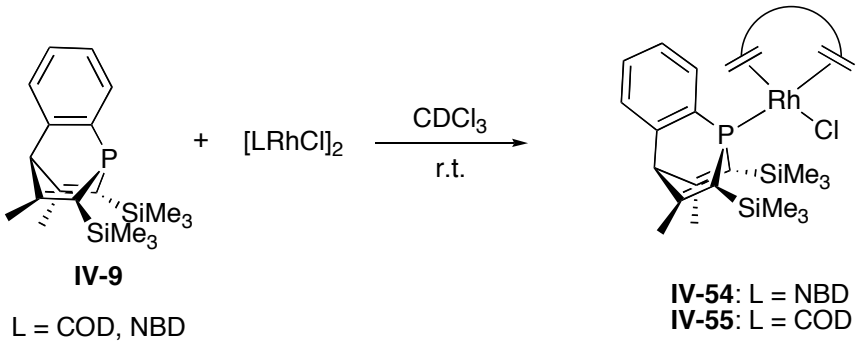
The ^{31}P NMR shows a signal at a chemical shift δ = 8.4 ppm with a $^{1}J_{PRh}$ coupling constant of 182 Hz. The infrared spectrum of **IV-53** shows a very intense carbonyl band at 1967 cm^{-1} for the Rh-CO and two less intense ketone carbonyl bands for the acac ligand at 2001 and 2067 cm^{-1}.



IV-9 **IV-53**

Scheme 33: *Synthesis of complex* ***IV-53****.*

Diolefin rhodium complexes **IV-54** and **IV-55** can be obtained by the reaction of ligand **IV-9** with $[LRhCl]_2$ (L= COD, NBD) in deuterated chloroform at room temperature (Scheme 34). The ^{31}P NMR spectra show signals at chemical shifts of δ = -15.1 ppm (d, $^1J_{PRh}$ = 177 Hz) for **IV-54** and δ = -18.9 ppm (d, $^1J_{PRh}$ = 181 Hz) for **IV-55**.



Scheme 34: *Synthesis of rhodium diolefin phosphabarrelene complexes* ***IV-54*** *and* ***IV-55*****.**

The molecular structure of complexes **IV-54** and **IV-55** are presented in Figure 17.

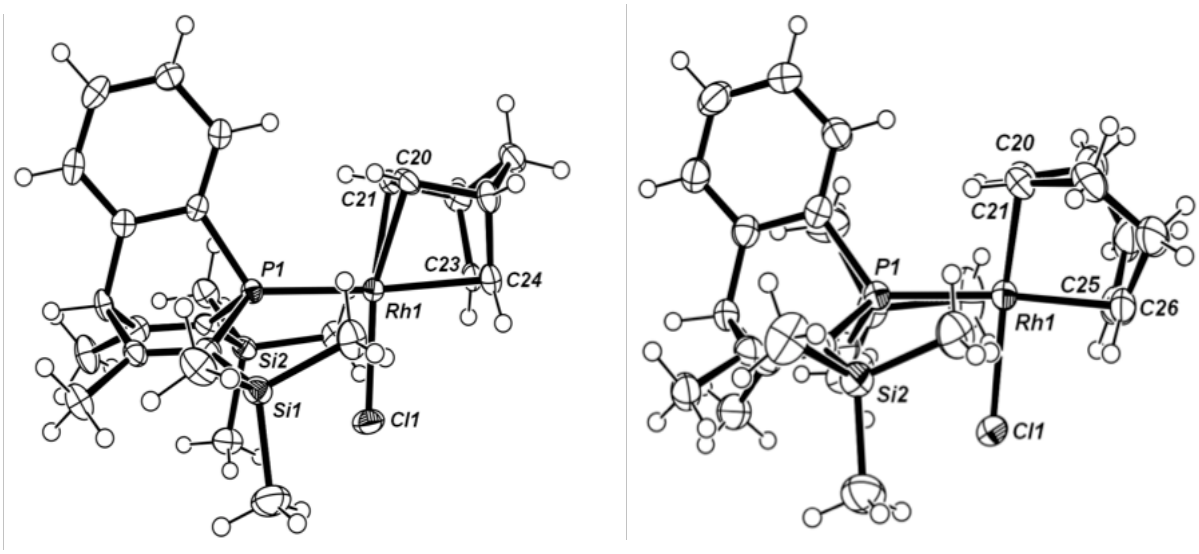


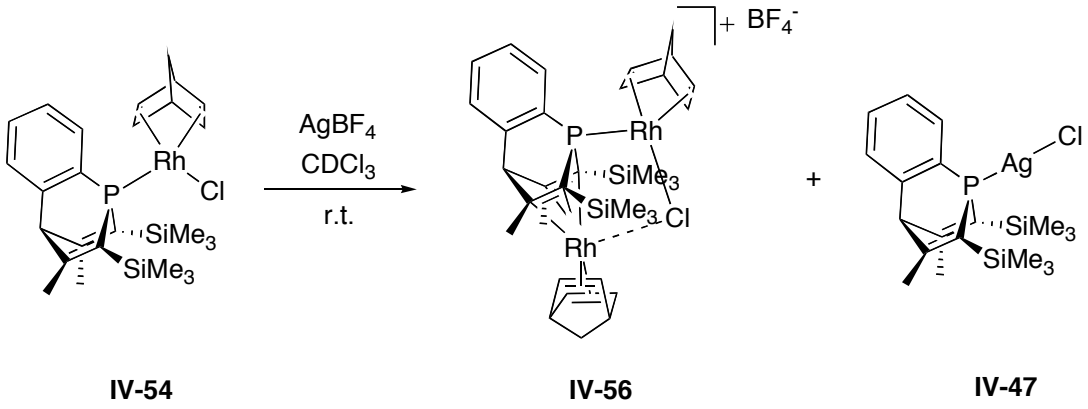
Figure 20: *Molecular structures (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complexes* ***IV-54*** *(left) and* ***IV-55*** *(right). Selected bond lengths [Å] and angles [°] for* ***IV-54****: Rh1-P1: 2.2940(6), Rh-Cl1:2.3687(7), Rh1-C20: 2.122(2), Rh1-C23: 2.199(2), C20-C21: 1.404(4), C23-C24: 1.379(4), C1-C2: 1.347(3), C4-C5: 1.350(3), P1-Rh1-Cl1: 87.20 . Selected bond lengths [Å] and angles [°] for* ***IV-55****: Rh1-P1: 2.3372(7), Rh-Cl1: 2.3712(7), Rh1-C20: 2.126(3), Rh1-C25: 2.200(3), C20-C21: 1.389(5), C25-C26: 1.511(4), P1-Rh1-Cl1: 84.43(3).*

The central rhodium atom adopts in both structures a slightly distorted square planar coordination mode. The P1-Rh1-Cl1 angle is slightly smaller in **IV-55** than in **IV-54**, due more

important steric demand of the COD ligand. Interestingly the bond length of the olefin ligand in *trans* to the phosphorus atom is significantly larger in the case of cyclooctadiene complex **IV-55**. This might be related to a stronger interaction of cyclooctadiene ligand with the rhodium center compared to the norbornadiene ligand due to the very constraint geometry of the bicyclic norbornadiene ligand.

The generation of a cationic rhodium complex was investigated with silver tetrafluoroborate starting from complex **IV-54** (Scheme 35). This reaction leads to the formation of two products: the well-known silver chloride complex **IV-47**, and a rhodium containing species **IV-56**.

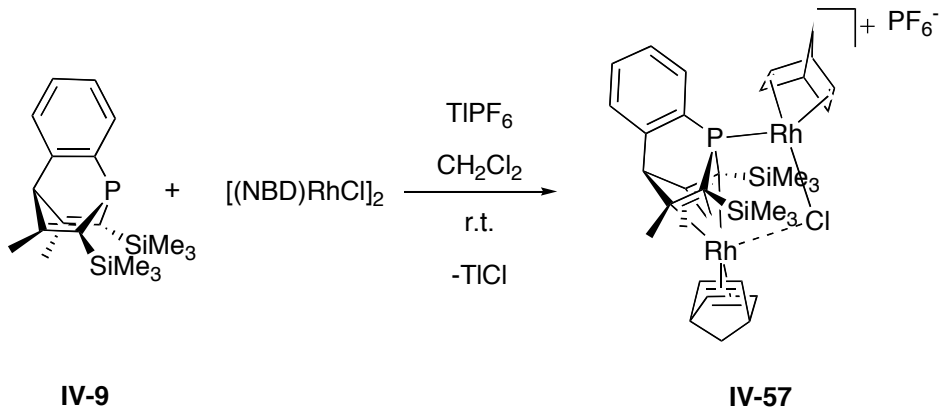
The ^{31}P NMR of this rhodium complex **IV-56** shows a signal at a chemical shift of δ = 22.6 ppm, with a surprising doublet of doublet coupling pattern with a very small coupling constant of J = 2.6 Hz and a large $^{1}J_{PRh}$ coupling constant of 170 Hz.



IV-54 **IV-56** **IV-47**

Scheme 35: *Attempted chloride abstraction from* ***IV-54*** *with one silver tetrafluoroborate.*

To prevent the formation of silver complex **IV-47** the abstraction of the chloride atom was performed with thalium hexafluorophosphate. The ^{31}P NMR spectrum of the crude reaction mixture shows the decoordination of one equivalent of ligand **IV-9** with the concomitant formation of a very similar rhodium species **IV-57**. A rational synthesis with a Rh/**IV-9**/Tl ratio of 2:1:1 led to the quantitative formation of **IV-57** (Scheme 36).



Scheme 36: *Rational synthesis of complex* ***IV-57****.*

The X-Ray crystal structure analysis of reveals the formation of an unexpected dinuclear rhodium complex. The molecular structure of **IV-57** is presented in Figure 21.

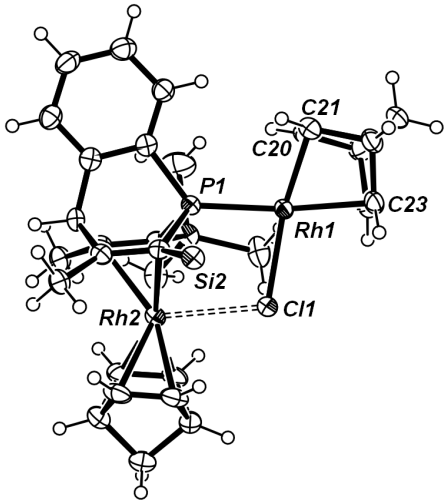
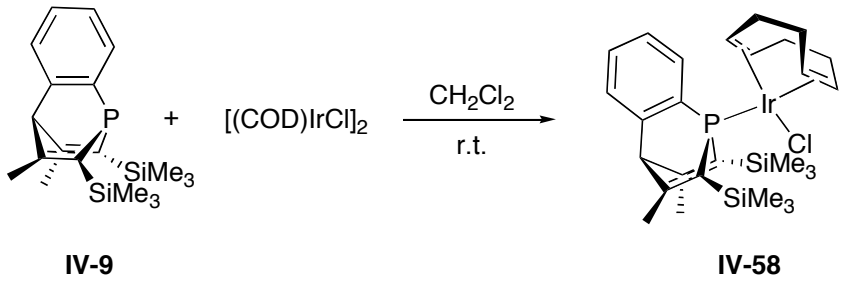


Figure 21: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex* ***57****. Selected bond lengths [Å] and angles [°]: Rh1-P1: 2.2611(8), Rh-Cl1: 2.4062(8), Rh2-Cl1: 2.7439(7), Rh1-C20: 2.102(3), Rh1-C23: 2.232(3), Rh2-C1: 2.188(3), Rh2-C2: 2.391(3), Rh2-C4: 2.443(3), Rh2-C5: 2.273(3), C1-C2: 1.402 (4), C4-C5: 1.390(4), C20-C21: 1.395(4), C23-C24: 1.363(4), P1-Rh1-Cl1: 82.73(3) .*

The structural parameters around Rh1 are only slightly altered. A minor interaction of Cl1 with Rh2 can be observed at 2.7339(7) Å , leading to the decrease of the P1-Rh1-Cl1- angle from 87.2 ° in **IV-54** to 82.7 ° in **IV-57**. The coordination of Rh2 to the double bonds of ligand **IV-9** results in an increase of the C1-C2 and C4-C5 distances (0.04 and 0.05 Å respectively).

III.2. Iridium

The synthesis of iridium complex **IV-58** could be achieved by stirring a suspension of $[(COD)IrCl]_2$ and ligand **IV-9** at room temperature (Scheme 37).



IV-9 **IV-58**

Scheme 37: *Synthesis of iridium complex* ***IV-58***.

The X-Ray crystal structure analysis allowed for the confirmation of the structure of complex **IV-58** and is presented in Figure 22.

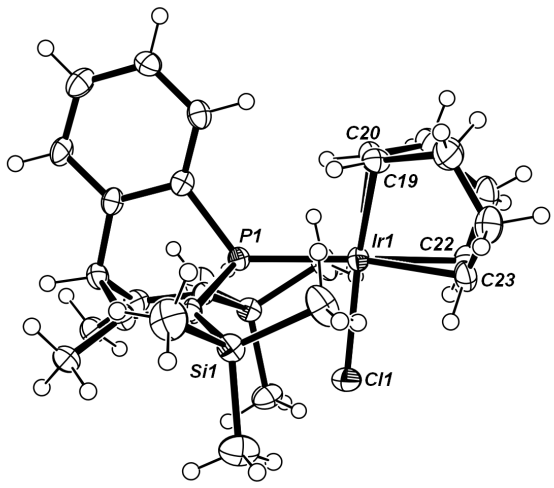
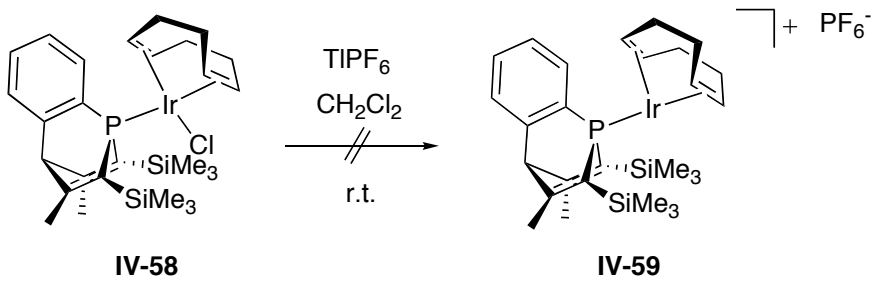


Figure 22: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex* ***58***. *Selected bond lengths [Å] and angles [°]: Ir1-P1: 2.325, Ir1-Cl1: 2.382, Ir1-C19: 2.108, Ir1-C23: 2.176, C19-C20: 1.425, C23-C24: 1.390 P1-Ir1-Cl1: 84.63.*

The iridium atom in complex **IV-58** shows the expected square planar coordination geometry.

The synthesis of a cationic derivative of **IV-59** was envisaged to generate an analogue of the Crabtree catalyst,[36, 37] but no reaction could be observed upon mixing compound **IV-58** with $TlPF_6$ (Scheme 38).



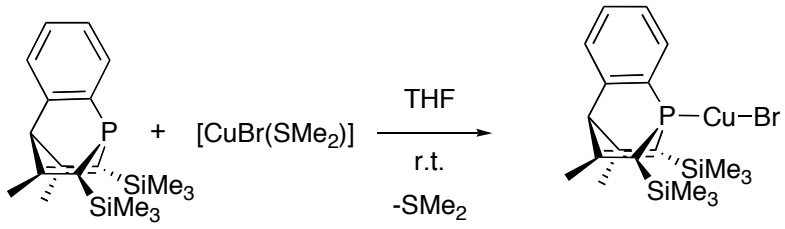
IV-58 **IV-59**

Scheme 38: *Attempted generation of cationic iridium complex IV-59.*

IV. COMPLEXES OF GROUP 11

IV.1. Copper

A copper (I) complex of ligand **IV-9** could be readily obtained by the reaction with the Me_2S adduct of copper(I) bromide (Scheme 39). Upon addition of the ligand to a solution of the metal precursor in THF, the reaction mixture turns from brown to colorless and a white precipitate is formed.



IV-9 **IV-60**

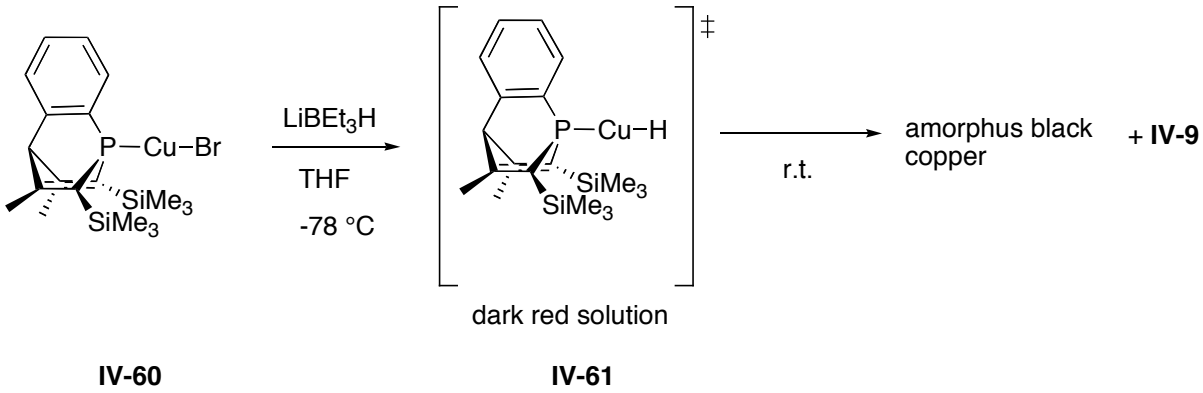
Scheme 39: *Synthesis of a copper (I) complex IV-60.*

The ^{31}P NMR of **IV-60** in $CDCl_3$ shows a large signal at a chemical shift of δ = -47. 3 ppm. The formation of the desired copper (I) bromide complex could be confirmed by the ^{1}H NMR spectrum, that shows a characteristic shift of the H-8 proton to lower field (δ = 8.23 ppm).

Crystals of complex **IV-60** could be grown by the slow evaporation of a solution of **IV-60** in toluene, but were constantly twinned.

Starting from **IV-60** it was tried to synthesize a copper hydride complex, a phosphabarrelene based equivalent of the Stryker reagent.[38] In analogy to a procedure reported by Osborn and coworkers,[39] the reaction of **IV-60** with a borohydride reagent was investigated (Scheme 40). Upon addition of lithium triethylborohydride, at -78 °C to complex **IV-60** in THF, the color of the reaction mixture turned deep red. When the reaction medium was allowed to

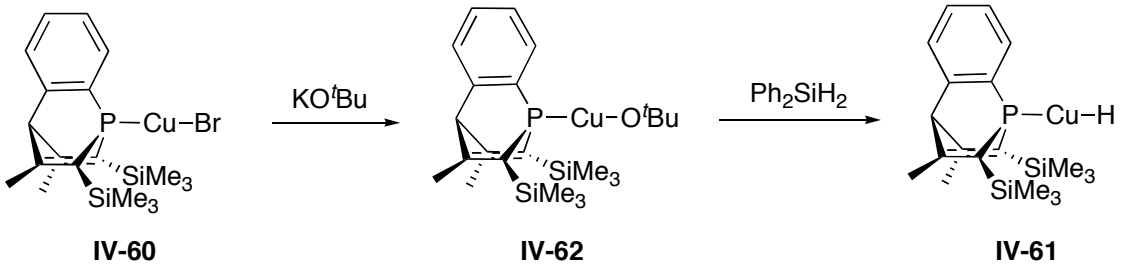
return to room temperature, decomposition of the possibly formed hydride complex **IV-61** was observed. A black precipitate of amorphous copper metal was formed and in the ^{31}P NMR, the signal of the free ligand could be observed.



Scheme 40: *Attempted synthesis of a copper (I) hydride* ***IV-61****.*

Due to the important steric demand of ligand **IV-9** it was postulated that the copper hydride complex **IV-61** was highly reactive and therefore difficult to isolate.

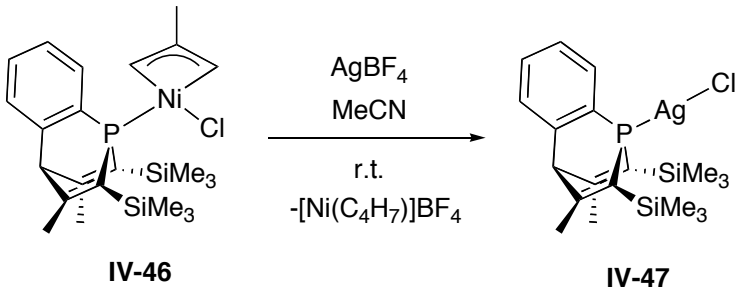
In order to develop phosphabarrelene based copper hydride catalyst for hydrogenation or hydrosilylation reactions, this copper(I) hydride species requires to be used after its formation. A possible way to generate **IV-61** *in-situ* could be the reaction of **IV-60** with KO^{t}Bu and the subsequent addition of a silane, such as Ph_2SiH_2 (Scheme 41). This strategy has proved to be efficient in the case of NHC-ligands[40, 41] and is currently under investigation.



Scheme 41: *Envisaged in-situ formation of CuH-catalysts from CuBr.*

IV.2. Silver

During the course of our studies on the study of cationic nickel and rhodium complexes, the formation of silver chloride complexes of phosphabarrelene ligand **IV-9** was observed in several instances (Scheme 42).



IV-46 **IV-47**

Scheme 42: *Formation of silver complex* ***IV-47****.*

Reaction of complex **IV-46** with silver tetrafluoroborate in acetonitrile led to the formation of pale yellow crystals. The ^{31}P NMR spectrum of the reaction mixture shows the complete absence of any phosphorus species. The ^{31}P NMR of the isolated crystals, that are soluble in $CDCl_3$ shows a characteristic signal of two doublets at a chemical shift of δ = -37.6 ppm with characteristic $^{1}J_{PAg}$ coupling constants of 522.5 Hz and 603.9 Hz. As should be expected from the isotope ratio of the silver isotopes ^{107}Ag and ^{109}Ag of 0.52/0.48 both signals show almost equal intensity.

The molecular structure of complex **IV-47** is presented in Figure 23:

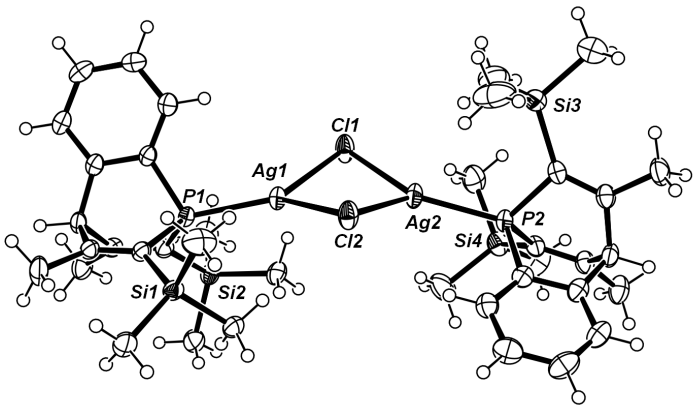


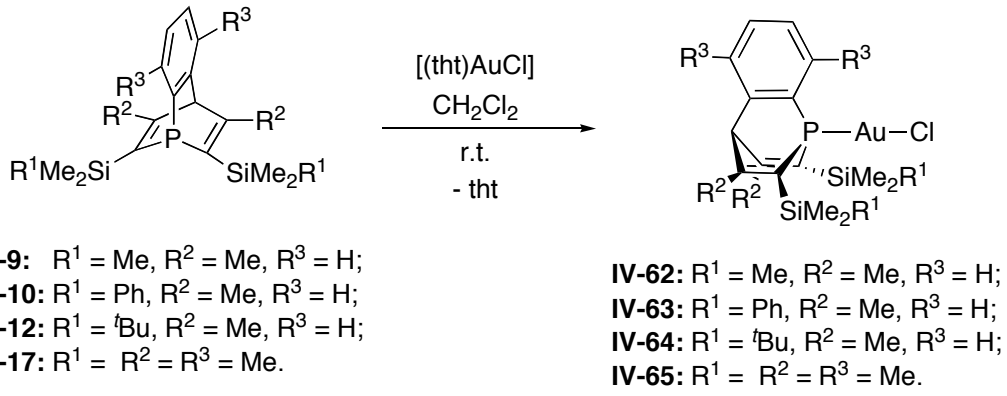
Figure 23: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex* ***IV-47****. Selected bond lengths [Å] and angles [°]: Ag1-P1: 2.3757(5), Ag1-Cl1: 2.5744(6), Ag1-Cl2:2.5148(5), P1-Ag1-Cl1: 130.70(2), P1-Ag1-Cl2: 138.52(2), Cl1-Ag1-Cl2: 90.77(2).*

The X-Ray crystal structure analysis reveals the dimeric structure of complex **IV-47** in the solid state. The silver atoms show a distorted trigonal planar coordination mode with a very small Cl1-Ag1-Cl2 angle of 90.8 °.

IV.3. Gold

In the last 10 years gold complexes of phosphine and NHC-ligands have attracted high interest. Cationic gold complexes present a promising catalytic activity for cycloisomerization and catalytic addition reactions.[42]

The synthesis of gold complexes was studied with phosphabarrelenes **IV-9**, **IV-10**, **IV-12** and **IV-17** bearing sterically demanding silyl groups, with the aim of synthesizing gold complexes with different steric and electronic properties. The corresponding gold complexes could be obtained in quantitative yields by the reaction of the ligands with [(tht)AuCl] (Scheme 43).



IV-9: R^1 = Me, R^2 = Me, R^3 = H;
IV-10: R^1 = Ph, R^2 = Me, R^3 = H;
IV-12: R^1 = ^{t}Bu, R^2 = Me, R^3 = H;
IV-17: R^1 = R^2 = R^3 = Me.

IV-62: R^1 = Me, R^2 = Me, R^3 = H;
IV-63: R^1 = Ph, R^2 = Me, R^3 = H;
IV-64: R^1 = ^{t}Bu, R^2 = Me, R^3 = H;
IV-65: R^1 = R^2 = R^3 = Me.

Scheme 43: *Synthesis of gold complexes.*

Single crystals suitable for X-Ray crystal structure analysis could be obtained for complexes **IV-62**, **IV-63** and **IV-65** by slow evaporation of solutions of these complexes in toluene. The molecular structures of complexes **IV-62** and **IV-63** are presented in Figure 24. The molecular structure of **IV-65** is presented in Figure 25.

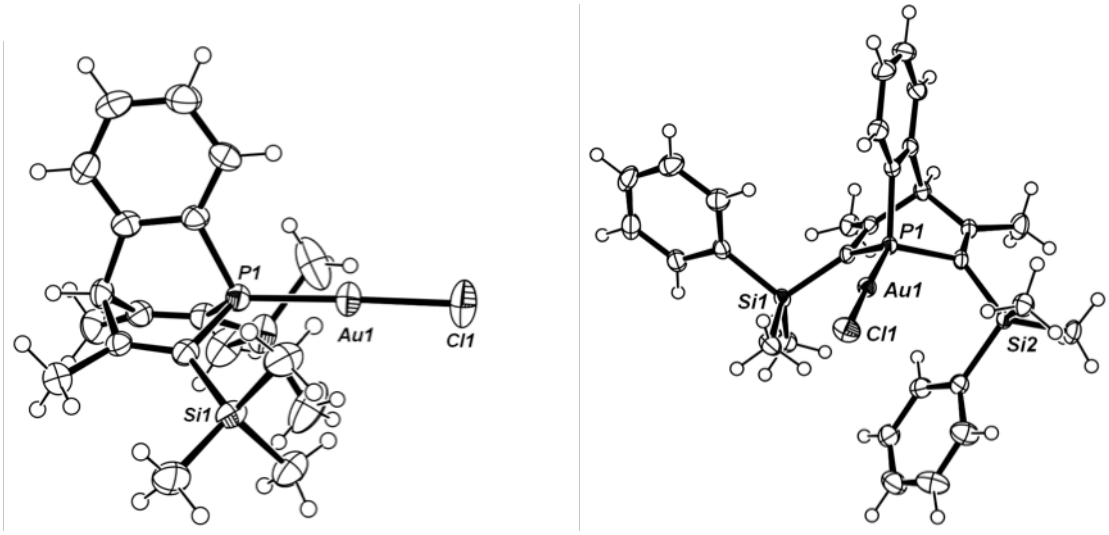


Figure 24: *Molecular structures (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complexes* **IV-62** *(left) and* **IV-63** *(right). Selected bond lengths [Å] and angles [°] for* **IV-62***: Au1-P1: 2.220(2), Au1-Cl1: 2.282(2), P1-Au1-Cl1: 176.29(8). Selected bond lengths [Å] and angles [°] for* **IV-63***: Au1-P1: 2.2243(7), Au1-Cl1: 2.2885(7), P1-Au1-Cl1: 176.29(2).*

In all three cases the Au1-P1 distance and Au1-Cl1 distances of about 2.23 Å and 2.28 Å are essentially equal. Additionally the P1-Au1-Cl1 angle in all three complexes shows a value of 176 °.

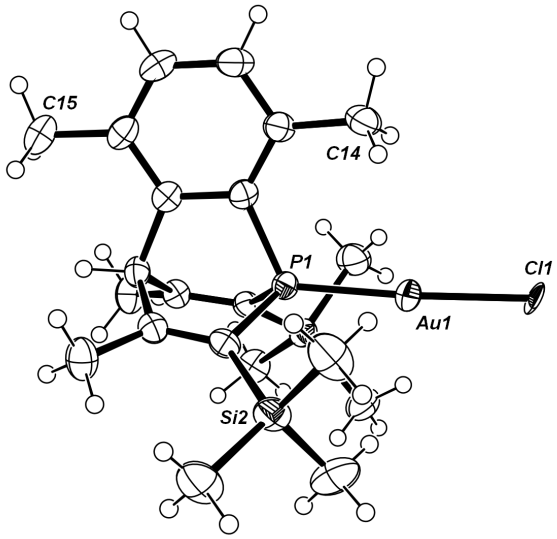
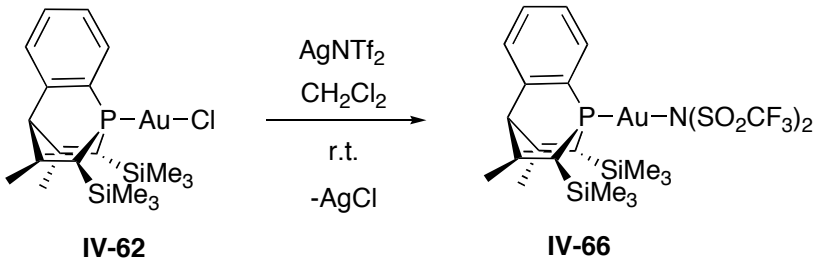


Figure 22: *Molecular structure (ORTEP-representation, thermal ellipsoids at a 50 % probability) of complex* **IV-65** *(A bromine/chlorine disorder was omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1-P1: 2.2313(7), Au1-Cl1: 2.26(1), P1-Au1-Cl1: 176.7(2).*

Air and moisture stable cationic gold (I) complexes can be conveniently prepared by the reaction of gold (I) chloride complexes with silver bis(trifluoromethanesulfonyl)imidate.[43] By this method, a cationic derivative of complex **IV-66** could be obtained. (Scheme 44)

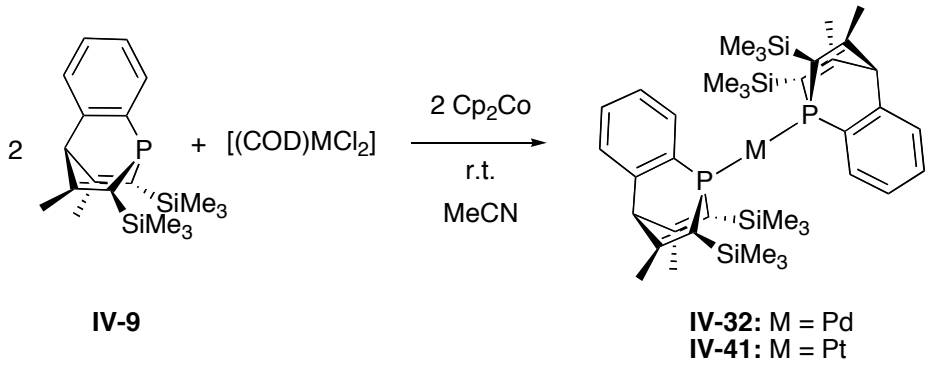


Scheme 44: *Formation of a cationic gold(I) phosphabarrelene complex IV-66.*

V. CONCLUSIONS AND PERSPECTIVES

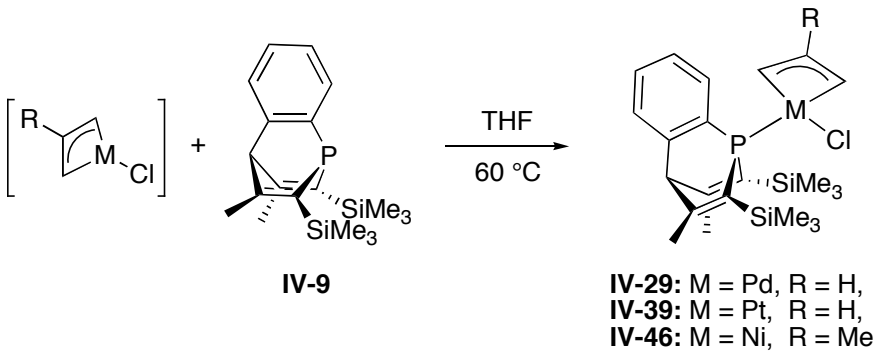
In this chapter the results of our studies concerning the coordination chemistry of 1-phosphabarrelene ligands with late transition metals (groups 9-11) were presented.

The initial studies that were conducted with palladium and platinum in combination with 1-phosphabarrelene **IV-9** have shown that these ligands are suitable for the kinetic stabilization of highly reactive 14 VE complexes and a protocol that easily allows for the synthesis of this type of complexes in high yield (~90 %) under mild conditions has been developed using cobaltocene as a reducing agent in acetonitrile (Scheme 45).



Scheme 45: *Synthesis of 14 VE palladium and platinum complexes.*

Furthermore the synthesis of allyl complexes M = Ni, Pd, Pt) could be achieved by several methods. In this case, the best results were obtained when preformed [(allyl)MCl] were used (Scheme 46). The palladium and platinum complexes are stable to air and moisture for extended periods of time.

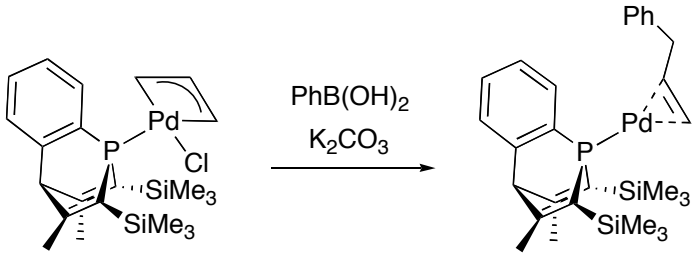


IV-9

IV-29: M = Pd, R = H,
IV-39: M = Pt, R = H,
IV-46: M = Ni, R = Me

Scheme 46: *Synthesis of group 9 allyl phosphabarrelene complexes.*

The intense study of the palladium complex **IV-29** has shown, that this complex can serve as a precursor for the highly reactive monophosphine palladium complex **IV-35** (Scheme 47), which makes complex **IV-29** a very interesting class of catalyst precursors for many catalytic reactions.

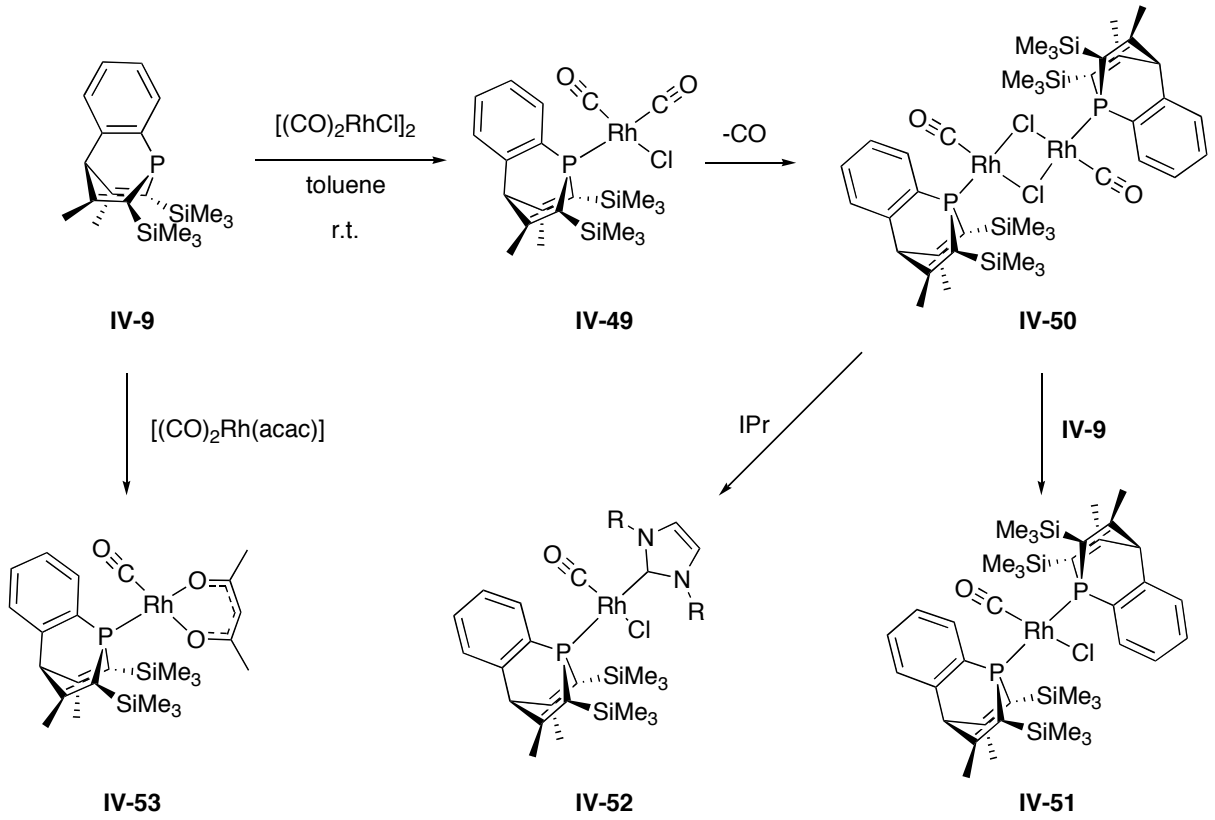


IV-29 **IV-35**

Scheme 47: *Reduction of complex IV-29 by phenylboronic acid and potassium carbonate.*

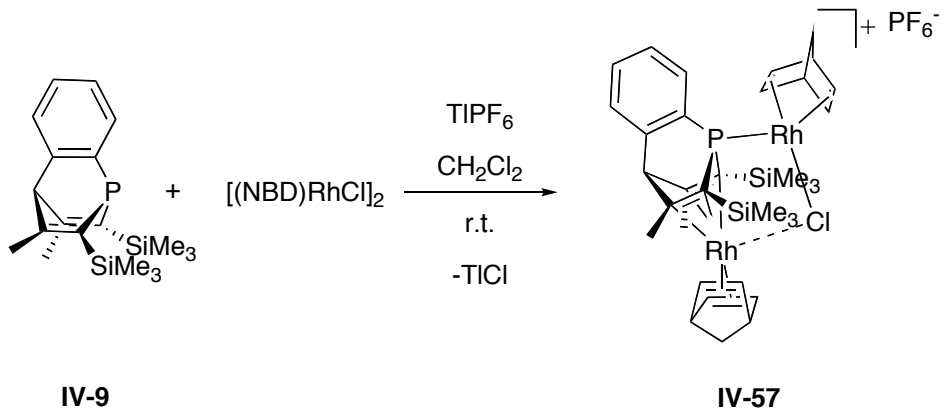
The application of the palladium and platinum complexes studied in this chapter in cross-coupling and hydrosilylation reactions will be the subject of the following chapter.

In the second part of this chapter the coordination chemistry of phosphabarrelene ligand **IV-9** with common rhodium and iridium precursors was studied. Especially the rhodium carbonyl complexes are of high interest, as this type of rhodium complexes are among the most active catalysts for the hydroformylation of internal olefins in the absence of olefin isomerisation (Scheme 48). As this process is of great industrial interest, the precise study of the reactivity of the catalyst precursors under the reaction conditions (pressure of CO and H_2) might allow for the detection of the active species in the catalytic cycle. This could allow a deeper understanding of the outstanding performance of phosphabarrelene rhodium complexes in hydroformylation reactions and allow for the development of more active and selective catalysts.



Scheme 48: *Synthesis of rhodium carbonyl complexes IV-49 – IV-53.*

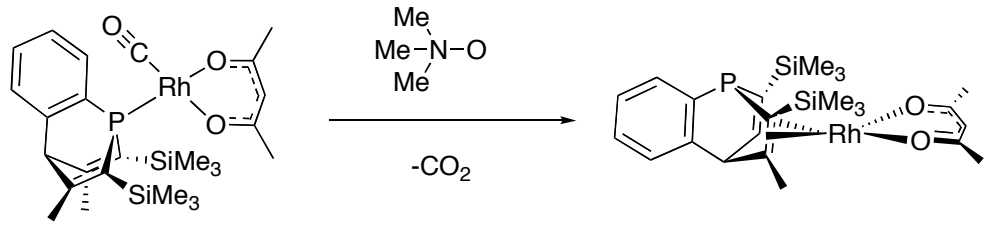
The use of diolefin-rhodium precursors has allowed for the synthesis of the first complex **IV-57** in which the phosphabarrelene coordinates to a metal center via the double bonds of the ligand framework (Scheme 49).



Scheme 49: *Synthesis of the first phosphabarrelene complex with η^4-coordination of the double bonds of the phosphabarrelene.*

The application of these rhodium complexes in homogeneous catalysis will be studied the near future. The use of cationic complex **IV-57** might be of interest in the hydrosilylation of alkynes.[44] In this regard it could be interesting to study a possible cooperative effect of the second rhodium center.

Furthermore, the selective transformation of the η^1 phosphorus coordinated rhodium complexes such as **IV-50** and **IV-53** into η^4 coordinated complexes *via* oxidation of the CO ligand to CO_2 with trimethylamine-N-oxide could be studied (Scheme 50). This would provide information on the accessibility of the $\eta^1 \rightarrow \eta^4 \rightarrow \eta^1$ interconversion during catalytic processes. This would point toward a novel type of hemilability of a ligand (2 e^- donor or 4 e^- donor).



IV-53

Scheme 50: *Envisaged synthesis of a η^4 diolefine coordinated phosphabarrelene rhodium complex.*

Finally the coordination of selected phosphabarrelene ligands with a gold(I)-precursor was studied. This has allowed for the preparation of gold(I) complexes with a variable steric demand in the coordination sphere of the gold atom. Furthermore it was shown, that isolable cationic gold(I) complexes that are active catalysts in a variety of reactions can be generated by the abstraction of the chloride ion with $AgNTf_2$. The use of these gold complexes is cycloisomerization reactions is envisaged. In this regard, the use of phosphabarrelene ligands with modulable steric and electronic properties might be well adapted to tune the catalyst activity and selectivity.

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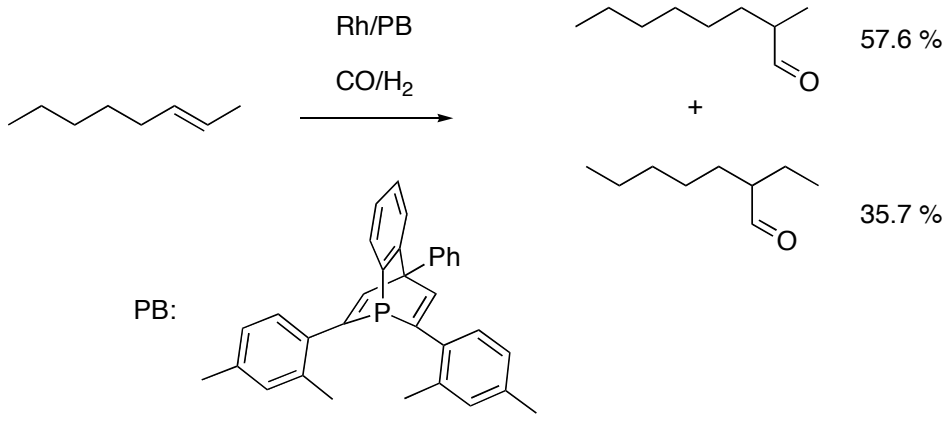
CHAPTER 3: APPLICATION OF 1-PHOSPHABARRELENES AS LIGANDS IN HOMOGENEOUS CATALYSIS

I. INTRODUCTION

Although the synthesis of phosphabarrelenes has already been reported in 1971 by Märkl, their application in transition metal catalysis was reported for the first time in 2004 by Breit and coworkers in the hydroformylation of olefines.[1, 2]

The rhodium complexes of phosphabarrelenes turned out to be highly active catalysts for this industrially important reaction and most interestingly internal alkenes can be used yielding internal aldehydes and no alkene isomerisation was observed.

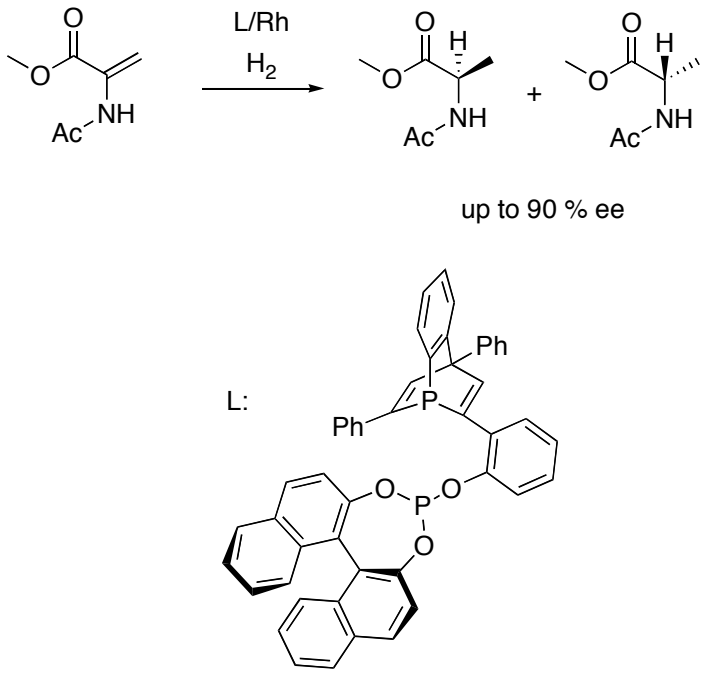
For example if oct-2-ene was used as a substrate (Scheme 1), 2-methyloctanal (57.6 mol%) and 2-ethylheptanal (35.7 mol%) were observed as the main products, together with unreacted starting material (6.5 mol%) and a small amount of 2-pentylhexanal (0.2 mol%).



Scheme 1: *Hydroformylation of oct-2-ene with phosphabarrelene rhodium catalyst.*

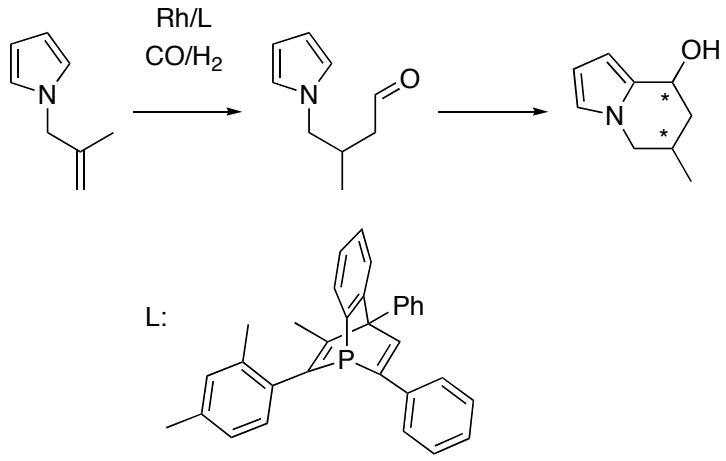
The use of bidentate, diasteromerically pure phosphabarrelene phosphite ligands has been reported by Breit *et al.* in the Rh-catalyzed asymmetric hydrogenation of prochiral substrates (Scheme 2).

For example in the case of the methyl acetamido acrylate as a substrate, enantioselectivities of ee = 9 % (R) and 90 % (S) were found with the system Rh/L depending on the configuration of the phosphorus atom in the bicyclic framework of the phosphabarrelene.



Scheme 2: *Hydrogenation of methyl acetamido acrylate with bidentate phosphabarrelene phosphite rhodium catalysts.*

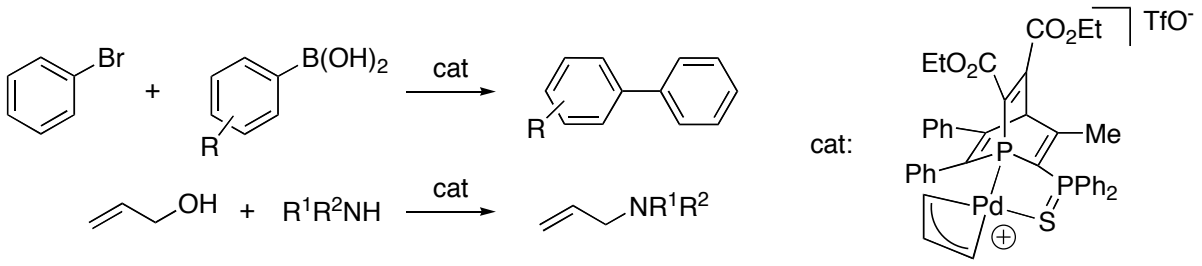
More recently Müller and coworkers have reported the application of a monodentate chiral phosphabarrelene ligand in a cascade reaction (Scheme 3).[3] In this case, an allyl moiety is hydroformylated in a first step. The resulting aldehyde subsequently undergoes a cyclisation reaction to the bicyclic product.



Scheme 3: *Cascade reaction leading to functionalized indolizine-derivatives.*

Apart from these rhodium-catalyzed reactions, only one further example for the application of phosphabarrelenes in homogeneous catalysis has been reported so far. In our group the

application of a bidentate phosphabarrelene phosphinesulfide ligand in the palladium catalyzed Suzuki-Miyaura coupling of bromoarenes with phenylboronic acid and the allylation of secondary amines were developed (Scheme 4).[4]



Scheme 4: *Cross-coupling and allylation reactions catalyzed by a phosphabarrelene palladium complex.*

Interestingly, the Suzuki Miyaura coupling reactions of bromo arenes can be carried out low catalyst loadings of 10^{-5} mol %, leading to high turnover numbers of up to $7 * 10^6$. In contrast, no conversion could be observed in the case of the less reactive chloro arenes. This catalyst show high activity for the allylation of secondary amines with allylic alcohol.

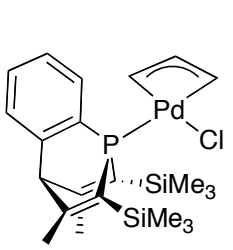
II. PALLADIUM CATALYZED CROSS-COUPLING REACTIONS

II.1 Suzuki Miyaura Coupling

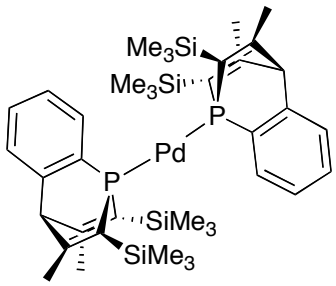
Palladium metal-mediated cross-coupling reactions represent an extremely versatile tool in organic synthesis. Reactions leading to C-C bond formation are often key steps in a wide range of organic processes ranging from pharmaceutical chemistry to natural product synthesis.[5] One of the most prominent methods in this regard is surely the palladium catalyzed coupling of boronic acid derivatives, which is mentioned above.[6]

Advances have been made in the way of reaction scope, including the use of aryl chlorides as substrates and the possibility of conducting coupling reactions at room temperature and at low catalyst loadings.[7, 8] The most efficient ligands used for these reactions are phosphines[9-12] or *N*-heterocyclic carbenes (NHC)[13] bearing sterically demanding substituents.

To evaluate the catalytic properties of ligand **IV-9** in the Suzuki-Miyaura coupling reaction, the use of the previously synthesized catalyst precursors **IV-29** and **IV-32** was envisaged (Scheme 5).



IV-29



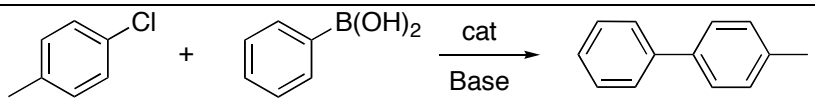
IV-32

Scheme 5: *Catalyst precursors for the use in Suzuki-Miyaura coupling reactions.*

We first focused on the (allyl)chloropalladium(II) derivative because π-allyl-palladium-NHC-complexes have been shown to be to be very efficient catalysts in Suzuki couplings of poorly reactive chloroarenes.[13]

In a first series of experiments, **IV-29** was used in the presence of a second equivalent of **IV-9** to determine the best experimental conditions. The nature of the base has been reported to be crucial in this type of coupling reactions.[14] The best results were obtained when reactions were carried out in toluene at 80°C using carbonate or phosphate as bases. Surprisingly the use of alkoxides resulted complete in complete loss of activity (Table 1), whereas they are the most efficient bases for the NHC system.[13, 14]

Table 1: *Screening of different bases.*



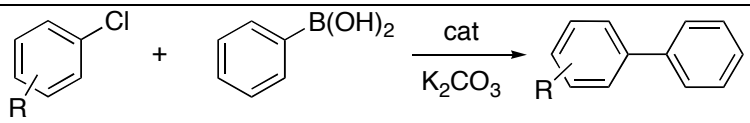
Entry	Base	Conversion %
1	KO^{t}Bu	0
2	Et_3N	17
3	KOH	58
4	$Cs_2(CO_3)$	76
5	K_3PO_4	82
6	K_2CO_3	91

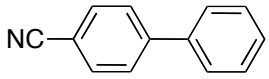
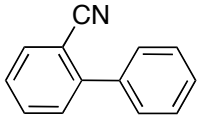
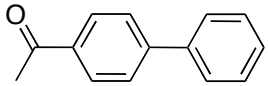
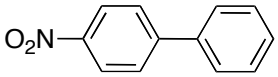
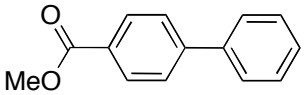
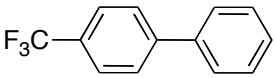
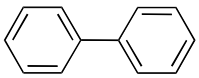
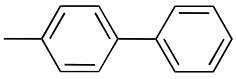
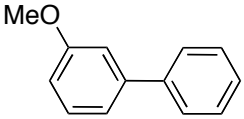
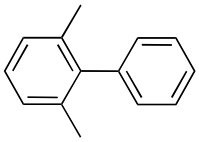
[a]*Reaction Conditions:* ArCl (1.0 mmol), $PhB(OH)_2$ (1.2mmol), Base (3 mmol),Toluene (2 mL), 0,002 mmol of **IV-29**, 0.002 mmol of **IV-9**, 80 °C. [b]Conversions as judged by GC analysis.

Various substituted chloroarenes were coupled with phenylboronic acid under these conditions in very good yields using either 0.2 mol% of catalyst **IV-29** or **IV-32** (see Table 2).

Interestingly, both catalysts show essentially the same performances under these conditions. Acceptor substituted biphenyls were obtained in excellent yields after short reaction times. Donor substituted arylchlorides required somewhat longer reaction times but the coupling still proceeded smoothly and delivered the products in high yields. 2,6-dimethylchlorobenzene, which is deactivated and also sterically hindered was not reactive under these conditions (Entry 13). Interestingly, reduction of the arylchlorides was not observed and only trace amounts of biphenyl (< 1%), resulting from the homo-coupling of phenylboronic acid were detected.

Table 2: *Substrates used in the Suzuki-Miyaura coupling with* ***IV-29*** *and* ***IV-32***.

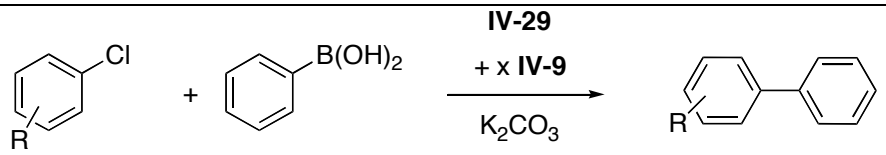


Entry	R	cat	Product	t h	Yield %
1	4-CN	**IV-29**		1	98
2		**IV-32**		1	99
3	2-CN	**IV-29**		1	99
4	4-Ac	**IV-29**		2	95
5	4-NO_2	**IV-29**		2	96
6	4-COOMe	**IV-29**		2	99
7	4-CF_3	**IV-29**		2	94
8	H	**IV-29**		12	97
9	4-Me	**IV-29**		20	91
10		**IV-32**		20	90
11	3-OMe	**IV-29**		20	96
12		**IV-32**		20	92
13	2,6-Me	**IV-29**		20	5

[a]*Reaction Conditions:* ArCl (1.0 mmol), $PhB(OH)_2$ (1.2mmol), K_2CO_3 (3 mmol),Toluene (2 mL), cat: 0.002 mmol of **IV-29** and 0.002 mmol of **IV-9** or 0.002 mmol of **IV-32**. [b]Isolated yield.

Additional reactions involving a different Ligand/Pd ratio were carried out to gain further insight into the nature of the active species. No difference in the catalytic activity was observed using 1 or 2 equivalents of ligand when performing the reaction at 80 °C. In contrast, the use of ten fold amount of ligand led to a significant decrease of the catalytic activity (see Table 3).

Table 3: *Further studies.*



Entry	R	Cat %	L/Pd	T °C	t h	Yield %[b]
1	4-CN	0.2	1	80	1	>99
2	4-CN	0.2	2	80	1	>99
3	4-CN	0.2	10	80	1	37
4	4-CN	1.0	1	25	12	99
5	4-CN	1.0	2	25	12	5
6	4-CN	1.0[c]	0	25	12	traces
7	4-NO_2	1.0	1	25	16	91
8	4-COOMe	1.0	1	25	24	89

[a]*Reaction Conditions:* ArCl (1.0 mmol), $PhB(OH)_2$ (1.2mmol), K_2CO_3 (3 mmol), Toluene (2 mL), [b]GC yield. [c]$[Pd(allyl)Cl]_2$ (0.5 mmol).

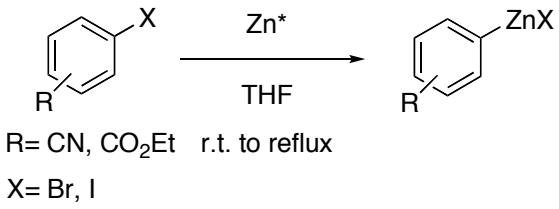
Finally the catalytic activity of **IV-29** at room temperature was also evaluated. Excellent yields were obtained after 12 h-24 h at room temperature when operating at a Ligand/Pd ratio of 1 for activated chloroarenes (Table 3 Entries 4,7 and 8). In contrast to other catalytic systems that allow the use of chlorarenes at room-temperature, catalyst **IV-29** shows an important activity with potassium carbonate as a base and there is no need for expensive fluorine or cesium salts or strong alkoxides bases. Importantly, when using L/Pd ratios of 2 or higher the catalytic activity decreased significantly (Table 3, Entry 5) thus suggesting that a monophosphine palladium complex may act as the active species.[10, 15] Note also that in the absence of ligand only trace amounts of the desired biphenyl-product were formed (Table 3 Entry 6).

II.2. Negishi Coupling Reactions

As it was mentioned before the formation of C-C bonds by palladium-catalyzed reactions is a very powerful tool in synthetic organic chemistry. The most widely studied of these reactions are Stille and Suzuki-Miyaura coupling reactions, involving organotin and organoboron reagents. Reactions involving organozinc reagents, Negishi type coupling have been less studied, due to the

fact that these reagents are not commercially available and have to be prepared prior to use. Moreover, compared to the Stille reaction, the use of zinc is by far more environmentally friendly and does only generate zinc halides as waste that can easily be treated in contrast to alkyltinhalides.

Two main strategies were employed to obtain aryl zinc reagents. The first one consists in the use of activated zinc. For example Rieke zinc, that is obtained by the reduction of zinc chloride with sodium naphthalenide, readily inserts into aryl halogen bonds (Br, I) to give the corresponding aryl zinc reagents in quantitative yield (Scheme 6).[16]

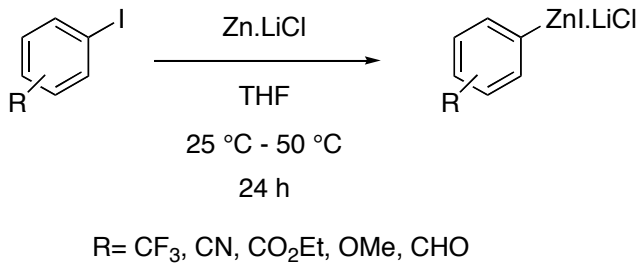


Scheme 6: *Preparation of arylzinc reagents with Rieke zinc.*

The drawback of this method is the preparation and the handling of the highly active zinc metal, this imposes to work under very strict reaction conditions.

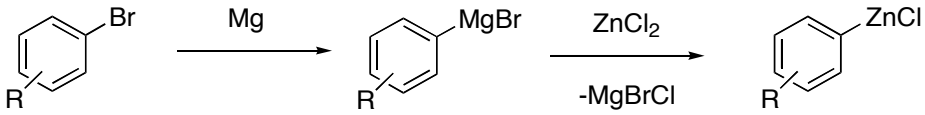
Alternative methods employing commercial zinc powder have been reported by Knochel and Ikegami. In this case highly polar solvents had to be used as the reaction medium.

More recently Knochel reported, that the use of lithium chloride could be beneficial for the direct synthesis of arylzinc reagents from zinc powder in THF. By this method functional arylzinc reagents could be obtained in high yield after 24 h under mild reaction conditions (Scheme 7).



Scheme 7: *Preparation of arylzinc reagents with Zn and LiCl.*

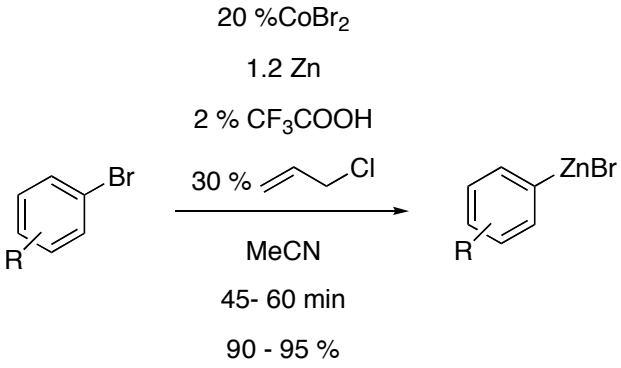
The second strategy consists in the transmetallation of organolithium or Grignard reagents with zinc chloride.[17, 18] In this case functional aryl zinc reagents can be obtained when the reactions are carried out at low temperature (- 100 °C for ArLi and -40 to -25 °C for ArMgX). (Scheme 8).



Scheme 8: *Preparation of organozinc reagents from Grignard reagents.*

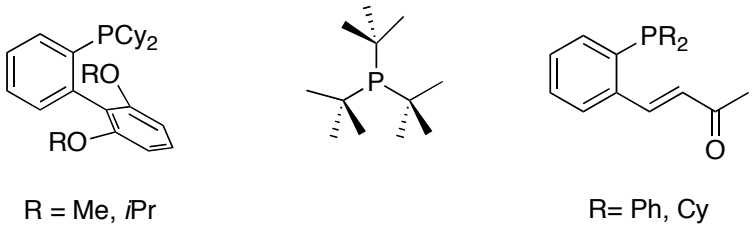
In contrast, Gosmini and coworkers developed during the last years a synthetic procedure that allows for the direct preparation of organozinc reagents from aryl bromides, catalyzed by a simple cobalt catalyst (Scheme 9). [19, 20]

By this method various organozinc reagents can be prepared from aryl bromides, chlorides and triflates under convenient conditions, after short reaction times (< 1h) in high yield (90- 95 %).



Scheme 9: *Preparation of organozinc reagents by cobalt catalysis.*

For the application in synthetic organic chemistry $Pd(PPh_3)_4$ is still a widely used catalyst in Negishi coupling reactions at high catalyst loadings of up to 5% of Pd. Although more active catalysts have been developed throughout the last decade.[21-23] As in the case of the Suzuki-coupling reaction, palladium complexes of phosphine ligands with sterically demanding substituents show the highest activity (Scheme 10).

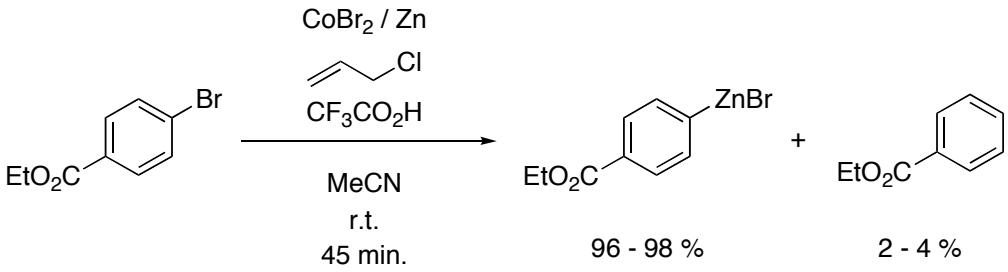


Scheme 10: *Phosphine ligands used in Negishi-coupling reactions.*

Luo *et al.* recently reported that the combination of a strongly donating phosphine ligand with an electron-deficient, strongly π-accepting olefin ligand could be beneficial for the reactivity

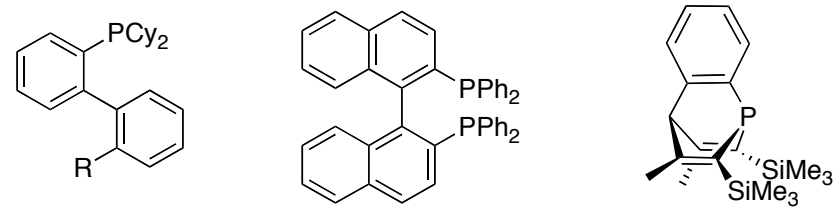
of a palladium catalyst used in the Negishi coupling of iodoarenes and alkylzinc reagents by accelerating the reductive elimination step.[24]

For our studies we prepared arylzinc reagents according to the method of Gosmini *et al.*[19, 20] from bromoarenes, who has joined our group in 2007. To prevent catalyst degradation, the preparation of the arylzinc compounds was carried out under a nitrogen atmosphere in freshly distilled acetonitrile. To separate the excess amount of zinc powder and precipitated cobalt metal, the reaction mixture was filtered prior to the addition to the palladium catalyst. In the case of *p*-bromoethylbenzoate, the yield of the corresponding aryl zinc reagent was confirmed after the filtration by GC analysis and showed to be reproducible in the range of 96 - 98 % with some traces of reduction to ethyl benzoate (Scheme 11).



Scheme 11: *Preparation of the aryl zinc reagent from p-ethyl bromo benzoate.*

The reaction of p-ethylbenzoatezincbromide with *p*-bromobenzonitrile was used for the optimization of the reaction conditions. In addition to phosphabarrelene **IV-9**, Buchwald-type phosphine ligands **IV-67 – IV-69** and *R*-BINAP **IV-70** were tested as ligands (Scheme 12)



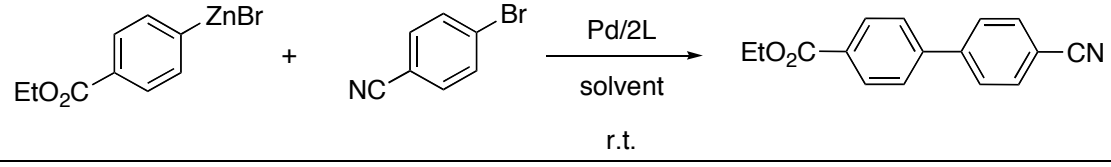
IV-67: R = H
IV-68: R= Me
IV-69: R= NMe_2

IV-70

IV-9

Scheme 12 : *Ligands tested in Negishi coupling reactions*

Table 4: *Screening of ligands and Pd-precursors.*



Entry	Ligand	Pd-source	Solvent	Yield %
1	**IV-67**	$Pd(OAc)_2$ (1 %)	Toluene	56
2	**IV-68**	$Pd(OAc)_2$ (1 %)	Toluene	61
3	**IV-69**	$Pd(OAc)_2$ (1 %)	Toluene	89
4	**IV-70**[d]	$Pd(OAc)_2$ (1 %)	Toluene	85
5	**IV-9**	$Pd(OAc)_2$ (1 %)	Toluene	40
6[c]	**IV-9**	**IV-29** (0.2%)	Toluene	80
7[c]	**IV-9**	**IV-29** (0.2%)	THF	88

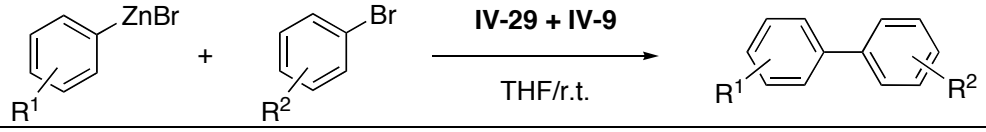
[a]*Reaction Conditions:* Arylzincbromide (5.5 mmol)/MeCN (5 mL), Arylbromide (5 mmol)/THF (2 mL). [b]Isolated Yield. [c]Complex **IV-29** + Ligand **IV-9.** [d]1 equivalent.

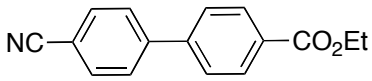
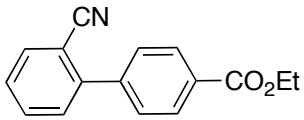
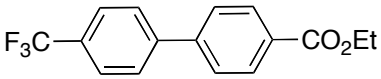
In the case of ligands **IV-67 – IV-70** best results were obtained by the dropwise addition at ambient temperature of the aryl zinc reagent in acetonitrile to a toluene solution of the catalyst and the substrate. Full conversion of the substrate was observed at a catalyst loading of 1 % (Table 4, Entries 1-4). Under these conditions only poor yields were obtained with ligand **IV-9**. In contrast, high activity was observed when Ligand **IV-9** was used with $[Pd(allyl)Cl]_2$ as a source of palladium. This catalyst is extremely active shown by the fact that the reaction mixture starts refluxing, if the arylzinc reagent is added in a single portion.

In this regard, the use of THF as a solvent has shown to be beneficial. When the catalyst substrate mixture is prepared in THF, the arylzinc reagent can be added in a single step. The reaction turns out to be significantly slower but full conversion of the *p*-bromobenzonitrile could be observed after 2 h and an excellent yield of 88 % of the desired coupling product was obtained.

To test the scope of our catalyst further experiments were performed with various substituted bromo arenes (Table 5). Bromo-arenes substituted with electron withdrawing substituents can be smoothly converted to the corresponding diaryls and were obtained in good yield.

Table 5: *Screening of Substrates.*



Entry	R^1	R^2	Product	t h	Yield %
1	4-CO_2Et	4-CN		2	88[b]
2	4-CO_2Et	2-CN		2	57[b]
3	4-CO_2Et	4-CF_3		2	85[c]

[a]*Reaction Conditions:* Arylzincbromide (5.5 mmol)/MeCN (5 mL), Arylbromide (5 mmol)/THF (2 mL), **IV-29** (0.01 mmol), **IV-9** (0.01 mmol). [b]Isolated Yield. [c]GC Yield

This study shows that by the combination of the cobalt catalyzed preparation of arylzinc reagents and the use of phosphabarrelene ligand in combination with the palladium allyl precursor, various substituted biaryls can be readily obtained. Moreover the high reactivity of the phosphabarrelene based catalyst allows for the use of poorly reactive acceptor substituted arylzinc reagents.

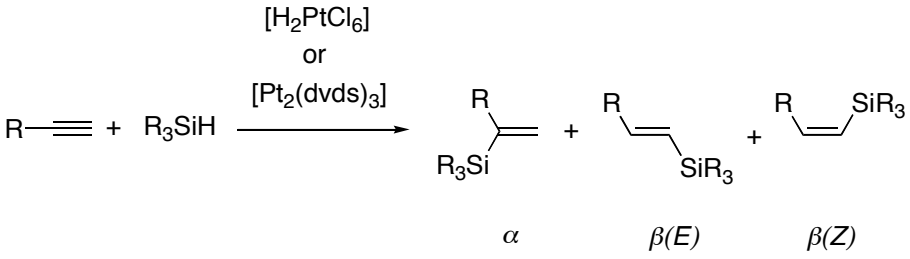
Further studies will be focused on the use of alkylzinc reagents as well as primary and secondary alkyl halides allowing to broaden the scope of this method.

III. PLATINUM CATALYZED HYDROSILYLATION

Vinylsilanes are versatile organometallic intermediates that can be used for further transformations such as Tamao–Fleming oxidation,[25], Pd-catalyzed cross-coupling,[26] protodesilylation,[27] and cycloaddition.

Of the available methods for preparation of vinylsilanes, the hydrosilylation of alkynes is the most direct and atom-economical approach.[28] A number of transition metal catalysts have been devised to execute these reactions in a regio- and stereocontrolled fashion.

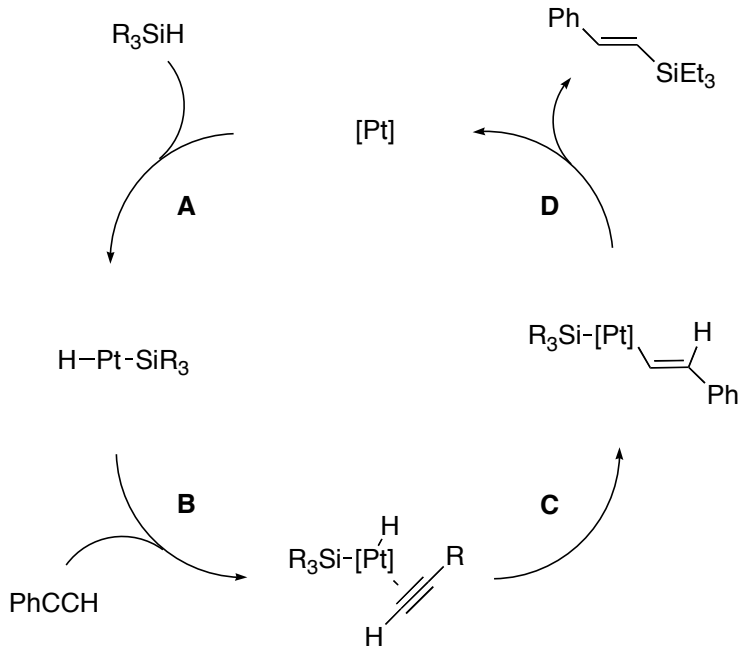
Among those platinum complexes such as Speier's catalyst[29] [H_2PtCl_6] as well as Karstedt's catalyst[30] [$Pt_2(dvds)_3$] are the highly active catalysts for the hydrosilylation of terminal alkynes providing high turnovers numbers (> 10 000) (Scheme13). Unfortunately those catalysts do not provide a good regioselectivity so that the corresponding vinylsilanes are generally obtained as a mixture of the α and $\beta(E)$-regioisomer, for various combinations of different alkynes and silanes. For example in the case of phenylacetylene and triethylsilane, a mixture of $\alpha/\beta(E)/\beta(Z)$ of 18/81/1 is obtained.[30]



Scheme 13: *Hydrosilylation of terminal alkynes with the Speier or the Karstedt catalyst.*

Studies that focused on the improvement of the regioselectivity of this reaction were carried out during the last decades, and zerovalent platinum catalysts with bulky phosphine[26, 31-37] and *N*-heterocyclic carbene ligands[38] have shown to be very selective.

For the platinum catalysts, that selectively form $\alpha/\beta(E)$-vinylsilanes, the Chalk-Harrod mechanism was proved, based on the oxidative addition of a silane to an unsaturated platinum(0) complex **A**, followed by alkyne coordination **B**. In the next step, a vinylplatinum compound is formed by migratory insertion **C**, that eliminates vinylsilane reductively **D** to regenerate the starting platinum (0) complex (Scheme 14). [39]

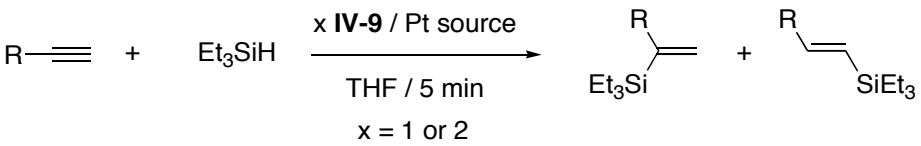


Scheme 14: Chalk-Harrod mechanism for the hydrosilylation of alkynes.

The role of the phosphine ligands in this mechanism is to stabilize the low valent platinum species prior to the oxidative addition on the one hand. On the other hand the steric interaction between the bulky tertiary silyl group and the substituents of the ligand leads to an increase in the regioselectivity.

As we could show in the case of palladium, phosphabarrelenes are suitable ligands for the stabilization of low valent transition metal centers (*vide supra*). Therefore we decided to test activity of ligand **IV-9** in the platinum catalyzed hydrosilylation of terminal alkynes. Additionally we expected that the important steric demand of the trimethylsilyl groups could have a beneficial influence on the regioselectivity of this reaction.

Preliminary experiments with ligand **IV-9** were conducted in the case of the silylation of phenylacetylene with triethylsilane, a transformation which is well documented and often used as a benchmark (Scheme 15).



Scheme 15: *Platinum catalyzed hydrosilylation of terminal alkynes using ligand **29**.*

In a standard experiment **IV-9** (0.2 equiv) was reacted first with [Pt(COD)Cl_2] (0.1 equiv) in the presence of triethylsilane (120 equiv) in THF at 60 °C for 2 min. prior to the addition of

phenylacetylene (100 equiv). The resulting mixture was then placed in a water bath at 20 °C and the progress of the reaction monitored by GC analysis.

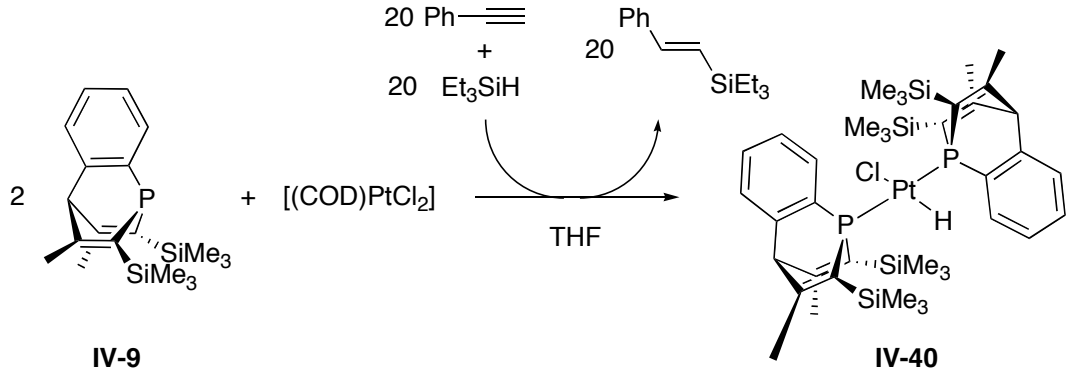
As can be seen in Table 1, entry 2, the presence of ligand **IV-9** results in an important increase of both the reaction rate and the selectivity, compared to those for the $[Pt(COD)Cl_2]$-based catalyst (entry 1), despite a 10 times lower catalyst loading. A complete conversion with a β-(*E*)/α ratio of 99/1 was obtained after only 5 min (entry 2). Note that, at lower catalyst loadings (0.01%), the catalytic activity decreased while the regioselectivity was slightly altered (entry 3). As the first catalytically active species in this transformation involves a Pt(0) complex, the combination of 1 equiv. of **IV-9** with the Karstedt catalyst $[Pt_2(dvds)_3]$ was tested. The 16-electron complex **IV-43** resulted in a less efficient catalyst (Entry 4). To the best of our knowledge, combination of **IV-9** and $[Pt(COD)Cl_2]$ turns out to be the most efficient phosphine-based catalyst reported to date. To evaluate the scope of our catalyst, further experiments were conducted with other silanes and alkynes (see Table 6). Apart from the case of triphenylsilane where no reaction was observed (entry 6), conversions were complete within 5 min. and good regioselectivities were obtained.

Table 6: *Substrate and Silane screening.*

Entry	Pt source	L/Pt	S/Pt	substrate	silane	t min	conv %	β-(*E*)/α
1	$[(COD)PtCl_2]$	0	100	PhCCH	Et_3SiH	60	100	80/20
2	$[(COD)PtCl_2]$	2	1000	PhCCH	Et_3SiH	5	100	99/1
3	$[(COD)PtCl_2]$	2	10000	PhCCH	Et_3SiH	1440	100	92/8
4	$[Pt_2(dvds)]$	1	100	PhCCH	Et_3SiH	60	85	97/3
5	$[Pt(PCy_3)_2]$	2	100	PhCCH	Et_3SiH	5	100	92/8
6	$[(COD)PtCl_2]$	2	1000	PhCCH	$PhMe_2SiH$	5	100	99/1
7	$[(COD)PtCl_2]$	2	1000	PhCCH	Ph_3SiH	60	0	n.d.
8	$[(COD)PtCl_2]$	2	1000	hex-1-yne	Et_3SiH	5	99	99/1
9	$[(COD)PtCl_2]$	2	1000	hex-1-yne	$PhMe_2SiH$	5	98	99/1
10	$[(COD)PtCl_2]$	2	1000	$HCCCH_2OH$	Et_3SiH	5	99	99/1
11	$[(COD)PtCl_2]$	2	1000	hex-3-yne	Et_3SiH	5	99	
12	$[(COD)PtCl_2]$	2	1000	PhCCPh	Et_3SiH	5	99	

[a]Conditions: alkyne (1 mmol), silane (1.2 mmol), THF (0.5 mmol). Abbreviations: n.d. = not determined; S = substrate; L = ligand. [b]The ratio of isomers was determined by GC; the β(*Z*) isomer was not detected.

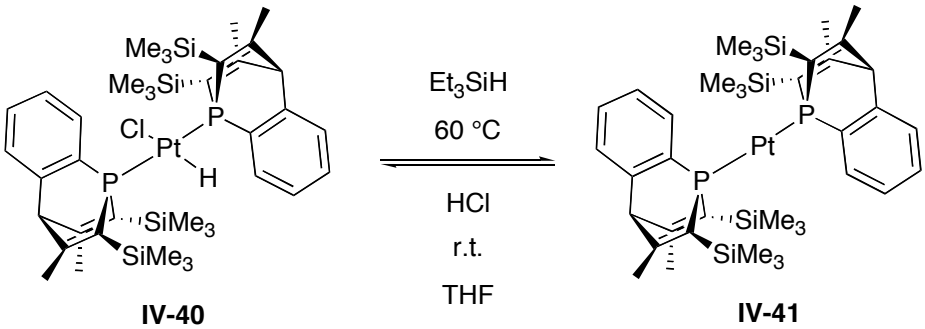
In order to get further insight into the mechanism of this transformation, observation/isolation of intermediates was sought. The reaction was therefore carried out with higher catalyst loading (5% [(COD)$PtCl_2$], 10% **IV-9**) allowing the direct observation of Pt species by NMR spectroscopy. As expected from the first results (cf. table 1), the reaction of Et_3SiH with phenylacetylene is complete within 5 minutes and a single new platinum complex is observed in the ^{31}P NMR spectrum, as shown by the presence of Pt satellites (I = ½, nat abundance 33%). This complex was identified to be the *trans*-[Pt(**IV-9**)$_2$HCl] complex **IV-40** (Scheme 16).



IV-9 **IV-40**

Scheme 16: *Catalytic test reaction at 5 % catalyst loading.*

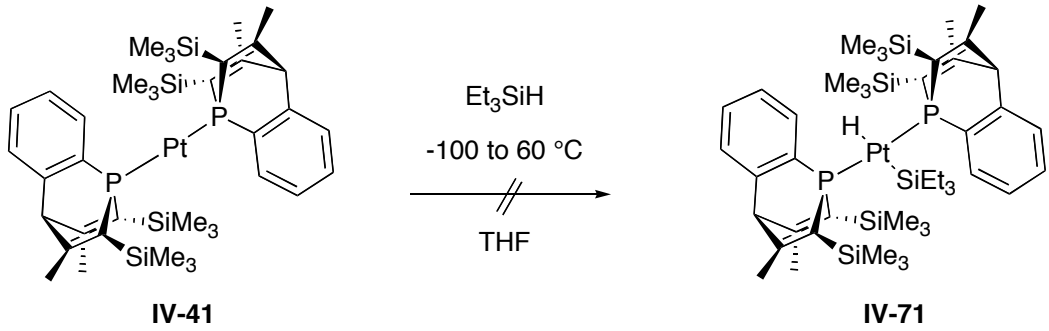
This complex was completely structurally characterized and is a deactivated form of the catalyst. Indeed, according to ^{31}P NMR spectroscopy, in a first attempt, heating a solution of **IV-40** in a NMR tube in the presence of triethylsilane in excess (10 equiv.) in THF at 60 °C resulted in the appearance of a new platinum complex **IV-41** characterized by a signal of weak intensity at δ = 5.6 ppm (J_{PPt} = 4644.0 Hz). (Scheme 17)



IV-40 **IV-41**

Scheme 17: *Reduction of complex* ***IV-40*** *wit triethylsilane.*

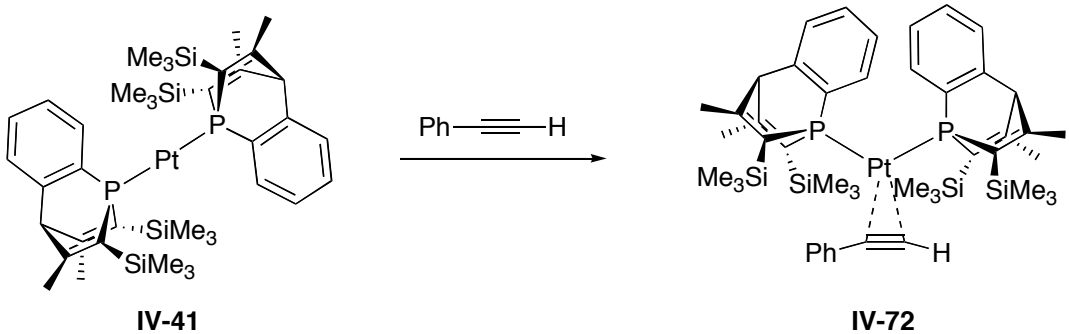
However, under these conditions, complex **IV-41**, which was only formed in a small amount, could not be isolated. Supposing that complex **IV-41** could be the corresponding 14 VE complex which equilibrates with **IV-40** through the oxidative addition of HCl in solution, experiments were conducted under a stream of nitrogen to eliminate HCl. Under these new conditions, the slow but quantitative formation of **IV-41** was observed. This complex could be prepared in a straightforward manner from the reaction of **IV-9** (2 equiv.) with $[Pt(COD)Cl_2]$ in the presence of $[CoCp_2]$ (2 equiv.) as a reducing agent in acetonitrile as solvent (see Chapter 2 for further details). As expected **IV-41** is indeed a very good catalytic precursor and the experiments reported in table 1 were successfully reproduced using 0.1 % of catalyst under the same experimental conditions. In order to get further insight on the initial steps of the catalytic pathway, complex **IV-41** was reacted with Et_3SiH. Surprisingly no reaction occurred even at elevated temperature (in a THF solution at reflux). This result contrasts sharply with the well known reactivity of the $[Pt(PCy_3)_2]$ complex with silanes between –78°C and 0°C (Scheme 18).



IV-41 **IV-71**

Scheme 18: *Reactivity of complex* ***IV-41*** *towards triethylsilane.*

On the other hand, **IV-41** reacted readily at room temperature with phenylacetylene to afford a new complex **IV-72** characterized by a AX spin system pattern in ^{31}P NMR spectroscopy (δ = -11.2 ppm, d+sat(J_{PP} = 35.9 Hz, J_{PtP} = 3680 Hz), -17.7 ppm, d+sat(J_{PP} = 35.9 Hz, J_{PtP} = 3640 Hz)) (Scheme 19).



IV-41 **IV-72**

Scheme 19: *Reaction of* ***IV-41*** *with phenylacetylene.*

This characteristic spin-pattern of complex **IV-72** correlates well with the formation of a 16 VE alkyne adduct. The ^{31}P NMR spectrum of complex **IV-72** is presented in Figure 1:

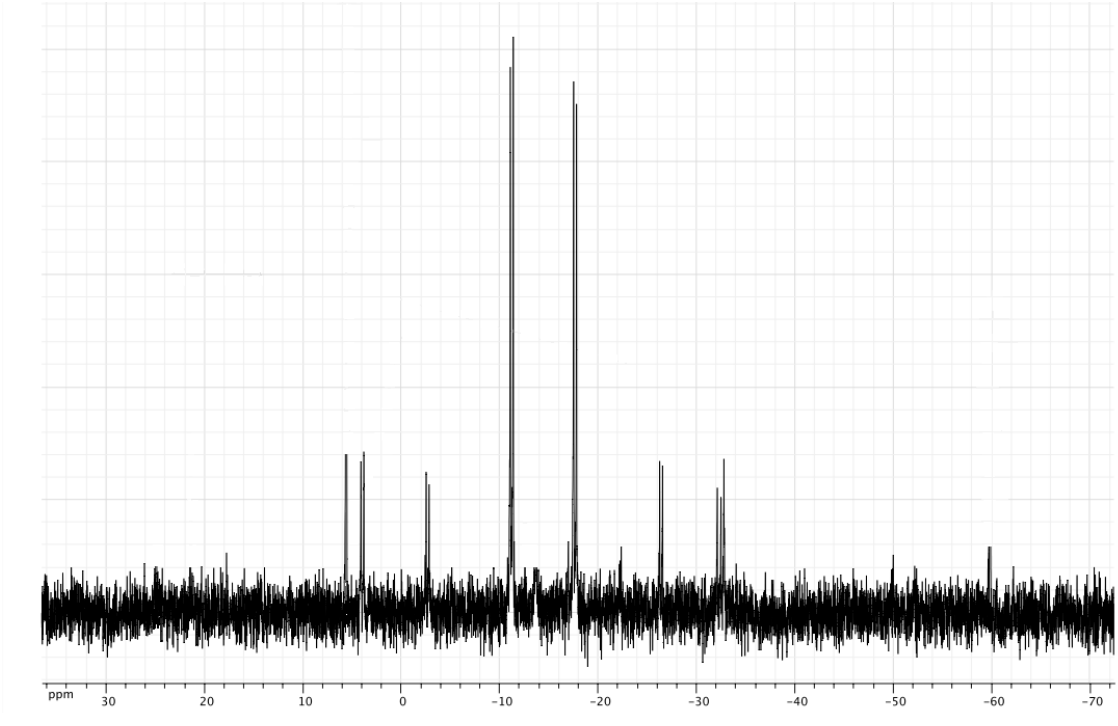
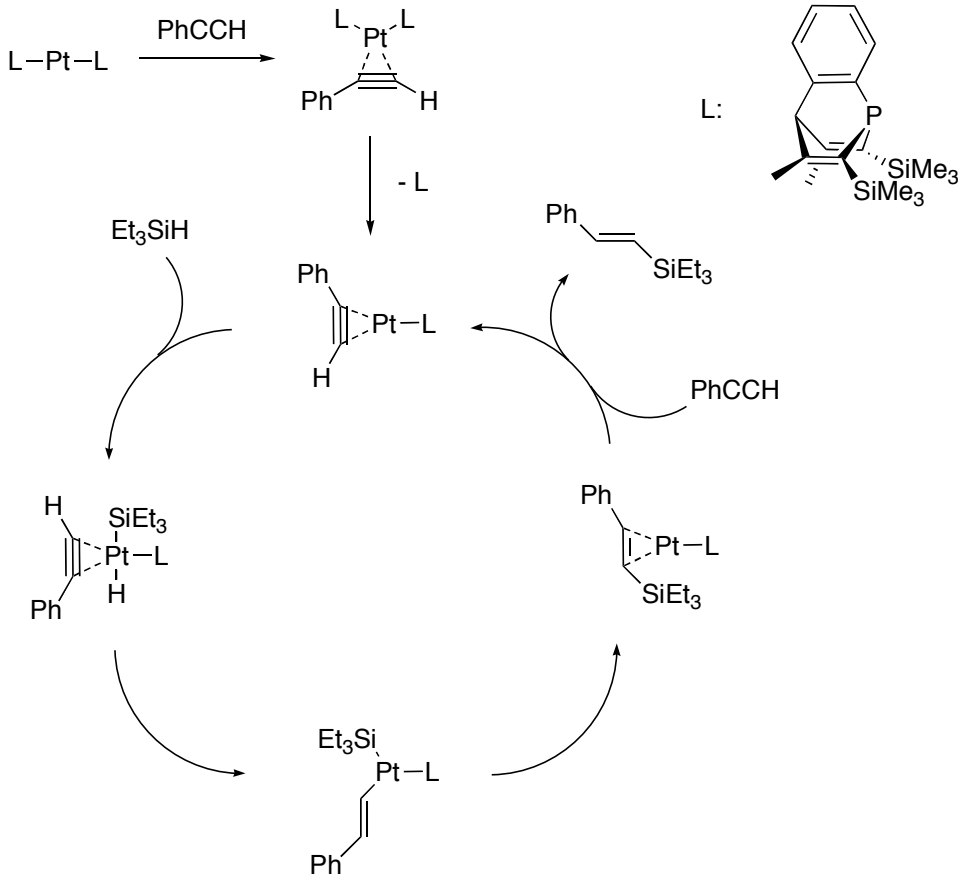


Figure 1: *^{31}P NMR spectrum of the reaction of* ***IV-41*** *with phenylacetylene leading to* ***IV-72****.*

Importantly, this complex subsequently reacted with one equivalent of Et_3SiH at 60°C to yield complex **IV-41** and the *trans*-triethyl-stirylsilane according to ^{1}H and ^{31}P NMR data.

Overall, these results led us to conclude that, unlike for other Pt complexes reported so far, the first step of the catalytic cycle with complex **IV-41** involves coordination of the alkyne and not the oxidative addition of silane on a low valent platinum(0) complex (Scheme 14).

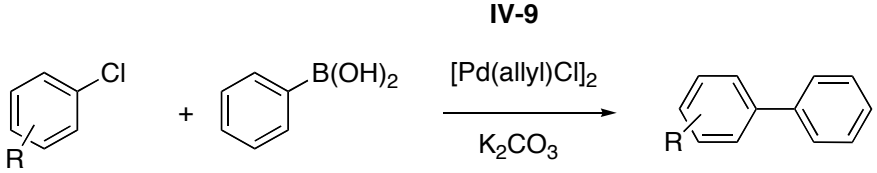


Scheme 20: *Proposed catalytic cycle with ligand* ***IV-9****.*

IV. CONCLUSIONS AND PERSPECTIVES

In this chapter it could be shown that phosphabarrelenes are a promising class of ligands, that can be used in palladium catalyzed C-C bond forming reactions and platinum catalyzed hydrosilylation reactions.

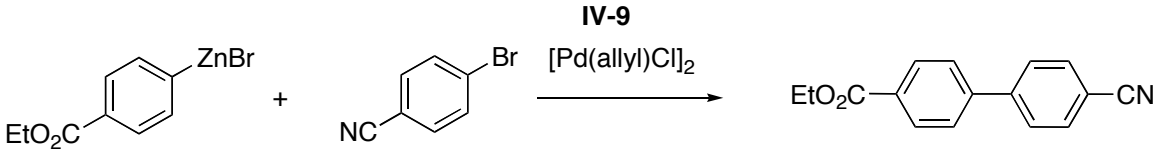
The bulky phosphabarrelene ligand **IV-9** can for example be employed in the Suzuki Miyaura coupling with poorly reactive chloro arenes (Scheme 21).



Scheme 21: *Suzuki Miyaura coupling of chloro arenes with ligand* ***IV-9****.*

Interestingly it could be shown that this catalyst system shows the highest reactivity with potassium carbonate as a base. Overall the reactions can be conducted under very mild conditions in the absence of strong bases and at relatively low catalyst loadings (0.1 – 1 %). Studies with variable ligand concentrations (1-10 equivalents of **IV-9**/Pd) show that the catalytically active species might be a highly reactive monophosphabarrelene Pd-species.

Additionally it could be shown that the combination of $[Pd(allyl)Cl]_2$ and ligand **IV-9** is a very reactive catalyst system, that can be used for the Negishi coupling of poorly reactive acceptor substituted aryl zinc bromides with bromo arenes (Scheme 22).



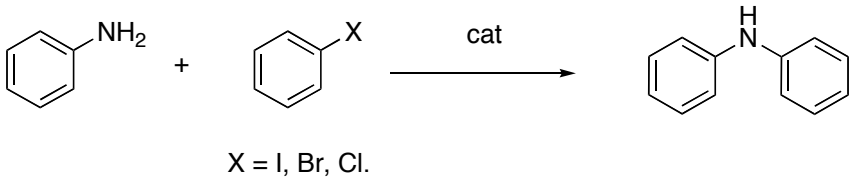
Scheme 22: *Negishi coupling reactions of aryl zincbromides with ligand* ***IV-9***.

It could be shown, that this catalyst system is more reactive than a combination of $Pd(OAc)_2$ with ligands **IV-67 – IV-70**.

A protocol for the highly regioselective hydrosilylation of terminal alkynes with $[(COD)PtCl_2]$ and ligand **IV-9** was developed. This system is the most active and selective phosphine-based catalyst for this transformation to date.

The identification of the intermediates of the catalytic cycle has revealed that the platinum(0) complex **IV-41**, that can equally serve as a catalyst precursor does not react with triethylsilane, in contrast to the well known $[(PCy_3)_2Pt]$ complex. Additionally it could be shown, that the reaction of complex **IV-41** with phenylacetylene leads to the formation of a species **IV-72** that shows a characteristic ^{31}P NMR spectrum that proves the formation of an alkyne adduct of complex **IV-41**. Therefore it was supposed, that in the case of ligand **IV-41**, alkyne coordination might be the first step of the catalytic cycle and not the oxidative addition of the silane as for $[(PCy_3)_2Pt]$.

Based on these results and on the studies of the coordination chemistry of the phosphabarrelenes in Chapter 2 it can be imagined that phosphabarrelenes are of potential use in various catalytic processes. A type of reactions that has been intensly studied in the last decades is the catalytic formation of C-N bonds, as amine are among the most important functional groups in pharmaceuticals. In this regard, the catalytic palladium catalyzed Buchwald-Hartwig-Amination, is one of the most important reactions (Scheme 23).[5] The catalysts used in this reactions are tertiary phosphines[40] and NHC-ligands[13] bearing sterically demanding substituents.



Scheme 23: *Palladium catalyzed amination of haloarenes.*

The rhodium phosphabarrelene complexes might be a good starting point for the development of rhodium catalyzed addition reactions. The use of rhodium complexes which is well established in hydrosilylation reactions[41] and in recent studies it was reported, that rhodium complexes can serve as catalysts for hydrothiolation[42, 43] reactions.

Scheme 24: *Rhodium(I) catalyzed hydrothiolation of terminal alkynes.*

This reaction shows a high regioselectivity, when arylalkynes are employed as substrates but for linear n-alkynes such as hex-1-yne 1:1 mixtures of the α and $\beta(E)$ isomers are usually obtained. Therefore it could be interesting to see whether or not this could be overcome by the use of the sterically hindered phosphabarrelene ligand such as **IV-9**.

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PART V:
Experimental Part

EXPERIMENTAL PART

I. GENERAL CONSIDERATIONS

I.1. Synthetic procedures

All manipulations were performed under exclusion of air or moisture on a vacuum line using Schlenk techniques or in dry boxes under purified argon. THF, diethyl ether and hexanes were distilled from sodium benzophenone ketyl. Toluene was distilled from sodium and triethylamine from calcium hydride. Dichloromethane and pivalonitrile were distilled from P_2O_5. All solvents were degassed by three freeze-pump-thaw cycles prior to use. Deuterated solvents (C_6D_6, C_6D_{12}, CD_3CN, CD_2Cl_2 Tol-d_8 and THF-d_8) purchased from Sigma-Aldrich were stored over activated 4 Å molecular sieves. $CDCl_3$ was distilled from P_2O_5 prior to use.

I.2. Spectroscopic characterization

I.2.a. NMR-Spectroscopy

NMR measurements were obtained using a Bruker 300 Avance spectrometer operating at 300 MHz for ^{1}H, 75.5 MHz for ^{13}C and 121.5 for ^{31}P. The spectra were recorded at 20 °C unless mentioned otherwise. Chemical shifts δ are reported in parts per million (ppm) relative to $SiMe_4$ (internal reference) for ^{1}H and ^{13}C and relative to 85% H_3PO_4 (external reference) for ^{31}P. The following abbreviations are used for the description of the NMR spectra: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad).

I.2.b. X-Ray-Diffraction analysis

Data were collected at 150.0-(1) K on a Nonius Kappa CCD diffractometer using a Mo Kα (λ= 0.71070 Å) X-ray source and a graphite monochromator. All data were measured using phi and omega scans. The crystal structures were solved using SIR 97 and Shelx-97. ORTEP drawings were made using ORTEP III for Windows. Crystallographic data for all X-Ray crystal structures are listed in Annex 2.

I.2.c. Microanalysis

Elemental analyses were performed by the "Service de microanalyse du CNRS" at Gif-sur-Yvette, France.

I.2.d. High resolution mass spectrometry

High-resolution mass spectra were recorded by electron impact ionization (EI) on a JMS-GCmateII mass spectrometer. The quoted masses are accurate to ± 5 ppm.

I.2.e. Electrospray mass spectrometry

A hybrid 7 T Fourier transform ion cyclotron resonance (FTICR) mass spectrometer was used for the mass spectroscopic study. High-resolution mass spectra, recorded in the 200-2000 m/z range in positive mode, were obtained by Fourier transformation of a time- domain transient signal averaged over 16 scans. Sample solutions of the Pd complexes (10^{-5} M) were infused via syringe pump at a flow rate of 140 μL/h. Standard ESI conditions were used, with a capillary voltage of 4 kV and a heater temperature of 200 °C. The FT-ICR instrument (Bruker Apex IV Qh) features a quadrupole mass filter followed by a hexapole cell pressurized at ~10^{-3} mbar with Ar for collision-induced dissociation (CID) experiments. CID experiments were performed at a collision energy of 20 V after selection of precursor ions with an isolation width of 10 Da.

I.2.f. Infrared spectroscopy

Infrared spectra were obtained with a Perkin Elmer 297 spectrometer in transmission mode using anhydrous KBr as a support or by evaporating a drop of a solution of a compound on the crystal of an ATR-unit.

I.3. Metal precursors

The metal precursors that were used in this work were prepared by the following synthetic procedures. The precursors that are not listed here are commercially available.

$[(COD)RhCl]_2$	G. Giordano, R.H. Crabtree, R. M. Heintz, D. Forster, D. E. Morris, in Inorganic Syntheses, Vol. 28, (Ed.: R. J. Angelici, John) Wiley & Sons, Inc. New York, **1990**, p. 88.
$[(NBD)RhCl]_2$	identical procedure to that of $[(COD)RhCl]_2$ using norbornadiene.
$[(tht)_3RhCl_3]$	E. A. Allen, W. Wilkinson, J. Chem. Soc., Dalton Trans. **1972**, 613.
$[(COE)_2IrCl]_2$	J. L. Herde, J. C. Lambert, C. V. Senoff, M. A. Cushing in *Inorganic Syntheses, Vol 15*. Ed.: G. W. Parshall, R. E. Krieger Publishing Company, Malabar, Florida, **1982**, p.19.
$[(COD)_2Ni]$	D. J. Krysan, P. B. Mackenzie, *J. Org. Chem.* **1990**, *55*, 4229.
$[(COD)PdCl_2]$	D. Drew, J.R. Doyle *in Inorganic Syntheses*, Vol. 28, (Ed.: R. J. Angelici) John Wiley & Sons, Inc. New York, **1990**, p. 110.
$[(PhC_3H_4)PdCl]$	N. Marion, O. Navarro, J. G. Mei, E. D. Stevens, N.M. Scott, S. P. Nolan, *J. Am. Chem. Soc.* **2006,** *128*, 4101.
$[(COD)PtCl_2]$	J.X. McDermott, J.F. White, J.F. Whitesides, *J. Am. Chem. Soc.* **1976**, *98*, 6521.
$[(PEt_3)PtCl_2]_2$	G. W. Parshall, in *Inorganic Syntheses, Vol 12*. Ed.: R. W. Parry, McGraw-Hill Book Company, New-York, **1970**, p.27.

$[(C_3H_5)PtCl]_4$ J. Lukas in *Inorganic Syntheses, Vol 15*. Ed.: G. W. Parshall, R. E. Krieger Publishing Company, Malabar, Florida, **1982**, p.79.

[(tht)AuCl] R. Uson, A. Laguna, *in Organometallic Syntheses*, Vol. 3 (Ed.: R. B. King, J. Eisch), Elsevier Science, Amsterdam, **1986**, p. 324.

I.4. Phosphinines

The phosphinines used in this work were prepared, with the exception of 2,4,6-triphenylphosphinine, *via* the 1,3,2-diazaphosphinine method. 1,3,2-diazaphosphinine was prepared *via* the procedure reported by M. Doux: *Nouveaux ligands mixtes phosphore soufre: coordination, catalyse et étude théorique,* Doctoral Studies, Ecole Polytechnique, Palaiseau, **2005**.

II. SYNTHETIC PROCEDURES OF PART II

The synthesis of the following products was reported before and was achieved according to literature methods:

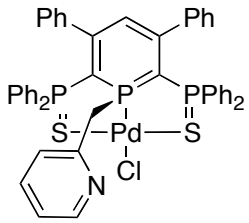
SPS **(II-1)** [(SPS^{Bu})PdCl] **(II-9)** and SP**(II-20)**: Doux, M. *Nouveaux ligands mixtes phosphore soufre: coordination, catalyse et étude théorique,* Doctoral Thesis, Ecole Polytechnique, Palaiseau, **2005**.

$dppmS_2$**(II-25)**: Grimm, S.O., Mitchell, J.D. *Inorg. Chem.* **1977**, *16*, 1762.

$dppm(BH_3)_2$**(II-30)**: Schmidbaur, H., Stutzer, A., Bissinger P., Schier, A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1519.

II.1. Chapter 1

II.1.a. [(SPS^{Pic})PdCl] II-2



A freshly prepared solution of α-Li-picoline (500 µL, 0.31 mmol) was added to a stirred solution of **II-1** (200 mg, 0.29 mmol) in THF (5 mL) at -78 °C. The solution turned immediately deep red and was allowed to return to room temperature during 15 min. $[(COD)PdCl_2]$ (83.6 mg, 0.29 mmol) was added as a solid and the resulting brick-red solution was stirred for 2 h at room

temperature. The solvent was evaporated and the resulting solid was rinced with hexanes (3 x 10 mL) and diethylether (2 x10 mL). The residue was dissolved in CH_2Cl_2 and filtered through a pad of celite. After evaporation of the solvent the title compound was obtained as a brick-red powder. Single crystals suitable for a X-Ray crystal structure analysis were grown from a concentrated solution of $CHCl_3$.

Yield: 200 mg (0.215 mmol, 74 %).

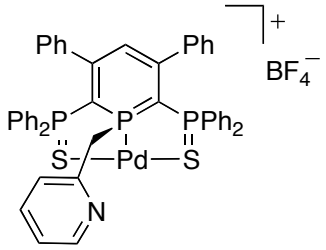
Elemental analysis for $[C_{47}H_{37}ClNP_3PdS_2]$ (914.7) : calculated: C 61.71, H 4.08 ; found: C 61.86, H 3.89.

^{1}H NMR($CDCl_3$):δ 3.83 (d, $^2J_{HPCPic=}$ = 12.5 Hz, 2H, CH2), 5.46 (t, $^4J_{HPPh2}$ = 4.3 Hz, 1H, C_4H), 6.74-7.52 (m, 31H, CH of Ph and CH of Py), 7.71-7.83 (m, 2H, CH of Py), 8.53 (d, J_{HH} = 3.9 Hz, 1H, CH of Py).

^{13}C NMR ($CDCl_3$) : δ 47.7 (d, $^1J_{PC}$ = 22.7 Hz, CH_2), 72.3 (ddd, $^1J_{PC}$ = 92.9, $^1J_{PC}$ = 51.5, $^3J_{PC}$ = 3.1 Hz, C_2, C_6), 119.3 (*pseudo*-q, $^3J_{PC}$ = 11.3 Hz, C_4H), 121.9 (d, J_{CP} = 3.0 Hz, CH of Py), 126.8 (d, J_{CP} = 3.0 Hz, H of Py), 127.8-129.0 (m, CH of Ph), 131.5 (dd, $^1J_{PC}$ = 83.8 Hz, $^3J_{CP}$ = 9.1 Hz of PPh_2), 132.3-132.5 (m, CH of Ph), 132.9 (m, C of PPh_2), 132.9-133.2 (m, CH of Ph), 136.6 (d, J_{PC} = 2.3, CH of Py), 140.0 (dt, $^2J_{PC}$ = 7.6 Hz, $^4J_{PC}$ = 3.0 Hz, C_3, C_5), 149.6 (d, J_{PC} = 2.3 Hz, CH of Py), 153.4 (d, $^2J_{CP}$ = 7.6 Hz, C of Py), 159.6 (s, C of Ph).

^{31}P NMR ($CDCl_3$): δ 48.4 (AB_2, m, $^2J_{PP}$ = 89.0 Hz, PPh_2), 51.9 (AB_2, m, $^2J_{PP}$ = 89.0 Hz, PPic).

II.1.b. [(SPS^{Pic})Pd](BF$_4$) II-3



To a solution of complex **II-2** (82 mg, 0.09 mmol) in CH_2Cl_2 (2 mL) was added solid $AgBF_4$ (20 mg, 0.10 mmol). The resulting orange-red solution was stirred for 2 h at room temperature. AgCl was separated by centrifugation. After evaporation of the solvent the title compound was obtained as a red powder.

Yield: 75 mg (0.08 mmol, 86 %).

Elemental analysis for $[C_{47}H_{37}BF_4NP_3PdS_2]$ (966.1): calculated: C 58.43, H 3.86 ; found: C 58.24, H 3.81.

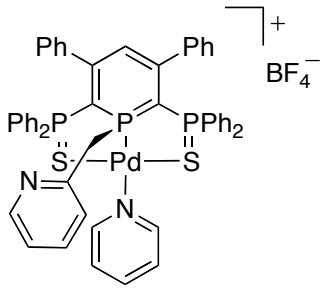
^{1}H NMR(CD_2Cl_2): δ 4.08 (dd, $^2J_{HH}$ = 13.6 Hz, $^2J_{HPPic}$ = 8.9 Hz, 1H, CH_2), 4.39 (*pseudo* t, $^2J_{HPPic}$ = $^2J_{HH}$ = 13.6 Hz, 1H, CH_2), 6.08 (t, $^4J_{HPPh2}$ = 4.7 Hz, 1H, H4), 6.24 (dd, $^2J_{HPPic}$ = 14.0 Hz, $^2J_{HH}$

= 7.3 Hz, 2H, CH of Ph) 6.77-7.79 (m, 30H, CH of Ph and CH of Py), 7.99 (td, J_{HH} = 7.8 Hz, J_{HH} = 1.3 Hz, 1H, CH of Py), 8.43 (d, J_{HH} = 5.7 Hz, 1H, CH of Py).

^{13}C NMR (CD_2Cl_2): δ 44.3 (d, $^1J_{CP}$ = 20.0 Hz, CH_2), 65.6 (m, C_2 or C_6), 72.1 (m, C_2 or C_6), 119.9 (*pseudo* q, $^3J_{PC}$ = 10.6 Hz, C_4H), 123.3 (s, CH of Py), 127.0-132.8 (m, CH of Py, CH and C of Ph), 136.7 (m, Σ J = 12.8 Hz, C_3 or C_5), 137.3 (m, Σ J = 13.6 Hz, C_3 or C_5), 138.6 (s, CH of Py), 151.0 (d, $^2J_{CP}$ = 6.0 Hz, C of Py), 153.0 (s, CH of Py), 159.7 (s, C of Ph), 160.0 (s, C of Ph).

^{31}P NMR (CD_2Cl_2): δ 45.4-49.8 (m, PPic, PPh_2, PPh_2).

II.1.c. [(SPS^{Pic})Pd(Pyr)](BF$_4$) II-4



Pyridine (10 μL, 0.12 mmol) was added to a solution of complex **II-3** (98 mg, 0.10 mmol) in CH_2Cl_2 (2 mL). After evaporation of the solvent the title compound was obtained as a red powder.

Yield: 94.6 mg (0.98 mmol, 98 %).

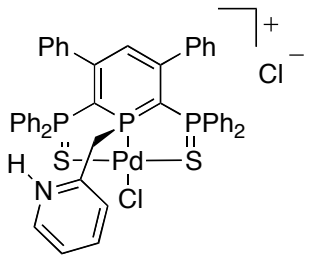
Elemental analysis for [$C_{52}H_{42}BF_4N_2P_3PdS_2$] (1045.18): calculated: C 59.76, H 4.05 ; found: C 59.54, H 4.09.

^{1}H-NMR ($CDCl_3$): δ 3.94 (d, $^2J_{HPPic}$ = 11.5 Hz, 2H, CH_2), 5.58 (t, $^4J_{HPPPh2}$ = 4.4 Hz, 1H, C_4H), 6.82-8.74 (m, 29H, CH of Py and CH of Ph).

^{13}C-NMR($CDCl_3$): δ = 48.5 (s, CH_2), 71.1 (s, C_2, C_6), 119.6 (s, C_4H), 122.7 (s, CH of α-picoline), 124.2 (s, CH of Py), 126.1 (s, CH of α-picoline), 128.1-129.3 (s, 5 x CH of Ph), 130.1 (s, C of PPh_2), 131.2 (s, C of PPh_2), 131.9-133.4 (s, 4 x CH of Ph), 136.5 (s, CH of Py), 138.7 (s, CH of α-picoline), 139.0 (s, C3, C5), 150.2 (s, CH of Py), 150.6 (s, CH of α-picoline), 151.1 (s, C of α-picoline), 160.9 (s, C of Ph).

^{31}P NMR ($CDCl_3$): δ 45.7 (AB2, m, $^2J_{PP}$ = 79.5 Hz, PPh_2), 47.6 (AB_2, m, $^2J_{PP}$ = 79.5, PPic).

II.1.d. [(SPS^{PicH})PdCl]Cl II-6



A 2M solution of HCl in diethyl ether (120 μL, 240 mmol) was added to a solution of **3** (200 mg, 0.22 mmol) in CH_2Cl_2 (5 mL). The solution turned immediately from deep red to light orange. The title compound was obtained by evaporation of the solvents as an orange powder. Single crystals suitable for X-Ray crystal structure analysis were grown by the diffusion of hexanes into a concentrated solution of the product in CH_2Cl_2.

Yield: 200 mg (0.21 mmol, 95 %).

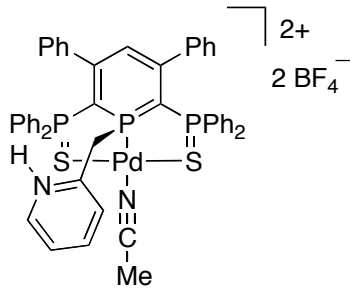
Elemental analysis for [$C_{47}H_{38}Cl_2NP_3PdS_2$] (951.19): calculated: C 59.35, H 4.03; found: C 59.30, H 4.07.

^{1}H NMR (CD_2Cl_2): δ 4.29 (d $^2J_{PH}$ = 12.7 Hz, 2H, CH_2), 5.72 (t, $^4J_{PH}$= 4.6 Hz, 1H, C_4H), 6.70-7.1 (m, 10H, CH of Ph), 7.20-7.65 (m, 20H, CH of PPh_2) 7.69, (br, 1H, CH of Py), 8.31 (br, 1H, CH of Py) 8.60 (br, 1H, CH of Py) 8.68 (br, 1H, CH of Py)

^{13}C NMR(CD_2Cl_2): δ 42.2 (CH_2), 72.3(C_2, C_6) 119.9(s, C_4H), 124.5 (CH of Py), 127.1(CH of Ph), 127.6(CH of Ph), 128.2(CH of Ph and PPh_2), 130.2(CH of Py), 131.1 (CH of PPh_2), 131.9(CH of PPh_2), 138.7(C_3, C_5), 144.1 (CH of Py), 148.5(C of Py), 160.0(C of Ph).

^{31}P NMR (CD_2Cl_2): δ 48.2 (m, AB_2, $^2J_{PP}$ = 91.0 Hz), 51.9 (m, AB_2, $^2J_{PP}$ = 91.0 Hz).

II.1.e. [(SPS^{PicH})Pd(MeCN)](BF$_4$)$_2$ II-8



$AgBF_4$ (8.2 mg, 0.04 mmol) was added as a solid to a solution of **6** (20 mg, 0.02 mmol) in CH_2Cl_2 (2 mL). The solution turned immediately deep red. AgCl was eliminated by centrifugation. Acetonitrile (10 μL, 0.2 mmol) was added via a microsyringe. Evaporation of the

solvents led to the partial reformation of the desolvated product. The NMR-Spectrum of **7** was fully restored after the addition of 1 eqv. MeCN-d_6 (~1 µl).

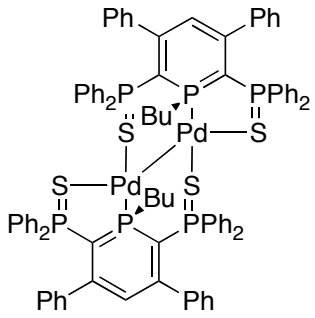
Yield:16.6 mg (0.015 mmol, 75 %).

^{1}H NMR (CD_2Cl_2): δ 2.03 (br, 3H, MeCN), 4.20 (d, $^2J_{PH}$= 12.3 Hz, 2H, CH_2), 5.93 (t, $^4J_{PH}$ = 4.7 Hz, 1H, C_4H), 6.80-7.70 (m, 30H, CH of Ph and PPh_2), 8.15(m, 2H, CH of Py) 8.79(t, $^3J_{HH}$=7.5Hz, 1H, CH of Py), 8.96 (br, 1H, CH of Py).

^{13}C NMR(CD_2Cl_2): δ 1.39 (hep, MeCN), 42.9(d, $^1J_{PC}$= 17.9 Hz, CH_2), 70.8 (dd, $^1J_{PC}$= 57.1 Hz, $^1J_{PC}$ = 93.0 Hz, C2,C6), 118.0(br, MeCN), 120.7(pseudo-q, ΣJ= 11.7 Hz), 126.2(s, CH of Py), 128.1(CH of Ph), 128.6(CH of Ph), 128.9(CH of Ph), 129.1(CH of Ph), 129.2(CH of Ph), 129.3(CH of Ph), 130.2(d, $^1J_{CP}$ = 4.1 Hz, C of PPh_2), 130.3(CH of Py), 132.4(CH of Ph), 132.5(CH of Ph), 132.6(CH of Ph), 133.2(CH of Ph), 133.4(CH of Ph), 137.8 (dt, C3,C5), 142.4 (s, CH of Py), 147.2(d, C of Py), 147.5(s, CH of Py), 161.2(s, C of Ph).

^{31}P NMR ($CDCl_3$) : 44.7 (m, AB2, J_{PP} = 80.4 Hz), 47.7 (m, AB_2, J_{PP} = 80.4 Hz).

II.1.f. [(SPS^{Bu})Pd]$_2$ II-11



A solution of $LiBEt_3H$ (1M, 230 µL, 0.230 mmol) in THF was added drop wise to a solution of complex **II-9** [(SPS^{Bu})PdCl] (200 mg, 0.227 mmol) at -78 °C. The color changed immediately from brick-red to dark red. Upon return to room temperature, the reaction mixture was taken to dryness and the resulting residue was rinsed with hexanes (3 x 2 mL). The dark-red solid was recovered and dried under vacuum.

Yield: 148 mg (0.088 mmol, 77 %)

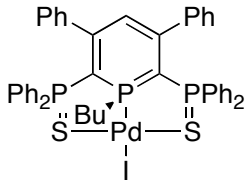
Elemental analysis for [$C_{47}H_{38}Cl_2NP_3PdS_2$] (951.19): calculated: C 59.35, H 4.03; found: C 59.30, H 4.07.

^{1}H NMR ($CDCl_3$): δ 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_2), 1.20 (m, 4H, CH_2), 1.97 (m, 4H, CH_2), 2.3 (m, 4H, CH_2), 5.56 (t, $^4J_{PH}$ = 4.0 Hz, 2H, C_4H), 6.70-7.15 (m, 36 H, CH of Ph), 7.30-7.50 (m, 16 H, CH of Ph), 7.55-7.68 (m, 4 H, CH of Ph), 7.70 (m, 4 H, CH of Ph).

^{13}C NMR ($CDCl_3$): δ 14.1 (s, CH_3), 22.4 (s, CH_2), 24.6 (d, $^2J_{PC}$ = 14.7 Hz, PCH_2) 32.4 (d, $^1J_{PC}$ = 30.2 Hz, PCH_2), 73.2 (m, C2, C6), 120.6 (m, C_4H), 126.5-138.3 (C and CH of Ph), 142.4 (m, C3, C5), 154.3 (C of Ph).

^{31}P NMR ($CDCl_3$) : 19.5 (dd, $^2J_{PP}$ = 96.1 Hz), 44.4 ppm (d, $^2J_{PP}$ = 87.9 Hz), 46.0 ppm (d, $^2J_{PP}$ = 104.2 Hz).

II.1.g. [(SPS^{Bu})PdI] II-12



A solution of complex **II-11** (30 mg, 0.017 mmol) and iodobenzene (ml, 0.03 mmol) in toluene (2 mL) was heated to 100 °C for 4h. The reaction was followed by ^{31}P NMR. Upon complete conversion of the starting product, the reaction mixture was taken to dryness and the resulting residue was rinsed with hexanes (3 x 2 mL). The solid was recovered and dried under vacuum.

Yield: 30.7 mg (0.032 mmol, 89 %).

^{1}H NMR ($CDCl_3$): δ 1.06 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3), 1.58 (m, 2H, CH_2), 2.02 (m, 2H, CH_2), 2.20 (m, 2H CH_2), 5.53 (t, $^4J_{PH}$ = 4.3 Hz, 1H, C_4H), 6.70-7.50 (m, 30H, CH of Ph).

^{13}C NMR ($CDCl_3$): δ 14.3 (s, CH_3), 24.5 (m, CH_2), 29.8 (m, CH_2), 33.9 (m, CH_2), 71.9 (m, C_2, C_6) 118.8 (m, C_4H), 127.5-132.9 (m, CH and C of Ph), 140.5 (m, C_3, C_5), 158.7 (s, C of Ph).

^{31}P NMR ($CDCl_3$) : 55.9 (AB_2, m, $^2J_{PP}$ = 94.9 Hz, PPh_2S), 64.4 (AB_2, m, $^2J_{PP}$ = 94.9 Hz, PBu)

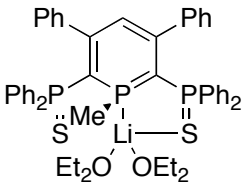
II.1.h. General procedure for the allylation of aldehydes

Representative procedure for the allylation of *p*-bromobenzaldehyde with allyltributyltin in the presence of complex **II-9**: A dried Schlenk was charged with *p*-bromobenzaldehyde (92.5 mg, 0.5 mmol), complex **II-9** (4.4 mg, 0.0050 mmol, 1.0 mol %), and THF (0.5 mL) under nitrogen. Allyltributyltin (186 μL 0.6 mmol) was then added *via* a syringe. The resulting solution was stirred at the desired temperature for 24 h. Thereafter the reaction mixture was evaporated, diluted into water, and extracted with ether. The organic layer was separated, washed with brine, dried (Na_2SO_4), and concentrated. The crude product was then purified by flash column chromatography (hexanes/EtOAc) to give the homoallylic alcohol as a colorless oil.

The NMR data obtained for the coupling product are in agreement with the corresponding literature.[3]

II.2. Chapter 2

II.2.a. [(SPS^{Me})Li(Et$_2$O)$_2$] II-14

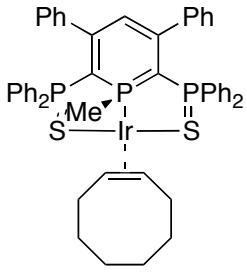


A solution of methyllithium in diethylether (1.6 M, 1 mL, 1.6 mmol) was added to a suspension of 2,6-bis(diphenylphosphine sulfide)-3,5-diphenylphosphinine **II-1** (1.0 g, 1.6 mmol) in Et_2O (10 mL) in a centrifugation tube in a glove box at room temperature. The centrifugation tube was sealed and shaken during 1 min. The formation of an orange precipitate was observed immediately. The precipitate was separated by centrifugation. The supernatent solution was decanted and the precipitate was transferred to a Schlenk tube. The desired product could be obtained as an orange powder after the evaporation of the residual solvent.

Yield: 1.2 g (1.55 mmol, 97 %)

^{31}P NMR (C_6D_6) : δ -66.3 (t, $^2J_{PP}$ = 156.7 Hz, PMe), 44.9 (t, $^2J_{PP}$ = 156.7 Hz, PPh_2S)

II.2.b. [(SPS^{Me})Ir(COE)] II-15



[(COE)$_2$IrCl]$_2$ (11.2 mg, 0.0125 mmol) was added to a solution of **II-14** (20 mg, 0.025 mmol) in deuterated benzene (500 μL). The color changed immediately from light orange to dark red. The 31P{1H} NMR spectrum of the reaction mixture shows the quantitative formation of the desired product. The product was stable in solution for 30 min under inert gas atmosphere at room temperature.

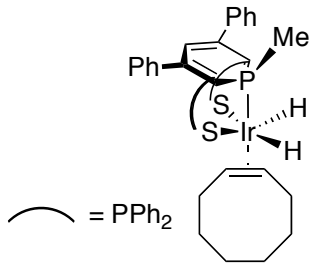
NMR-Yield: 100%

^{1}H NMR (Tol-d$_8$): δ 4.28 (br, 2H, CH of COE), 5.76 (t, $^4J_{PH}$ = 4.6 Hz 1H, C_4H), 6.60-7.15 (m, 24H, CH of Ph),7.40-7.58 (m, 4H, CH of Ph), 7.82-7.95 (m, 4H, CH of Ph). The signals of

PMe could not be identified in the spectrum, due to the superposition of its signal with those of non-coordinated COE.

^{31}P NMR (Tol-d_8) : δ 13.4 (dd, $^2J_{PP}$ = 110.3 Hz, $^2J_{PP}$ = 114.7 Hz, PMe), 32.8 (*pseudo*-d, $^2J_{PP}$ = 112.5 Hz, PPh_2S).

II.2.c. [(SPS^{Me})IrH$_2$(COE)] II-16

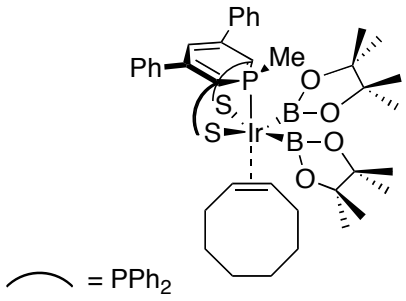


$[(COE)_2IrCl]_2$ (11.2 mg, 0.0125 mmol) was added to a solution of **II-14** (20 mg, 0.025 mmol) in toluene (2 mL). The color changed immediately from light orange to dark red. Hydrogen was bubbled through the reaction mixture for 5 seconds. The color changed from dark red to brown. The 31P NMR showed the formation of the desired product and compound **II-17**. The product could not be separated from the impurities.

^{1}H NMR (C_6D_6) (Selected data): δ -19.5 (d, $^2J_{PH}$ = 17.0 Hz, IrH), 5.70 (t, $^4J_{PH}$ = 5 Hz, 1H, C_4H).

^{31}P NMR (C_6D_6): δ 13.4 (dd, $^2J_{PP}$ = 110.3 Hz, $^2J_{PP}$ = 114.7 Hz, PMe), 32.8 (*pseudo*-d, $^2J_{PP}$ = 112.5 Hz, PPh_2S).

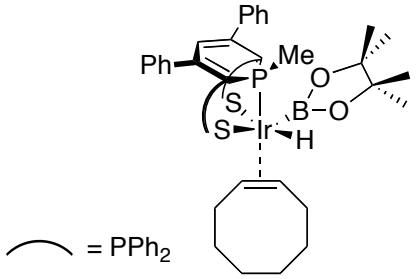
II.2.d. [(SPS^{Me})Ir(Bpin)$_2$(COE)] II-18



$[(COE)_2IrCl]_2$ (11.2 mg, 0.0125 mmol) was added to a solution of **II-14** (20 mg, 0.025 mmol) in toluene (2 mL). The color changed immediately from light orange to dark red. bispinacoleborane (63.5 mg, 0.25 mmol) was added as a solid and the reaction mixture was stirred at room temperature for 1 h.

^{31}P NMR (C_6D_6): δ 22.7 (t, $^2J_{PP}$ = 90 Hz), 43.3 (d, $^2J_{PP}$ = 90 Hz.)

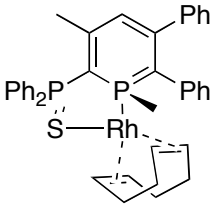
II.2.e. [(SPS^{Me})IrH(Bpin)(COE)] II-19



$[(COE)_2IrCl]_2$ (11.2 mg, 0.0125 mmol) was added to a solution of **II-14** (20 mg, 0.025 mmol) in toluene (2 mL). The color changed immediately from light orange to dark red. pinacoleborane (28.2 μL, 0.25 mmol) was added *via* a syringe and the reaction mixture was stirred at room temperature for 1 h. In the ^{31}P NMR spectrum the formation of three products **II-16**, **II-18** and **II-19** in a 1:2:7 ratio can be observed.

^{1}H NMR (C_6D_6) (Selected data): δ -15.2 (d, $^2J_{PH}$ = 20.2 Hz, IrH),
^{31}P NMR (C_6D_6): δ 15.9 ppm (dd, $^2J_{PP}$= 80.7 Hz, $^2J_{PP}$= 109.6 Hz, PMe), 45.9 ppm (d, $^2J_{PP}$= 80.7 Hz, PPh_2S), 50.5 (d, $^2J_{PP}$= 109.6 Hz, PPh_2S).

II.2.f. [(SP^{Me})Rh(COD)] II-21



A solution of methyl lithium in diethylether (1.6 M, 0.156 mL, 0.25 mmol) was added to a solution of ligand **II-20** (120 mg, 0.25 mmol) in THF (5 mL) at -78 °C. After return to room temperature, $[(COD)RhCl]_2$ (59 mg, 0.125 mmol) was added as a solid and the reaction mixture was stirred et room temperature for 1 h. The reaction mixture was taken to dryness and the resulting residue was suspended in CH_2Cl_2. This suspension was filtered over a sintered glass filter covered with celite. The product was obtained as a dark yellow solid after evaporation of the solvent.

Yield 172 mg (0.235 mmol, 94 %).

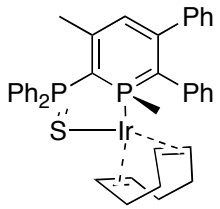
^{1}H NMR (C_6D_6): δ 1.27 (d, $^2J_{PH}$ = 7.8 Hz, 3H, P*A*-Me), 1.40-1.55 (m, 3H, CH_2 of COD), 1.60-1.72 (m, 3H, CH_2 of COD), 1.83 (s, 3H, Ar-CH_3), 1.85-1.95 (m, 1H, CH_2 of COD), 2.07-2.15 (m, 1H, CH_2 of COD), 3.16 (l s, 1H, CH of COD), 3.88 (l s, 1H, CH of COD), 5.23

(s, 1H, CH of COD), 5.46 (s, 1H, CH of COD), 6.01 (d, $^4J_{PH}$ = 5.2 Hz, 1H, C_4H), 6.82-8.34 (m, 20H, CH of Ph).

^{13}C NMR (THF-d_8): δ 11.6 (m, P-CH_3), 27.5 (s, Ar-CH_3), 29.7 (d, $^2J_{RhC}$ = 29.7 Hz, CH_2 of COD), 31.5 (d, $^2J_{RhC}$ = 26.2 Hz, CH_2 of COD), 33.3 (d, $^2J_{RhC}$ = 12.0 Hz, CH_2 of COD), 35.7 (s, CH_2 of COD), 55.5 (m, C_2), 74.7 (d, $^1J_{RhC}$ = 11.3 Hz, CH of COD), 80.6 (d, $^1J_{RhC}$ = 12.8 Hz, CH of COD), 98.7 (d, $^1J_{RhC}$ = 6.8 Hz, CH of COD), 99.5 (d, $^1J_{RhC}$ = 6.8 Hz, CH of COD), 111.0 (ABX, dd, J_{PAC} = 47.1 Hz, J_{PBC} = 2.3 Hz, C_6), 116.8 (dd, $^3J_{PAC}$ = 12.1 Hz, $^3J_{PBC}$ = 9.8 Hz, C_4H), 126.4-130.2 (m, 6 x CH of Ph), 130.4 (s, C of Ph), 130.8 (s, CH of Ph), 131.8 (m, C of Ph), 132.8-134.8 (m, 4 x CH of Ph), 138.4 (s, C), 138.5 (s, C), 144.1 (d, J_{RhC} = 2.3 Hz, C), 146.4-146.6 (d, J_{RhC} = 14.3 Hz, C).

^{31}P NMR (THF): δ 17.8 (dd, $^2J_{PMe\text{-}PPh2S}$ = 128.8 Hz, J_{PMeRh} = 140.3 Hz, PMe), 47.0 (d, $^2J_{PMe\text{-}PPh2S}$ = 128.8 Hz, PPh_2S).

II.2.g. [(SP^{Me})Ir(COD)] II-22



A solution of methyl lithium in diethylether (1.6 M, 0.156 mL, 0.25 mmol) was added to a solution of ligand II-20 (120 mg, 0.25 mmol) in THF (5 mL) at -78 °C. After return to room temperature, $[(COD)IrCl]_2$ (84 mg, 0.125 mmol) was added as a solid and the reaction mixture was stirred et room temperature for 1 h. The reaction mixture was taken to dryness and the resulting residue was suspended in CH_2Cl_2. This suspension was filtered over a sintered glass filter coverd with celite. The product was obtained as a dark brown-yellow solid after evaporation of the solvent.

Yield: 160 mg (0.200 mmol, 80%)

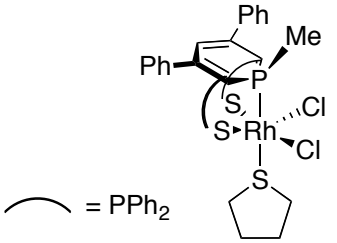
^{1}H NMR ($CDCl_3$): δ 1.13 (d, $^2J_{PH}$ = 8.3 Hz, PCH_3), 1.18-1.35 (m, CH_2 of COD, 2H) 1.50-1.62 (m, CH_2 of COD, 2H), 1.76 (s, 3H, CH_3-Ar), 1.86-2.23 (m, 4H, CH_2 of COD), 2.42 (m, 1H, CH of COD), 3.40 (m, 1H, CH_2 of COD), 3.77 (m, 1H, CH of COD), 4.58 (m, 1H, CH of COD), 5.02 (m, 1H, CH of COD), 5.72 (d, $^4J_{PH}$ = 5.2 Hz, 1H, C_4H), 6.98-7.61 (m, 18H, CH of Ph and PPh_2), 8.01-8.13 (m, CH of PPh_2).

^{13}C NMR (C_6D_6): 10.4 (d, $^1J_{PC}$= 33.2 Hz, PMe), 25.6 (s, Ar-CH_3), 27.6 (s, CH_2 of COD), 30.7 (s, CH_2 of COD), 31.5 (s, CH_2 of COD), 35.1 (s, CH_2 of COD), 51.4 (dd, J_{PC} = 111.5 Hz, J_{PC}

= 58.5 Hz, C_2), 57.0 (s, CH of COD), 63.3 (s, CH of COD), 82.9 (d, $^2J_{PC}$ = 14.6 Hz, CH of COD), 85.6 (d, $^2J_{PC}$ = 12.0 Hz, CH of COD), 109.6 (dd, $^1J_{PMeC}$ = 47.6 Hz, $^3J_{PPh2C}$ = 2.3 Hz, C_6) 115.4 (dd, $^3J_{PC}$ = 13.0Hz, $^3J_{PC}$ = 11.0 Hz, C_4H), 124.2-133.0 (CH and C of Ph), 134.2-134.6 (m, C_3 or C_5), 142.1 (dd, $^2J_{PC}$ = 9.1 Hz , J_{PC} = 1.7 Hz, C of Ph), 143.2 (d, J_{PC} = 12.8 Hz, C_3 or C_5), 144.1 (d, J_{PC} = 8.1 Hz, C of Ph), 144.5 (s, C of Ph).

^{31}P NMR ($CDCl_3$): 13.0 (d, $^2J_{PP}$ = 120.3), 49.7 (d, $^2J_{PP}$ = 120.3)

II.2.h. [(SPS^{Me})RhCl$_2$(tht)] II-23



A solution of [$RhCl_3(tht)_3$] (mg, 0.1 mmol) in toluene (2 mL) was added dropwise to a solution of ligand **II-14** (mg, mmol) in toluene (2 mL). The formation of an orange precipitate was observed. The precipitate was recovered by filtration on a sintered glass-filter and rinsed twice with hexanes (1 mL). The resulting residue was suspended in CH_2Cl_2. This suspension was filtered over a sintered glass filter coverd with celite. The product was obtained as an orange solid after evaporation of the solvent.

Yield 172 mg (75 %).

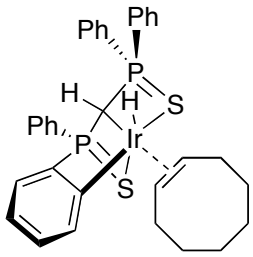
^{31}P NMR (THF): δ 49.7 (m), 58.8-61.0 (m).

ESI-MS: m/z 921 $[M\text{-}Cl]^+$

The product is extremely insoluble in all organic solvents and could therefore not be characterized by ^{1}H and ^{13}C NMR-spectroscopy.

II.3. Chapter 3

II.3.a. [(SCS)IrH(COE)] II-27



1,1-Bis(diphenylphosphinosulfide)methane **II-25** (143 mg, 0.32 mmol) was placed in a Schlenk tube equipped with a stirring bar. The tube was flushed with nitrogen and toluene (2 mL) was added at room temperature. The resulting solution was cooled to -78°C, and MeLi (0.2 mL, 1,6 M in Et_2O, 0.32 mmol) was added. The mixture was then slowly warmed to room-temperature (30 min). $[Ir(COE)_2(Cl)]_2$ (143 mg, 143 mmol) (COE = cyclooctene) was added as a solid in a glove box and the brown-red reaction mixture was stirred at r.t. during 2 h. The reaction mixture was taken to dryness and the remaining solid was washed with hexanes (2 x 5 ml). The resulting residue was dried under vacuum to give the title complex **II-27** as a brown solid, insensitive towards air or moisture. Single crystals suitable for X-Ray-crystal structure analysis were grown by the diffusion of hexanes into a concentrated solution of **II-27** in dichloromethane.

Yield: 217.5 mg (90 %, 0.29 mmol).

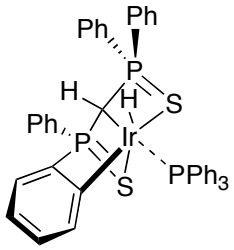
Elemental analysis for $[C_{33}H_{35}IrP_2S_2]$: calculated: C 52.85, H 4.70, found: C 52.8, H 4.8.

^{1}H NMR (C_6D_6): δ -18.10 (d, $^3J_{PAH}$= 4.4 Hz, 1H, IrH), 1.20-1.80 (m, 8H, CH_2 of COE), 2.33 – 2.54 (m, 2 H, CH_2 of COE), 2.62 (dt, $^2J_{PBH}$ = 5.9 Hz, $^2J_{PAH}$ = 1.3 Hz, 1 H, PCHP), 2.82 (dt, $^3J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 3.3 Hz, 2 H, CH_2 of COE), 4.20 – 4.31 (m, 1 H CH of COE), 5.09 – 5.21 (m, 1H, CH of COE), 6.47-6.52(m, 2H CH-meta of P_BPh), 6.52-6.59 (m, 1H, CH of P_APh-orthometallated), 6.62-6.60 (m, 2 H, CH-para of P_BPh), 6.73-6.92 (m, 7 H, 5 CH of P_APh and 2 CH-meta of P_BPh), 7.16-7.25 (m, 3H, 2 CH-ortho of P_APh and CH-ortho of P_APh-orthometallated), 7.32-7.41 (m, 2 H, CH-ortho of PhP_B), 7.55-7.63 (m, 2 H, CH-ortho of PhP_B).

^{13}C NMR (C_6D_6): δ -7.4 (dd, $^1J_{PC}$ = 60.5 Hz, $^1J_{PC}$ = 47.7 Hz, PCHP), 26.7 (s, CH_2 of COE), 26.9 (s, CH_2 of COE), 30.5 (s, CH_2 of COE), 31.9 (s, CH_2 of COE), 32.7 (s, CH_2 of COE),32.8 (s, CH_2 of COE), 69.4 (s, CH of COE), 70.2 (s, CH of COE), 121.4 (d, $^3J_{PC}$ = 14.9 Hz, CH meta of P_APh), 127.4 (CH-para of P_BPh), 128.0 (CH-meta of P_APh), 128.5 (d, $^4J_{PC}$ = 4.6 Hz, CH-para of P_APh), 128.9 (d, $^3J_{PC}$ = 11.7 Hz, 2x CH of P_BPh), 129.5 (d, $^2J_{PC}$ = 12.4 Hz, 2x CH-ortho of P_APh), 129.9 (d, $^3J_{PC}$ = 10.1 Hz, 2x CH-ortho of P_BPh), 130.3 (s, CH of P_BPh), 131.2 (d, $^3J_{PC}$ = 3.1 Hz, CH of P_APh), 131.4 -5(m, 1 x CH-meta' of P_APh-orthometallated), 131.6 (d, $^2J_{PC}$= Hz, 2 x CH-ortho of P_BPh), 134.0 (d, $^2J_{PC}$ = 15.1 Hz, CH-ortho of P_APh-orthometallated), 135.8 (d, $^1J_{PC}$ = 64.7 Hz, C of P_BPh), 136.3 (dd, $^1J_{PC}$ = 73.6 Hz, $^3J_{PC}$ = 6.8 Hz, C of P_BPh), 138.4 (d, $^2J_{PC}$ = 43.2 Hz, C of P_APh), 146.8 (d, $^2J_{PC}$ = 15.8 Hz, C-Ir), 149.2 (dd, $^1J_{PC}$ = 108.8 Hz, $^3J_{PC}$ = 3.3 Hz, C of P_APh).

^{31}P NMR (C_6D_6, 25): δ -0.3 (d, $^2J_{PP}$ = 2.9 Hz, P_A), 60.4 (d, $^2J_{PP}$ = 2.9 Hz, P_B).

II.3.b. [(SCS)IrH(PPh$_3$)] II-28



A solution of triphenylphosphine (26.2 mg, 0.1 mmol) in THF (1 mL) was added dropwise to a solution of **2** (93.6 mg, 0.1 mmol) in THF (10 mL). The reaction was followed by ^{31}P-NMR and the immediate conversion of compound **II-27** to compound **II-28** could be observed at room temperature. The reaction mixture was taken to dryness and the resulting residue was washed with hexanes (3 x 3 mL). The remaining solid was dried under vacuum to give the title compound as a brown solid. Single crystals suitable for X-Ray-crystal structure analysis were obtained by the slow evaporation of a concentrated solution of **II-28** in dichloromethane.

Yield: 86 mg (95 %, 0.095 mmol)

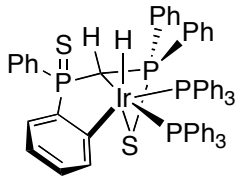
Elemental analysis for [$C_{43}H_{36}IrP_3S_2$]: calculated C 57.3, H 4.0, found: C 57.4, H 3.9.

^{1}H-NMR ($CDCl_3$): δ -19.74 (dd, $^2J_{PPh3H}$= 18.2 Hz, $^3J_{PAH}$= 3.8 Hz, IrH), 2.30 (td, $^2J_{PBH}$= 5.2 Hz, $^3J_{PIrH}$ = 0.7 Hz, 1H, PCHP), 6.45 (m, 1H, CH-para of P_APh-orthometallated), 6.68 (m, 1H, CH-meta of P_APh-orthometallated), 6.78 (m, 1H, CH-meta' of P_APh-orthometallated), 6.88-6.96 (m, 1H, CH-ortho of P_APh-orthometallated), 7.10-7.85 (m, 40 H, 5 CH of P_APh, 10 CH of P_BPh and 15 CH of PPh_3).

^{13}C-NMR ($CDCl_3$): δ -8.0 ($^1J_{PC}$ = 45.8 Hz, $^1J_{PC}$ = 53.9 Hz, PCHP), 120.1 (d, $^3J_{PC}$= 14.8 Hz, CH-meta of P_APh-orthometallated), 125.3 (s, CH of PPh_3), 126.4 (d, $^4J_{PC}$= 3.3 Hz, CH-para of P_APh-orthometallated) 127.5-129.4 (m, CH of P_APh-orthometallated, CH of P_BPh and CH of PPh_3), 131.6 (d, $^2J_{PC}$ = 11.8 Hz, CH-ortho of P_BPh), 134.3 (d, $^2J_{PC}$ = 10.5 Hz, CH-ortho of P_APh and P_BPh), 135.3(dd, $^1J_{PC}$ = 76.0 Hz, $^3J_{PC}$ = 7.4 Hz, C of P_BPh), 136.0 (dd, $^1J_{PC}$ = 64.0 Hz, $^3J_{PC}$ = 4.0 Hz, C of P_BPh), 139.0 (ddd, J_{PC} = 43.0, J_{PC} = 3.5 Hz, J_{PC} = 1.4 Hz, C of PPh_3), 139.1 (dd, J_{PC} = 2.4 Hz, J_{PC} = 15.1 Hz, CH of P_APh-orthometallated), 148.7 (ddd, $^1J_{PC}$ = 108.7 Hz, $^3J_{PC}$ = 4.6 Hz, $^2J_{PC}$ = 2.6 Hz, C of P_APh-orthometallated) 149.2 (ddd, J_{PC} = 15.0 Hz, J_{PC} = 6.0 Hz, J_{PC} = 2.0 Hz, C-Ir).

^{31}P-NMR (CD_2Cl_2): δ -1.1 (dd, $^2J_{PP}$ = 4.6 Hz, $^2J_{PP}$ = 19.5 Hz, P_A), 13.4 (*pseudo*-t, $^2J_{PP}$ = 19.0 Hz, PPh_3), 53.9 (dd, $^2J_{PP}$ = 4.6 Hz, $^2J_{PP}$ = 18.1 Hz, P_B)

II.3.c. [(SCS)IrH(PPh$_3$)$_2$] II-29



Triphenylphosphine (26.2 mg, 0.1 mmol) was added as a solid to a solution of **II-28** (46.8 mg, 0.05 mmol) in THF (5 mL). The resulting solution was stirred at room temperature for 30 min. The solution was taken to dryness and the resulting residue was washed with diethylether (3 x 3 mL). The title compound was obtained as an off-white powder after drying under vaccum. Single crystals suitable for X-Ray-crystal structure analysis were grown by the diffusion of hexanes into a concentrated solution of **II-29** in dichloromethane.

Yield: 51 mg (87 %, 0.044 mmol).

Elemental analysis for: [$C_{61}H_{51}IrP_4S_2$]: calculated: C 62.9 H 4.4, found: C 62.8 H 4.6.

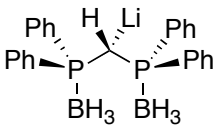
^{1}H-NMR (CD_2Cl_2): δ -21.98 (m, 1H, IrH), 2.52 (m, 1H, PCHP), 6.19-6.31 (m, 2H, CH of P_APh-orthometallated and CH of P_BPh), 6.70-7.80 (m, 49 H, CH of Ph).

^{13}C-NMR (CD_2Cl_2): δ 8.7 (m, PCHP), 120.8 (d, $^3J_{PC}$ = 13.8 Hz, CH-meta of P_APh), 124.9 (d, J_{PC} = 12.6 Hz, CH of P_BPh), 126.0-129.0 (m, CH of PPh_3, CH of P_BPh and CH-para of P_APh), 130.2 (d, J_{PC} = 2.7 Hz, CH of P_BPh_2), 130.7 (dd, $^1J_{PC}$ = 43.7 Hz, $^3J_{PC}$ = 3.4 Hz, C of P_BPh), 131.7 (dd, $^2J_{PC}$ = 19.0 Hz, $^4J_{PC}$ = 4.2 Hz, CH-ortho of P_APh), 133.5 (d, J_{PC} = 11.0 Hz, CH of P_BPh), 133.9 (m, C of PPh_3), 139.9 (dd, $^1J_{PC}$ = 81.7 Hz, $^3J_{PC}$ = 2.0 Hz, C of P_APh), 140.4 (dd, $^1J_{PC}$ = 87.4 Hz, $^3J_{PC}$ = 9.4 Hz, C of P_APh-orthometallated), 143.4 (ddd, J_{PC} = 2.9 Hz, J_{PC} = 10.0 Hz, J_{PC} = 17.0 Hz, CH-ortho of P_APh-orthometallated). 151.1 (m, C-Ir).

^{31}P-NMR (CD_2Cl_2): δ 10.0 (ddd, J_{PP} =21.0 Hz, J_{PP} = 3.6 Hz, J_{PP} =9.5 Hz, PPh_3), 15.3 (dd, J_{PP} = 9.3 Hz, J_{PP} = 23.2 Hz, PPh_3), 66.4 (ddd, J_{PP} = 23.2 Hz, J_{PP} = 6.8 Hz, J_{PP} = 9.5 Hz, P_B), 76.7 (dd, J_{PP} = 6.8 Hz, J_{PP} = 21.0 Hz, P_A).

II.4. Chapter 4

II.4.a. [(BH$_3$Ph$_2$P)$_2$CHLi] II-31



A 1.6 M ethereal solution of MeLi (0.410 mL, 0.655 mmol) was added to a dry diethylether (5 mL) solution of dppm$(BH_3)_2$ **II-30** (270 mg, 0.655 mmol) and stirred for 36 h at room temperature. The solvent was then removed under vacuum and the resulting solid washed copiously with dry pentane and dried under vacuum. The resulting compound was obtained as 1/1 lithium salt/diethylether adduct **II-31** as a white solid in nearly quantitative yield.

Yield: 312 mg (0.635 mmol, 97 %)

$^{31}P\{^1H\}$ NMR (C_6D_6, 121.495 Hz): δ 8.95 (m);

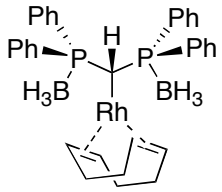
$^{11}B\{^1H\}$ NMR (C_6D_6, 75.768 Hz): δ -33.2 (bd, $^1J_{BP}$ = 64 Hz, BH_3);

^7Li (C_6D_6, 155.505 MHz): δ 0.95;

^1H (C_6D_6, 300.130 Hz): δ 7.83-7.96 (m, 8H, CH arom.), 7.00-7.13 (m, 12H, CH arom.), 4.00 (q, 4H, $^3J_{HH}$ = 7.06 Hz, CH_2 Et_2O), 1.45 (bs, BH_3), 1.33 (t, 1H, $^2J_{HP}$ = 13.60 Hz, PCH(Li)P), 0.87 (t, 6H, $^3J_{HH}$ = 7.06 Hz, CH_3 Et_2O);

$^{13}C\{^1H\}$ NMR (C_6D_6, 100.613 MHz): δ 140.59 (d, $^1J_{CP}$ = 68.63 Hz, C arom.), 132.25 (pt, J_{CP} = 4.79 Hz, CH arom.), 129.44 (s, CH arom.), 128.47 (pt, J_{CP} = 5.03 Hz, CH arom.), 66.67 (s, CH_2, Et_2O), 14.97 (s, CH_3 Et_2O), 8.53 (t, $^1J_{CP}$ = 70.46 Hz, CHLi).

II.4.b. [$(BH_3Ph_2P)_2CH$)Rh(COD)] II-33



A C_6D_6 solution of **II-31** (0.067g, 0.136 mmol) was added to a room temperature C_6D_6 stirred solution of $[(COD)RhCl]_2$ (0.0336g, 0.068 mmol) and the reaction was monitored by ^{31}P NMR spectroscopy. After completion, the solvent was removed under vacuum. Pentane was added and the resulting suspension was filtered over cellite. Removal of the solvent and drying under vacuum lead to complex **II-33** that was obtained as a greenish powder.

Yield: 40 mg (0.064mmol, 47%).

Elemental analysis for $[C_{33}H_{39}B_2P_2Rh]$: calculated: C, 63.71; H, 6.32. Found: C, 63.51; H, 6.65.

$^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.88 (bs);

$^{11}B\{^1H\}$ NMR (C_7D_8, 353 K): δ -40.62 (d, $^1J_{PB}$ = 73 Hz, B);

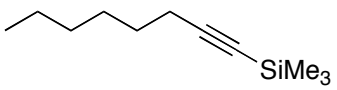
^1H NMR (C_6D_6): δ 8.10-8.20 and 7.50-7.60 (2 x m, 4H, CH arom.), 7.00-7.13 and 6.60-6.80 (2 x m, 6H, CH arom.), 4.90 (m, 4H, CH=CH COD), 2.72 and 1.29 (bm, COD), 1.11 (t, $^2J_{HP}$ = 11.07 Hz, PCH(Rh)P), 1.09 (bm, BH_3);

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 135.70 (d, $^{1}J_{PC}$ = 33.40 Hz, C_{ipso} Ar), 134.37 (dd, $^{1}J_{PC}$ = 66.04 Hz, $^{3}J_{PC}$ = 9.68 Hz, C_{ipso} Ar), 132.63 and 131.75 (2 x d, J_{PC} = 9.5 Hz, CH Ar), 130.78 and 130.11 (2 x d, $^{4}J_{PC}$ = 2.01 Hz, CH Ar), 128.82 and 128.35 (2 x d, J_{PC} = 9.85 Hz, CH Ar), 89.35 and 72.32 (2 x bs, CH COD), 31.88 and 29.04 (2 x bs, CH_2 COD), -3.72 (td, $^{1}J_{PC}$ = 15.42 Hz, $^{1}J_{RhC}$ = 18.89 Hz, CHRh).

III. SYNTHETIC PROCEDURES OF PART III

III.1. Chapter 1

III.1.a. 1-Trimethylsilyl-oct-1-yne



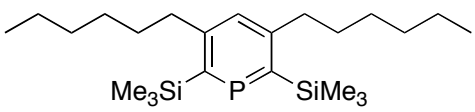
To a solution of oct-1-yne (14.8 mL, 100 mmol) in THF (100 mL) was added a 1.6 M solution of n-BuLi in hexanes (62.5 mL, 100 mmol) at -78°C. The resulting solution was allowed to warm to 0 °C and stirred for 30 minutes. Trimethylsilylchloride (12.8 mL, 100 mmol) was added dropwise at 0 °C. The resulting suspension was stirred at room temperature for 30 minutes. After evaporation of the solvent the resulting residue was treated with water (50 mL) and the title compound was extracted with hexanes (3x 20 mL). The combined organic phases were tried over anhydrous $MgSO_4$. After evaporation of the solvent, the title compound was obtained as a yellow oil.

Yield: 17.3 g (95 %).

^{1}H-NMR ($CDCl_3$): δ 0.00 (s, $SiMe_3$, 9H), 0.75 (t, $^{3}J_{HH}$= 6.9 Hz, CH_3, 3H), 1.37 (m, CH_2, 2H), 1.10-1.30 (m, CH_2, 6H), 2.07 (t, $^{3}J_{HH}$=7.2 Hz, CH_2, 2H).

^{13}C-NMR ($CDCl_3$): δ 0.03 (s, $SiMe_3$), 13.86 (s), 19.62 (s), 22.38 (s), 28.34 (s), 28.48 (s), 31.15 (s), 84.05 (s), 107.57 (s).

III.1.b. 2,6-Bis(trimethylsilyl)-3,5-bis(hexyl)phosphinine III-2



A mixture of 1,3,2-diazaphosphinine (10 mmol) and 1-trimethylsilyl-oct-1-yne (1.82 g, 20 mmol) in toluene (10 mL) was heated to reflux during 5 days, following the reaction by ^{31}P NMR. After evaporation of the solvent, the resulting oily residue was dispersed in a minimal quantity of

hexanes and placed on top of column (80g SiO_2). The title compound was eluted with hexanes (500 mL). After evaporation of the solvents the title compound was obtained as a highly viscous nearly colorless oil.

Yield: 3.4 g (83 %).

^{1}H NMR ($CDCl_3$): δ 0.28 (s, $SiMe_3$, 18H), 0.78(t, $^3J_{HH}$= 6.6 Hz, Me, 6H), 1.15-1.35(m, CH_2, 12H), 1.48(m, CH_2, 4H), 2.60-2.68 (pseudo-t, CH_2, 4H), 6.98(s, H-4, 1H).

^{13}C NMR ($CDCl_3$): δ 0.0 (d, $^3J_{PC}$= 11.1 Hz, $SiMe_3$), 12.1 (s), 20.7 (s), 27.8 (s), 30.0 (s), 30.8(s), 37.8(s), 129.2(d, $^2J_{PC}$= 23.0 Hz), 152.7(d, $^3J_{PC}$=11.7 Hz), 161.5(d, $^3J_{PC}$=85.5 Hz).

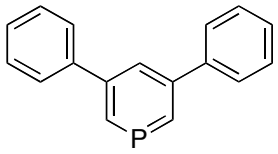
^{31}P NMR ($CDCl_3$): δ 268.1 (s).

HRMS EI+: 408.2812 (calcd 408.2797 for $C_{23}H_{45}Si_2P$).

III.1.c. General protodesilylation procedure

A 2 M solution of HCl in Et_2O (3 mL, 6 mmol) was added to a solution of 2,6-Bis(phenyl)-3,5-bis(hexyl)phosphinine (785 mg, 2 mmol) in Et_2O (20 mL). The reaction mixture was stirred for 30 min at 25 °C. 3,5-Bis(phenyl)phosphinine was obtained pure by evaporation of the volatiles. Yield: 486 mg (1.96 mmol, 98%).

III.1.d. 3,5-Bis(phenyl)phosphinine III-5



Yield: 486 mg (1.96 mmol, 98 %)

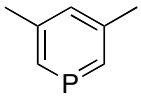
^{1}H NMR (CD_2Cl_2): δ 7.45 (m, CH of phenyl, 6H), 7.70 (d, $^2J_{PH}$= 37.8 Hz, 4H).

^{13}C NMR (CD_2Cl_2): δ 127.5 (s), 128.0 (s), 128.9 (s), 129.6 (d, $^2J_{PC}$= 18.9 Hz, C3), 142.7 (d, $^3J_{PC}$= 15.1 Hz, C4), 147.7 (d, $^1J_{PC}$= 49.6 Hz, C2).

^{31}P-NMR (CD_2Cl_2): δ 150.8 (t, $^2J_{PH}$= 37.8 Hz).

HRMS EI+: 248.0745 (calcd 248.0755 for $C_{17}H_{13}P$)

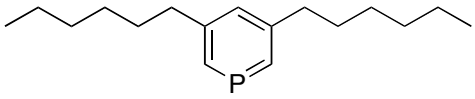
III.1.e. 3,5-Bis(methyl)phosphinine III-6



Yield: 186 mg (1.5 mmol, 75 %).

^{1}H NMR(C_6D_6): δ 2.07 (s, 6H, CH3), 6.79 (s, 1H, H4), 8.17 (d, $^{2}J_{PH}$= 38.1Hz).
^{13}C NMR (C_6D_6): δ 24.5 (d, $^{3}J_{PC}$=2.8 Hz, CH3), 132.5 (d, $^{2}J_{PC}$= 18.7 Hz), 133.4 (d, $^{3}J_{PC}$=15.2 Hz), 150.5 (d, $^{1}J_{PC}$=50.1 Hz).
^{31}P NMR (CD_2Cl_2): δ 203.7 (t, $^{2}J_{PH}$= 38.1 Hz).
HRMS EI+: 124.0447 (calcd 124.0442 for C_7H_9P)

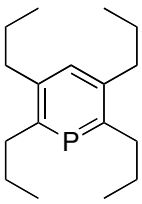
III.1.f. 3,5-Bis(hexyl)phosphinine III-7



Yield: 502 mg (1.9 mmol, 95 %).

^{1}H NMR (CD_2Cl_2): δ 0.80(pseudo-s, CH_3, 6H), 1.22 (m, CH_2, 12H), 1.54 (m, CH_2, 4H), 2.58 (t, $^{3}J_{HH}$= 7.8 Hz, CH_2, 4H), 7.1 (s, H-4, 1H), 8.24 (d, $^{2}J_{PH}$= 37.8 Hz, H-2, H-6, 2H).
^{13}C NMR (CD_2Cl_2): δ 13.1 (s, CH_3), 21.9 (s, CH_2), 28.8 (s, CH_2), 30.9 (d, CH_2), 31.0 (s, CH_2), 38.6(s, CH_2), 130.9(d, $^{2}J_{PC}$= 18.9 Hz, C3), 148.6(d, $^{3}J_{PC}$= 15.1 Hz, C4), 149.3(d, $^{1}J_{PC}$= 49.6 Hz, C2).
^{31}P NMR (CD_2Cl_2): 204.1 (t, $^{2}J_{PH}$= 37.8 Hz).
HRMS EI+: 264.2003 (calcd 264.2007 for $C_{17}H_{29}P$).

III.1.g. 2,3,5,6-tetrapropylphosphinine III-8



A mixture of 1,3,2-diazaphosphinine (10 mmol) and 4-octyne (2.2 mL, 15 mmol) in toluene (20 mL) was heated to 120 °C in a schlenk tube. The reaction was finished after 7 days. After evaporation of the solvent, the resulting oily residue was dispersed in a minimal quantity of

hexanes and placed on top of column (10 g SiO_2). The title compound was eluted with hexanes (500 mL). After evaporation of the solvents the title compound was obtained a colorless oily liquid.

Yield: 2.22 g (8.4 mmol, 84 %)

^{1}H NMR (CD_2Cl_2): δ 1.03 (t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_3), 1.06 (t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_3), 1.67 (m, 8H, CH_2), 2.67 (t, $^3J_{HH}$ = 8.1 Hz, 4H, CH_2), 2.87 (t, $^3J_{HH}$ = 8.1 Hz, 2H, CH_2), 2.93 (d, 3JHH = 7.8 Hz, 2H, CH2), 7.10 (d, $^3J_{PH}$ = 3.6 Hz, 1H, C_4H).

^{13}C NMR (CD_2Cl_2): δ 14.1 (s, CH_3), 24.9 (s, CH_2), 26.9 (d, J_{PC} = 10.2 Hz, CH_2), 36.0 (s, CH_2), 37.0 (d, J_{PC} = 33.8 Hz, CH_2), 134.6 (d, $^2J_{PC}$ = 15.8 Hz, C_3, C_5), 144.2 (d, $^3J_{PC}$ = 12.8 Hz, C_4H), 168.0 (d, $^1J_{PC}$ = 49.2 Hz, C_2, C_6).

^{31}P NMR (CD_2Cl_2): 210.7 (s).

CI-MS(NH_3): *m/z*: 265 [M+1]

IR(KBr): (selected data): 738, 963, 1038, 1159, 1263, 1466, 1641, 2873, 2933, 2962 cm^{-1}.

III.2. Chapter 2

III.2.a. Synthesis of gold nanoparticles AuNP(III-7)

A solution of phosphinine **III-7** (27 mg, 0.1 mmol) and [(tht)AuCl] (32 mg, 0.1 mmol) was stirred for 15 min in THF (5 mL) at room temperature. A solution of $NaBH_4$ (38 mg, 1 mmol) in H_2O (1 mL) was added to the solution of the gold precursor rapidly in one single portion. The color of the reaction mixture changed immediately from colorless to dark brown. The reaction mixture was stirred for 1 h in a Schlenk tube under a flux of nitrogen. The reaction mixture was diluted with H_2O (10 mL). The nanoparticles were extracted from this solution with dichlormethane (3 x 10 mL).

The sample for TEM analysis were prepared from this solution by evaporating a drop of this solution on a microscopy grid.

The nanoparticles were isolated as red-brown solid after evaporation of the solvent.

Yield: 20 mg.

III.2.c. AuNP(III-8)

IR(KBr): 803, 1023, 1094, 1262, 1458, 1624, 2870, 2938, 2960 cm^{-1}.

III.2.d. Synthesis of nickel-nanoparticles

A solution of $[Ni(COD)_2]$ (0.072 mmol) and phosphinine in toluene (2 mL) was heated to 120 °C for 2 h. The reaction mixture turned from light red to black.

The sample for TEM analysis were prepared from this solution by evaporating a drop of this solution on a microscopy grid.

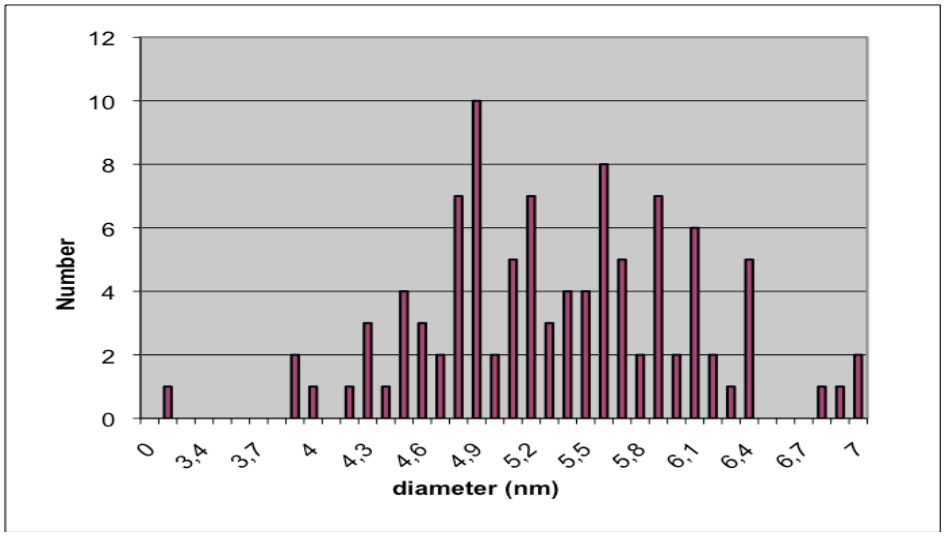
The samples for IR-analysis were thoroughly washed with hexanes until no more free ligand could be observed in solution.

III.2.e. NiNP(1-III-7)

The absolute number of nanoparticles detected was too small to allow statistical treatment of the results.

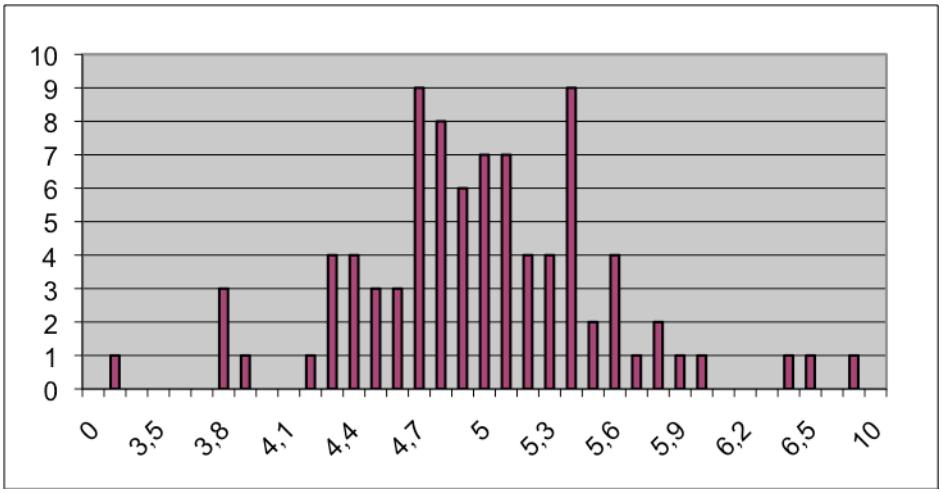
III.2.f. NiNp(0.5-III-8)

The analysis of the TEM images shows a mean diameter of 5 nm with a standard deviation of 0.7 nm on 102 nanoparticles.



III.2.g NiNp(1-III-8)

The analysis of the TEM images shows a mean diameter of 5 nm with a standard deviation of 0.6 nm on 88 nanoparticles.

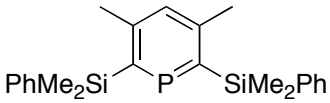


IR(KBr): 803, 1021, 1094, 1262, 2871, 2940, 2963 cm^{-1}.

IV. SYNTHETIC PROCEDURES OF PART IV

IV. 1. Chapter 1

IV.1.a. 2,6-Di(dimethylphenylsilyl)-3,5-dimethyl-phosphinine IV-3



A mixture of 1,3,2-diazaphosphinine (10 mmol) and 1-dimethylphenylsilylpropyne (3.5 g, 20 mmol) in toluene (10 mL) was heated to reflux during 3 days, following the reaction by ^{31}P NMR. After evaporation of the solvent, the resulting oily residue was dispersed in a minimal quantity of hexanes and placed on top of column (80g SiO_2). The title compound was eluted with hexanes (500 mL). After evaporation of the solvents the title compound was obtained as a white solid.

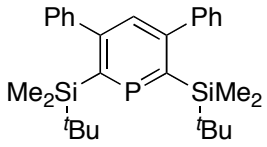
Yield: 2.98 g (7.6 mmol, 76 %)

^1H NMR ($CDCl_3$): δ 0.80 (s, $SiMe_2$, 12H), 2.35 (s, Me, 6H), 7.1 (s, H-4, 1H), 7.35-7.42 (m, CH meta and para of Ph, 6H), 7.58-7.65 (m, CH ortho of Ph, 4H).

^{13}C NMR ($CDCl_3$): δ 27.3 (d, $^3J_{PC}$=5.5 Hz, Me), 127.3 (s, *o*-CH of SiPh), 127.7 (s, *p*-CH of SiPh), 128.1 (d, J_{PC}= 32.4 Hz, C_4), 133.7 (s, *m*-CH of SiPh), 133.8 (s, C ipso of Ph), 135.4 (d, $^2J_{PC}$ =13.5 Hz, C_3, C_5), 165.9 (d, $^1J_{PC}$=80.4 Hz, C_2,C_6).

^{31}P NMR ($CDCl_3$): δ 268.6 (s).

IV.1.b. 2,6-Di(dimethyl-*t*-butyl-silyl)-3,5-diphenyl-phosphinine IV-5



The synthesis of **IV-5** could achieved by the same procedure as for **IV-3** using 1-(dimethyl-^{t}-butyl-silyl)-2-phenylacetylene.

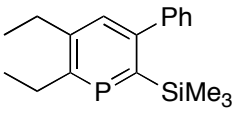
Yield: 1.1 g (2.3 mmol, 73 %)

^{1}H NMR ($CDCl_3$): δ 0.02 (s, 12H, $SiMe_2$) 0.96 (s, 18H, CH3 of ^{t}BuSi), 7.12(s, C4H), 7.28-7.38 (m, 10H, CH of Ph).

^{13}C NMR ($CDCl_3$): δ -1.43(d, J_{PC} = 12.8 Hz, $SiMe_2$), 17.9 (s, C-ipso of ^{t}BuSi), 27.8 (s, CH_3 of ^{t}BuSi), 127.1 (s, *p*-CH of Ph) 127.3(s, *o*-CH of Ph) 129.3(s, *m*-CH of Ph), 133.2 (d, J_{PC} = 22.2 Hz, C_4), 146.0 (s, C-ipso of Ph), 153.1 (d, $^1J_{PC}$ = 93.0 Hz, C_3, C_5), 161.1 (d, $^1J_{PC}$ = 93.0 Hz, C_2, C_6).

^{31}P NMR ($CDCl_3$): δ 282.0 (s).

IV.1.c. 2,3-Diethyl-5-phenyl-6-(trimethylsilyl)-phosphinine IV-7



A mixture of 1,3,2-diazaphosphinine (10 mmol) and 3-hexyne (1.2 mL, 10 mmol) in toluene (10 mL) was heated to 80 °C. After 12 h the complete conversion of 1,3,2-diazaphosphinine monoaza-intermediate **IV-6** at δ = 269.8 ppm) to the monoaza-intermediate **IV-6** (^{31}P NMR: δ = 270.5 ppm) could be observed. 1-trimethylsilyl-3-phenyl-acteylene (2.6 g, 15 mmol) was added and the reaction mixture was heated to 120 °C. The complete conversion of monoazaphosphinine **IV-6** to **IV-7** could be observed by ^{31}P NMR after 12h. After evaporation of the solvent, the resulting oily residue was dispersed in a minimal quantity of hexanes and placed on top of column (80g SiO_2). The title compound was eluted with hexanes (500 mL). After evaporation of the solvents the title compound was obtained an off-white solid.

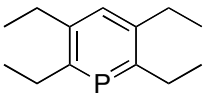
Yield: 2.46 g (8.2 mmol, 82 %)

^{1}H NMR (C_6D_6): δ 0.25 (d, $^{4}J_{PH}$=1.5 Hz, 9H, $SiMe_3$), 1.02 (t, $^{3}J_{HH}$=7.9 Hz, 3H, CH_3 of Et of C_5), 1.29 (t, $^{3}J_{HH}$=7.5 Hz, 3H, CH_3 of Et on C_6), 2.47 (qd, $^{3}J_{HH}$=7.7 Hz, $^{4}J_{PH}$=1.1 Hz, 4H, CH_2 of Et of C_5), 2.98 (dq, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=15.4 Hz, 2H, CH_2 of Et of C_6), 7.07-7.15 (m, 3H, C_4H, CH_{ortho} of Ph), 7.24 (m, 2H, CH_{meta} of Ph), 7.47 (m, 1H, CH_{para} of Ph).

^{13}C NMR (C_6D_6): δ 2.6 (d, $^{3}J_{PC}$=10.5 Hz, $SiMe_3$), 16.1 (d, $^{4}J_{PC}$=1.4 Hz, CH_3 of Et of C_5), 18.8 (d, $^{3}J_{PC}$=10.9 Hz, CH_3 of Et on C_6), 27.5 (d, $^{3}J_{PC}$=1.3 Hz, CH_2 of Et of C_5), 28.8 (d, $^{2}J_{PC}$=35.9 Hz, CH_2 of Et of C_6), 127.8 (s, CH_{meta} of Ph), 129.8 (d, $^{4}J_{PC}$=0.9 Hz, CH_{ortho} of Ph), 132.6 (s, CH_{para} of Ph), 133.8 (d, $^{3}J_{PC}$=18.7 Hz, C_4H), 146.9 (d, $^{3}J_{PC}$=4.2 Hz, C_{ipso} of Ph), 148.0 (d, $^{2}J_{PC}$=10.1 Hz, C_5), 153.3 (d, $^{2}J_{PC}$=12.7 Hz, C_3), 166.1 (d, $^{1}J_{PC}$=79.9 Hz, C_2), 171.0 (d, $^{1}J_{PC}$=60.3 Hz, C_6).

^{31}P NMR (C_6D_6): δ 238.3 (s).

IV.1.d. 2,3,5,6-tetraethyl-phosphinine IV-8



A mixture of 1,3,2-diazaphosphinine (1 mmol) and 3-hexyne (0.6 mL, 5 mmol) in toluene (3 mL) was heated to 140 °C in a sealed schlenk tube. The reaction was finished after 7 days. After evaporation of the solvent, the resulting oily residue was dispersed in a minimal quantity of hexanes and placed on top of column (10 g SiO_2). The title compound was eluted with hexanes (200 mL). After evaporation of the solvents the title compound was obtained an off-white solid.

Yield: 120 mg (0.57 mmol, 57 %)

^{1}H NMR (C_6D_6): δ 1.09 (t, $^{3}J_{HH}$=7.6 Hz, 6H, CH_3 of Et of C_3, C_5), 1.29 (t, $^{3}J_{HH}$=7.5 Hz, 6H, CH_3 of Et of C_2, C_6), 2.51 (qd, $^{3}J_{HH}$=7.6 Hz, $^{4}J_{PH}$=1.2 Hz, 4H, CH_2 of Et of C_3, C_5), 2.92 (dq, $^{3}J_{HH}$=7.5 Hz, $^{3}J_{PH}$=15.9 Hz, 4H, CH_2 of Et on C_2, C_6), 7.01 (d, $^{4}J_{PH}$=3.6 Hz, C_4H).

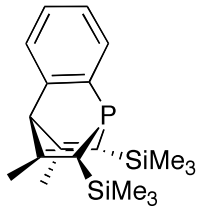
^{13}C NMR (C_6D_6): δ 16.3 (d, $^{4}J_{PC}$=1.5 Hz, CH_3 of Et of C_3, C_5), 18.6 (d, $^{3}J_{PC}$=11.6 Hz, CH_3 of Et of C_2, C_6), 27.3 (d, $^{3}J_{PC}$=1.6 Hz, CH_2 of Et of C_3, C_5), 28.7 (d, $^{2}J_{PC}$=36.1 Hz, CH_2 of Et of C_2, C_6), 133.7 (d, $^{3}J_{PC}$=15.5 Hz, C_4H), 146.1 (d, $^{2}J_{PC}$=12.7 Hz, C_3, C_5), 170.4 (d, $^{1}J_{PC}$=49.3 Hz, C_2, C_6).^{31}P NMR (C_6D_6): δ 207.6 (s).

IV.1.e. General procedure for the synthesis of phosphabarrelenes with o-bromofluorobenzene

2-Bromofluorobenzene (0.57 mL, 5.21 mmol) was slowly added to a mixture of phosphinine **IV-9** (1.00 g, 3.72 mmol) and magnesium turnings (135.7 mg, 5.58 mmol) in THF

(20 mL) at room temperature. The reaction mixture is stirred during 4 h at room temperature. The solvent was evaporated and the resulting residue was extracted with hexanes (3 x 5 mL). After evaporation of the solvent the title compound was obtained as an off-white crystalline solid. Further purification could be performed by recrystallization from MeOH, when needed.

IV.1.f. Phosphabarrelene IV-9



Yield: 960.2 mg (2.79 mmol, 75 %).

Elemental analysis for [$C_{19}H_{29}PSi_2$]: Calculated: C: 66.2; H: 8.5. Found: C 66.4; H, 8.5.

^{1}H NMR ($CDCl_3$): δ 0.20 (s, 18 H, $SiMe_3$), 2.20 (s, 6H, Me), 4.95 (s, 1H, C_4H), 7.05(t, $^3J_{HH}$= 7.0 Hz, 1H, C_9H), 7.13(t, $^3J_{HH}$=7.2 Hz, 1H, $C_{10}H$), 7.36 (d, $^3J_{HH}$= 7.2 Hz, 1H, $C_{11}H$), 7.60(t, $^3J_{HH}$=7.2 Hz, 1H C_8H).

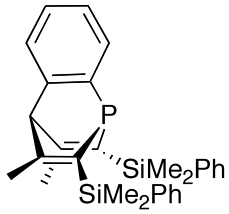
^{13}C NMR($CDCl_3$): δ 0.5 (d+ sat $^3J_{PC}$=7.3 Hz, $^1J_{SiC}$=52.8 Hz, $SiMe_3$), 24.2 (d, $^3J_{PC}$= 2.9 Hz, Me), 71.5 (d, $^3J_{PC}$= 9.4 Hz, C_4H), 123.7 (d, $^3J_{PC}$= 0.9 Hz, $C_{11}H$), 124.4 (d, $^4J_{PC}$=11.5 Hz, $C_{10}H$), 126.4 (d, $^3J_{PC}$=1.5 Hz, C_9H), 129.8 (d, $^2J_{PC}$= 36.1 Hz, C_8H), 135.9 (d, $^1J_{PC}$=46.2 Hz, C_2,C_6), 143.1 (d, $^2J_{PC}$=20.3 Hz, C_{12}), 148.3(d, $^1J_{PC}$=3.6 Hz, C_7), 167.3 (d, $^2J_{PC}$=4.4 Hz, C_3,C_5).

^{31}P NMR($CDCl_3$): δ -60.1(s).

HRMS EI+: 344.1551 (calcd 344.1545 for $C_{19}H_{29}PSi_2$)

Single crystals were grown by recrystallization of **IV-9** from methanol.

IV.1.g. Phosphabarrelene IV-10



Yield: 1.83 g (3.9 mmol, 78 %)

^{1}H NMR (CD_2Cl_2): δ 0.40-0.45 (m, 12H, $SiMe_2$) 2.10(s, 6H, Me), 5.01 (s, 1H, C_4H), 7.09-7.18 (m, 2H, C_9H and $C_{10}H$), 7.25-7.42 (m, 11H, 10 CH of Ph and $C_{11}H$), 7.55 (m, 1H, C_8H).

^{13}C NMR (CD_2Cl_2): 24.3 (d, $^{3}J_{PC}$=2.5 Hz, Me), 71.6 (d, $^{3}J_{PC}$=8.7 Hz, C_4H), 124.0 (s, $C_{11}H$), 124.4(d, J_{PC} = 11.5 Hz, $C_{10}H$), 126.5(s, C_9H), 127.6 (s, *o*-CH of SiPh), 127.9 (s, CH of Ph), 128.7 (s, *p*-CH of SiPh), 128.9 (s, C_{ipso} of Ph), 129.0 (s, CH of Ph), 129.8 (d, $^{2}J_{PC}$=36.4 Hz, C_8H), 133.3 (s, C ipso of SiPh), 133.8 (s, *m*-CH of SiPh), 133.9 (d, $^{1}J_{PC}$=45.8 Hz, C_2, C_6) 134.1 (s, CH of Ph), 143.0 (d, $^{2}J_{PC}$=20.7 Hz, C_{12}), 148.1 (d, $^{2}J_{PC}$=2.9 Hz, C_7), 170.1 (d, $^{1}J_{PC}$=3.8 Hz, C_3, C_5).

^{31}P NMR (CD_2Cl_2): δ -59.5 (s).

IV.1.h. Phosphabarrelene IV-11

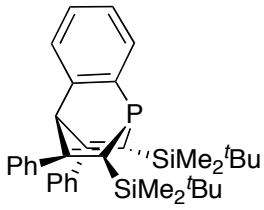
Yield: 150 mg (0.47 mmol, 63%)

^{1}H NMR (C_6D_6): δ 0.22 (s, 18H, $SiMe_3$), 5.27 (t, $^{3}J_{PC}$=6.2 Hz, 1H, C_4H), 6.91 (m, 1H, $C_{10}H$), 7.00 (m, 1H, C_9H), 7.31 (m, 1H, $C_{11}H$), 7.58 (m, 2H, C_3H, C_5H), 7.77 (m, 1H, C_8H), 8.01 (m, 1H).

^{13}C NMR (C_6D_6): δ 0.34 (d, $^{3}J_{PC}$=6.0 Hz, $SiMe_3$), 57.1 (d, $^{3}J_{PC}$=9.7 Hz, C_4H), 124.9 (d, $^{4}J_{PC}$=12.1 Hz, $C_{10}H$), 125.2 (s, $C_{11}H$), 127.5 (d, $^{3}J_{PC}$=1.6 Hz, C_9H), 131.7 (d, $^{2}J_{PC}$=36.7 Hz, C_8H), 138.7 (d, $^{1}J_{PC}$=12.0 Hz. C_2,C_6), 143.1 (d, $^{2}J_{PC}$=20.5 Hz, C_{12}), 149.4 (d, $^{1}J_{PC}$=47.0 Hz, C_7), 157.9 (d, $^{2}J_{PC}$=4.5 Hz, C_3, C_5).

^{31}P NMR (C_6D_6): δ -78.6 (s).

IV.1.i. Phosphabarrelene IV-12



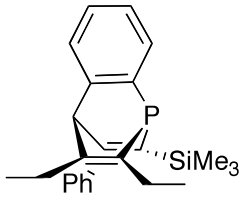
Yield: 213 mg (0.49 mmol, 80 %).

^{1}H NMR (CD_2Cl_2): δ -0.40 (s, 6H, $SiMe_2$), -0.06 (s, 6H, $SiMe_2$), 0.83 (s, 18H, Si^tBu), 5.44 (d, J_{PH} = 1.5 Hz, C_4H), 7.01 (m, CH of Ph), 7.15 (m, C_9H, 1H), 7.21 (m, $C_{10}H$, 1H), 7.28 (m, CH of Ph, 2H), 7.35 (m, $C_{11}H$, 1H), 7.76 (s, C_8H, 1H).

^{13}C NMR (CD_2Cl_2): δ -3.8 (m, $SiMe_2$), 18.1 (s, C ipso of Si^tBu), 27.5 (d, J_{PC} = 4.2 Hz, CH_3 of Si^tBu), 73.3 (d, $^3J_{PC}$= 6.4 Hz, C_4H), 124.3 (d, J_{PC}=1.1 Hz, $C_{11}H$), 124.4 (d, $^3J_{PC}$=11.3 Hz, C_9H), 126.9 (d, $^4J_{PC}$= 0.6 Hz, $C_{10}H$), 127.0 (s, CH ortho of Ph), 127.8 (m, CH meta and para of Ph), 130.7 (d, $^2J_{PC}$=35.7 Hz, C_8H), 139.4 (d, J_{PC}= 53.8 Hz, C_2, C_6), 142.9 (d, J_{PC}= 22.3 Hz, C_{12}), 144.5 (d, J_{PC}= 3.1 Hz, C ipso of Ph), 148.0 (d, J_{PC}= 3.0 Hz, C_7), 172.6 (d, J_{PC}= 2.9, C_3, C_5).

^{31}P NMR (CD_2Cl_2): δ -54.8 (s).

IV.2.j. Phosphabarrelene IV-13



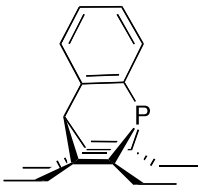
Yield: 400 mg (1.06 mmol, 60 %).

^{1}H NMR (CD_2Cl_2): δ 0.1 (d, $^4J_{PH}$=1.0 Hz, 9H, $SiMe_3$), 1.11 (t, $^3J_{HH}$=7.5 Hz, 3H, CH_3 of Et of C_5), 1.23 (t,d $^3J_{HH}$=7.6 Hz, J_{PH}=0.8 Hz, 3H, CH_3 of Et of C_6), 2.32 (m, 4H, CH_2 of Et), 5.48 (s, 1H, C_4H), 7.20 (m, 3H, C_9H, CH of Ph), 7.31 (m, 1H, $C_{10}H$), 7.43-7.52 (m, 3H, CH of Ph), 7.49 (m, 1H, $C_{11}H$), 7.69 (t, J_{HH}=7.4 Hz, 1H, C_8H).

^{13}C NMR (CD_2Cl_2): δ 0.23 (d, $^3J_{PC}$=1.1 Hz, $SiMe_3$), 13.5 (d, $^4J_{PC}$=0.8 Hz, CH_3 of Ethyl on C_5), 14.8 (d, $^3J_{PC}$=8.0 Hz, CH_3 of Ethyl on C_6), 25.6 (d, $^2J_{PC}$=34.0 Hz, CH_2 of Ethyl on C_6), 26.4 (d, $^3J_{PC}$=2.0 Hz, CH_2 of Ethyl on C_5), 68.2 (d, $^3J_{PC}$=4.1 Hz, C_4H), 124.5 (m, CH of Ph and $C_{11}H$), (d, $^4J_{PC}$=11.7 Hz, $C_{10}H$), 127.4 (d, $^3J_{PC}$=1.6 Hz, C_9H), 127.5 (m, CH of Ph), 128.5 (CH of Ph), 131.0 (d, $^2J_{PC}$=35.8 Hz, C_2), 131.7 (m, C_8H), 142.2 (d, $^2J_{PC}$=5.5 Hz, C_{12}), 142.7 (d, J= 7.2 Hz, C_6), 144.6 (d, $^3J_{PC}$=3.7 Hz, C_{ipso} of Ph), 148.9 (d, $^1J_{PC}$=3.6 Hz, C_7), 155.1 (d, $^2J_{PC}$=4.6 Hz, C_5), 171.7 (d, $^2J_{PC}$=3.7 Hz, C_3).

^{31}P NMR (CD_2Cl_2): δ -59.1 (s).

IV.1.k. Phosphabarrelene IV-14



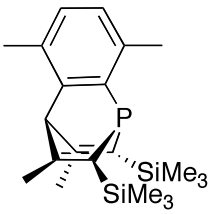
Yield: 320 mg (1.13 mmol, 55 %)

^{1}H NMR (CD_2Cl_2): δ 0.96 (td, $^{4}J_{PH}$=0.8 Hz, $^{3}J_{HH}$=7.4 Hz, 6H, CH_3 of Et of C_2, C_6), 0.98 (t, $^{3}J_{HH}$=7.6 Hz, 6H, CH_3 of Et of C_3, C_5), 2.29 (m, 8H, CH_2 of Et), 4.71 (s, 1H, C_4H), 6.96 (m, 1H, C_{10}H), 7.05 (m, 1H, C_9H), 7.30 (m, 1H, C_{11}H), 7.56 (m, 1H, C_8H).

^{13}C NMR (CD_2Cl_2): δ 13.2 (s, CH_3 of Et on C_3,C_5), 14.7 (d, $^{3}J_{PC}$=7.7 Hz, CH_3 of Et of C_2,C_6), 25.8 (d, $^{2}J_{PC}$=33.0 Hz, CH_2 of Et of C_2,C_6), 26.2 (d, $^{3}J_{PC}$=2.3 Hz, CH_2 of Et of C_3,C_5), 63.1 (d, $^{3}J_{PC}$=1.8 Hz, C_4H), 124.0 (d, $^{3}J_{PC}$=0.9 Hz, C_{11}H), 124.2 (d, $^{4}J_{PC}$=11.6 Hz, C_{10}H),127.1 (d, $^{3}J_{PC}$=1.8 Hz, C_9H), 130.6 (d, $^{2}J_{PC}$=35.1 Hz, C_8H), 132.6 (br, C_2, C_6) 143.2 (d, $^{2}J_{PC}$=14.6 Hz, C_{12}), 152.4 (d, $^{1}J_{PC}$=3.1 Hz, C_7), 155.7 (d, $^{2}J_{PC}$=5.3 Hz, C_3,C_5).

^{31}P NMR (CD_2Cl_2): δ -59.3 (s).

IV.1.l. Phosphabarrelene IV-17



A mixture of 2,6-di(trimethylsilyl)-3,5-methyl-phosphinine (100 mg, 0.37 mmol), 2-bromo-3,5-dimethyl-phenyltriflate (173.2 mg, 0.52 mmol) and magnesium turnings (15 mg, 0.6 mmol) in THF (10 mL) was heated to 60 °C. The reaction was followed by 31P-NMR. After complete conversion of the phosphinine, the reaction mixture was taken to dryness and the resulting residue was extracted with hexanes (3 x 10 mL). The desired product could be observed as a white solid after evaporation of the solvent.

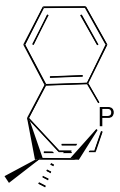
Yield: 83 mg (0.22 mmol, 60 %).

^{1}H NMR: δ 0.29 (s, 18H, $SiMe_3$), 2.00 (d, 6H, 3,5-Me), 2.31 (s, 3H, 11-Me), 2.70 (s, 3H, 8-Me), 5.16 (d, J_{PC}= 1.5 Hz, C_4H), 6.73-6.74 (m, 2H, C_9H, C_{10}H).

^{13}C NMR: δ 0.39 (d+sat, $^{3}J_{PC}$= 7.4 Hz, $^{1}J_{SiC}$= 52.0 Hz, $SiMe_3$), 24.6 (d, J_{PC} = 2.9 Hz, 3,5-Me), 19.2 (s, Me), 21.0 (d, J_{PC}= 19.5 Hz, Me), 67.5 (d, J_{PC}= 8.8 Hz, C_4H), 125.4 (d, J_{PC}= 6.0 Hz, CH), 128.2 (CH), 129.2 (), 136.0 (d, J_{PC} = 46.8 Hz), 137.0 (d, J_{PC}= 25.7 Hz,), 142.0 (d, J_{PC}= 21.6 Hz, C_{12}), 146.6(d, J_{PC}= 4.0 Hz, C_7), 168.1 (d, J_{PC}= 3.5 Hz, C_3, C_5).

^{31}P NMR: δ -70.3 (s).

IV.1.m. Phosphabarrelene IV-19



A mixture of ligand **IV-9** (20 mg, 0.06 mmol) and [$(Bu_4N)F.H_2O$] (76 mg, 0.24 mmol) in THF (2 mL) was stirred for 24 h at 60 °C. After return to r.t. the reaction mixture was taken to dryness and the resulting residue was extracted with hexanes (3 x 5 mL). The filtrate was extracted with H_2O (3 x 10 ml) and the organic layer was dried over anhydrous $MgSO_4$. The product could be obtained as an off white solid after evaporation of the solvent.

Yield: 8 mg (0.04 mmol, 67 %)

^{1}H NMR: δ 1.81 (s, 6H, 3,5-Me), 4.32 (s, 1H, C_4H), 6.40 (d, $^{2}J_{PH}$ = 53.4 Hz, C_2H, C_6H), 6.91-7.06 (m, 2H C_9H and $C_{10}H$) 7.20 (m, 1H, $C_{11}H$), 7.75-7.84 (m, 1H, C_8H).

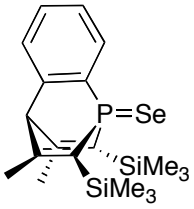
^{13}C NMR: δ 23.7 (s, 3,5-Me), 65.1 (d, $^{3}J_{PC}$ = 2.7 Hz, C_4H), 124.4-124.9 (m, $C_{10}H$ and $C_{11}H$), 126.8 (br, C_9H) 128.4 (C_2, C_6) 131.4 (d, $^{2}J_{PC}$ = 36.2 Hz, C_8), 144.1 (d, J_{PC}= 12.1 Hz, C_{12}), 149.6 (d, J_{PC}= 4.3 Hz, C_7), 161.6 (d, J_{PC}= 5.8 Hz, C_3, C_5).

^{31}P NMR: δ -79.9 (dt, $^{2}J_{PH}$ = 53.4 Hz, $^{3}J_{PH}$= 7.4 Hz).

IV.1.n. General procedure for the preparation of phosphabarrelene selenides

A mixture of phosphabarrelene **IV-9** (20 mg, 0.058 mmol) and selenium (40 mg) in toluene was heated under reflux. The reaction was followed by ^{31}P NMR. After the consumption of all starting material the reaction mixture was filtered through a plug of celite. The product was obtained as a colorless crystalline solid by slow evaporation of the solvent.

IV.1.o. Phosphabarrelene selenide IV-21



Yield: 24.1 mg (0.057 mmol, 98 %)

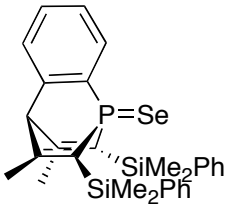
^{1}H NMR ($CDCl_3$): δ 0.38(s, 18H, $SiMe_3$), 2.24(s, 6H, Me), 4.73 (d, J(P-C)= 4.3 Hz, 1H, H-4), 7.19-7.36 (m, 3H, H-9, H-10, H-11), 8.02 (dd, J(H-H)= 7.1 Hz, J(P-H)= 12.8 Hz, 1H, H-8),

^{13}C NMR ($CDCl_3$): δ 2.6 (d, J(P-C)=2.1 Hz, $SiMe_3$), 24.5 (d, J(P-C)=15.0 Hz, Me), 68.4 (d, J(P-C)=44.5 Hz, C_4H), 122.9 (d, J_{PC} =5.9 Hz, $C_{11}H$),125.5 (d, J_{PC} = 12.7 Hz, $C_{10}H$), 127.9 (d, J_{PC} = 2.3 Hz, C_9H), 128.3 (d, J_{PC} = 10.2 Hz, C_8H), 131.3 (d, J_{PC} = 14.8 Hz, C_{12}), 135.3 (m, C_2, C_6), 142.9 (d, J_{PC} =1.9 Hz, C_7), 168.8 (d, J_{PC} =8.6 Hz, C_3, C_5).

^{31}P NMR ($CDCl_3$): δ 4.3 (s +sat, $^{1}J_{PSe}$=772 Hz)

HRMS EI^{+}: 424.0711 (calcd 424.0711 for $C_{19}H_{29}PSi_2Se$)

IV.1.p. Phosphabarrelene selenide IV-22



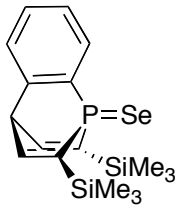
Yield: 28 mg (0.05 mmol, 92 %)

^{1}H NMR ($CDCl_3$): δ 0.54 (s, 6H, $SiMe_2$), 0.65 (s, 6H, $SiMe_2$), 1.80 (s, 6H, Me), 4.56 (d, J_{PC} = 3.9 Hz, C_4H), 7.08-7.43 (m, C_9H, $C_{10}H$, $C_{11}H$ and CH of Ph) 7.92-8.00 (m, 1H, C_8H).

^{13}C NMR ($CDCl_3$): δ 0.83 (s, $SiMe_2$), 1.13 (s, $SiMe_2$), 24.9 (d, J_{PC} = 13.8 Hz, Me), 68.8 (d, J_{PC} = 44.0 Hz, C_4H), 123.0 (d, J_{PC} = 5.9 Hz, $C_{11}H$), 125.7 (d, J_{PC} = 12.8 Hz, C_9H) 128.3 (br, $C_{10}H$), 128.5 (d, J_{PC} = 10.4 Hz, C_8H) 134.9 (m, C_2, C_6), 143.0 (s, C_7), 170.9 (m, C_3, C_5).

^{31}P NMR ($CDCl_3$): δ 4.8 (s + sat, $^{1}J_{31P77Se}$= 776 Hz).

IV.2.q. Phosphabarrelene selenide IV-23



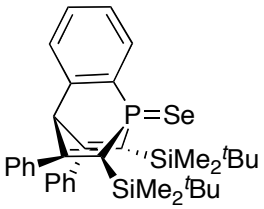
Yield: 24.0 mg (0.06 mmol, 96 %).

^{1}H NMR ($CDCl_3$): δ 0.27 (s, 18H, $SiMe_3$), 5.37 (t, $^{3}J_{HH}$ = 6.4 Hz, C_4H), 7.15-7.30 (m, C_9H, $C_{10}H$, $C_{11}H$) 7.59 (dd, J_{HH} = 6.4 Hz, J_{PC} = 37.2 Hz, C_3H, C_5H), 8.05 (m, C_8H).

^{13}C NMR ($CDCl_3$): δ -0.53 (s, $SiMe_3$), 53.4 (d, J_{PC} = 47.3 Hz, C_4H), 124.1 (d, J_{PC} = 5.6 Hz, $C_{11}H$), 125.5 (d, J_{PC} = 12.5 Hz, C_9H), 128.3 (s, $C_{10}H$), 129.1 (d, J_{PC} = 10.1 Hz, C_8H), 135.4 (m, C_2, C_6), 143.7 (m, C_7 and C_{12}) 158.9 (d, J_{PC} = 10.2 Hz, C_3H, C_5H),

^{31}P NMR ($CDCl_3$): δ -2.7 (s + sat, $^{1}J_{31P77Se}$= 787 Hz).

IV.2.r. Phosphabarrelene selenide IV-24



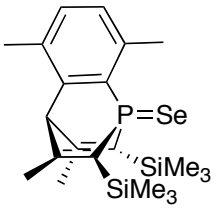
Yield: 38 mg (0.06 mmol, 94 %).

^{1}H NMR ($CDCl_3$): δ 5.19 (d, J_{PC} = 4.1 Hz, C_4H), 6.60-7.51 (m, C_9H, $C_{10}H$, $C_{11}H$ and CH of Ph), 8.23 (m, C_8H).

^{13}C NMR ($CDCl_3$): δ -0.2 (m, $SiMe_2$), 18.2 (s, C_{ipso} of Si^{t}Bu), 29.2 (Me of Si^{t}Bu), 70.2 (d, J_{PC} = 40.2 Hz, C_4H), 123.3 (d, J_{PC} = 6.0 Hz, $C_{11}H$), 125.6 (d, J_{PC} = 12.5 Hz, C_9H), 126.6 (s, CH of Ph), 127.8 (s, CH of Ph), 128.2 (s, CH of Ph), 128.4 (s, $C_{10}H$), 129.6 (d, J_{PC} = 9.9 Hz C_8H), 136.3 (d, J_{PC} = 9.6 Hz, C_7) 143.1 (s, C_{ipso} of Ph), 143.2 (d, J_{PC} = 14.9, C_{12}), 173.7 (d, J_{PC} = 8.8 Hz, C_3, C_5).

^{31}P NMR ($CDCl_3$): δ -2.7 (s + sat, $^{1}J_{31P77Se}$= 787 Hz).

IV.2.s. Phosphabarrelene selenide IV-25



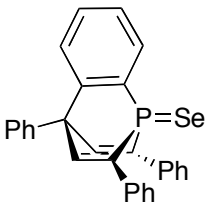
Yield: 23.5 mg (0.05 mmol, 97 %).

^{1}H NMR ($CDCl_3$): δ 0.37 (d, $^{4}J_{PH}$=0.7 Hz, 18H, $SiMe_3$), 2.21 (dd, J=0.7 Hz, J=1.8 Hz, 6H, Me), 2.43 (s, 3H, C_{11}-Me), 3.00 (s, 3H, C_8-Me), 4.99 (d, $^{4}J_{PH}$=4.8 Hz, 1H, C_4H), 6.71 (dd, $^{3}J_{HH}$=7.9 Hz, $^{4}J_{PH}$=5.0 Hz, 1H, C_9H), 6.88 (d, $^{3}J_{HH}$=7.9 Hz, C_{10}H).

^{13}C NMR ($CDCl_3$): δ 3.4 (d, $^{3}J_{PC}$=2.0 Hz, $SiMe_3$), 19.6 (d, $^{4}J_{PC}$=1.4 Hz, C_{11}-Me), 21.2 (d, $^{3}J_{PC}$=3.6 Hz, C_8-Me), 25.2 (d, $^{3}J_{PC}$=14.7 Hz, Me), 65.0 (d, $^{3}J_{PC}$=45.6 Hz, C_4H), 128.5 (d, $^{4}J_{PC}$=9.4 Hz, C_{10}H), 129.5 (d, $^{3}J_{PC}$=5.6 Hz, C_9H), 129.7 (d, $^{3}J_{PC}$=12.1 Hz, C_{11}), 130.0 (d, $^{2}J_{PC}$=2.7 Hz, C_8), 134.0 (d, $^{1}J_{PC}$=17.6 Hz, C_2, C_6), 142.8 (d, $^{2}J_{PC}$=2.7 Hz, C_{12}), 146.5 (d, $^{1}J_{PC}$=2.7 Hz, C_7), 168.6 (d, $^{2}J_{PC}$=8.9 Hz, C_3, C_5).

^{31}P NMR ($CDCl_3$): δ 1.1 (s + sat, $^{1}J_{31P77Se}$=762 Hz).

IV.2.t. Phosphabarrelene selenide IV-26



Yield: 22.7 mg (0.05 mmol, 95 %).

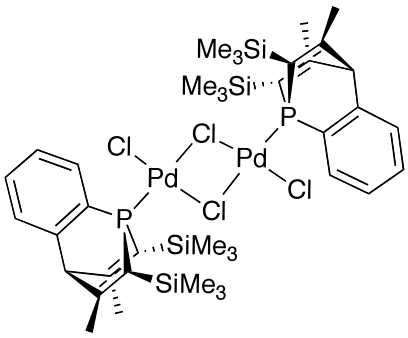
^{1}H NMR ($CDCl_3$): δ 6.62 (m, C_{11}H), 7.15-7.80 (m, 19H, C_8H, C_9H, C_{10}H, CH of Ph), 7.98 (d, J_{PC} = 29.8 Hz, 2H, C_3H, C_5H)

^{13}C NMR ($CDCl_3$): δ 58.5(d, J_{PC} = 21.8 Hz, C_4H), 123.9 (d, J_{PC} = 6.2 Hz, C_{11}H), 125.1 (d, J_{PC} = 13.2 Hz, C_9H) 126.1-130.2 (m, C and CH of Ph), 135.4 (d, J_{PC} = 10.6 Hz, C_2, C_6), 137.9 (C of Ph), 139.2 (s, C_{12}), 145.6 (s, C_7), 149.5 (s, C_3H, C_5H).

^{31}P NMR ($CDCl_3$): δ 6.6 (s + sat, $^{1}J_{31P77Se}$=840 Hz).

IV.2. Chapter 2

IV.2.a. Complex IV-27



A suspension of ligand **IV-9** (34.5 mg, 0.10 mmol) and [(COD)$PdCl_2$] (mg, 0.10 mmol) in toluene is stirred for 30 min. at 80 °C. After return to r.t. the orange precipitate is filtered and rinsed twice with hexanes (2 mL). The orange solid was dried under vacuum.

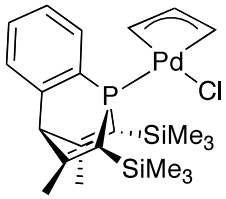
Yield: mg (0.045 mmol, 90 %).

^{1}H NMR: δ 0.59 (s, 18H, $SiMe_3$), 2.19 (s, 6H, CH_3), 4.67 (s, C_4H), 7.00 (m, 2H, CH), 7.12 (m, 1H, CH), 8.46 (t, J=7.6 Hz, 1H, CH).

^{13}C NMR: δ 5.5 ($SiMe_3$), 28.1 (d, $^{3}J_{PC}$=13.5 Hz, Me), 68.2 (d, $^{3}J_{PC}$= 38.4 Hz, C_4H), 123.8 (d, $C_{11}H$), 125.5 (d, $^{4}J_{PC}$ = 10.9 Hz, $C_{10}H$), 127.5 (s, C_9H), 132.2 (m, C_8H), 133.5 (d, J_{PC} = 12.3 Hz, C_{12}), 136.4 (d, J_{PC} = 41 Hz, C_7), 167.6 (d, J_{PC} = 11.6 Hz, C_3, C_5).

^{31}P NMR: δ 2.1 (s).

IV.2.b. Complex IV-29



A mixture of ligand **IV-9** (34.5 mg, 0.10 mmol) and $[Pd(C_3H_5)Cl]_2$ (18.3 mg, 0.05 mmol) in CH_2Cl_2 (10 mL) was stirred for 15 min at r.t.. The color of the solution turned from light green to pale yellow. The title compound was obtained as an off-white solid after evaporation of the solvent.

Yield: 51.6 mg (0.098 mmol, 98 %).

Elemental composition for [$C_{22}H_{34}PSi_2PdCl$]: Calculated: C: 50.09; H: 6.50. Found: C 49.95; H, 6.53.

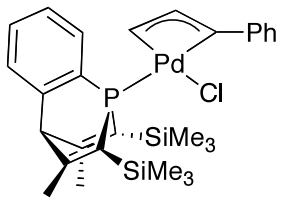
^{1}H NMR($CDCl_3$): δ 0.22-0.34 (m, 18H, $SiMe_3$), 2.27 (s, 6H, Me), 2.98 (d, $^{3}J_{HH}$=11.4 Hz, 1H, $C_{15}H_2$), 3.87 (dd, $^{3}J_{HH}$=10.6 Hz, $^{2}J_{PH}$= 13.3 Hz, 1H, $C_{13}H_2$), 4.40 (d, $^{3}J_{HH}$=5.3 Hz, 1H, $C_{15}H_2$), 4.87 (br, 2H, $C_{13}H_2$ and C_4H) 5.43-5.60 (m, $C_{14}H$), 7.13 (m, 2H, C_9H and $C_{10}H$), 7.30 (m, 1H, $C_{11}H$), 7.77 (m, 1H, C_8H).

^{13}C NMR($CDCl_3$): δ 2.53 (s, $SiMe_3$), 26.1 (d, $^{3}J_{PC}$=9.1 Hz, CH_3), 51.6 (d, $^{2}J_{PC}$=2.5 Hz, CH_2 of allyl), 70.1 (d, $^{2}J_{PC}$=27.4 Hz, C_4H), 79.8 (d, $^{2}J_{PC}$=32.4 Hz, CH_2 of allyl), 115.6 (d, $^{3}J_{PC}$=5.7 Hz, CH of allyl), 124.3(d, J_{PC}=3.2 Hz, $C_{11}H$), 125.3(d, J_{PC}=11.9 Hz, C_9H), 127.5 (d, J_{PC}=2.0 Hz, $C_{10}H$), 129.5 (d, J_{PC}=19.4 Hz, C_8H), 133.2 (dd, J_{PC}=8.1 Hz, $^{1}J_{PC}$=54.1 Hz, C_2,C_6), 139.2 (d, J_{PC}=27.3Hz, C_{12}), 146.9 (d, J_{PC}=2.7 Hz, C_7), 169.9 (dd, J_{PC}=6.6 Hz, J_{PC}=11.1 Hz, C_3, C_5).

^{31}P NMR ($CDCl_3$): δ -6.1 (s).

HRMS EI^{+}: 526.0653 (calcd 526.0660 for $C_{22}H_{34}PSi_2PdCl$).

IV.2.c. Complex IV-30



A mixture of ligand **IV-9** (34.5 mg, 0.10 mmol) and $[Pd(PhC_3H_4)Cl]_2$ (26 mg, 0.05 mmol) in CH_2Cl_2 (10 mL) was stirred for 15 min at r.t.. The color of the solution turned from light yellow to colorless. The title compound was obtained as an off-white solid after evaporation of the solvent.

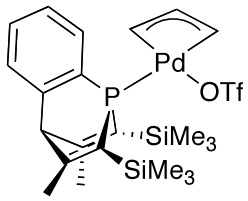
Yield: 57 mg (0.095 mmol, 95 %).

^{1}H NMR (CD_2Cl_2): δ 0.27 (s, 9H, $SiMe_3$), 0.35 (s, 9H, $SiMe_3$), 2.30 (s, 6H, Me), 3.12 (d, $^{3}J_{HH}$=10.7 Hz, 1H, CH_2 of allyl), 4.46 (d, J_{HH}=5.3 Hz, 1H, CH_2 of allyl), 4.93 (d, J_{PH}=2.6 Hz, 1H, C_4H), 5.30-5.42 (m, CHPh), 5.98 (m, 1H, CH_2CH), 7.18 (m, 2H, C_9H, $C_{10}H$), 7.30-7.55 (m, 4H, $C_{11}H$, CH of Ph), 7.60-7.64 (2H, CH of Ph), 7.92 (m, 1H, C_8H).

^{13}C NMR (CD_2Cl_2): δ 1.82 (s, $SiMe_3$), 25.5 (d, J_{PC}=9.0 Hz, Me) 47.2 (s, CH_2 allyl), 69.5 (d, J_{PC}=27.6 Hz), 97.6 (d, J_{PC}=30.1 Hz, CH_2CH), 109.1 (d, J_{PC}=6.1 Hz, CHPh), 124.1 (d, J_{PC}=2.5 Hz), 124.8 (d, J=11.9 Hz), 127.0 (s), 127.6-128.0 (m, C_{ipso} of Ph), 128.7 (s), 132.9 (d, J_{PC}=74.4 Hz, C_2, C_6), 137.2 (d, J_{PC}=6.4 Hz), 139.0 (d, J_{PC}=26.6 Hz, C_{12}), 146.8 (d, J_{PC}=2.0 Hz, C_7), 169 (d, J_{PC}=9.6 Hz, C_3, C_5).

^{31}P NMR: δ = -9.0 (s).

IV.2.d. Complex IV-31



A suspension of complex **IV-29** (52.7 mg, 0.10 mmol) and AgOTf (28.3 mg 0.11 mmol) is stirred in CH_2Cl_2 at room temperature for 45 min. The light yellow suspension is filtered through a pad of celite and the resulting solution is taken to dryness.

Yield: mg (0.08 mmol, 83 %).

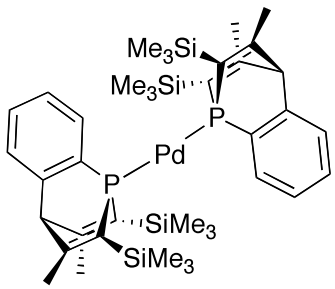
^{1}H NMR: δ 0.30 (s, 18H, $SiMe_3$), 2.28 (s, 6H, CH_3), 3.02(br, 1H, CH_2 of allyl trans to OTf), 4.16 (br, 1H, CH_2 of allyl trans to OTf), 4.34(m, 1H CH_2 of allyl trans to P) 4.93 (d, $^4J_{PH}$=2.8 Hz, C_4H), 5.55 (m, 1H, CH_2 of allyl trans to P), 5.75 (m, 1H, CH of allyl), 7.15-7.2 (m, 2H, CH), 7.36(d, $^3J_{HH}$=6.6 Hz), 7.70 (m, CH).

^{13}C NMR: δ 1.4 (d, $^3J_{PC}$=4 Hz, $SiMe_3$), 25.6 (d, $^3J_{PC}$=9.1 Hz, Me), 48.0 (s, C_aH_2 of allyl) , 70.1 (d, $^3J_{PC}$=28.9 Hz, C_4H), 86.6 (d, J_{PC}=25.8Hz, C_bH_2 of allyl), 116.1 (d, J_{PC}=4.7 Hz, CH of allyl), 124.4(d, J_{PC}=3.4 Hz, $C_{11}H$), 125.3 (d, J_{PC}=12.1 Hz, C_9H), 127.7(d, J_{PC}=2.0 Hz, $C_{10}H$), 129.2 (d, J_{PC}=19.1 Hz, C_8H), 131.6 (br, $C_{2,6}$) 137.4 (d, J_{PC}=31.2 Hz, C_{12}), 145.5 (d, J_{PC}=2.5 Hz, C_7), 170.8 (br, $C_{3,5}$).

^{31}P NMR: δ -12.1 (s).

HRMS EI$^+$: 640.0482 (calcd 640.0492 for $C_{23}H_{34}PSi_2PdSO_3F_3$)

IV.2.e. Complex IV-32



To a mixture of ligand **IV-9** (69.0 mg, 0.20 mmol) and [(COD)$PdCl_2$] (28.5 mg, 0.10 mmol) in acetonitrile (10 mL) cobaltocene (37.8 mg, 0.20 mmol) was added as a solid. The reaction mixture was stirred for 24 h at r.t.. The resulting dark-green suspension was taken to dryness and the residue was extracted with hexanes (10 mL). The product was isolated as a pale yellow solid after evaporation of the solvent.

Yield: 71.6mg (0.09 mmol, 90 %)

Elemental composition for [$C_{38}H_{58}P_2Si_4Pd$] Calculated C, 57.4; H, 6.5. Found: C, 57.35; H,6.4 %.

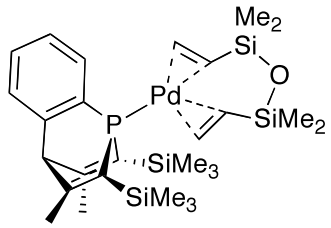
^{1}H NMR (C_6D_6): δ 0.65 (s, 18H, SiMe3); 2.03 (s, 6H, Me), 4.61 (s, 1H, C_4H), 6.94(t, $^3J_{HH}$=7.3 Hz, 1H, C_{10}H), 7.05 (t, $^3J_{HH}$=7.3 Hz , 1H, C_9H), 7.12 (d, $^3J_{HH}$=7.3 Hz, 1H, C_{11}H), 8.85 (*pseudo*-q, $^3J_{HH}$=7.5 Hz , 1H, C_8H).

^{13}C NMR (C_6D_6): δ 2.0 (*pseudo*-t, ΣJ_{PC}=6.3 Hz, $SiMe_3$); 24.0 (*pseudo*-t, ΣJ_{PC}=7.5 Hz, CH_3); 70.3 (*pseudo*-t, Σ*J*PC=22.7 Hz, C_4H) 123.2 (s, C_{11}H), 124.3 (*pseudo*-t, ΣJ_{PC}=13.3 Hz, C_9H), 126.8 (s, C_{10}H), 133.2 (*pseudo*-t, ΣJ_{PC}=30.2 Hz, C_8H), 135.7 (*pseudo*-t, ΣJ_{PC}=15.8 Hz, C_2,C_6), 142.1 (*pseudo*-t, ΣJ_{PC}=20.7 Hz, C_{12}), 146.5 (s, C_7) 169.9 (*pseudo*-t, ΣJ_{PC}=6.5 Hz, C_3,C_5).

^{31}P NMR (C_6D_6): δ -28.8 (s).

Single crystals were grown from a concentrated solution of **IV-32** in hexanes at -20 °C.

IV.2.f. Complex IV-33



To a solution of complex **IV-29** (52.7 mg, 0.1 mmol) in toluene were added consecutively at room temperature, potassium carbonate (14 mg, 0.1 mmol) and phenylboronic acid (12 mg, 0.1 mmol). The solution was stirred at room temperature for 5 min and dvds (50 μl, 0.2 mmol) was added. The reaction mixture was then stirred for 2 h at room temperature. The light yellow solution was taken to dryness and the resulting residue was washed with MeOH (3 x 1 mL).

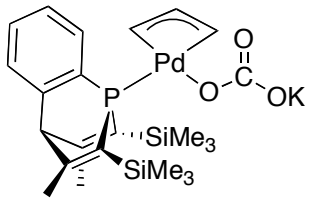
Yield: 41 mg (0.065 mmol, 65 %)

^{1}H NMR (C_6D_6): δ 0.3 (br, $SiMe_2$, $SiMe_3$, 24H), 0.4 (s, $SiMe_2$, 6H) 2.05 (d, J_{PC}= 2.0 Hz, 6H, Me), 3.51 (ddd, J_{PH}=5.3 Hz, J_{HH}=12.6 Hz, J_{PH}=16.2 Hz, CHSiMe$_2$), 3.82 (ddd, J_{PH}=1.4 Hz, J_{HH}=4.7 Hz, J_{PH}=16.2 Hz, CH_2), 4.18 (ddd, J_{PH}=1.4 Hz, J_{HH}=7.9 Hz, J_{HH}=12.6 Hz, CH_2), 4.65 (d, J_{PH}=2.0 Hz, 1H, C_4H), 7.00-7.08 (m, 2H, C_9H, C_{10}H), 7.17-7.23 (m, 1H, C_{11}H), 8.05 (m, 1H, C_8H).

^{13}C NMR (C_6D_6): δ 1.7 (br, $SiMe_2$, $SiMe_3$), 25.2 (d, J_{PC}=6.5 Hz, Me), 66.5-66.9 (m, CH$_2$CHSiMe$_2$), 70.1 (d, J_{PC}=19.5 Hz, C_4H), 123.7 (s, C_{11}), 124.8 (d, J_{PC}=11.9 Hz, C_{10}), 126.9 (s, C_9H), 130.7 (d, J_{PC}=24.9 Hz, C_8H), 135.7 (d, J_{PC}=21.7 Hz, C_2, C_6), 142.7 (d, J_{PC}=16.2 Hz, C_{12}), 146.5 (s, C_7), 169.3 (d, J_{PC}=8.6 Hz, C_3, C_5).

^{31}P NMR (C_6D_6): δ -28.8 (s).

IV.2.g. Complex IV-34



Potassium carbonate (14 mg, 0.1 mmol) was added to a solution of complex **IV-29** (52.7 mg, 0.1 mmol) in toluene. The pale yellow reaction mixture was stirred for 30 min. at room temperature. The resulting suspension was filtered over celite. The pale yellow product could be isolated by evaporation of the solvent under vacuum.

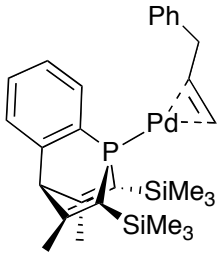
Yield: 53 mg (0.083 mmol, 83 %)

^{1}H NMR (C_6D_6): δ 0.40 (s, 9H, $SiMe_3$), 0.47 (s, 9H, $SiMe_3$), 2.00 (br, 6H, Me), 2.64 (d, J_{HH} = 12.3 Hz, 1H, CH_2 of allyl trans to carbonate), 3.61 (dd, J_{HH}= 10.5 Hz, J_{HH}= 13.8 Hz, 1H, CH_2 of allyl trans to P), 4.14 (d, J_{HH}= 6.3 Hz, 1H, CH_2 of allyl trans to carbonate), 4.65 (d, 1H, C_4H), 4.72 (*pseudo*-t, $\Sigma(J_{PH},J_{HH})$ = 7.5 Hz, CH_2 of allyl trans to P), 5.10 (m, CH of allyl), 6.87-7.00 (m, 2H, C_9H, $C_{10}H$), 7.06 (d, J=6.9 Hz, 1H, $C_{11}H$), 7.76 (m, 1H, C_8H).

^{13}C NMR (C_6D_6): δ 2.4 (s, $SiMe_3$), 23.2 (s, allyl-CH), 25.5 (d, J_{PC}=9.1 Hz, Me), 48.9 (s, allyl-CH_2-trans to carbonate), 69.5 (d, J_{PC}=27.1 Hz, C_4H), 76.8 (d, J_{PC}=34.7 Hz, allyl-CH_2-trans to P), 115.2 (d, J_{PC} = 5.5 Hz, CH of allyl), 123.8 (d, J_{PC}=2.2 Hz, $C_{11}H$), 125.0 (d, J_{PC}=11.9 Hz, C_9H), 127.6 (s, $C_{10}H$), 129.2 (m, C_8H), 134.0 (m, C_2, C_6), 139.7 (d, J_{PC}=24.6 Hz, C_{12}), 147.5 (d, J_{PC}=2.1 Hz, C_7), 168.6 8 (d, J_{PC}=10.7 Hz, C_3, C_5).

^{31}P NMR (C_6D_6): δ -11.0 (s).

IV.2.h. Complex IV-35



After the addition of phenylboronic acid (12 mg, 0.1 mmol) to a mixture of complex **IV-29** (52.7 mg, 0.1 mmol)and potassium carbonate (14 mg, 0.1 mmol) in toluene (2 mL), the color of

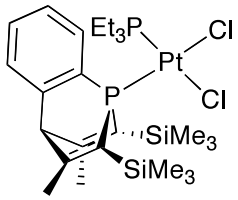
the initially pale yellow solution changed to bright yellow. The resulting suspension was filtered over celite and the product could be isolated as a bright yellow solid after evaporation of the solvent under vacuum.

Yield: 44.8 mg (0.079 mmol, 79 %)

^{1}H NMR (C_6D_6): δ 0.43 (s, 9H, $SiMe_3$), 0.47 (s, 9H, $SiMe_3$), 1.95-2.10 (m, 8H, Me, CH_2), 3.17 (d, J_{PH}= 7.2 Hz, 1H), 3.82 (q, J_{PH}=7.2 Hz, 1H), 4.61 (s, 1H), 4.95 (d, J_{HH}=13.8 Hz, 1H), 6.90-7.18 (m, 8H, CH of Ph, C_9H, $C_{10}H$, $C_{11}H$), 8.21 (m, C_8H, 1H).

^{31}P NMR (C_6D_6): δ -21.0 (s).

IV.2.i. Complex IV-37



A solution of ligand **IV-9** (20 mg, 0.058 mmol) and $[(PEt_3)PtCl_2]_2$ (22.3 mg, 0.029 mmol) in dichloromethane (2 mL) was stirred for 30 min at room temperature. The product could be isolated as a colorless crystalline solid after recrystallization from chloroform.

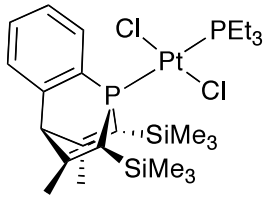
Yield: 41 mg (0.056 mmol, 97 %)

^{1}H NMR ($CDCl_3$): δ 0.39 (s, 18H, $SiMe_3$) 1.20-1.38 (m, 9H, $PCH_2\underline{CH_3}$), 2.24 (br, 6H, Me), 2.25-2.35 (m, $\underline{PCH_2}CH_3$), 6H, 4.73 (d, J_{PC} = 2.6 Hz, 1H, C_4H), 7.05 (m, 2H, C_9H, $C_{10}H$), 7.36 (m, 1H, $C_{11}H$), 8.98 (m, 1H, C_8H).

^{13}C NMR ($CDCl_3$): δ 3.0 (s, $SiMe_3$), 19.0 (d, J_{PC} = 38.2 Hz, $P\underline{CH_2}CH_3$) 26.3 (d, J_{PC} = 10.1 Hz, Me) 69.6 (d, J_{PC} = 29.5 Hz, C_4H), 123.5 (s, $C_{11}H$), 125.1 (d, J_{PC} = 10.4 Hz, C_9H), 126.7 (s, $C_{10}H$), 131.3 (d, J_{PC} = 12.8 Hz, C_8H) 134.2 (m, C_2, C_6), 135.5 (m, C_{12}), 144.3 (s, C_7), 165.9 (d, J_{PC} = 10.0 Hz, C_3, C_5)

^{31}P NMR ($CDCl_3$): δ -19.8 (d+sat, $^{1}J_{PPt}$=3837.0 Hz, $^{2}J_{PP}$=13.9 Hz, PB), 3.5 (d+sat, $^{1}J_{PPt}$=3536.2 Hz, $^{2}J_{PP}$=13.9 Hz, PEt_3).

IV.2.j. Complex IV-38



Yellow crystals of complex **IV-36** were obtained by the recrystallization of compound **IV-35** in a mixture of dichloromethane and diethyl ether (1/1).

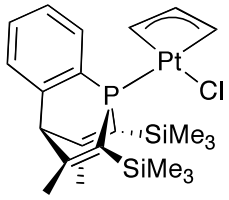
^{1}H NMR ($CDCl_3$): δ 0.44 (s, 18H, $SiMe_3$), 1.20-1.38 (m, 9H, $PCH_2\underline{CH_3}$), 2.00-2.10 (br, 6H, $P\underline{CH_2}CH_3$), 2.26 (s, 6H, Me), 4.30 (s, 1H, C_4H), 7.02-7.30 (m, 3H, C_9H, $C_{10}H$, $C_{11}H$), 7.27 (br, 1H, $C_{11}H$), 8.43 (m, 1H, C_8H).

^{13}C NMR ($CDCl_3$): δ 3.1 (s, $SiMe_3$), 7.6 (s, $PCH_2\underline{CH_3}$), 12.8 (d, J_{PC} = 32.4 Hz, $P\underline{CH_2}CH_3$), 24.3 (m, Me), 64.4 (d, J_{PC}= 21.3 Hz, C_4H), 125.6 (s, $C_{11}H$), 126.0 (d, J_{PC} = 6.2 Hz, C_9H), 129.5 (s, $C_{10}H$), 132.2 (d, J_{PC} = 11.5 Hz, C_8H), 132.6 (m, C_2,C_6) 138.7(m, C_{12}), 144.8 (m, C_7), 169.3 (m, C_3, C_5)

^{31}P NMR ($CDCl_3$): δ -20.5 (d+sat, $^{1}J_{PPt}$=2525.4 Hz, $^{2}J_{PP}$=500.6 Hz, PB), 7.5 (d+sat, $^{1}J_{PPt}$=2585.6 Hz, $^{2}J_{PP}$=500.6 Hz, PEt_3).

Yellow crystals were obtained by slow evaporation of a solution of **IV-35** in chloroform.

IV.2.k. Complex IV-39



Method A:

A suspension of $[Pt(C_3H_5)Cl]_4$ (mg, mmol) and ligand **IV-9** in THF (2 mL) is heated to 60 °C during 4h. The solution is taken to dryness and the title compound is obtained as a white solid.

Single-Crystals suitable for X-Ray-crystal structure analysis were obtained by cooling a concentrated solution to -18 °C.

Yield: (95 %)

Method B:

A suspension of ligand **IV-9**, $[(COD)PtCl_2]$ and allyltributyltin in THF (2 mL) is heated to 60 °C for ca. 1 h. Upon complete conversion of the free ligand as judged by ^{31}P-NMR the solution was taken to dryness and the resulting off-white solid was rinsed twice with hexanes. The title compound is obtained as an off-white powder.

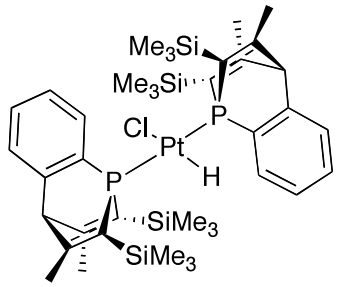
Yield (60 %)

^{1}H-NMR (CD_2Cl_2): δ 0.27 (*pseudo*-d, 18H, $SiMe_3$), 2.30 (s, 6H, Me), 2.46 (m, 1H, allyl-CH_2 trans Cl), 3.19 (m, 1H, allyl-CH_2 trans P), 4.18 (br, 1H, allyl-CH_2 trans Cl), 4.45 (m, 1H, allyl-CH_2 trans P), 4.75-4.90 (m, CH of allyl), 4.92 (d, J_{PH}= 2.9 Hz, C_4H), 7.13-7.17 (m, 2H, C_9H, $C_{10}H$) 7.30-7.34 (m, 1H, $C_{11}H$), 7.71-7.81 (m, 1H, C_8H).

^{13}C-NMR (CD_2Cl_2): δ 2.5 (s, $SiMe_3$), 26.2 (br, Me), 37.6 (s+sat, $^{1}J_{PtC}$=132.6 Hz, allyl-CH_2), 68.7 (allyl-CH_2) 70.0 (C_4H) 105.4 (s+sat, J_{PtC}=28.0 Hz, CH of allyl), 124.5 (d, J_{PC}=3.8 Hz, $C_{11}H$), 125.3 (d, J_{PC}= 11.3 Hz, C_{10}), 127.6 (s, C_9), 129.5 (d, J_{PC}= 16 Hz, C_8), 133.3 (d, J_{PC}= 78.1 Hz, C_2, C_6), 138.7 (d, J_{PC}= Hz, C_{12}), 147.2 (s, C_7), 171.0 (br, C_3, C_5).

^{31}P-NMR (CD_2Cl_2): δ 7.01 (s+sat, J_{PPt}=4577 Hz).

IV.2.l. Complex IV-40



A mixture of ligand **IV-9** (37 mg, 0.1 mmol), [(COD)PtCl2] (20 mg, 0.05 mmol) and Et_3SiH (20 μL, 0.12 mmol) was heated to 60 °C during 5 min in a sealed schlenk tube. The colorless suspension turned pale yellow. The solvent was evaporated under vacuum and the resulting solid were extracted with hexanes (3 x 5 mL). The residue was dissolved in toluene and filtered through a plug of celite. The title compound was obtained as an off-white powder after evaporation of the solvent. Single crystals suitable for X-Ray-crystal structure analysis were obtained from a concentrated solution of **IV-40** in THF at -20 °C.

Yield: 38 mg (0.041 mmol, 82 %)

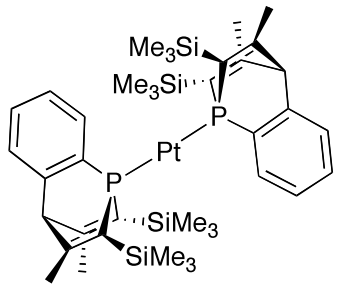
Elemental analysis for **IV-40** calc. for $C_{38}H_{59}ClP_2PtSi_4$: C 49.6, H 6.5, found: C 49.6, H 6.6.

^{1}H-NMR: δ -15.56 (t+sat, J_{PtH}=588.4 Hz, $^{2}J_{PH}$=15.3 Hz, 1H, Pt-H), 0.63 (s, 36H, $SiMe_3$), 1.96 (s, 12H, CH_3), 4.53 (s, 2H, C_4H), 6.93 (t, $^{3}J_{HH}$= 7.3 Hz, 2H, CH), 7.05 (d, C_9H),7.13 ($C_{10}H$), 7.20($C_{11}H$), 9.26 (*pseudo*-q, 2H, C_8H).

13C-NMR: δ 2.8 (s, $SiMe_3$), 25.0 (*pseudo*-t, $\Sigma J_{PP,PC}$=5.5 Hz, Me), 70.3 (*pseudo*-t, $\Sigma J_{PP,PC}$=16.8 Hz, C_4H), 123.2 (br, $C_{11}H$), 124.4 (*pseudo*-t, $\Sigma J_{PP,PC}$=6.8 Hz, $C_{10}H$), ,127.5 (C_9H), 132.8 (C_{12}), 134.6 (C_8H), 138.1 (*pseudo*-t, $\Sigma J_{PP,PC}$=23.1 Hz, C_2, C_6), 145.4 (s, C_7), 169.5 (*pseudo*-t, $\Sigma J_{PP,PC}$=2.9 Hz, C_3, C_5).

^{31}P-NMR: δ -13.0(s+sat, $^{1}J_{PPt}$= 3120 Hz).

IV.2.m. Complex IV-41



Method A:

Cobaltocene (38 mg, 0.2 mmol) was added as a solid to a solution of [(COD)$PtCl_2$] (37 mg, 0.1 mmol) and ligand **IV-9** (70 mg, 0.2 mmol) in MeCN (10 mL) at r.t.. The suspension turned immediately from colorless to intense yellow and after 1h to dark green. After 1 h the reaction mixture was taken to dryness. The residue was extracted with hexanes (3 x 5 mL). The title compound was obtained as a pale yellow powder upon evaporation of the solvent. Colorless crystals were obtained from a concentrated solution of the product in MeCN.

Yield: 84 mg (0.095 mmol, 95%)

Method B:

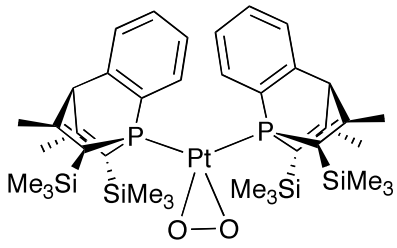
A mixture of phosphabarrelene **IV-9** (34 mg, 0.1 mmol), [(COD)$PtCl_2$] (20 mg, 0.05 mmol) and Et_3SiH (43 μL, 0.26 mmol) was heated to 60 °C during 2 h in a schlenk tube under a flux of nitrogen. The reaction was monitored in ^{31}P NMR.

^{1}H NMR (C_6D_{12}): δ 0.50 (s, 36H, SiMe3), 2.12 (s, 12H, Me), 4.61 (br, 2H, C_4H), 6.90 (m, 4H, C_9H, $C_{10}H$), 7.13 (d, $^{3}J_{HH}$=6.9 Hz, 2H, $C_{11}H$), 8.51 (pseudo-q, $\Sigma J_{HH,PH}$ =5.8 Hz, 2H, C_8H).

^{13}C NMR(C_6D_{12}): δ 3.0 (*pseudo*-t, $\Sigma J_{PP,PC}$=1.8 Hz, $SiMe_3$), 24.8 (*pseudo*-t $\Sigma J_{PP,PC}$=5.0 Hz, Me) 72.6 (*pseudo*-t, J_{PC}=14.6 Hz C_4H), 123.5 (m, C_9H), 124.1 (pseudo-t, J_{PC}=6.2 Hz, $C_{11}H$), 127.2 (m, $C_{10}H$), 134.3 (pseudo-t, J_{PC}=10.0 Hz, C_8H), 136.9 (pseudo-t, J_{PC}=1.1 Hz, C_2, C_6), 142.6 (pseudo-t, J_{PC}=20.7 Hz, C_{12}) 148.5 (s, C_7), 167.3 (pseudo-t, J_{PC}=2.8 Hz C_3, C_5).

^{31}P NMR (C_6D_{12}): δ 5.6 (s+ sat, $^{1}J_{PtP}$=4644 Hz).

IV.2.n. Complex IV-42



Upon exposure of an acetonitrile solution of complex **IV-41** (20 mg, mmol) to oxygen, the formation of brown crystals was observed after 3 days. The crystals are rinsed with acetonitrile and dried under vacuum.

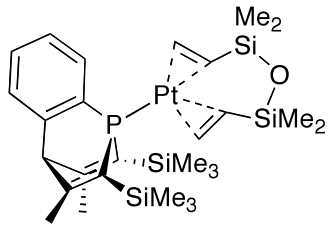
Yield: 21 mg (0.023 mmol, 76 %)

^{1}H NMR: δ 0.58 (s, 9H, $SiMe_3$), 0.68 (s, 9H, $SiMe_3$), 1.89 (s, 3H, Me), 2.06 (s, 3H, Me), 4.46 (s, 2H, C_4H), 6.28 (t, $^{3}J_{HH}$= 6.8 Hz, $C_{10}H$), 6.64 (t, $^{3}J_{HH}$=5.8 Hz, C_9H) 6.87 (d, $^{3}J_{HH}$=5.8 Hz, $C_{11}H$), 7.11 (m, C_8H).

^{13}C NMR: δ 3.1 (d, J_{PC}=2.5 Hz, CH_3 of $SiMe_3$), 3.5 (d, J_{PC}=3.0 Hz, CH_3 of $SiMe_3$), 24.9 (d, J_{PC}=11.1 Hz, CH_3), 25.2 (d, J_{PC}=9.9 Hz, CH_3'), 71.2 (C_4), 71.6 (C_4') 123.2-123.5 (m, $C_{10}H$, $C_{11}H$), 127.6 (d, J_{PC}=27.6 Hz, C_9H), 133.2 (m, C_8H), 135.0 (m, C_2, C_6) 136.9 (d, J_{PC}=42.6 Hz, C_{12}), 144.9 (d, J_{PC}=2.2 Hz, C_7), 168.8 (d, J_{PC}=10.3 Hz, C_3, C_5), 169.6 (d, J_{PC}=10.3 Hz, C_3', C_5').

^{31}P NMR: δ -25.2 (s, +sat, J_{PPt}=4277 Hz).

IV.2.o. Complex IV-43



A mixture of ligand **IV-9** (10 mg, 0.03 mmol) in toluene (200 μL) and [Pt_2(DVDS)$_3$] (313 μl, 2.1-2.4 % solution in xylene, 0.0145 mmol) is heated to 60 °C for 2 min. The complete formation of complex **IV-43** is verified by ^{31}P-NMR spectroscopy. The title compound was obtained as an off-white powder upon evaporation of the volatiles under vacuum. Single crystals, suitable for X-Ray-crystal structure analysis, were obtained by slow evaporation of a solution of **IV-43** in diethyl ether.

Yield: 19 mg (0.026 mmol, 88 %)

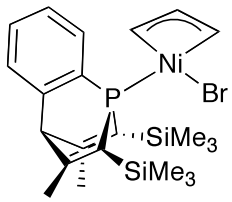
^{1}H NMR (C_6D_6): δ 0.24 (s, 18H, $SiMe_3$), 0.27 (s, 6H, $SiMe_2$), 0.77 (s, 6H, $SiMe_2$) 2.04 (s, 6H, CH_3) 2.63 (m, 2H, CHSiMe$_2$), 3.02 (m, 2H, CH_2CH), 3.41 (m, 2H, CH_2CH), 4.60 (s, C_4H), 6.98 (t, $^{3}J_{HH}$=7.2 Hz $C_{10}H$), 7.06 (t, $^{3}J_{HH}$=7.2 Hz CH-2), 7.16 (d $^{3}J_{HH}$= 7.0 Hz, 1H, $C_{11}H$), 8.24 (t, $^{3}J_{HH}$=8.5 Hz, 1H, C_8H).

^{13}C NMR (C_6D_6): δ 1.8 (br, $SiMe_2$, $SiMe_3$), 25.6 (d, J_{PC}=8.7 Hz, Me), 42.4 (d+sat, J_{PC}=11.5 Hz, J_{PtC}=131.0 Hz, CHSiMe$_2$), 46.6 (d+sat, J_{PC}=5.7 Hz, J_{PtC}=160.3 Hz, CH_2CHSiMe$_2$), 69.6 (d,

J_{PC}=25.9 Hz, C_4H), 123.7 (d, J_{PC}=3,4 Hz, C_{11}H), 124.9(d, J_{PC}=11.7 Hz), 127.0 (d, J_{PC}=2.0 Hz, C_{10}H), 129.9 (m, C_8H), 142.3 (d, J_{PC}=29.8 Hz, C_2, C_6), 146.6 (d, J_{PC}=1.9 Hz, C_7), 169.9 (d+ sat, J_{PC}=9.4 Hz, J_{PtC}=39.7 Hz, C_3, C_5).

^{31}P NMR (C_6D_6): δ -16.71 (s +sat, J_{PtP}=3764 Hz).

IV.2.p. Complex IV-45

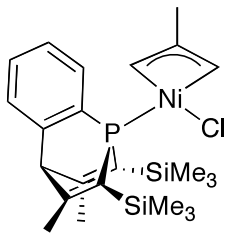


Allylbromide (10 μL, 0.11 mmol) was added to a solution of ligand **IV-9** (34.4 mg, 0.1 mmol) and [Ni(COD)$_2$] (27.5 mg, 0.1 mmol) in toluene (2 mL) at -78 °C. The color changed from yellow to orange immediately. After return to room temperature, the solvent was evaporated under vacuum and the resulting residue was rinsed with hexanes (3 x 1 mL). The product was obtained as a pale orange powder after drying the solid under vacuum.

Yield: 37 mg (0.07 mmol, 70 %)

^{31}P NMR (C_6D_6): δ -12.7 (s)

IV.2.q. Complex IV-46



A solution ligand **IV-9** (20 mg, 0.06 mmol) and methallylnickel chloride dimer (9 mg, 0.03 mmol) was stirred in benzene for 30 min. The quantitative formation of the desired product could be observed in ^{31}P NMR spectrum. The title compound could be isolated as a brick-red solid after evaporation of the solvent.

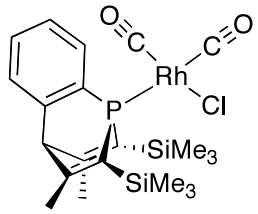
Yield: 27 mg (0.055 mmol, 92 %)

^{1}H NMR (C_6D_6): δ 0.36 (s, 6H, $SiMe_3$), 0.44 (s, 6H, $SiMe_3$), 2.10 (m, 1H, CH_2 of methallyl trans to Cl), 2.22 (s, 6H, Me), 2.26 (s, 3H, CH_3 of methallyl), 3.38 (br, 1H CH_2 of methallyl trans to P), 3.50 (m, 1H, CH_2 of allyl trans to Cl), 4.03 (m, 1H, CH_2 of allyl trans to P), 4.84 (d, J_{PC} = 1.9 Hz, C_4H), 6.67-6.93 (m, 2H, C_9H, $C_{10}H$), 7.03 (m, 1H, C11H), 7.63-7.72 (m, 1H, C_8H).

^{13}C NMR (C_6D_6): δ 2.64 (m, $SiMe_3$) 24.3 (br, Me), 26.0 (m, CH_3 of methallyl), 43.8 (d, JPC = 4.7 Hz, CH_2 of methallyl trans to Cl), 69.7 (d, J_{PC} = 25.4 Hz C_4H), 73.3 (d, J_{PC} = 21.5 Hz, CH_2 of allyl trans to P), 123.2 (s, C of methallyl), 124.4 (s, $C_{11}H$), 125.6 (d, J_{PC} = 10.9 Hz, C_9H), 127.2 (s, $C_{10}H$), 129.0 (d, J_{PC} = 17.5 Hz, C_8H), 133.0 (m, C_2, C_6), 139.6 (d, J_{PC} = 25.4 Hz, C_{12}), 148.0 (s, C_7), 169.5 (m, C_3, C_5).

^{31}P NMR (C_6D_6): δ -12.6 (s)

IV.2.r. Complex IV-49



A mixture of ligand **IV-9** (20 mg, 0.06 mmol) and $[Rh(CO)_2Cl]_2$ (11.3 mg, 0.03 mmol) was stirred in C_6D_6 (1 mL) for 15 min. The quantitative formation of the desired product could be observed by ^{31}P NMR-spectroscopy. The product could not be isolated as a solid as it losses one molecule of CO and transforms to **IV-50** upon drying under vacuum.

NMR-Yield: 100 %

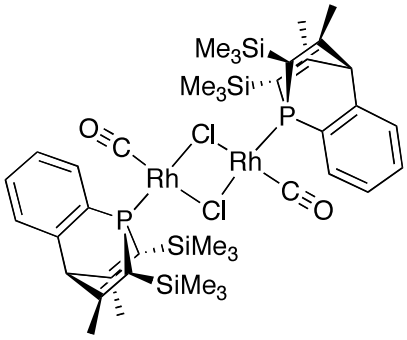
^{1}H NMR (C_6D_6): δ 0.42 (s, 18H, $SiMe_3$), 1.91 (s, 6H, Me), 4.44 (d, $^{4}J_{PH}$=2.8 Hz, 1H, C_4H), 6.82 (m, 2H, C_9H, $C_{10}H$), 6.95 (m, 1H, $C_{11}H$), 8.10 (m, 1H, C_8H).

^{13}C NMR (C_6D_6): δ 3.4 (d, $^{3}J_{PC}$=3.4 Hz, $SiMe_3$), 26.1 (d, $^{3}J_{PC}$=10.7 Hz, Me), 69.6 (d, $^{3}J_{PC}$=31.1 Hz, C_4H), 124.1 ($C_{11}H$), 124.6 (d, $^{4}J_{PC}$=3.6 Hz, $C_{10}H$), 126.2 (d, $^{3}J_{PC}$=11.3 Hz, C_9H), 128.0 (s, C_8H), 133.7 (d, $^{1}J_{PC}$=1.0 Hz, C_2,C_6), 137.5 (dd, $^{3}J_{CRh}$=2.8 Hz, $^{2}J_{PC}$=32.5 Hz, C_{12}), 147.5 (dd, $^{1}J_{PC}$=1.2 Hz, $^{2}J_{CRh}$=1.0 Hz, C_7), 169.4 (dd,$^{2}J_{PC}$=11.0 Hz, $^{3}J_{CRh}$=1.2 Hz, C_3,C_5), 182.9 (dd, $^{2}J_{PC}$=128.6 Hz, $^{1}J_{RhC}$=60.2 Hz, CO-*trans*-P), 185.6 (dd, $^{1}J_{RhC}$=70.9 Hz, *J*=15.8 Hz, CO-*cis*-P).

^{31}P NMR (C_6D_6): δ -3.6 (d, $^{1}J_{PRh}$ = 130.0 Hz).

IR(ATR): 1972 cm^{-1}, 1998 cm^{-1}, 2085 cm^{-1}.

IV.2.s. Complex IV-50



A mixture of ligand **IV-9** (20 mg, 0.06 mmol) and $[Rh(CO)_2Cl]_2$ (11.3 mg, 0.03 mmol) was stirred in toluene (5 mL) for 48 h. The quantitative formation of product **IV-50** could be observed by ^{31}P NMR-spectroscopy. The product was isolated as a light orange solid after evaporation of the solvent.
Yield: 27 mg (0.026 mmol, 87 %).

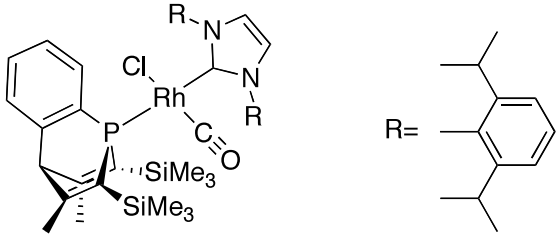
^{1}H NMR (C_6D_6): δ 0.70 (s, 18H, $SiMe_3$), 1.93 (s, 6H, Me), 4.44 (d, $^{4}J_{PH}$=2.4 Hz, 1H, C_4H), 6.76 - 6.91 (m, 2H, C_9H, $C_{10}H$), 6.96 (d, J_{HH}=7.2 Hz, 1H, $C_{11}H$), 8.61 (dd, J_{HH}= 7.7 Hz, J_{PH}= 10.0 Hz, 1H, C_8H).

^{13}C NMR (C_6D_6): δ 3.9 (s, $SiMe_3$), 25.9 (d, $^{3}J_{PC}$=10.3 Hz, Me), 70.0 (d, $^{3}J_{PC}$=32.9 Hz, C_4), 124.1 (d, $^{3}J_{PC}$=4.1 Hz, C_{11}), 126.2 (d, $^{4}J_{PC}$=11.8 Hz, C_{10}), 127.9 (d, $^{3}J_{PC}$=1.2 Hz, C_9), 131.0 (d, $^{2}J_{PC}$=15.4 Hz, C_8), 135.3 (d, $^{1}J_{PC}$=1.9 Hz, C_2,C_6), 138.8 (dd, $^{2}J_{PC}$=39.4 Hz, $^{3}J_{RhC}$=2.6 Hz, C_{12}), 145.9 (s, C_7), 169.9 (m, C_3,C_5), 187 (m, CO).

^{31}P NMR (C_6D_6): δ 10.5 (d, $^{1}J_{PRh}$ = 182.0 Hz).

IR (ATR): 1972 cm^{-1}.

IV.2.t. Complex IV-51



IPr (8 mg, 0.02 mmol) is added as a solid to a solution of complex **II-50** (10 mg, 0.01 mmol) in C_6D_6 (500 μL). The solution is heated to 40 °C for 2h in an oil bath. The quantitative

formation of the desired product can be observed by ^{31}P NMR spectroscopy. The product is obtained as a light orange solid upon evaporation of the solvent.

Yield: 16 mg, (0.018 mmol, 88 %)

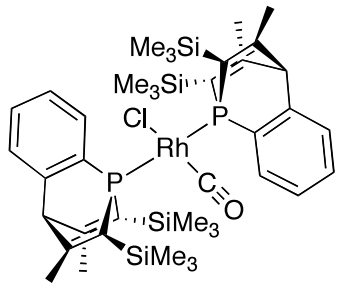
^{1}H NMR (C_6D_6): δ 0.29 (s, 18H, $SiMe_3$), 1.13 (d, $^{3}J_{HH}$=6.8 Hz, 12H, CH_3 of ^{i}Pr), 1.55 (d, $^{3}J_{HH}$=6.8 Hz, 12H, CH_3' of ^{i}Pr), 1.82 (s, 6H, Me), 3.42 (hept, $^{3}J_{HH}$=6.8 Hz, 4H, CH of ^{i}Pr), 4.38 (d, $^{4}J_{PH}$=2.3 Hz, 1H, C_4H), 6.79 (m, 2H, NCH=CHN), 6.98 (m, 2H, C_9H, $C_{10}H$), 7.24-7.42 (m, 7H, $C_{11}H$ and C_{ar} of IPr), 7.78 (dd, J_{HH}= 7.6 Hz, $^{3}J_{PH}$= 9.9 Hz, 1H, C_8H).

^{13}C NMR (C_6D_6): δ 2.9 (d, *J*=3.7 Hz, $SiMe_3$), 23.3 (s, $CH\underline{Me_2}$), 25.5 (d, *J*=9.1 Hz, Me), 27.2 (s, $CH\underline{Me_2}$), 29.4 (s, $\underline{CH}Me_2$), 70.1 (d, $^{3}J_{PC}$=25.1 Hz, C_4H), 123.0 (br, $C_{11}H$), 124.6 (s, $C_{ar}H$ of IPr), 125.4 (m, NCH=CHN), 127.7 (m, C_9H), 129.1(m, $C_{10}H$), 130.6 (s $C_{ar}H$ of IPr), 136.1 (d, *J*=21.2 Hz C_8H), 137.4 (s, C_{12}), 142.5 (d, $^{2}J_{PC}$=34 Hz, C_7), 145.4 (NC_{ipso}) 147.5 (s, $C_{ar}{}^{i}$Pr), 169.1 (dd, *J*=9.8 Hz, *J*=1.1 Hz, C_3,C_5), 187.0 (m, C carbonic of IPr), 189.5 (m, CO).

^{31}P NMR (C_6D_6): δ 10.5 (d, $^{1}J_{PRh}$ = 182.0 Hz).

IR (ATR): 1952 cm^{-1}.

IV.2.u. Complex IV-52



Ligand **IV-9** (3.5 mg, 0.01 mmol) is added as a solid to a solution of comlplex **II-50** (10 mg, 0.01 mmol) in C_6D_6 (500 μL). The quantitative formation of the desired product can be observed by ^{31}P NMR spectroscopy. The product is obtained as a light yellow solid upon evaporation of the solvent.

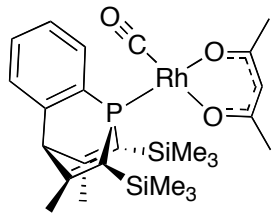
Yield: 13 mg (0.01 mmol, 99%)

^{1}H NMR (CD_2Cl_2): δ 0.39 (s, 18H, $SiMe_3$), 2.24 (s, 6H, Me), 4.94 (s, 1H, C_4H), 7.16 (m, 1H, $C_{10}H$), 7.25 (t, J_{HH}=7.4 Hz, 1H, C_9H), 7.41 (d, J_{HH}=7.4 Hz, 1H, $C_{11}H$), 8.99 (m, 1H, C_8H).

^{13}C NMR (CD_2Cl_2): δ 2.6 (t, $^{3}J_{PC}$=1.8 Hz, $SiMe_3$), 26.0 (*pseudo*-t, ΣJ_{PC}=5.3 Hz, Me), 70.4 (*pseudo*-t, ΣJ_{PC}=14.2 Hz, C_4H), 124.0 (*pseudo*-t, ΣJ_{PC}=1.7 Hz, $C_{11}H$), 124.8 (*pseudo*-t, ΣJ_{PC}=6.3 Hz, $C_{10}H$), 128.5 (m, C_9H), 134.0 (d, $^{2}J_{PC}$=2.5 Hz, C_8H), 135.4 (*pseudo*-t, ΣJ_{PC}=10.1 Hz, C_2,C_6), 140.8 (*pseudo*-t, ΣJ_{PC}=17.0 Hz, C_{12}), 145.5 (br, C_7), 171.6 (br, C_3,C_5), 187.5 (m, CO).

^{31}P NMR (CD_2Cl_2): δ -5.6 (d, $^1J_{PRh}$ = 135 Hz).
IR (ATR): 1963 cm^{-1}.

IV.2.v. Complex IV-53



A solution of ligand **IV-9** (10 mg, 0.03 mmol) and [Rh(acac)(CO)$_2$] (7.6 mg, 0.03 mmol) in C_6D_6 (500 μL) was heated to 40 °C for 4 h. The title compound could be obtained as a light yellow solid after evaporation of the solvent.

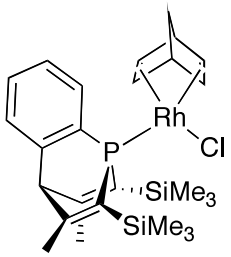
Yield: 14 mg (0.024 mmol, 81 %).

^{1}H NMR (C_6D_6): δ 0.45 (s, 18H, $SiMe_3$), 1.85 (s, 3H, ac-Me), 1.94 (s, 6H, Me), 1.95 (s, 3H, ac-Me), 4.44 (d, $^3J_{PC}$=3.2 Hz, C_4H), 5.41 (s, CH of acac), 6.85 (m, 1H???, $C_{10}H$), 7.01 (m, 1H, C_9H), 7.12 (d, J=Hz, 1H, $C_{11}H$), 8.51 (m, 1H, C_8H).

^{13}C NMR (C_6D_6): δ 3.3 (d, $^3J_{PC}$=2.9 Hz, $SiMe_3$), 25.7 (d, J=10.2 Hz, Me), 27.8 (t, J=1.2 Hz, Me of acac), 28.2 (d, J = 6.0 Hz, Me of acac), 70.4 (d, $^3J_{PC}$=31.5 Hz, C_4H), 101.8 (dd, J_{PC}=2.5 Hz, J_{RhC} = 40.8 Hz, C of acac), 124.2 (d, $^3J_{PC}$=3.9 Hz, $C_{11}H$), 126.1(br, C_9H), 127.6 (d, J = 2.3 Hz, $C_{10}H$), 130.7 (m, C_8H), 135.0 (m, C_2,C_6), 138.2 (br, C_{12}), 146.5 (br, C_7), 169.1 (dd, $^2J_{PC}$=10.4 Hz, $^3J_{RhC}$=1.6 Hz, C_3,C_5), 184.6 (d, J=0.6 Hz, ac-CO), 184.9 (d, $^1J_{RhC}$=72.8 Hz, CO), 188.3 (d, $^1J_{RhC}$=85.3 Hz, CO).

^{31}P NMR (C_6D_6): δ 8.4 (d, $^1J_{PRh}$=182 Hz).
IR (ATR): 1967 cm^{-1}.

IV.2.w. Complex II-54



Ligand **IV-9** (10 mg, 0.03 mmol) and $[Rh(NBD)Cl]_2$ (6.7 mg, 0.015 mmol) were mixed in C_6D_6. An intense yellow solution was obtained immediately at room temperature. ^{31}P NMR reveals the quantitative formation of the title product. After evaporation of the solvent the product was obtained in quantitative yield as a yellow solid.

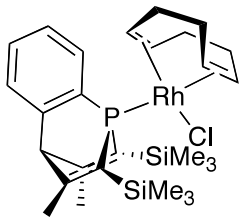
Yield: 15 mg (0.024 mmol, 83 %).

^1H NMR(C_6D_6): 0.86 (s, 18H, Me_3Si),1.19 (d, J_{HH}= 8.2 Hz, CH_2) 1.26(d, J_{HH}= 8.2 Hz, 1H, CH_2) 2.09 (s, 6H, Me), 3.66 (s, 2H, $\underline{CH}CH_2$), 4.40 (s, 2H, $CH_{olefinic}$), 4.54 (d, J= 2.7 Hz, 1H, CH-4), 5.45(s, 2H, $CH_{olefinic}$), 6.82-6.89 (m, 1H, CH), 6.93 (t, J=7.2 Hz, 1H, CH), 7,03-7.13 (m, 2H, CH).

^{13}C NMR (C_6D_6): 2.8 (d, *J*= 3.4 Hz, Me_3Si), 25.5 (d, J= 9.0 Hz, Me), 46.1 (d, J= 11.6 Hz, $CH_{olefinic}$), 51.2 (dd, J=2.4 Hz, J= 1.9 Hz, $\underline{CH}CH_2$), 63.2 (dd, J= 2.2 Hz, J= 5.0 Hz, CH_2), 69.2 (d, J= 26.8 Hz, CH-4), 82.2 (dd, J= 5.8 Hz, 12.5 Hz, $CH_{olefinic(transP)}$), 124.0 (d, J= 3.0 Hz, $C_{11}H$), 124.7 (d, J= 10.1 Hz, C_9H), 126.5 (d, J= 1.9 Hz, $C_{10}H$), 127.0 (d, J= 14.1 Hz, $C_{11}H$), 134.8 (dd, J= 1.3 Hz, J= 5.2 Hz, C_{12}), 139.8 (dd, J= 3.0 Hz, J= 24.2 Hz, C_2, C_6), 147.9 Hz (dd, J=1.5 Hz, J= 2.7 Hz, C_7), 167.9 (dd, *J*= 1.4 Hz, *J*= 10.3 Hz, C_3, C_5).

^{31}P NMR (C_6D_6): -14.4 (d, J_{PRh}= 177.4 Hz).

IV.2.x. Complex IV-55



A solution of ligand **IV-9** (20 mg, 0.06 mmol) and $[Rh(COD)Cl]_2$ (14.3 mg, 0.03 mmol) in $CDCl_3$ (500 μL) was heated to 40 °C for 2 h. The reaction mixture was taken to dryness and the title compound was obtained as a microcrystalline solid after recrystallization from toluene/MeOH at -18 °C.

Yield: 20.4 mg (0.033 mmol, 55 %).

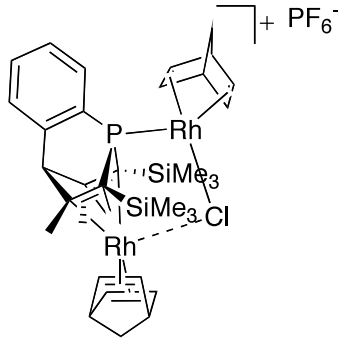
^1H NMR(C_6D_6): 0.56 (s, 18H, $SiMe_3$), 1.85-2.10 (m, 4H, CH_2 of COD), 2.21 (s, 6H, Me), 2.37-2.51 (m, 4H, CH_2 of COD), 4.67 (d, J_{PC} = 2.7 Hz, C_4H), 4.91 (m, 2H, CH of COD), 5.41 (m, 2H, CH of COD), 7.05 (m, C_9H), 7.23 (m, $C_{10}H$) 7.33 (m, $C_{11}H$), 7.53 (m, 1H C_8H).

^{13}C NMR (C_6D_6): 3.08 (s, $SiMe_3$), 24.2 (J_{PC} = 9.3 Hz, Me), 31.3 (m, 2 x CH_2 of COD) 64.7 (d, J_{PC} = 19.7 Hz, C_4H), 66.9 (d, J_{RhC} = 13.9 Hz, CH of COD trans to Cl) 100.2 (dd, J_{PC} = 13.9 Hz,

J_{RhC} = 8.1 Hz, CH of COD trans to P), 125.7 (s, $C_{11}H$), 126.3 (m, C_9H), 127.7 (s, $C_{10}H$), 130.6 (m, C8H) 133.3 (m, C_2, C_6), 135.5 (br, C_{12}), 145.6 (br, C_7), 169.4 (d, J_{PC} = 9.3 Hz, C_3, C_5)

^{31}P NMR (C_6D_6): -18.9 (d, J_{PRh} = 149.5 Hz)

IV.2.y. Complex IV-57



A mixture of $[Rh(NBD)Cl]_2$ (26.8 mg, 0.12 mmol), $TlPF_6$ (20.3 mg, 0.06 mmol) and ligand **IV-9** (20mg, 0.06 mmol) in dichloromethane (2 mL) is stirred at room température for 2h. The formation of a white precipitate could be observed. The solution was filtered over a sintered glass-filter covered with celite. The air-stable product could be obtained as an orange solid after evaporation of the solvent.

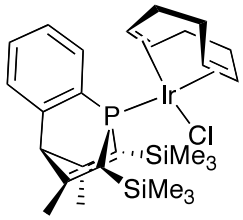
Yield: 49 mg (0.055 mmol, 92 %)

^{1}H NMR (CD_2Cl_2): δ 0.29 (s, 18H, $SiMe_3$), 1.39 (t, J_{HH}=1.5 Hz, 2H, CH_2 of NBD'), 1.58 (m, 1H, CH_2 of NBD), 1.72 (m, 1H, CH_2 of NBD), 2.26 (s, 6H, Me), 3.92 (m, 2H, CHCH$_2$ of NBD'), 4.12 (m, 2H, CHCH2 of NBD), 4,51 (dd, *J*=2.1 Hz, *J*=5.1 Hz, 4H, $CH_{olefininc}$ of NBD'), 4.62 (m, 2H, $CH_{olefininc}$ of NBD), 5.28 (d, $^4J_{PH}$=2.7 Hz, 1H, C_4H), 5.60 (m, 2H, $CH_{olefininc}$ of NBD), 6.80 (t, *J*=8.0 Hz, 1H, C_9H), 7.22 (tdd, *J*=7.5 Hz, *J*=3.0 Hz, *J*=1.1 Hz, 1H, C_8H), 7.36 (tt, *J*=7.5 Hz, *J*=1.1 Hz, 1H, $C_{10}H$), 7.57 (d, *J*=7.5 Hz, 1H, $C_{11}H$).

^{13}C NMR (CD_2Cl_2): δ 3.2 (d, $^3J_{PC}$=2.9 Hz, $SiMe_3$), 29.1 (dd, $^3J_{PC}$=5.3 Hz, J=1.0 Hz, Me), 50.0 (d, *J*=1.9 Hz, $CH_{olefininc}$ of NBD'), 50.8 (d, *J*=11.8 Hz, $CH_{olefininc}$ of NBD'), 53.1 (m, $CH_{olefininc}$ of NBD), 62.7 (d, $^3J_{PC}$=24.8 Hz, C_4H), 63.7 (d, *J*=5.3 Hz, CH_2 of NBD'), 65.0 (dd, *J*=1.7 Hz, *J*=5.4 Hz, CH_2 of NBD), 70.0 (d, *J*=7.1 Hz, $CH_{olefinic}$ NBD'), 87.2 (dd, *J*=5.6 Hz, *J*=12.1 Hz, $CH_{olefininc}$ NBD), 116.3 (m, C_3, C_5), 126.1 (d, $^3J_{PC}$=15.4 Hz C_9H), 126.9 (d, $^4J_{PC}$=3.2 Hz $C_{11}H$,), 128.5 (br, C_8H), 130.5 (br, $C_{10}H$, C_{12}), 137.3 (m, $^1J_{PC}$=4.3 Hz, C_2, C_6), 149.0 (C_7).

^{31}P NMR (CD_2Cl_2): δ 22.6 (dd, J_{PRh}=2.6 Hz, $^2J_{PRh}$=170.1 Hz), -144.2 (hept, $^2J_{PF}$=705 Hz).

IV.2.z. Complex IV-58



A mixture of $[Ir(COD)Cl]_2$ (19.5 mg, 0.03 mmol) and ligand IV-9 (20 mg, 0.06 mmol) was stirred at 40 °C in $CDCl_3$ (1 mL) for 36 h. The reaction was followed by ^{31}P NMR. The title product could be obtained by evaporation of the solvent.

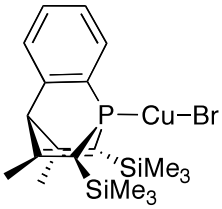
Yield: 38.4 mg (0.054 mmol, 90 %)

^{1}H NMR ($CDCl_3$): δ 0.39 (s, 18H, $SiMe_3$), 1.67 (m, 4H, CH_2 of COD), 2.23 (s, 6H, Me), 2.23-2.46 (m, 4H, CH_2 of COD), 4.47 (m, 2H, CH of COD), 4.69 (d, 1H, J_{PC} = 2.7 Hz, C_4H), 5.02 (m, 2H, CH of COD), 6.92-7.10 (m, 2H, C_9H, $C_{10}H$), 7.21-7.28 (m, 1H, $C_{11}H$), 7.36 (m, 1H, C_8H).

^{13}C NMR ($CDCl_3$): δ 3.5 (s, $SiMe_3$), 26.1 (d, J_{PC} = 10.1 Hz, Me), 28.4 (s, CH_2 of COD), 34.3 (s, CH_2 of COD), 48.4 (s, CH of COD trans to Cl), 69.6 (d, J_{PC} = 28.8 Hz, C_4H), 89.5 (d, J_{PC} = 15.5 Hz, CH of COD trans to P), 124.0 (d, J_{PC} = 2.8 Hz, $C_{11}H$), 124.8 (d, J_{PC} = 9.8 Hz, C_9H), 126.4 (s, $C_{10}H$), 127.7 (d, J_{PC} = Hz, C_8H), 134.9 (s, C_{12}), 138.2 (m, C_2, C_6), 148.4 (s, C_7), 168.4 (d, J_{PC} = 9.9 Hz, C_3, C_5).

^{31}P NMR ($CDCl_3$): δ 21.5 (s).

IV.2.aa. Complex IV-60



A solution of $CuBr.SMe_2$ (6mg, 0.03 mmol) and ligand **IV-9** (10 mg, 0.03 mmol) was stirred in toluene (2 mL), for 30 min.. The title compound was obtained as a colorless solid upon evaporation of the solvents.

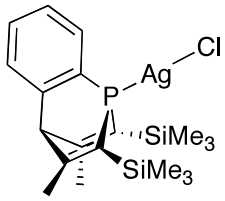
Yield: 13 mg (0.027mmol, 90 %)

^{1}H NMR ($CDCl_3$): δ 0.35 (s, 18H, $SiMe_3$) 2.21 (s, 6H, Me), 4.87 (d, J_{PC} = 2.7 Hz, C_4H), 7.13 (m, 2H, C_9H, $C_{10}H$), 7.31 (m, $C_{11}H$), 8.19 (m, C_8H).

^{13}C NMR ($CDCl_3$): δ 1.6 (m, $SiMe_3$), 24.7 (d, J_{PC} = 8.6 Hz, Me), 70.6 (d, J_{PC} = 26.7 Hz, C_4H), 124.2 (s, $C_{11}H$), 125.6 (d, J_{PC} = 12.7 Hz, C_9H), 127.7 (s, $C_{10}H$), 130.8 (d, J_{PC} = 21.6 Hz, C_8H), 131.5 (d, J_{PC} = 11.2 Hz, C_2, C_6) 137.0 (d, J_{PC} = 30.3 Hz, C_{12}) 145.9 (d, J_{PC} = 2.2 Hz, C_7) 169.1 (d, J_{PC} = 9.5 Hz, C_3, C_5).

^{31}P NMR ($CDCl_3$): δ -47.3 (br).

IV.2.ab. Complex IV-47



$AgBF_4$ (11 mg, 0.05 mmol) was added as a solid to a solution of complex **IV-46** (25 mg, 0.05 mmol) in toluene (2 mL). The color changed immediately from red to yellow. The reaction mixture was taken to dryness and the resulting residue was solubilized in acetonitrile (1 mL). The formation of pale yellow crystals was observed. The supernatant was decanted and the crystals were rinsed with acetonitrile.

Yield: 17 mg (0.035 mmol, 70 %).

^{1}H NMR ($CDCl_3$): δ 0.34 (s, 18H, $SiMe_3$), 2.25 (s, 6H, Me), 4.98 (d, J_{PC} = 2.7 Hz, 1 H, C_4H), 7.08-7.22 (m, 2H, C_9H, $C_{10}H$), 7.34 (m, 1H, $C_{11}H$), 7.87 (m, 1H, C_8H).

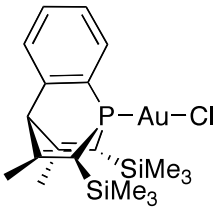
^{13}C NMR ($CDCl_3$): δ 1.11 (m, $SiMe_3$), 24.6 (d, J_{PC} = 8.7 Hz, Me), 70.7 (d, J_{PC} = 27.4 Hz, C_4H), 124.3 (s, $C_{11}H$), 125.8 (d, J_{PC} = 13.4 Hz, C_9H), 128.3 (s, $C_{10}H$), 130.5 (d, J_{PC} = 26.3 Hz, C_8H), 132.4 (m, C_2, C_6), 136.2 (m, C_{12}), 145.6 (s, C_7), 169.7 (d, J_{PC} = 10.1 Hz, C_3, C_5).

^{31}P NMR ($CDCl_3$): δ -37.6 (dd, $^{1}J_{PAg}$ = 522.5 Hz, $^{1}J_{PAg}$ = 603.9 Hz)

IV.2.ac. Synthesis of gold complexes IV-62 - IV-65

A solution of Ligand **IV-9** (10 mg, 0.03 mmol) and [AuCl(tht)] (9.3 mg, 0.03 mmol) was stirred in dichloromethane (2 mL) at room temperature 15 min. The desired product was obtained in quantitative yield as a white solid after evaporation of the solvent.

IV.2.ad. Complex IV-62



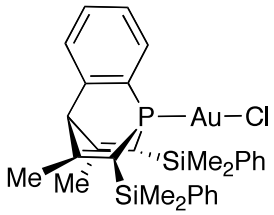
Yield: 16 mg (0.028 mmol, 92 %)

^{1}H NMR (CD_2Cl_2): δ 0.38 (d, $^{4}J_{PH}$=0.5 Hz, 18H, $SiMe_3$), 2.24 (d, $^{4}J_{PH}$=1.7 Hz, 6H, Me), 4.99 (d, $^{4}J_{PH}$=3.9 Hz, 1H, C_4H), 7.22 (m, 2H, C_9H, $C_{10}H$), 7.44 (m, 1H, $C_{11}H$), 7.82 (m, 1H, C_8H).

^{13}C NMR (CD_2Cl_2): δ 1.7 (d, $^{3}J_{PC}$=3.8 Hz, $SiMe_3$), 25.1 (d, $^{3}J_{PC}$=12.3 Hz, Me), 70.5 (d, $^{3}J_{PC}$=37.9 Hz, C_4H), 125.3 (d, $^{3}J_{PC}$=4.4 Hz $C_{11}H$), 126.1 (d, $^{4}J_{PC}$=13.1 Hz $C_{10}H$,), 128.1 (s, C_{12}), 129.4 (d, $^{3}J_{PC}$=2.4 Hz, C_9H), 130.5 (d, $^{2}J_{PC}$=17.5 Hz, C_8H), 135.3 (d, $^{1}J_{PC}$=52.5 Hz, C_2, C_6), 145.5 (d, $^{1}J_{PC}$=0.8 Hz, C_7), 171.7 (d, $^{2}J_{PC}$=11.1 Hz, C_3, C_5).

^{31}P NMR (CD_2Cl_2): δ -12.1 (s).

IV.2.ae. Complex IV-63



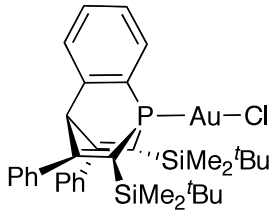
Yield: 19 mg (0.027 mmol, 90 %)

^{1}H NMR ($CDCl_3$): δ 0.55 (m, 12H, $SiMe_2$), 2.15 (br, 6H, Me), 4.98 (d, J_{PC} = 3.6 Hz, C_4H), 7.15-7.42 (m, 13H, CH of Ph, C_9H, $C_{10}H$, $C_{11}H$), 7.63-7.72 (m, 1H, C_8H).

^{13}C NMR ($CDCl_3$): δ 0.32 (m, $SiMe_2$), 25.2 (d, J_{PC} = 11.7 Hz, Me), 70.3 (d, J_{PC} = 11.7 Hz, C_4H), 124.4 (br, $C_{11}H$), 125.6 (d, J_{PC} = 13.3 Hz, CH), 128.2 (s, CH of SiPh), 128.8 (s, $C_{10}H$), 129.1 (m, C_{12}), 129.6 (s, CH of SiPh), 130.2 (d, J_{PC} = 18.1 Hz, C_8H), 134.2 (s, CH of SiPh), 135.0 (m, C_2, C_6) 135.3 (C_{ipso} of SiPh) 144.8 (s, C_7), 172.3 (d, J_{PC} = 9.7 Hz, C_3, C_5).

^{31}P NMR ($CDCl_3$): δ -10.5 (s).

IV.2.af. Complex IV-64



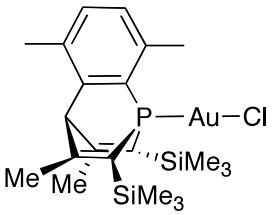
Yield: 20 mg (0.0255 mmol, 85 %)

^{1}H NMR ($CDCl_3$): δ -0.25 (s, 6H, Me of $SiMe_2$), 0.29 (s, 6H, Me of $SiMe_2$), 0.89 (s, 18H, Me of Si^{t}Bu), 5.44 (d, J_{PC} = 3.5 Hz, 1H, C_4H), 6.85-7.05 (br, 4H, CH of Ph, C_9H and C_{10}H), 7.26-7.50 (br, 9H, CH of Ph and C_{11}H), 8.05-8.15 (m, 1H, C_8H).

^{13}C NMR ($CDCl_3$): δ -1.6 (s, Me of $SiMe_2$), 18.9 (s, C ipso of Si^{t}Bu), 28.8 (s, Me of Si^{t}Bu), 72.1 (d, $^{3}J_{PC}$= 34.5 Hz, C_4H), 125.2 (d, J_{PC} = 4.4 Hz, C_{11}H), 126.0 (d, J_{PC} = 13.1 Hz C_9H), 126.4 (s, CH of Ph) 128.1 (s, CH of Ph), 128.3 (s, CH of Ph), 129.5 (s, C_{10}H), 131.5 (d, J_{PC} = 17.9 Hz, C_8H), 133.6 (s, C_{12}), 134.8 (m, C_2, C_6) 142.9 (d, J_{PC} = 13.0 Hz, C_7), 144.7 (C ipso of Ph), 175.6 (d, J_{PC} = 9.8 Hz, C_3, C_5).

^{31}P NMR ($CDCl_3$): δ - 5.5 (s).

IV.2.ag. Complex IV-65



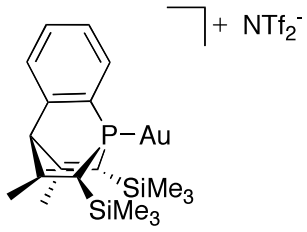
Yield: 17 mg (0.028 mmol, 94 %)

^{1}H NMR (C_6D_6): δ 0.29 (s, 18H, $SiMe_3$), 1.79 (d, J=1.7 Hz, 6H, Me), 2.13 (s, 3H, C_{11}Me), 3.00 (s, 3H, C_8-Me), 4.92 (d, $^{4}J_{PH}$=3.9 Hz, 1H, C_4H), 6.51 (m, 1H, C_9H), 6.60 (d, J=7.7 Hz, C_{10}H).

^{13}C NMR (C_6D_6): δ 1.2 (s, $SiMe_3$), 18.9 (d, $^{4}J_{PC}$=0.9 Hz, C_{11}Me), 23.1 (d,$^{3}J_{PC}$=11.3 Hz, C_8Me), 24.8 (d, $^{4}J_{PC}$=11.3 Hz, Me), 66.1 (d, $^{3}J_{PC}$= 39.4 Hz, C_4), 129.8 (d, $^{3}J_{PC}$=2.3 Hz, C_9), 130.3 (d, $^{4}J_{PC}$=5.0 Hz, C_{10}), 130.8 (d, $^{2}J_{PC}$=5.3 Hz, C_8), 132.0 (d, $^{1}J_{PC}$=47.3 Hz, C_2,C_6), 136.5 (d, $^{2}J_{PC}$=11.8 Hz, C_{12}), 143.5 (s, C_7), 170.8 (d, $^{2}J_{PC}$=10.3 Hz, C_3,C_5).

^{31}P NMR (C_6D_6): δ -25.3 (s).

IV.2.ah. Complex IV-66



$AgNTf_2$ (22.5 mg, 0.06 mmol), was added as a solid to a solution of Ligand **IV-9** (20 mg, 0.06 mmol) and [AuCl(tht)] (18.6 mg, 0.06 mmol) in dichloromethane (2 mL). The formation of a white precipitate could be observed immediately. The reaction mixture was stirred for 1 h at room temperature. The resulting suspension was filtered over a sintered glass filter covered with celite. The product could be obtained as a white solid after evaporation of the filtrate.

Yield: 41 mg (0.05 mmol, 83 %)

^{1}H NMR (CD_2Cl_2): δ 0.41 (s, 18H, SiMe3), 2.29 (s, 6H, Me), 5.12 (br, C_4H), 7.25-7.35 (m, 2H, C_9H, $C_{10}H$), 7.53 (m, 1H, $C_{11}H$), 7.68-7.82 (m, 1H, C_8H).

^{13}C NMR (CD_2Cl_2): δ 1.15 (s, $SiMe_3$), 24.8 (d, J_{PC} = 12.7 Hz, Me), 70.0 (d, J_{PC} = 39.1 Hz, C_4H), 125.5 (s, $C_{11}H$), 126.0 (d, J_{PC} = 13.1 Hz, C_9H), 128.4 (m, C_{12}), 129.3-129.9 (m, $C_{10}H$, C_8H), 133.0 (m, C_2, C_6), 144.6 (s, C_7), 173.1 (m, C_3, C_5).

^{31}P NMR (CD_2Cl_2): δ -8.7 (s).

IV.3. Chapter 3

IV.3.a. General procedure for Suzuki-Miyaura Coupling Reactions

An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with potassium carbonate (3 mmol, 414.6 mg) and phenylboronic acid (1.2 mmol, 146.3 mg). The Schlenk tube was sealed and then evacuated and backfilled with nitrogen (this sequence was repeated three times). Freshly distilled toluene (1.9 mL) was added via a rubber-septum. A solution of a 0.02 M solution of **IV-29** (0.002 mmol, 100 μL) in toluene was added via a microsyringe. Chloroarenes (1 mmol) were added in a single portion and the schlenk tube was sealed and placed into an oil bath at 80 °C. Upon complete consumption of starting material as judged by GC analysis, the reaction mixture was then allowed to cool to room temperature, diluted with diethyl ether (10 mL), filtered through a thin pad of silica gel (eluting with diethyl ether) and concentrated under reduced pressure. The crude material obtained was purified by flash chromatography on silica gel when necessary. All the biphenyl products reported are known compounds and were

characterized by favorable comparison of their ^{1}H and ^{13}C NMR to the previously reported data in the literature.

IV.3.b. Literature references for biaryls prepared *via* Suzuki-Miyaura-Coupling

4-Cyano-biphenyl, CAS-Registry-Nr.: 2920-38-9
Liu, L.; Zhang, Y.; Xin, B. *J. Org. Chem.* **2006**, 71, 3994-3997.

2-Cyano-biphenyl, CAS-Registry-Nr.: 24973-49-7
Zapf, A.; Beller, M.; *Chem Eur. J.* **2000**, *6*, 1830-1833

4-Acetyl-biphenyl CAS-Registry-Nr.: 92-91-1
Liang, L-C.; Chien, PS.; Huang, M-H. *Organometallics* **2005**, *24*, 353-357.

4-Nitro-biphenyl CAS-Registry-Nr.: 86-00-0
Liu, L.; Zhang, Y.; Xin, B. *J. Org. Chem.* **2006**, 71, 3994-3997.

Methyl 4-biphenylcarboxylate, CAS-Registry-Nr.: 720-75-2
Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P.; *J. Org. Chem.* **1999**, *64*, 3804-3805.

4-Trifluoromethyl-biphenyl CAS-Registry-Nr.: 398-36-7
Liu, L.; Zhang, Y.; Xin, B. *J. Org. Chem.* **2006**, 71, 3994-3997.

Biphenyl, CAS-Registry-Nr.: 92-52-4
Pickett, T. E.; Richards, *Tetrahedron Lett.* **2001**, 42, 3767-3769.

3-Methoxy-biphenyl CAS-Registry-Nr.: 2113-56-6
Zapf. A.; Ehrentraut, A.; Beller, M. *Angew. Chem., Int. Ed.* **2000**, 39, 4153-4155.

4-Methyl-biphenyl CAS-Registry-Nr.: 92-91-1
Liu, L.; Zhang, Y.; Xin, B. *J. Org. Chem.* **2006**, 71, 3994-3997.

IV.3.c. General procedure for the preparation of organozinc reagents

Allylchloride (300 μl, mmol), CF_3CO_2H (20 μl, mmol) and p-bromo ethylbenzoate (980 μl, 5.5 mmol) were added consecutively to a suspension of zinc powder (1g, 15.3 mmol) and $CoBr_2$ (220 mg, 1 mmol) in dry acetonitrile (5 mL). The reaction mixture was stirred at room

temperature for 45 min.. The resulting suspension was filtered over a sintered glass-filter covered with oven dried celite. The filter was rinsed with dry acetonitrile (2 x 1 mL). The organozinc reagent was immediately used in Negishi-coupling reactions.

IV.3.d. General procedure for Negishi coupling reactions

A solution of a freshly prepared organozinc reagent (7 mL, 5.5 mmol) was added in a single portion to a solution of complex **IV-29** (5.3 mg, 0.01 mmol), ligand **IV-9** (3.4 mg, 0.01 mmol), 4-bromo benzonitrile (910 mg, 5 mmol) in THF (2 mL). The reaction mixture was stirred for 2h at room temperature. The reaction mixture was quenched with dilute hydrochloric acid (50 mL, 2 M) and extracted with diethylether (3 x 50 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated. The pure product could be isolated by column chromatography (SiO_2/petrolether:Et_2O/95:5).

IV.3.e Literature references for biaryls prepared *via* Negishi coupling reactions

Ethyl-4-(4-cyanophenyl)benzoate, CAS-Registry-Nr.: 89409-89-2
M. Amatore, C.Gosmini, *Angew. Chem. Int. Ed.* **2008**, *47*, 2089.

Ethyl-4-(2-cyanophenyl)benzoate, CAS-Registry-Nr.: 501427-88-9
M. Amatore, C.Gosmini, *Angew. Chem. Int. Ed.* **2008**, *47*, 2089.

Ethyl-4-(4-trifluoromethylphenyl)benzoate, CAS-Registry-Nr.: 647842-34-0
M. Amatore, C.Gosmini, *Angew. Chem. Int. Ed.* **2008**, *47*, 2089.

IV.3.f. General hydrosilylation procedure

A solution containing phosphabarrelene **IV-9** (0.68 mg. 0.002 mmol), [(COD)$PtCl_2$] (0.37 mg, 0.001 mmol), Silane (1.2 mmol) and THF (0.5 mL) was heated to 60 °C for 2 min in a Schlenk tube capped with a rubber septum. The color of the reaction mixture changed from colorless to intense yellow. Alkyne (1 mmol) was added to the reaction mixture with a microsyringe.

The schlenk tube was immediately placed into a bath of water at 20 °C after the addition of the alkyne.

IV.3.g. Literature references for prepared vinylsilanes

(E)-1-triethylsilyl-2-phenylethene
Hamze, A.; Provot, O.; Brion, J.-D.; Alami, M. *J. Organomet. Chem.* **2008**, *693*, 2789.

(E)-1-dimethylphenylsilyl-2-phenylethene
Hamze, A.; Provot, O.; Brion, J.-D.; Alami, M. *J. Organomet. Chem.* **2008**, *693*, 2789.

(E)-1-triethylsilyl-hex-1-ene
Aneetha, H.; Wu, W.; Verkade, J.G. *Organometalics* **2005**, *24,* 2590.

(E)-1-dimethylphenylsilyl-hex-1-ene
Cauhan, M.; Hauck, B. J.; Keller, L. P.; Boudjouk, P. *J. Organomet. Chem.* **2002**, *645,* 1.

(E)-triethylsilyl-2-prop-2-en-1-ol
Hamze, A.; Provot, O.; Brion, J.-D.; Alami, M. *J. Organomet. Chem.* **2008**, *693*, 2789.

(E)-3-triethylsilyl-hex-3-ene
Cauhan, M.; Hauck, B. J.; Keller, L. P.; Boudjouk, P. *J. Organomet. Chem.* **2002**, *645,* 1.

(E)-1-triethylsilyl-1,2-diphenyl-ethene
Cauhan, M.; Hauck, B. J.; Keller, L. P.; Boudjouk, P. *J. Organomet. Chem.* **2002**, *645,* 1.

ANNEX 1: COMPUTATIONAL DETAILS

I. GENERAL CONSIDERATIONS

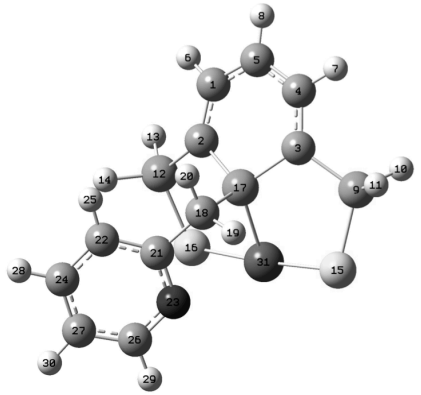
All calculations presented in this work were carried out with Gaussian 03 (Revision C.02). Stationary points were characterized as minima by full vibration frequencies calculations (no imaginary frequency) as well as transition states (one imaginary frequency). IRC calculations were realized on each transition structure obtained to check the validity of starting and final structures.

The full reference for Gaussian is:

Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, r., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

II. OPTIMIZED STRUCTURES OF PART II

II.1. Optimized geometry, three lower frequencies, thermochemistry and PCM energy for II-A



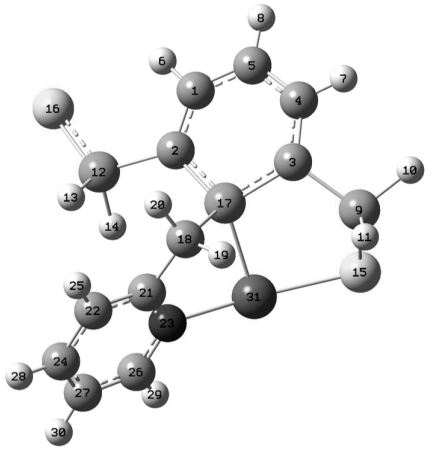
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.759621	-0.621280	-3.250645
2	6	0	-0.960169	-0.394414	-1.889351
3	6	0	1.802802	-0.190338	-1.849962
4	6	0	1.680190	-0.433018	-3.221654
5	6	0	0.472625	-0.547513	-3.911502
6	1	0	-1.615209	-0.942730	-3.844490
7	1	0	2.591722	-0.607657	-3.793556
8	1	0	0.500223	-0.742902	-4.977488
9	15	0	3.253514	-0.491236	-0.877850
10	1	0	3.858827	-1.686742	-1.326045
11	1	0	4.273663	0.452192	-1.112256
12	15	0	-2.380099	-0.941660	-0.980349
13	1	0	-3.045973	-1.892349	-1.781886
14	1	0	-3.356188	0.069122	-0.861149
15	16	0	2.778877	-0.440906	1.099751
16	16	0	-1.852344	-1.646580	0.849409
17	15	0	0.378175	0.115685	-0.843738
18	6	0	0.258752	1.898636	-0.356429
19	1	0	1.240377	2.142954	0.067317
20	1	0	0.125523	2.464097	-1.286409
21	6	0	-0.823134	2.192323	0.650665
22	6	0	-1.935905	2.967819	0.320242
23	7	0	-0.630963	1.681153	1.875544
24	6	0	-2.878011	3.239912	1.313005
25	1	0	-2.049656	3.373378	-0.681555
26	6	0	-1.537865	1.949124	2.816624
27	6	0	-2.675642	2.724960	2.588769
28	1	0	-3.747889	3.852148	1.091819
29	1	0	-1.344990	1.525358	3.799678
30	1	0	-3.377415	2.917391	3.394151
31	46	0	0.454374	-1.005471	1.049283

	1	2	3
	A	A	A
Frequencies --	22.8354	25.9897	45.1353
Red. masses --	6.0884	6.8554	5.6556
Frc consts --	0.0019	0.0027	0.0068
IR Inten --	1.1930	2.5004	0.9808

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.12	-0.02	-0.04	0.06	-0.01	-0.08	0.00	0.00	0.05
2	6	0.09	-0.05	-0.04	0.03	-0.03	-0.04	0.03	0.00	-0.07
3	6	0.01	0.01	0.00	0.00	0.00	-0.01	-0.04	0.01	0.04
4	6	0.06	0.04	-0.01	0.03	0.01	-0.05	-0.07	0.01	0.15
5	6	0.11	0.02	-0.03	0.07	0.00	-0.09	-0.06	0.00	0.16
6	1	0.16	-0.02	-0.06	0.09	-0.01	-0.10	0.02	-0.01	0.06
7	1	0.05	0.07	-0.01	0.03	0.03	-0.06	-0.09	0.01	0.22
8	1	0.14	0.04	-0.04	0.09	0.02	-0.12	-0.09	0.00	0.25
9	15	-0.03	0.03	0.03	-0.05	0.02	0.03	-0.02	0.00	0.05
10	1	-0.01	0.07	0.06	-0.06	0.09	0.02	0.02	-0.03	0.12
11	1	-0.08	0.04	0.04	-0.05	0.00	0.04	-0.09	0.01	0.07
12	15	0.10	-0.10	-0.05	0.03	-0.02	-0.04	0.13	-0.04	-0.17
13	1	0.24	0.01	-0.15	-0.03	-0.09	0.03	0.32	0.09	-0.27
14	1	0.15	-0.30	-0.09	0.01	0.08	-0.01	0.14	-0.26	-0.31
15	16	-0.05	0.00	0.00	-0.11	0.00	0.10	0.04	0.00	-0.06
16	16	-0.13	-0.03	0.12	0.16	-0.07	-0.15	-0.06	0.05	0.02
17	15	0.02	-0.05	-0.01	0.00	-0.03	-0.01	-0.02	0.00	-0.04
18	6	0.00	-0.09	-0.01	0.00	-0.07	-0.01	-0.03	-0.03	-0.04
19	1	0.04	-0.14	0.06	0.03	-0.09	0.03	-0.02	-0.03	-0.04
20	1	-0.06	-0.14	-0.05	-0.03	-0.09	-0.03	0.00	-0.03	-0.05
21	6	0.02	0.01	-0.03	0.00	0.01	0.01	-0.04	-0.02	0.02
22	6	-0.04	0.02	-0.14	-0.06	0.16	0.19	-0.02	0.00	0.09
23	7	0.09	0.10	0.07	0.06	-0.08	-0.12	-0.07	-0.02	0.03
24	6	-0.02	0.12	-0.16	-0.05	0.24	0.23	-0.04	0.03	0.19
25	1	-0.10	-0.05	-0.21	-0.10	0.22	0.28	0.00	0.00	0.08
26	6	0.11	0.20	0.05	0.06	0.00	-0.08	-0.09	0.00	0.11
27	6	0.06	0.21	-0.06	0.01	0.16	0.09	-0.08	0.03	0.20
28	1	-0.06	0.12	-0.25	-0.09	0.37	0.36	-0.03	0.05	0.26
29	1	0.17	0.27	0.14	0.11	-0.07	-0.19	-0.12	-0.01	0.12
30	1	0.08	0.29	-0.06	0.01	0.22	0.12	-0.09	0.05	0.28
31	46	-0.05	-0.03	0.03	-0.03	-0.02	0.01	0.04	0.00	-0.05

HF=-2428.3555166
 Sum of electronic and zero-point Energies= -2428.137520
 Sum of electronic and thermal Energies= -2428.118531
 Sum of electronic and thermal Enthalpies= -2428.117587
 Sum of electronic and thermal Free Energies= -2428.187541
Total free energy in solution:
  with all non electrostatic terms (a.u.) = -2428.432986

II.2. Optimized geometry, three lower frequencies, thermochemistry and PCM energy for II-B



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000687	-0.004922	0.000187
2	6	0	-0.000523	-0.003639	1.394311
3	6	0	2.752219	-0.001584	1.023859
4	6	0	2.420754	0.002268	-0.338140
5	6	0	1.122117	0.050499	-0.832685
6	1	0	-0.985579	-0.038755	-0.470030
7	1	0	3.232884	-0.081655	-1.059285
8	1	0	0.971969	0.062450	-1.906737
9	15	0	4.298024	-0.706457	1.570137
10	1	0	5.067847	-0.887695	0.405794
11	1	0	5.060610	0.231553	2.296086
12	15	0	-1.623386	-0.117048	2.245232
13	1	0	-1.562447	0.975660	3.147316
14	1	0	-1.402362	-1.188440	3.147050
15	16	0	3.988997	-2.434544	2.581417
16	16	0	-3.190714	-0.217793	1.106143
17	15	0	1.511372	-0.020908	2.265623
18	6	0	1.526251	1.371762	3.517575
19	1	0	2.582937	1.607407	3.705635
20	1	0	1.058890	2.264259	3.087159
21	6	0	0.855981	0.932370	4.790999
22	6	0	0.182678	1.813063	5.634782
23	7	0	0.951600	-0.382560	5.096032
24	6	0	-0.386957	1.329747	6.810673
25	1	0	0.114671	2.864768	5.375583
26	6	0	0.399143	-0.852249	6.228417
27	6	0	-0.277717	-0.025515	7.114267
28	1	0	-0.912240	2.004780	7.479750
29	1	0	0.503556	-1.917391	6.410528
30	1	0	-0.713418	-0.443234	8.015541
31	46	0	2.201442	-1.502338	3.852966

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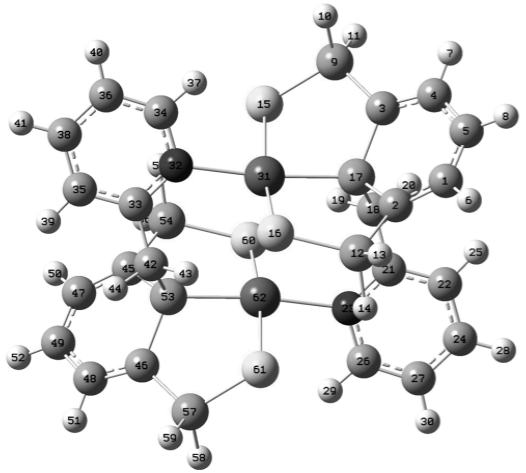
1 2 3

		A			A			A		
Frequencies --		30.9250			39.7351			51.5796		
Red. masses --		11.3722			6.2264			4.4763		
Frc consts --		0.0064			0.0058			0.0070		
IR Inten --		2.7426			1.8866			2.5100		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	-0.05	-0.22	-0.02	-0.02	0.02	0.05	0.00	-0.07	-0.02
2	6	-0.05	-0.12	-0.02	0.03	0.05	0.05	-0.01	0.05	-0.02
3	6	-0.05	-0.07	-0.02	0.02	-0.03	-0.03	-0.01	0.00	0.01
4	6	-0.05	-0.19	-0.02	-0.03	-0.04	-0.02	0.00	-0.11	0.01
5	6	-0.06	-0.28	-0.02	-0.04	-0.02	0.02	0.01	-0.16	-0.01
6	1	-0.06	-0.22	-0.01	-0.03	0.03	0.08	0.00	-0.09	-0.02
7	1	-0.05	-0.20	-0.02	-0.05	-0.07	-0.05	0.01	-0.15	0.02
8	1	-0.06	-0.37	-0.02	-0.07	-0.04	0.02	0.02	-0.25	-0.01
9	15	0.01	0.09	0.01	0.03	-0.04	-0.07	0.00	0.05	0.05
10	1	0.03	0.12	0.02	-0.02	-0.09	-0.09	0.05	0.10	0.07
11	1	-0.08	0.20	-0.03	0.07	-0.02	-0.13	-0.07	0.08	0.08
12	15	-0.06	0.04	-0.01	0.05	0.12	0.11	-0.03	0.24	-0.02
13	1	0.13	-0.05	0.08	0.05	0.22	-0.01	-0.08	0.48	-0.31
14	1	-0.22	-0.07	-0.10	0.11	0.22	0.22	-0.01	0.49	0.27
15	16	0.18	0.11	0.08	0.04	0.00	0.01	0.04	0.02	0.01
16	16	-0.08	0.38	-0.01	0.02	-0.04	0.18	0.01	-0.13	-0.03
17	15	-0.04	-0.07	-0.02	0.06	0.02	0.00	-0.02	0.02	0.00
18	6	-0.10	-0.05	-0.04	0.11	0.00	0.02	-0.02	0.00	0.02
19	1	-0.11	0.00	-0.05	0.11	-0.08	0.09	-0.02	0.00	0.01
20	1	-0.15	-0.08	-0.05	0.18	0.04	0.02	-0.02	0.01	0.04
21	6	-0.06	-0.06	-0.03	0.00	0.00	-0.04	0.00	-0.02	0.02
22	6	-0.10	-0.08	-0.03	-0.08	-0.02	-0.09	0.04	-0.03	0.06
23	7	0.00	-0.05	-0.01	-0.04	-0.01	-0.05	-0.01	-0.02	0.00
24	6	-0.07	-0.09	-0.02	-0.22	-0.04	-0.16	0.07	-0.04	0.07
25	1	-0.15	-0.09	-0.04	-0.05	-0.01	-0.08	0.04	-0.02	0.08
26	6	0.03	-0.07	0.00	-0.16	-0.03	-0.12	0.03	-0.04	0.01
27	6	-0.01	-0.09	-0.01	-0.26	-0.04	-0.18	0.07	-0.05	0.05
28	1	-0.10	-0.11	-0.03	-0.29	-0.05	-0.21	0.11	-0.04	0.10
29	1	0.08	-0.06	0.01	-0.18	-0.03	-0.12	0.02	-0.04	-0.02
30	1	0.02	-0.09	0.00	-0.36	-0.06	-0.24	0.10	-0.06	0.05
31	46	0.07	0.00	0.01	0.03	0.00	0.00	-0.02	-0.01	-0.03

HF=-2428.3528348

Sum of electronic and zero-point Energies= -2428.133871
Sum of electronic and thermal Energies= -2428.115215
Sum of electronic and thermal Enthalpies= -2428.114271
Sum of electronic and thermal Free Energies= -2428.182679
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2428.436875

II.3. Optimized geometry, three lower frequencies, thermochemistry and PCM energy for II-C



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.926296	-0.600107	1.421848
2	6	0	3.531378	-0.567440	1.322826
3	6	0	4.038036	1.220567	-0.724139
4	6	0	5.373315	0.975418	-0.398354
5	6	0	5.808446	0.036427	0.543295
6	1	0	5.369033	-1.098655	2.284021
7	1	0	6.141402	1.596027	-0.860447
8	1	0	6.873964	-0.068811	0.713706
9	15	0	3.412459	2.583450	-1.645258
10	1	0	3.914244	3.810643	-1.155799
11	1	0	3.860282	2.604540	-2.981216
12	15	0	2.418756	-0.852806	2.653634
13	1	0	3.137710	-0.861501	3.864743
14	1	0	1.854292	-2.145843	2.636251
15	16	0	1.371860	2.479341	-1.677177
16	16	0	0.932054	0.556676	2.666417
17	15	0	2.739558	0.178967	-0.085700
18	6	0	2.380378	-1.059080	-1.450848
19	1	0	1.614693	-0.586384	-2.075600
20	1	0	3.311613	-1.080639	-2.027485
21	6	0	2.004696	-2.468170	-1.110846
22	6	0	2.984099	-3.464977	-1.167130
23	7	0	0.717698	-2.780993	-0.832262
24	6	0	2.639021	-4.799899	-0.991844
25	1	0	4.011145	-3.185400	-1.379950
26	6	0	0.385682	-4.078528	-0.682616

27	6	0	1.303414	-5.115575	-0.764784
28	1	0	3.395068	-5.577377	-1.051439
29	1	0	-0.659904	-4.280527	-0.482612
30	1	0	0.969679	-6.141184	-0.648071
31	46	0	0.929580	1.404502	0.443156
32	7	0	-0.717813	2.781566	0.830860
33	6	0	-2.004817	2.468604	1.109304
34	6	0	-0.386149	4.079088	0.680318
35	6	0	-2.984534	3.465174	1.164448
36	6	0	-1.304213	5.115933	0.761325
37	1	0	0.659443	4.281269	0.480549
38	6	0	-2.639804	4.800056	0.988177
39	1	0	-4.011558	3.185468	1.377211
40	1	0	-0.970727	6.141542	0.643912
41	1	0	-3.396102	5.577357	1.046895
42	6	0	-2.380253	1.059704	1.450398
43	1	0	-1.614300	0.587510	2.075206
44	1	0	-3.311316	1.081580	2.027307
45	6	0	-3.532652	0.566069	-1.322307
46	6	0	-4.037241	-1.221155	0.725831
47	6	0	-4.927638	0.597935	-1.420599
48	6	0	-5.372827	-0.976919	0.400617
49	6	0	-5.808982	-0.038679	-0.541298
50	1	0	-5.371110	1.095854	-2.282759
51	1	0	-6.140322	-1.597715	0.863440
52	1	0	-6.874646	0.065857	-0.711234
53	15	0	-2.739638	-0.179219	0.086141
54	15	0	-2.420962	0.852085	-2.653749
55	1	0	-1.858450	2.145994	-2.637748
56	1	0	-3.140388	0.858719	-3.864600
57	15	0	-3.410690	-2.583307	1.647368
58	1	0	-3.913043	-3.810815	1.159289
59	1	0	-3.857188	-2.603441	2.983789
60	16	0	-0.932081	-0.555123	-2.665893
61	16	0	-1.370061	-2.479417	1.677236
62	46	0	-0.929302	-1.403979	-0.443051

	1	2	3
	A	A	A
Frequencies --	13.5330	35.5954	35.8405
Red. masses --	6.6933	6.7748	7.2071
Frc consts --	0.0007	0.0051	0.0055
IR Inten --	1.2313	0.7314	0.0049

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.06	0.09	-0.07	-0.01	-0.04	-0.05	0.09	0.01	-0.03
2	6	0.06	0.06	-0.03	-0.01	-0.05	-0.06	0.08	0.04	0.03
3	6	-0.04	0.02	-0.08	0.00	0.02	0.00	0.03	0.00	-0.01
4	6	-0.02	0.06	-0.12	0.00	0.02	0.00	0.04	-0.02	-0.07
5	6	0.02	0.09	-0.11	-0.01	0.00	-0.02	0.06	-0.02	-0.08
6	1	0.10	0.11	-0.08	-0.01	-0.07	-0.07	0.12	0.02	-0.05
7	1	-0.05	0.06	-0.16	0.00	0.03	0.02	0.03	-0.03	-0.11
8	1	0.03	0.11	-0.14	-0.01	0.00	-0.02	0.07	-0.04	-0.13
9	15	-0.08	-0.01	-0.09	0.00	0.05	0.03	0.01	0.01	0.01
10	1	-0.06	0.01	-0.15	0.02	0.03	0.05	0.03	0.00	0.00
11	1	-0.15	-0.04	-0.12	-0.03	0.07	0.02	-0.02	0.01	0.00
12	15	0.11	0.04	0.01	-0.03	-0.13	-0.10	0.14	0.06	0.09
13	1	0.14	0.13	-0.01	-0.04	-0.23	-0.09	0.18	0.20	0.06
14	1	0.19	0.00	0.07	-0.04	-0.12	-0.20	0.22	0.03	0.21
15	16	-0.09	0.00	0.01	-0.01	0.08	0.07	0.01	0.02	0.06
16	16	0.02	-0.06	-0.01	-0.01	-0.11	-0.01	0.04	-0.04	0.04
17	15	0.00	0.01	-0.02	-0.01	0.01	-0.03	0.04	0.02	0.04
18	6	-0.01	-0.03	0.02	-0.04	0.05	-0.05	0.00	0.00	0.06

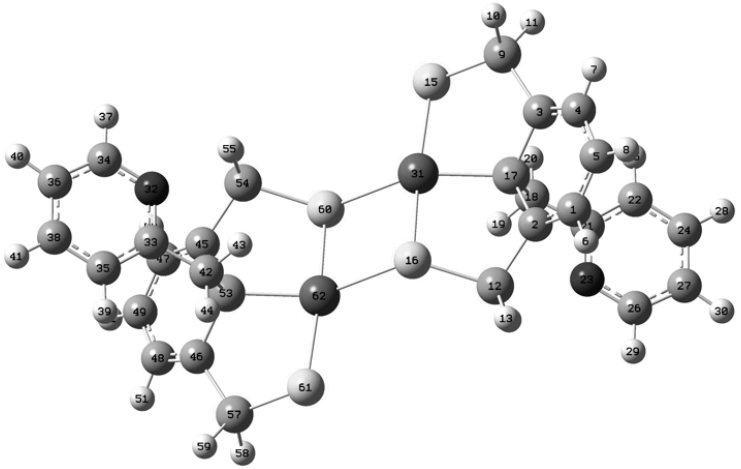
19	1	-0.01	-0.05	0.01	-0.08	0.04	-0.01	0.00	0.01	0.07
20	1	-0.01	-0.04	0.01	-0.07	0.07	-0.09	-0.01	-0.01	0.05
21	6	0.00	-0.02	0.06	0.00	0.04	-0.03	-0.01	0.01	0.06
22	6	0.01	-0.01	0.10	0.02	0.06	-0.08	0.00	0.02	0.16
23	7	0.00	-0.02	0.06	0.03	0.02	0.06	-0.04	0.00	-0.05
24	6	0.02	-0.01	0.14	0.06	0.06	-0.01	-0.01	0.01	0.14
25	1	0.01	-0.01	0.09	0.00	0.08	-0.16	0.02	0.02	0.26
26	6	0.01	-0.02	0.10	0.07	0.02	0.13	-0.04	0.00	-0.08
27	6	0.02	-0.02	0.14	0.09	0.04	0.10	-0.03	0.01	0.01
28	1	0.03	-0.01	0.17	0.08	0.08	-0.04	0.01	0.02	0.22
29	1	0.01	-0.03	0.10	0.09	0.00	0.21	-0.06	-0.01	-0.19
30	1	0.03	-0.02	0.17	0.12	0.03	0.17	-0.03	0.00	-0.03
31	46	-0.01	-0.02	0.01	0.01	0.00	0.03	0.05	0.01	0.06
32	7	0.00	-0.02	0.06	0.03	0.02	0.07	0.03	0.00	0.04
33	6	0.00	-0.02	0.06	0.00	0.04	-0.04	0.01	-0.02	-0.06
34	6	0.01	-0.02	0.10	0.07	0.02	0.14	0.03	0.00	0.06
35	6	0.01	-0.01	0.10	0.02	0.06	-0.10	0.00	-0.03	-0.15
36	6	0.02	-0.02	0.14	0.09	0.04	0.10	0.01	-0.01	-0.02
37	1	0.01	-0.03	0.10	0.10	0.00	0.24	0.04	0.01	0.15
38	6	0.02	-0.01	0.14	0.06	0.06	-0.03	0.00	-0.03	-0.14
39	1	0.01	-0.01	0.10	0.00	0.07	-0.20	-0.02	-0.04	-0.23
40	1	0.03	-0.02	0.17	0.12	0.03	0.17	0.01	-0.01	0.00
41	1	0.03	-0.01	0.17	0.07	0.07	-0.08	-0.02	-0.03	-0.21
42	6	-0.01	-0.03	0.02	-0.04	0.05	-0.06	0.01	-0.01	-0.05
43	1	-0.01	-0.05	0.01	-0.08	0.04	-0.03	0.01	-0.02	-0.06
44	1	-0.01	-0.04	0.01	-0.06	0.07	-0.10	0.02	0.00	-0.03
45	6	0.06	0.06	-0.03	-0.02	-0.05	-0.07	-0.08	-0.03	-0.02
46	6	-0.04	0.02	-0.08	-0.01	0.02	0.00	-0.03	-0.01	0.01
47	6	0.06	0.09	-0.07	-0.02	-0.04	-0.05	-0.09	0.00	0.04
48	6	-0.02	0.06	-0.12	-0.01	0.02	0.01	-0.03	0.02	0.07
49	6	0.02	0.09	-0.11	-0.02	0.00	-0.01	-0.06	0.02	0.09
50	1	0.10	0.11	-0.08	-0.03	-0.08	-0.06	-0.12	0.00	0.06
51	1	-0.05	0.06	-0.16	-0.01	0.04	0.04	-0.03	0.03	0.10
52	1	0.03	0.11	-0.14	-0.02	0.00	0.00	-0.06	0.04	0.13
53	15	0.00	0.01	-0.02	-0.01	0.01	-0.04	-0.04	-0.02	-0.04
54	15	0.11	0.04	0.01	-0.05	-0.14	-0.11	-0.14	-0.04	-0.07
55	1	0.19	0.00	0.07	-0.08	-0.13	-0.24	-0.21	-0.01	-0.17
56	1	0.14	0.13	-0.01	-0.07	-0.26	-0.10	-0.17	-0.16	-0.05
57	15	-0.08	-0.01	-0.09	0.00	0.05	0.03	-0.01	-0.02	-0.01
58	1	-0.06	0.01	-0.15	0.02	0.03	0.05	-0.03	-0.01	-0.01
59	1	-0.15	-0.04	-0.12	-0.02	0.07	0.02	0.02	-0.02	0.00
60	16	0.02	-0.06	-0.01	-0.02	-0.11	-0.02	-0.04	0.06	-0.03
61	16	-0.09	0.00	0.01	-0.01	0.08	0.06	-0.01	-0.03	-0.07
62	46	-0.01	-0.02	0.01	0.00	0.00	0.02	-0.05	-0.01	-0.07

HF=-4856.7252267

Sum of electronic and zero-point Energies= -4856.285791
Sum of electronic and thermal Energies= -4856.247062
Sum of electronic and thermal Enthalpies= -4856.246118
Sum of electronic and thermal Free Energies= -4856.358636

Total free energy in solution:
with all non electrostatic terms (a.u.) = -4856.899047

II.4. Cartesian coordinates, three lower frequencies thermochemistry and PCM energy for II-D



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.206579	0.222916	-0.815908
2	6	0	0.268422	0.646919	0.510156
3	6	0	2.994651	0.250964	0.188112
4	6	0	2.619063	-0.118348	-1.109455
5	6	0	1.318741	-0.073627	-1.612968
6	1	0	-0.776434	0.073699	-1.260930
7	1	0	3.388077	-0.519917	-1.769004
8	1	0	1.149855	-0.388954	-2.636385
9	15	0	4.502297	-0.201098	0.998125
10	1	0	4.921687	-1.454840	0.503118
11	1	0	5.594204	0.624497	0.665920
12	15	0	-1.077099	0.708432	1.643717
13	1	0	-2.246866	0.227655	1.026809
14	1	0	-1.370719	2.027171	2.036809
15	16	0	4.254466	-0.099825	3.029892
16	16	0	-0.516673	-0.471099	3.263616
17	15	0	1.816798	0.877167	1.343528
18	6	0	2.065232	2.663298	1.824328
19	1	0	1.607082	2.786594	2.811987
20	1	0	3.146093	2.792558	1.950028
21	6	0	1.464808	3.640794	0.850414
22	6	0	2.256197	4.378635	-0.031318
23	7	0	0.128845	3.763764	0.908202
24	6	0	1.637058	5.301985	-0.872269
25	1	0	3.334789	4.250898	-0.045808

26	6	0	-0.450902	4.653727	0.097895
27	6	0	0.255408	5.448527	-0.804727
28	1	0	2.226729	5.900511	-1.560692
29	1	0	-1.532844	4.741520	0.176885
30	1	0	-0.268521	6.161647	-1.433129
31	46	0	1.879402	-0.184198	3.314008
32	7	0	0.816476	-4.541389	8.150047
33	6	0	-0.519624	-4.422019	8.211996
34	6	0	1.400053	-5.437755	8.950496
35	6	0	-1.307403	-5.170123	9.088315
36	6	0	0.697543	-6.242776	9.847003
37	1	0	2.482015	-5.522284	8.868297
38	6	0	-0.684278	-6.100082	9.918969
39	1	0	-2.386268	-5.045152	9.106329
40	1	0	1.224472	-6.960667	10.467416
41	1	0	-1.271037	-6.706592	10.602878
42	6	0	-1.124439	-3.436766	7.248684
43	1	0	-0.668354	-3.549630	6.258836
44	1	0	-2.205338	-3.566946	7.124379
45	6	0	0.671778	-1.429161	8.576971
46	6	0	-2.054219	-1.041960	8.910773
47	6	0	0.736617	-1.018269	9.907093
48	6	0	-1.675660	-0.684796	10.210811
49	6	0	-0.373793	-0.732076	10.710243
50	1	0	1.720610	-0.871325	10.350699
51	1	0	-2.443486	-0.290969	10.876395
52	1	0	-0.202635	-0.426515	11.736243
53	15	0	-0.878460	-1.654906	7.746132
54	15	0	2.014188	-1.475530	7.438998
55	1	0	2.310386	-2.788966	7.030596
56	1	0	3.184455	-0.998407	8.057749
57	15	0	-3.564909	-0.584618	8.109041
58	1	0	-3.983410	0.665016	8.615040
59	1	0	-4.655070	-1.413595	8.438465
60	16	0	1.446708	-0.279989	5.833325
61	16	0	-3.323103	-0.670172	6.075997
62	46	0	-0.948919	-0.574080	5.786996

	1			2			3		
	A			A			A		
Frequencies --	5.9596			12.0408			21.5479		
Red. masses --	8.2820			7.3040			7.2047		
Frc consts --	0.0002			0.0006			0.0020		
IR Inten --	2.1959			0.0215			0.0001		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
1 6	-0.01	0.08	-0.02	-0.06	0.07	0.01	-0.04	0.06	0.01
2 6	-0.01	0.03	0.00	-0.03	0.06	0.01	-0.02	0.06	0.01
3 6	-0.01	0.06	-0.04	-0.05	-0.06	-0.02	-0.03	0.06	-0.01
4 6	-0.01	0.10	-0.05	-0.08	-0.03	-0.02	-0.04	0.06	-0.01
5 6	-0.02	0.11	-0.04	-0.08	0.03	0.00	-0.04	0.06	0.00
6 1	-0.02	0.08	-0.01	-0.07	0.11	0.02	-0.04	0.06	0.02
7 1	-0.02	0.13	-0.07	-0.10	-0.06	-0.03	-0.04	0.07	-0.02
8 1	-0.03	0.15	-0.05	-0.11	0.04	0.00	-0.05	0.06	0.00
9 15	0.00	0.04	-0.07	-0.06	-0.12	-0.04	-0.02	0.07	-0.02
10 1	0.00	0.06	-0.11	-0.12	-0.15	-0.03	-0.02	0.07	-0.03
11 1	0.00	0.05	-0.05	-0.02	-0.18	-0.06	-0.02	0.07	-0.03
12 15	0.00	-0.02	0.01	-0.01	0.10	0.03	-0.01	0.06	0.02
13 1	0.00	-0.01	0.00	-0.04	0.16	0.04	-0.02	0.08	0.03
14 1	0.00	-0.04	0.06	0.05	0.10	0.06	0.00	0.06	0.04
15 16	0.02	-0.02	-0.06	-0.03	-0.10	-0.03	0.00	0.06	-0.02
16 16	0.02	-0.08	-0.04	-0.03	0.04	0.00	0.00	0.04	0.01
17 15	0.00	0.01	-0.01	-0.01	-0.01	0.00	-0.02	0.06	0.00
18 6	-0.01	-0.01	0.06	0.08	-0.02	0.00	-0.03	0.06	-0.01
19 1	0.00	-0.05	0.07	0.10	0.00	0.01	-0.08	0.08	-0.04
20 1	-0.01	0.00	0.05	0.08	-0.07	-0.02	-0.04	0.06	0.04
21 6	-0.03	0.03	0.10	0.10	0.01	0.01	0.03	0.04	-0.07

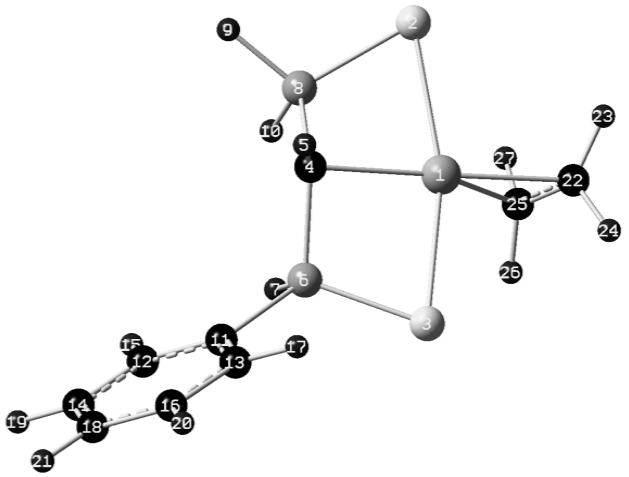
22	6	-0.04	0.07	0.12	0.12	-0.02	0.01	0.07	-0.01	-0.07
23	7	-0.03	0.01	0.12	0.11	0.06	0.03	0.03	0.06	-0.14
24	6	-0.06	0.10	0.17	0.14	0.01	0.02	0.12	-0.03	-0.13
25	1	-0.04	0.08	0.10	0.11	-0.06	-0.01	0.07	-0.02	-0.01
26	6	-0.05	0.04	0.16	0.13	0.09	0.05	0.07	0.03	-0.20
27	6	-0.06	0.08	0.19	0.15	0.07	0.04	0.12	-0.02	-0.20
28	1	-0.07	0.13	0.18	0.15	0.00	0.02	0.16	-0.07	-0.13
29	1	-0.04	0.03	0.18	0.13	0.13	0.06	0.07	0.05	-0.25
30	1	-0.07	0.10	0.22	0.16	0.09	0.06	0.16	-0.04	-0.25
31	46	0.02	-0.06	-0.05	-0.03	-0.01	0.00	0.00	0.05	-0.01
32	7	-0.03	0.01	0.12	0.11	0.06	0.03	-0.02	-0.06	0.14
33	6	-0.03	0.02	0.10	0.10	0.01	0.01	-0.03	-0.04	0.07
34	6	-0.04	0.04	0.16	0.13	0.09	0.05	-0.07	-0.03	0.20
35	6	-0.04	0.07	0.12	0.12	-0.01	0.01	-0.07	0.01	0.07
36	6	-0.06	0.08	0.19	0.15	0.07	0.04	-0.12	0.02	0.20
37	1	-0.04	0.03	0.18	0.13	0.13	0.06	-0.07	-0.05	0.25
38	6	-0.06	0.09	0.17	0.14	0.02	0.02	-0.12	0.03	0.13
39	1	-0.04	0.07	0.11	0.11	-0.06	-0.01	-0.07	0.02	0.02
40	1	-0.07	0.10	0.22	0.17	0.09	0.05	-0.15	0.04	0.26
41	1	-0.07	0.12	0.18	0.16	0.00	0.02	-0.16	0.07	0.13
42	6	-0.01	-0.01	0.06	0.08	-0.02	0.00	0.03	-0.06	0.02
43	1	0.00	-0.05	0.07	0.10	0.00	0.01	0.08	-0.08	0.04
44	1	-0.01	0.00	0.05	0.08	-0.07	-0.02	0.04	-0.06	-0.04
45	6	-0.01	0.03	0.00	-0.03	0.06	0.01	0.02	-0.05	-0.01
46	6	-0.01	0.06	-0.04	-0.05	-0.05	-0.02	0.03	-0.06	0.01
47	6	-0.01	0.08	-0.02	-0.06	0.07	0.01	0.04	-0.06	-0.01
48	6	-0.02	0.10	-0.05	-0.08	-0.03	-0.02	0.04	-0.06	0.01
49	6	-0.02	0.11	-0.04	-0.08	0.03	0.00	0.04	-0.06	0.00
50	1	-0.02	0.08	-0.01	-0.07	0.11	0.02	0.04	-0.05	-0.02
51	1	-0.02	0.13	-0.07	-0.10	-0.06	-0.03	0.04	-0.06	0.02
52	1	-0.03	0.15	-0.04	-0.10	0.04	0.00	0.05	-0.06	0.00
53	15	0.00	0.01	-0.01	-0.01	-0.01	0.00	0.02	-0.06	0.00
54	15	0.00	-0.02	0.01	-0.01	0.10	0.03	0.01	-0.06	-0.02
55	1	0.00	-0.04	0.07	0.05	0.10	0.06	0.00	-0.05	-0.04
56	1	0.00	-0.01	0.01	-0.04	0.16	0.04	0.02	-0.07	-0.03
57	15	0.00	0.04	-0.07	-0.06	-0.12	-0.04	0.02	-0.07	0.02
58	1	0.00	0.06	-0.11	-0.12	-0.14	-0.04	0.02	-0.07	0.03
59	1	0.00	0.05	-0.05	-0.02	-0.17	-0.06	0.02	-0.07	0.03
60	16	0.02	-0.08	-0.04	-0.03	0.04	0.00	0.00	-0.04	-0.01
61	16	0.02	-0.02	-0.06	-0.03	-0.10	-0.04	0.00	-0.06	0.02
62	46	0.02	-0.06	-0.05	-0.03	-0.01	-0.01	0.00	-0.05	0.01

HF=-4856.6953328

Sum of electronic and zero-point Energies= -4856.258911
Sum of electronic and thermal Energies= -4856.218933
Sum of electronic and thermal Enthalpies= -4856.217988
Sum of electronic and thermal Free Energies= -4856.337646

Total free energy in solution:
with all non electrostatic terms (a.u.) = -4856.871257

II.5. Cartesian coordinates, three lower frequencies and thermochemistry of II-E



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.003802	-0.008878	-0.029697
2	16	0	-0.033073	0.116119	2.415652
3	16	0	0.681180	-0.093177	-2.353760
4	6	0	2.107603	0.343123	0.255735
5	1	0	2.411095	1.390364	0.279079
6	15	0	2.325541	-0.549695	-1.257613
7	1	0	2.443929	-1.909119	-0.907533
8	15	0	1.803373	-0.463932	1.795681
9	1	0	2.795120	-0.191033	2.787980
10	1	0	2.008930	-1.846503	1.613037
11	6	0	3.900476	-0.267513	-2.133099
12	6	0	4.950321	-1.187572	-2.019674
13	6	0	4.069663	0.890559	-2.893244
14	6	0	6.164285	-0.941002	-2.660003
15	1	0	4.823122	-2.098012	-1.436308
16	6	0	5.278572	1.134890	-3.532236
17	1	0	3.246943	1.591657	-2.995833
18	6	0	6.328213	0.221318	-3.415582
19	1	0	6.977314	-1.657789	-2.575667
20	1	0	5.403063	2.036757	-4.126391
21	1	0	7.272806	0.413101	-3.918609
22	6	0	-2.105192	-0.223978	-0.322558
23	1	0	-2.669523	0.206497	0.502994
24	1	0	-2.408655	0.122836	-1.309137

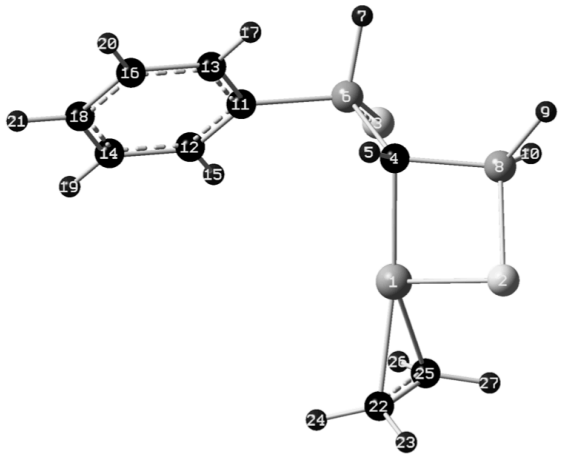
25	6	0	-1.505562	-1.491929	-0.178337
26	1	0	-1.343759	-2.122761	-1.051371
27	1	0	-1.604257	-2.038089	0.758892

	1	2	3
	A	A	A
Frequencies --	14.5026	41.0776	54.6490
Red. masses --	3.9555	5.8089	6.4102
Frc consts --	0.0005	0.0058	0.0113
IR Inten --	0.0974	0.4854	0.2041

Sum of electronic and zero-point Energies= -1934.225238
Sum of electronic and thermal Energies= -1934.208921
Sum of electronic and thermal Enthalpies= -1934.207977
Sum of electronic and thermal Free Energies= -1934.272179

HF=-1934.4219247

II.6. Cartesian coordinates, three lower frequencies and thermochemistry of II-ETSII-F



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.790771	-0.844567	0.500696
2	16	0	-0.839723	-0.831421	2.788392

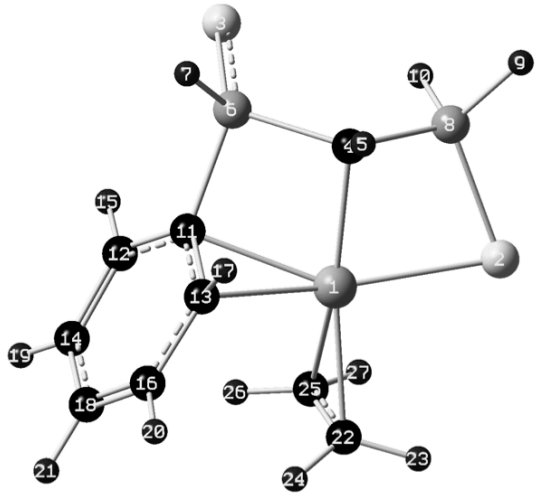
3	16	0	2.501998	-0.827489	-1.108764
4	6	0	0.631212	0.717246	0.895780
5	1	0	0.099016	1.643557	1.141514
6	15	0	1.815715	0.892211	-0.446967
7	1	0	2.839029	1.774059	-0.007575
8	15	0	1.055565	-0.187825	2.362623
9	1	0	1.681757	0.477466	3.465237
10	1	0	2.018193	-1.160369	2.036294
11	6	0	0.955214	1.944585	-1.664856
12	6	0	0.491658	1.401103	-2.865796
13	6	0	0.762793	3.299963	-1.393341
14	6	0	-0.180603	2.212895	-3.779979
15	1	0	0.675941	0.351270	-3.083450
16	6	0	0.096022	4.108649	-2.304694
17	1	0	1.139621	3.733095	-0.470421
18	6	0	-0.380985	3.564985	-3.499428
19	1	0	-0.540579	1.790112	-4.714688
20	1	0	-0.048486	5.164188	-2.087521
21	1	0	-0.901222	4.198397	-4.213806
22	6	0	-2.445588	-2.108402	0.086639
23	1	0	-3.168737	-2.168288	0.897451
24	1	0	-2.884178	-1.848026	-0.879286
25	6	0	-1.247442	-2.855459	0.124346
26	1	0	-0.765637	-3.159600	-0.808086
27	1	0	-1.014664	-3.500849	0.969855

	1	2	3
	A	A	A
Frequencies --	-34.0232	17.4073	28.9995
Red. masses --	11.1259	3.9665	7.6864
Frc consts --	0.0076	0.0007	0.0038
IR Inten --	2.0762	0.1323	0.2918

Sum of electronic and zero-point Energies= -1934.191007
Sum of electronic and thermal Energies= -1934.175222
Sum of electronic and thermal Enthalpies= -1934.174278
Sum of electronic and thermal Free Energies= -1934.237915

HF=-1934.3864469

II.7. Cartesian coordinates, three lower frequencies and thermochemistry of II-F



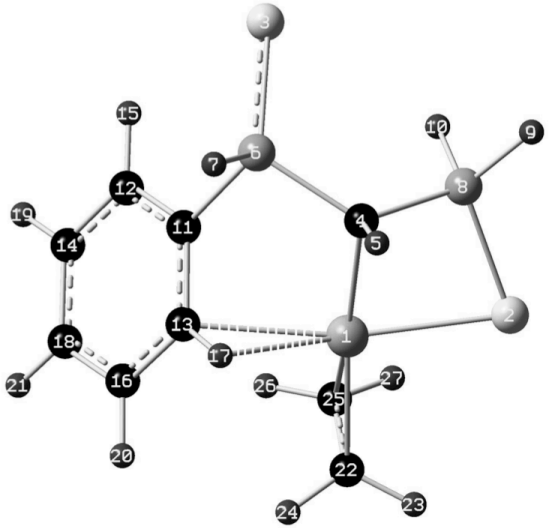
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.009361	-0.129690	-0.241778
2	16	0	0.185893	-0.385274	2.142643
3	16	0	4.091495	0.531210	-1.117280
4	6	0	1.286175	1.536420	0.178507
5	1	0	0.766983	2.493910	0.259922
6	15	0	2.289999	1.283782	-1.303668
7	1	0	2.279730	2.541296	-1.968014
8	15	0	1.774200	0.823944	1.713331
9	1	0	2.081790	1.736231	2.757840
10	1	0	2.990007	0.141688	1.515439
11	6	0	1.035825	0.254838	-2.156370
12	6	0	1.426502	-0.808645	-3.034696
13	6	0	-0.311626	0.769740	-2.210496
14	6	0	0.508978	-1.373670	-3.880286
15	1	0	2.460495	-1.145394	-3.013876
16	6	0	-1.219051	0.163312	-3.139239
17	1	0	-0.520873	1.803812	-1.943316
18	6	0	-0.833734	-0.889842	-3.925261
19	1	0	0.808054	-2.181864	-4.543791
20	1	0	-2.222167	0.575253	-3.228585
21	1	0	-1.539552	-1.337368	-4.621072
22	6	0	-1.616534	-1.541176	-0.397540
23	1	0	-2.099735	-1.614866	0.575261
24	1	0	-2.286914	-1.311685	-1.220835
25	6	0	-0.411909	-2.207056	-0.638780
26	1	0	-0.133571	-2.476668	-1.653333
27	1	0	0.061452	-2.801398	0.139733

	1 A	2 A	3 A
Frequencies --	37.8240	78.0712	102.3452
Red. masses --	6.5704	6.2247	3.3275
Frc consts --	0.0055	0.0224	0.0205
IR Inten --	1.6035	2.4690	0.0286

Sum of electronic and zero-point Energies= -1934.224158
Sum of electronic and thermal Energies= -1934.208542
Sum of electronic and thermal Enthalpies= -1934.207598
Sum of electronic and thermal Free Energies= -1934.267767

HF=-1934.4209172

II.8. Cartesian coordinates, three lower frequencies and thermochemistry of II-FTSII-G



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.001089	-0.005138	0.000270
2	16	0	0.004912	-0.009864	2.355500
3	16	0	4.650144	-0.004936	-0.621550
4	6	0	1.762400	1.128550	0.346421
5	1	0	1.538084	2.192352	0.475218
6	15	0	2.886164	0.766925	-1.011036
7	1	0	2.943612	2.005991	-1.701503

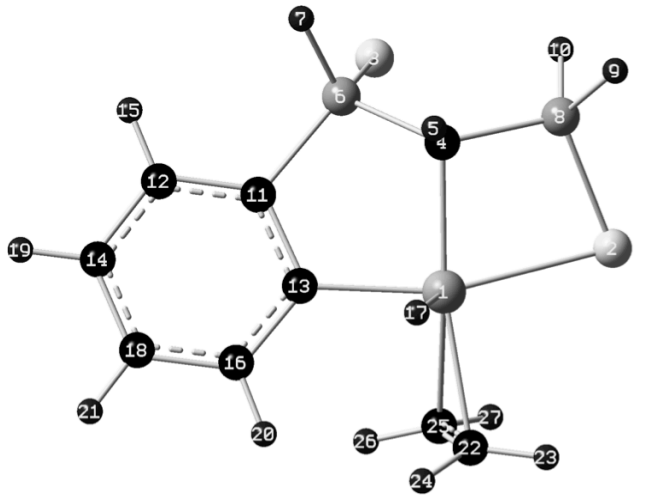
8	15	0	1.966815	0.293959	1.902134
9	1	0	2.700555	0.950547	2.931735
10	1	0	2.738527	-0.861453	1.693145
11	6	0	1.831718	-0.246546	-2.130526
12	6	0	2.368697	-1.336307	-2.823120
13	6	0	0.482432	0.104169	-2.326702
14	6	0	1.575133	-2.040017	-3.727154
15	1	0	3.403322	-1.620361	-2.645760
16	6	0	-0.299857	-0.599239	-3.247506
17	1	0	0.075966	1.041404	-1.895530
18	6	0	0.244184	-1.666929	-3.952424
19	1	0	1.998451	-2.882673	-4.268847
20	1	0	-1.336978	-0.310332	-3.397452
21	1	0	-0.362048	-2.214465	-4.669555
22	6	0	-2.000037	-0.751500	-0.199785
23	1	0	-2.594962	-0.536703	0.685784
24	1	0	-2.463444	-0.426738	-1.130640
25	6	0	-1.090266	-1.823967	-0.201442
26	1	0	-0.834261	-2.330192	-1.130044
27	1	0	-0.966145	-2.436347	0.689677

	1	2	3
	A	A	A
Frequencies --	-155.5287	30.1815	78.7781
Red. masses --	4.5892	7.0687	5.3043
Frc consts --	0.0654	0.0038	0.0194
IR Inten --	2.5229	3.6376	3.4311

Sum of electronic and zero-point Energies= -1934.205373
Sum of electronic and thermal Energies= -1934.189995
Sum of electronic and thermal Enthalpies= -1934.189051
Sum of electronic and thermal Free Energies= -1934.249504

HF=-1934.4008623

II.9. Cartesian coordinates, three lower frequencies and thermochemistry of II-G



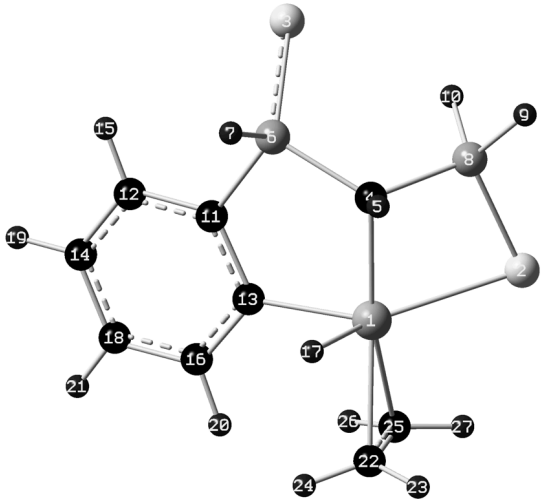
Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	77	-0.000011854	-0.000005640	-0.000006830
2	16	0.000006111	0.000003950	0.000007146
3	16	-0.000003584	-0.000004295	0.000002457
4	6	0.000007507	0.000001911	-0.000000955
5	1	0.000003108	-0.000002468	0.000001380
6	15	-0.000007763	-0.000000814	0.000003336
7	1	0.000001524	-0.000002622	0.000004697
8	15	-0.000011710	-0.000012717	0.000000046
9	1	0.000001556	-0.000003805	0.000004397
10	1	-0.000002706	-0.000002098	0.000004925
11	6	0.000006907	0.000002555	0.000006027
12	6	-0.000002765	-0.000003147	-0.000001980
13	6	0.000008829	-0.000000529	-0.000000847
14	6	0.000003352	0.000001840	0.000001229
15	1	0.000002412	-0.000001264	0.000003236
16	6	-0.000001347	-0.000001085	-0.000003733
17	1	0.000002784	0.000003837	0.000000619
18	6	0.000002106	0.000002933	0.000000190
19	1	0.000003731	0.000001059	0.000001008
20	1	0.000001203	0.000004505	-0.000003114
21	1	0.000002917	0.000003640	-0.000002152
22	6	-0.000000033	0.000001886	-0.000001139
23	1	-0.000001823	0.000001875	-0.000003590
24	1	0.000000395	0.000003767	-0.000003788
25	6	-0.000003621	0.000004975	-0.000007892
26	1	-0.000001924	0.000001940	-0.000001274
27	1	-0.000005310	-0.000000189	-0.000003397

	1	2	3
	A	A	A
Frequencies --	16.0151	44.9688	81.9702
Red. masses --	10.4701	8.5825	4.5083
Frc consts --	0.0016	0.0102	0.0178
IR Inten --	1.3347	1.6214	1.2801

Sum of electronic and zero-point Energies= -1934.233838
Sum of electronic and thermal Energies= -1934.218038
Sum of electronic and thermal Enthalpies= -1934.217094
Sum of electronic and thermal Free Energies= -1934.279059

HF=-1934.4285679

II.10. Cartesian coordinates, three lower frequencies and thermochemistry of II-GTSII-H



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.794305	-0.536099	0.469145
2	16	0	0.333114	-1.244586	2.571160
3	16	0	2.924958	2.427198	-0.212157
4	6	0	0.156130	1.274538	1.022171
5	1	0	-0.578036	1.957325	1.463138
6	15	0	0.997475	2.051227	-0.396989
7	1	0	0.241816	3.236818	-0.577463
8	15	0	1.191433	0.578360	2.291886

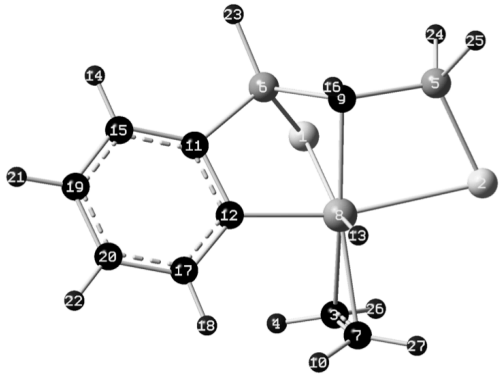
9	1	0	1.291119	1.350864	3.473831
10	1	0	2.523041	0.518906	1.839306
11	6	0	0.486884	0.962239	-1.747567
12	6	0	0.942873	1.224336	-3.045485
13	6	0	-0.361448	-0.128911	-1.455361
14	6	0	0.533694	0.424092	-4.106302
15	1	0	1.633094	2.049319	-3.213358
16	6	0	-0.776696	-0.900783	-2.551529
17	1	0	-1.955850	0.360212	-0.070441
18	6	0	-0.336449	-0.636708	-3.847980
19	1	0	0.885125	0.622813	-5.115282
20	1	0	-1.453957	-1.737552	-2.409432
21	1	0	-0.677124	-1.271738	-4.663533
22	6	0	-2.416824	-1.940440	0.078307
23	1	0	-3.070818	-1.927669	0.948644
24	1	0	-2.906251	-1.699914	-0.859908
25	6	0	-1.232761	-2.665657	0.105441
26	1	0	-0.742682	-2.988027	-0.808427
27	1	0	-0.963216	-3.233538	0.991123

	1	2	3
	A	A	A
Frequencies --	-28.9134	52.2218	65.7261
Red. masses --	6.2478	6.8930	3.7994
Frc consts --	0.0031	0.0111	0.0097
IR Inten --	2.1366	3.7539	0.2781

Sum of electronic and zero-point Energies= -1934.231596
Sum of electronic and thermal Energies= -1934.216867
Sum of electronic and thermal Enthalpies= -1934.215923
Sum of electronic and thermal Free Energies= -1934.274195

HF=-1934.4268864

II.11. Cartesian coordinates, three lower frequencies and thermochemistry of II-H



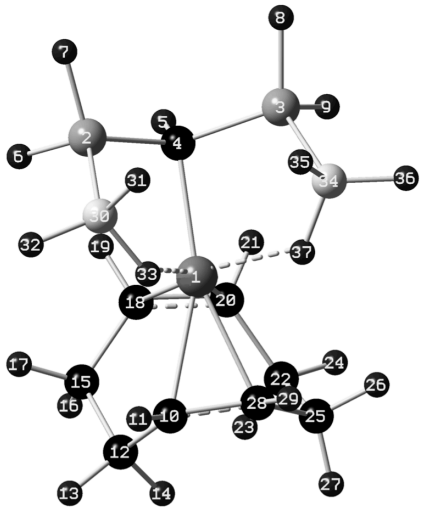
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.010005	-0.000621	0.010947
2	16	0	0.018175	-0.007406	3.761456
3	6	0	2.965568	0.001955	1.645742
4	1	0	3.388008	-0.152291	0.656825
5	15	0	-1.438737	-1.032262	2.840475
6	15	0	-0.532842	-1.940852	0.019666
7	6	0	3.276201	-0.864355	2.692508
8	77	0	1.301763	-1.370956	1.929130
9	6	0	-0.666081	-2.244630	1.775515
10	1	0	3.973526	-1.682810	2.547171
11	6	0	0.856159	-2.980965	-0.412167
12	6	0	1.887097	-2.676695	0.507508
13	1	0	1.644521	-2.464286	3.006577
14	1	0	0.166721	-4.070624	-2.156412
15	6	0	0.989872	-3.880993	-1.469608
16	1	0	-0.763020	-3.280694	2.101204
17	6	0	3.098506	-3.346742	0.311686
18	1	0	3.936876	-3.177039	0.982761
19	6	0	2.212431	-4.531331	-1.629486
20	6	0	3.255063	-4.256282	-0.738163
21	1	0	2.354073	-5.242700	-2.438996
22	1	0	4.209743	-4.764273	-0.862099
23	1	0	-1.640612	-2.263471	-0.814011
24	1	0	-2.338034	-0.230108	2.107523
25	1	0	-2.314138	-1.697515	3.731582
26	1	0	2.611181	1.008055	1.853256
27	1	0	3.168683	-0.537008	3.723147

	1	2	3
	A	A	A
Frequencies --	68.9140	87.1432	112.0303
Red. masses --	6.4859	5.9407	3.9261
Frc consts --	0.0181	0.0266	0.0290
IR Inten --	0.2350	1.7194	3.3684


```
 Sum of electronic and zero-point Energies=          -1934.243013
 Sum of electronic and thermal Energies=             -1934.227658
 Sum of electronic and thermal Enthalpies=           -1934.226714
 Sum of electronic and thermal Free Energies=        -1934.285728

HF=-1934.4384488
```

II.12. Cartesian coordinates, three lower frequencies and thermochemistry of II-I



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.040777	-0.020421	-0.002096
2	15	0	0.003793	0.038493	2.872377
3	15	0	2.705193	-0.018793	1.319031
4	6	0	1.124906	0.749851	1.674594
5	1	0	1.214774	1.833823	1.777856
6	1	0	-0.963768	1.053094	3.023816
7	1	0	0.537037	0.054560	4.197901
8	1	0	3.560859	-0.005893	2.459892
9	1	0	3.346644	0.985430	0.563662
10	6	0	-1.655453	-0.595864	-1.347221
11	1	0	-2.126518	-1.425286	-0.826774
12	6	0	-2.546175	0.590776	-1.653646
13	1	0	-3.592209	0.278049	-1.576578
14	1	0	-2.404132	0.894631	-2.694550
15	6	0	-2.288559	1.768260	-0.704904
16	1	0	-2.604154	2.717367	-1.165460

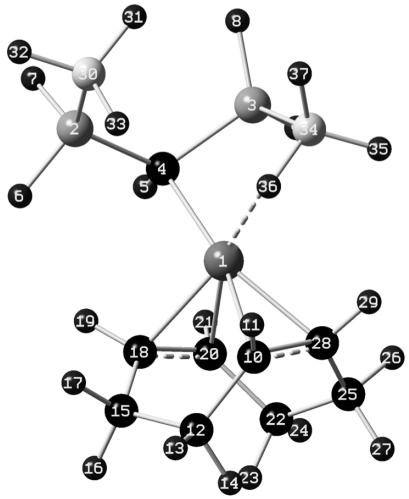
17	1	0	-2.909039	1.650584	0.190163
18	6	0	-0.847351	1.842835	-0.256996
19	1	0	-0.713296	2.459337	0.633851
20	6	0	0.297665	1.726643	-1.109405
21	1	0	1.188249	2.260608	-0.776728
22	6	0	0.215851	1.527101	-2.618442
23	1	0	-0.665599	2.042947	-3.014340
24	1	0	1.073211	2.013424	-3.094075
25	6	0	0.205199	0.040436	-3.013742
26	1	0	1.237443	-0.304485	-3.125207
27	1	0	-0.265228	-0.097830	-3.998759
28	6	0	-0.456052	-0.853188	-1.990578
29	1	0	-0.085098	-1.874943	-1.957772
30	5	0	-0.690482	-1.637470	2.226602
31	1	0	0.064366	-2.513471	2.561265
32	1	0	-1.833237	-1.753216	2.594231
33	1	0	-0.641276	-1.550276	0.975666
34	5	0	2.500894	-1.680179	0.366026
35	1	0	2.269602	-2.555628	1.157988
36	1	0	3.477065	-1.835433	-0.328241
37	1	0	1.502585	-1.442167	-0.340922

	1	2	3
	A	A	A
Frequencies --	33.4518	48.6973	93.7216
Red. masses --	2.9238	4.1380	2.2024
Frc consts --	0.0019	0.0058	0.0114
IR Inten --	7.2299	0.6810	0.7005

Sum of electronic and zero-point Energies= -1199.396863
Sum of electronic and thermal Energies= -1199.379274
Sum of electronic and thermal Enthalpies= -1199.378330
Sum of electronic and thermal Free Energies= -1199.441276

HF=-1199.6965408

II.12.Cartesian coordinates, three lower frequencies and thermochemistry of II-J



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-0.130167	-0.095920	0.132130
2	15	0	0.062849	-0.248535	3.373224
3	15	0	2.335723	0.306353	1.422863
4	6	0	0.665333	0.692142	1.949452
5	1	0	0.510686	1.763354	2.106197
6	1	0	-1.310423	0.084402	3.414505
7	1	0	0.485219	0.494527	4.508467
8	1	0	3.290483	0.277203	2.482552
9	1	0	2.769989	1.471791	0.759794
10	6	0	-1.357077	-1.148693	-1.360169
11	1	0	-1.210886	-2.199530	-1.116753
12	6	0	-2.791654	-0.659714	-1.329988
13	1	0	-3.462188	-1.524278	-1.345502
14	1	0	-3.012544	-0.100675	-2.243211
15	6	0	-3.096612	0.189987	-0.084223
16	1	0	-3.971590	0.833387	-0.261687
17	1	0	-3.378099	-0.473043	0.740549
18	6	0	-1.920095	1.015426	0.379660
19	1	0	-1.982376	1.330467	1.420717
20	6	0	-1.046882	1.742734	-0.446633
21	1	0	-0.475404	2.536560	0.032151
22	6	0	-1.197421	1.882592	-1.952039
23	1	0	-2.256675	1.839106	-2.221590
24	1	0	-0.858743	2.878850	-2.253051
25	6	0	-0.394610	0.823102	-2.725288
26	1	0	0.629925	1.182404	-2.865899
27	1	0	-0.806344	0.692473	-3.737121
28	6	0	-0.312741	-0.502702	-2.010366
29	1	0	0.566828	-1.096350	-2.248978
30	5	0	0.465717	-2.120913	3.559182

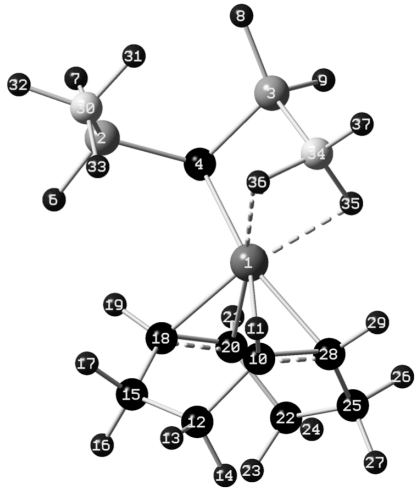
31	1	0	1.678863	-2.170950	3.562271
32	1	0	-0.021043	-2.398914	4.635724
33	1	0	-0.047287	-2.684772	2.620722
34	5	0	2.204975	-1.247939	0.278028
35	1	0	2.719075	-1.030253	-0.787788
36	1	0	0.962790	-1.541237	0.173383
37	1	0	2.607853	-2.211440	0.871471

	1	2	3
	A	A	A
Frequencies --	32.5912	44.8499	52.3678
Red. masses --	3.2132	4.2388	3.1577
Frc consts --	0.0020	0.0050	0.0051
IR Inten --	4.5389	1.8882	4.1545

Sum of electronic and zero-point Energies= -1199.396470
Sum of electronic and thermal Energies= -1199.378530
Sum of electronic and thermal Enthalpies= -1199.377586
Sum of electronic and thermal Free Energies= -1199.442059

HF=-1199.6962136

II.13. Cartesian coordinates, three lower frequencies and thermochemistry of II-K



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-0.214773	-0.441561	-0.533046
2	15	0	-0.183308	0.218538	2.719237
3	15	0	2.227960	-0.503450	1.115526
4	6	0	0.725510	0.507122	1.174587
5	1	0	0.945536	1.572692	1.063789
6	1	0	-1.347833	1.005240	2.587125
7	1	0	0.484054	1.010632	3.692535
8	1	0	2.795599	-0.765676	2.392471
9	1	0	3.235782	0.323140	0.573778
10	6	0	-1.660406	-1.636709	-1.700033
11	1	0	-1.564012	-2.633945	-1.276294
12	6	0	-3.051807	-1.035580	-1.663589
13	1	0	-3.778164	-1.835249	-1.488889
14	1	0	-3.297909	-0.621485	-2.645546
15	6	0	-3.191798	0.032938	-0.572033
16	1	0	-4.020065	0.720246	-0.803275
17	1	0	-3.459792	-0.452475	0.372261
18	6	0	-1.908686	0.795633	-0.341233
19	1	0	-1.890791	1.325776	0.608507
20	6	0	-1.047858	1.305012	-1.347325
21	1	0	-0.419831	2.146548	-1.056600
22	6	0	-1.333164	1.218083	-2.840666
23	1	0	-2.413819	1.247279	-3.011042
24	1	0	-0.936314	2.110384	-3.334927

25	6	0	-0.713016	-0.031311	-3.486181
26	1	0	0.312220	0.197458	-3.794652
27	1	0	-1.249063	-0.299415	-4.408858
28	6	0	-0.647720	-1.214414	-2.551288
29	1	0	0.144324	-1.927102	-2.768138
30	5	0	-0.470665	-1.581571	3.338799
31	1	0	0.634401	-2.088425	3.353810
32	1	0	-0.931866	-1.428755	4.450471
33	1	0	-1.228543	-2.099577	2.552160
34	5	0	1.618081	-1.873151	-0.083284
35	1	0	1.573816	-1.169381	-1.115275
36	1	0	0.477504	-2.138444	0.347486
37	1	0	2.273774	-2.857542	-0.269927

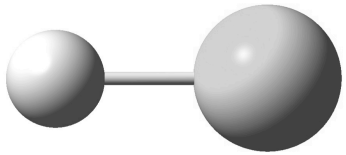
	1	2	3
	A	A	A
Frequencies --	35.6757	52.1924	91.2401
Red. masses --	3.9425	3.0952	3.6385
Frc consts --	0.0030	0.0050	0.0178
IR Inten --	2.1237	7.2823	1.5845

Sum of electronic and zero-point Energies= -1199.395247
Sum of electronic and thermal Energies= -1199.377719
Sum of electronic and thermal Enthalpies= -1199.376774
Sum of electronic and thermal Free Energies= -1199.439499

HF=-1199.6951394

III. OPTIMIZED STRUCTURES OF PART III

III.1. Cartesian coordinates, frequency and PCM energy for HCl



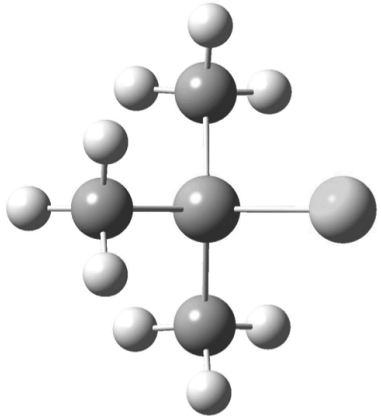
Center Number	Atomic Number	Atomic Type	X	Y	Z
1	17	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.290000

	1
	SG
Frequencies --	2925.1381
Red. masses --	1.0360
Frc consts --	5.2228
IR Inten --	13.3195

Atom AN	X	Y	Z
1 17	0.00	0.00	0.03
2 1	0.00	0.00	-1.00

Total free energy in solution:
with all non electrostatic terms (a.u.) = -460.838192

III.2. Cartesian coordinates, three lower frequencies and PCM energy for Me_3SiCl



Center Number	Atomic Number	Atomic Type	X	Y	Z
1	14	0	0.069998	0.000000	0.025602
2	6	0	-0.005089	0.000000	1.905982
3	1	0	1.006727	0.000000	2.332778
4	1	0	-0.529441	0.885933	2.282481
5	1	0	-0.529441	-0.885933	2.282481
6	6	0	0.893252	-1.556740	-0.638005
7	1	0	0.891913	-1.570090	-1.734111
8	1	0	1.936982	-1.615092	-0.301471
9	1	0	0.376562	-2.458905	-0.290565
10	6	0	0.893252	1.556740	-0.638005
11	1	0	1.936982	1.615092	-0.301471
12	1	0	0.891913	1.570090	-1.734111
13	1	0	0.376562	2.458905	-0.290565
14	17	0	-1.921637	0.000000	-0.677689

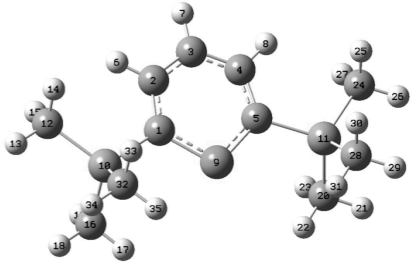
	1	2	3
	A	A	A
Frequencies --	137.0923	158.8477	159.0506
Red. masses --	1.0116	1.0238	1.0258
Frc consts --	0.0112	0.0152	0.0153
IR Inten --	0.0000	0.0022	0.0040

Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
1 14	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00
2 6	0.00	0.00	0.00	-0.02	0.00	0.00	0.00	0.01	0.00
3 1	0.00	0.42	0.00	-0.03	0.00	0.02	0.00	-0.38	0.00
4 1	-0.36	-0.20	-0.02	-0.03	0.00	0.00	0.35	0.22	0.01
5 1	0.36	-0.20	0.02	-0.03	0.00	0.00	-0.35	0.22	-0.01
6 6	0.00	-0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00

7	1	0.25	0.11	0.01	-0.35	-0.18	0.01	0.27	0.15	0.00
8	1	-0.09	-0.15	0.25	0.13	0.22	-0.32	-0.08	-0.14	0.25
9	1	-0.18	0.01	-0.21	0.26	-0.01	0.33	-0.16	0.02	-0.23
10	6	0.00	-0.01	-0.01	0.01	0.00	0.01	-0.01	0.01	0.00
11	1	0.09	-0.15	-0.25	0.13	-0.22	-0.32	0.08	-0.14	-0.25
12	1	-0.25	0.11	-0.01	-0.35	0.18	0.01	-0.27	0.15	0.00
13	1	0.18	0.01	0.21	0.26	0.01	0.33	0.16	0.02	0.23
14	17	0.00	0.00	0.00	0.00	0.00	-0.01	0.00	-0.02	0.00

Total free energy in solution:
with all non electrostatic terms (a.u.) = -869.603925

III.3. Cartesian coordinates, three lower frequencies and PCM energy for III-A



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.178160	-0.002022	-0.166711
2	6	0	-0.024271	-0.007957	1.227546
3	6	0	1.207804	-0.009362	1.890388
4	6	0	2.440095	-0.004855	1.227974
5	6	0	2.594450	0.001457	-0.166237
6	1	0	-0.916282	-0.011786	1.854424
7	1	0	1.207621	-0.014123	2.978525
8	1	0	3.331899	-0.006437	1.855155
9	15	0	1.208349	0.004377	-1.245302
10	14	0	-1.912761	-0.000877	-0.957565
11	14	0	4.329329	0.007066	-0.956475
12	6	0	-3.233696	-0.004043	0.402337
13	1	0	-4.233774	-0.003224	-0.050352
14	1	0	-3.166158	-0.892667	1.042347
15	1	0	-3.166382	0.881850	1.046140
16	6	0	-2.114916	1.547425	-2.029651
17	1	0	-1.363325	1.579198	-2.827846
18	1	0	-3.105801	1.571022	-2.501908
19	1	0	-2.005146	2.462747	-1.434808
20	6	0	4.528428	1.556675	-2.027244
21	1	0	5.519459	1.582920	-2.499053
22	1	0	3.777104	1.587350	-2.825736
23	1	0	4.416298	2.471268	-1.431720
24	6	0	5.649795	0.005757	0.403885
25	1	0	5.584100	-0.883585	1.043086
26	1	0	6.650024	0.009322	-0.048456
27	1	0	5.580198	0.890923	1.048447
28	6	0	4.534372	-1.535615	-2.036085
29	1	0	5.525378	-1.555183	-2.508270

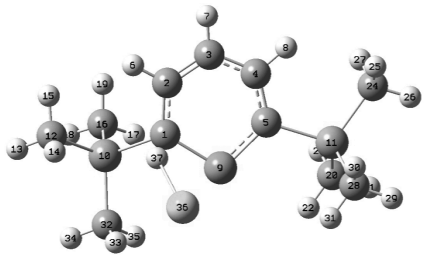
30	1	0	4.426070	-2.454045	-1.445785
31	1	0	3.782962	-1.564728	-2.834555
32	6	0	-2.114026	-1.544872	-2.036004
33	1	0	-2.003746	-2.462587	-1.444958
34	1	0	-3.104875	-1.567088	-2.508400
35	1	0	-1.362362	-1.572875	-2.834277

	1	2	3
	A	A	A
Frequencies --	26.1033	26.8375	54.3917
Red. masses --	3.5938	2.9016	4.8346
Frc consts --	0.0014	0.0012	0.0084
IR Inten --	0.1050	0.0000	0.7422

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.11	0.00
2	6	0.00	0.15	0.00	0.00	-0.01	0.00	0.00	-0.03	0.00
3	6	0.00	0.22	0.00	0.00	0.00	0.00	0.00	-0.08	0.00
4	6	0.00	0.15	0.00	0.00	0.00	0.00	0.00	-0.03	0.00
5	6	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.11	0.00
6	1	0.00	0.21	0.00	0.00	-0.01	0.00	0.00	-0.12	0.00
7	1	0.00	0.32	0.00	0.00	0.00	0.00	0.00	-0.18	0.00
8	1	0.00	0.21	0.00	0.00	0.01	0.00	0.00	-0.12	0.00
9	15	0.00	-0.08	0.00	0.00	0.00	0.00	0.00	0.26	0.00
10	14	0.00	-0.03	0.00	0.00	0.02	0.00	0.00	-0.02	0.00
11	14	0.00	-0.03	0.00	0.00	-0.01	0.00	0.00	-0.02	0.00
12	6	0.00	-0.18	0.00	0.00	-0.14	0.00	0.00	-0.10	0.00
13	1	0.00	-0.25	0.00	0.00	-0.16	0.00	0.00	-0.20	0.00
14	1	0.08	-0.19	-0.02	0.04	-0.18	-0.06	0.07	-0.09	0.01
15	1	-0.08	-0.19	0.02	-0.05	-0.18	0.06	-0.07	-0.09	-0.01
16	6	-0.08	0.03	0.09	-0.04	0.11	0.14	-0.14	-0.07	-0.05
17	1	-0.08	0.11	0.10	-0.04	0.20	0.14	-0.13	-0.02	-0.04
18	1	-0.08	0.01	0.09	-0.04	0.13	0.14	-0.13	-0.19	-0.07
19	1	-0.13	0.00	0.15	-0.06	0.06	0.22	-0.25	-0.04	-0.08
20	6	0.08	0.02	0.09	-0.04	-0.11	-0.14	0.14	-0.07	-0.05
21	1	0.08	0.00	0.09	-0.04	-0.13	-0.14	0.13	-0.19	-0.07
22	1	0.08	0.11	0.09	-0.04	-0.20	-0.14	0.13	-0.02	-0.04
23	1	0.12	0.00	0.14	-0.07	-0.06	-0.23	0.25	-0.04	-0.08
24	6	0.00	-0.17	0.00	0.00	0.14	0.00	0.00	-0.10	0.00
25	1	-0.08	-0.18	-0.02	0.05	0.18	0.06	-0.07	-0.09	0.01
26	1	0.00	-0.25	0.00	0.00	0.17	0.00	0.00	-0.20	0.00
27	1	0.08	-0.18	0.02	-0.05	0.18	-0.06	0.07	-0.09	-0.01
28	6	-0.08	0.02	-0.09	0.04	-0.11	0.14	-0.14	-0.07	0.05
29	1	-0.08	0.00	-0.09	0.04	-0.13	0.14	-0.13	-0.19	0.07
30	1	-0.12	0.00	-0.14	0.06	-0.06	0.22	-0.25	-0.04	0.08
31	1	-0.08	0.10	-0.09	0.04	-0.20	0.14	-0.13	-0.02	0.04
32	6	0.08	0.03	-0.09	0.04	0.11	-0.14	0.14	-0.07	0.05
33	1	0.12	0.00	-0.15	0.06	0.06	-0.22	0.25	-0.04	0.08
34	1	0.08	0.01	-0.09	0.04	0.13	-0.14	0.13	-0.19	0.07
35	1	0.08	0.11	-0.09	0.04	0.20	-0.14	0.13	-0.02	0.04

Total free energy in solution:
with all non electrostatic terms (a.u.) = -1352.415030

III.4. Cartesian coordinates, three lower frequencies and PCM energy for III-ATSIII-B



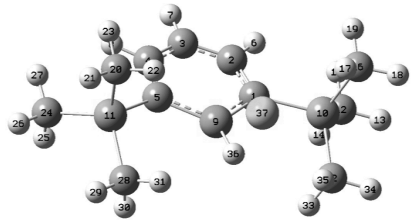
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.041064	-0.450681	0.089697
2	6	0	0.012721	-0.038344	1.468386
3	6	0	1.173655	0.165069	2.183954
4	6	0	2.458786	-0.017458	1.624743
5	6	0	2.748864	-0.414959	0.313591
6	1	0	-0.933861	0.097582	1.991990
7	1	0	1.106573	0.466465	3.226031
8	1	0	3.295719	0.177521	2.296491
9	15	0	1.478746	-0.788694	-0.837008
10	14	0	-1.512515	0.320635	-0.957658
11	14	0	4.557809	-0.655065	-0.265756
12	6	0	-3.106507	-0.074906	-0.026374
13	1	0	-3.970779	0.277809	-0.604163
14	1	0	-3.222536	-1.155875	0.116846
15	1	0	-3.157566	0.407668	0.957196
16	6	0	-1.249359	2.189679	-1.071699
17	1	0	-0.312443	2.432356	-1.587954
18	1	0	-2.067982	2.658279	-1.633744
19	1	0	-1.217256	2.657223	-0.079997
20	6	0	4.817535	0.312841	-1.871333
21	1	0	5.845673	0.185918	-2.234403
22	1	0	4.143864	-0.032204	-2.665105
23	1	0	4.644471	1.386770	-1.728464
24	6	0	5.727590	0.002680	1.071369
25	1	0	5.647772	-0.558045	2.011032
26	1	0	6.765981	-0.091638	0.728235
27	1	0	5.553291	1.063338	1.292088
28	6	0	4.869630	-2.494933	-0.558421
29	1	0	5.895324	-2.664309	-0.911350
30	1	0	4.729177	-3.076794	0.360545
31	1	0	4.184436	-2.904075	-1.310519
32	6	0	-1.508404	-0.480933	-2.659825
33	1	0	-1.458819	-1.573185	-2.582508
34	1	0	-2.429245	-0.215403	-3.195665
35	1	0	-0.660670	-0.148978	-3.270147
36	17	0	-0.036723	-3.390282	-0.483228
37	1	0	-0.453005	-1.561517	0.017513

	1	2	3
	A	A	A
Frequencies --	-257.4581	14.8037	30.3433
Red. masses --	5.4904	3.1712	4.0448
Frc consts --	0.2144	0.0004	0.0022
IR Inten --	45.5563	0.5715	2.1729

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.08	-0.06	-0.08	0.00	-0.01	0.00	-0.01	-0.08	0.02
2	6	0.01	-0.10	-0.11	0.00	-0.04	0.01	-0.02	-0.09	0.02
3	6	0.00	-0.09	-0.02	0.00	-0.05	0.01	-0.02	-0.07	0.02
4	6	0.00	-0.03	0.05	0.00	-0.03	0.01	-0.02	-0.03	0.02
5	6	0.04	0.06	0.01	0.00	-0.01	0.00	-0.01	-0.03	0.02
6	1	-0.01	-0.04	-0.15	0.00	-0.05	0.01	-0.02	-0.11	0.02
7	1	-0.07	-0.10	-0.02	0.00	-0.07	0.02	-0.02	-0.07	0.02
8	1	-0.02	-0.09	0.09	0.00	-0.05	0.02	-0.02	0.00	0.01
9	15	0.11	0.22	-0.04	0.00	0.02	-0.01	-0.01	-0.08	0.03
10	14	0.01	-0.10	0.01	0.00	0.02	0.02	0.05	0.02	0.00
11	14	0.02	0.01	0.00	0.00	-0.01	0.01	-0.01	0.07	-0.01
12	6	0.00	-0.03	0.01	0.00	-0.01	0.01	0.02	0.21	0.03
13	1	0.01	-0.01	0.00	0.00	0.00	0.02	0.05	0.27	0.01
14	1	-0.04	-0.03	0.02	0.00	-0.02	-0.02	-0.08	0.23	0.08
15	1	0.01	-0.02	0.00	0.00	-0.04	0.02	0.07	0.26	0.01
16	6	0.02	-0.08	0.03	-0.01	0.02	0.07	0.24	-0.02	-0.09
17	1	0.01	-0.07	0.02	-0.01	0.04	0.09	0.24	-0.13	-0.13
18	1	0.00	-0.10	0.03	-0.01	0.03	0.09	0.26	0.04	-0.08
19	1	0.02	-0.08	0.02	-0.02	-0.01	0.09	0.32	0.02	-0.11
20	6	0.02	0.00	0.00	-0.05	-0.20	-0.11	-0.08	0.09	0.00
21	1	0.01	0.00	-0.01	-0.04	-0.21	-0.10	-0.08	0.15	-0.02
22	1	0.01	0.00	0.00	-0.04	-0.32	-0.06	-0.07	0.05	0.00
23	1	0.01	0.00	-0.01	-0.08	-0.18	-0.24	-0.15	0.08	0.00
24	6	0.02	0.00	0.00	-0.01	0.19	-0.08	-0.03	0.13	-0.02
25	1	0.01	0.00	0.00	0.04	0.29	-0.02	0.02	0.12	-0.02
26	1	0.03	0.01	0.01	-0.01	0.20	-0.09	-0.03	0.18	-0.03
27	1	0.02	0.00	0.01	-0.06	0.21	-0.19	-0.08	0.12	-0.01
28	6	0.00	0.01	0.01	0.06	-0.03	0.23	0.10	0.09	-0.02
29	1	0.00	0.00	0.01	0.06	-0.04	0.24	0.10	0.15	-0.05
30	1	-0.01	0.01	0.01	0.10	0.07	0.31	0.15	0.07	-0.02
31	1	0.00	0.02	0.00	0.06	-0.15	0.29	0.10	0.05	-0.01
32	6	-0.02	-0.01	-0.03	0.00	0.06	0.00	-0.03	-0.06	0.03
33	1	-0.06	-0.02	-0.08	0.00	0.06	-0.03	-0.12	-0.06	0.08
34	1	-0.01	0.03	-0.03	0.00	0.08	0.00	-0.02	0.00	0.03
35	1	0.00	-0.02	-0.01	0.00	0.08	0.01	-0.01	-0.15	0.01
36	17	-0.20	0.02	0.08	0.01	0.01	-0.08	-0.10	-0.08	-0.03
37	1	0.52	-0.60	-0.30	0.00	0.00	-0.03	-0.07	-0.05	0.00

Total free energy in solution:
with all non electrostatic terms (a.u.) = -1813.216528

III.5. Cartesian coordinates, three lower frequencies and PCM energy for III-ATSIII-C



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.439580	-0.821815	0.008684
2	6	0	1.240572	-2.083803	-0.578812
3	6	0	-0.000015	-2.677963	-0.850567

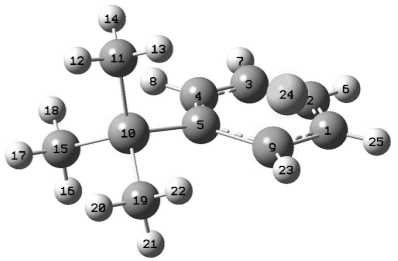
4	6	0	-1.240596	-2.083793	-0.578816
5	6	0	-1.439594	-0.821803	0.008681
6	1	0	2.126675	-2.655480	-0.852414
7	1	0	-0.000018	-3.663595	-1.308599
8	1	0	-2.126703	-2.655461	-0.852420
9	15	0	-0.000004	0.010896	0.417020
10	14	0	3.169682	-0.020798	0.218901
11	14	0	-3.169692	-0.020779	0.218899
12	6	0	4.385934	-1.411598	0.630116
13	1	0	5.388138	-0.992527	0.787925
14	1	0	4.102036	-1.944638	1.545712
15	1	0	4.469688	-2.148516	-0.178186
16	6	0	3.603448	0.820975	-1.409418
17	1	0	2.857683	1.589557	-1.645860
18	1	0	4.586750	1.304941	-1.344529
19	1	0	3.634971	0.107220	-2.241842
20	6	0	-3.603489	0.820931	-1.409446
21	1	0	-4.586791	1.304898	-1.344557
22	1	0	-2.857731	1.589503	-1.645938
23	1	0	-3.635029	0.107141	-2.241839
24	6	0	-4.385939	-1.411563	0.630182
25	1	0	-4.102029	-1.944571	1.545792
26	1	0	-5.388142	-0.992488	0.787988
27	1	0	-4.469703	-2.148510	-0.178093
28	6	0	-3.090634	1.233574	1.626300
29	1	0	-4.089707	1.650378	1.808423
30	1	0	-2.746401	0.786284	2.567288
31	1	0	-2.432478	2.074287	1.374990
32	6	0	3.090647	1.233503	1.626350
33	1	0	2.746413	0.786183	2.567323
34	1	0	4.089726	1.650288	1.808483
35	1	0	2.432500	2.074232	1.375072
36	1	0	0.000003	1.349372	0.859319
37	17	0	0.000051	2.730016	-0.811651

		1			2			3		
		A			A			A		
Frequencies --		-641.9771			33.1562			35.2473		
Red. masses --		1.1437			2.9909			3.4700		
Frc consts --		0.2777			0.0019			0.0025		
IR Inten --		109.1872			0.4766			0.9005		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	-0.01	-0.03	0.01	-0.01	0.00	0.00	-0.01	0.03
2	6	0.01	-0.01	0.00	0.00	-0.01	0.00	0.00	-0.04	0.11
3	6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.06	0.14
4	6	-0.01	-0.01	0.00	0.00	0.01	0.00	0.00	-0.04	0.11
5	6	0.00	-0.01	-0.03	0.01	0.01	0.00	0.00	-0.01	0.03
6	1	0.00	-0.02	0.00	0.00	-0.01	0.00	0.00	-0.06	0.14
7	1	0.00	0.00	0.00	-0.01	0.00	0.00	0.00	-0.09	0.20
8	1	0.00	-0.02	0.00	0.00	0.01	0.00	0.00	-0.06	0.14
9	15	0.00	-0.02	0.05	0.01	0.00	0.00	0.00	0.01	-0.01
10	14	0.00	0.00	0.00	0.01	-0.01	0.01	0.00	0.01	-0.01
11	14	0.00	0.00	0.00	0.01	0.01	-0.01	0.00	0.01	-0.01
12	6	0.00	0.00	0.00	0.03	-0.04	-0.13	0.05	0.01	-0.16
13	1	0.00	0.00	0.00	0.03	-0.04	-0.12	0.04	0.03	-0.18
14	1	0.00	0.00	0.00	0.06	-0.12	-0.17	0.10	-0.06	-0.19
15	1	0.00	0.00	0.00	0.02	0.03	-0.20	0.03	0.07	-0.22
16	6	0.00	0.00	0.00	-0.04	0.14	0.08	-0.10	0.13	0.03
17	1	0.00	0.00	0.00	-0.05	0.15	0.16	-0.13	0.13	0.11
18	1	0.00	0.00	0.00	-0.04	0.14	0.11	-0.11	0.16	0.02
19	1	0.00	0.00	0.00	-0.04	0.21	0.02	-0.11	0.19	-0.02
20	6	0.00	0.00	0.00	-0.04	-0.14	-0.08	0.10	0.14	0.03
21	1	0.00	0.00	0.00	-0.04	-0.14	-0.11	0.11	0.16	0.02
22	1	0.00	0.00	0.00	-0.05	-0.15	-0.16	0.13	0.13	0.11
23	1	0.00	0.00	0.00	-0.04	-0.21	-0.02	0.11	0.19	-0.02
24	6	0.00	0.00	0.00	0.03	0.04	0.13	-0.05	0.01	-0.16
25	1	0.00	0.00	0.00	0.06	0.12	0.17	-0.10	-0.06	-0.19

26	1	0.00	0.00	0.00	0.03	0.04	0.12	-0.04	0.03	-0.18
27	1	0.00	0.00	0.00	0.02	-0.03	0.20	-0.03	0.07	-0.22
28	6	0.00	0.00	0.00	0.03	0.14	-0.13	-0.04	-0.08	0.08
29	1	0.00	0.00	0.00	0.04	0.16	-0.15	-0.04	-0.09	0.07
30	1	0.00	0.00	0.00	0.05	0.23	-0.10	-0.08	-0.16	0.06
31	1	0.00	0.00	0.01	0.03	0.11	-0.22	-0.02	-0.07	0.17
32	6	0.00	0.00	0.00	0.03	-0.14	0.13	0.04	-0.08	0.08
33	1	0.00	0.00	0.00	0.05	-0.23	0.10	0.08	-0.16	0.06
34	1	0.00	0.00	0.00	0.04	-0.16	0.15	0.04	-0.09	0.07
35	1	0.00	0.00	0.01	0.03	-0.11	0.22	0.02	-0.07	0.17
36	1	0.00	0.42	-0.90	0.02	0.00	0.00	0.00	0.02	-0.05
37	17	0.00	0.03	0.00	-0.05	0.00	0.00	0.00	-0.03	-0.09

Total free energy in solution:
with all non electrostatic terms (a.u.) = -1813.230288

III.6. Cartesian coordinates, three lower frequencies and PCM energy for III-AbTSIII-Cb



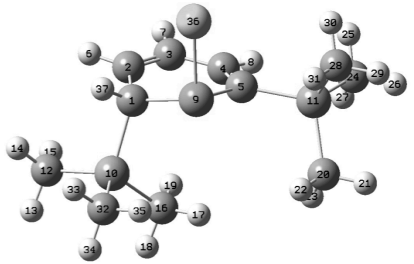
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.841740	-0.040172	-0.501854
2	6	0	-3.100152	-1.255280	0.134310
3	6	0	-2.101675	-2.119344	0.600496
4	6	0	-0.726455	-1.864630	0.487487
5	6	0	-0.125791	-0.727412	-0.080132
6	1	0	-4.139679	-1.546438	0.269737
7	1	0	-2.408767	-3.045386	1.078292
8	1	0	-0.059150	-2.626511	0.888016
9	15	0	-1.213979	0.443586	-0.698584
10	14	0	1.776295	-0.447382	-0.058605
11	6	0	2.225393	0.299417	1.610268
12	1	0	3.306302	0.481914	1.672225
13	1	0	1.705538	1.255534	1.741912
14	1	0	1.948559	-0.361646	2.440876
15	6	0	2.581631	-2.144827	-0.294369
16	1	0	2.275598	-2.618578	-1.235121
17	1	0	3.673178	-2.031259	-0.321140
18	1	0	2.352742	-2.838217	0.524272
19	6	0	2.235299	0.706485	-1.477498
20	1	0	3.325732	0.824793	-1.521191
21	1	0	1.908995	0.321694	-2.452058
22	1	0	1.807190	1.705068	-1.328605
23	1	0	-0.833252	1.724936	-1.161681
24	17	0	-0.397233	2.978619	0.510272
25	1	0	-3.647512	0.601714	-0.843175

1	2	3

		A			A			A		
Frequencies --		-719.1250			42.1275			51.1155		
Red. masses --		1.1346			3.5081			9.3553		
Frc consts --		0.3457			0.0037			0.0144		
IR Inten --		146.9400			1.6847			9.2191		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	-0.01	0.02	-0.01	-0.03	0.01	0.11	0.13	-0.03
2	6	-0.01	-0.01	0.00	0.00	0.00	0.06	0.04	0.20	0.07
3	6	0.00	0.00	0.00	0.00	0.02	0.09	-0.01	0.18	0.15
4	6	0.00	-0.01	0.00	0.00	0.02	0.06	0.01	0.08	0.11
5	6	-0.01	0.00	0.02	-0.01	0.00	0.01	0.07	-0.01	-0.01
6	1	0.00	-0.02	0.00	0.00	0.01	0.09	0.03	0.27	0.11
7	1	0.00	0.00	0.00	0.01	0.04	0.13	-0.06	0.25	0.25
8	1	-0.01	-0.02	0.00	0.01	0.04	0.09	-0.04	0.08	0.19
9	15	0.00	-0.03	-0.05	-0.02	-0.03	-0.03	0.14	-0.01	-0.12
10	14	0.00	0.00	0.00	-0.01	0.01	0.02	0.07	-0.10	-0.04
11	6	0.00	0.00	0.00	-0.04	-0.19	0.12	0.11	-0.15	-0.02
12	1	0.00	0.00	0.00	-0.04	-0.20	0.17	0.11	-0.14	-0.04
13	1	0.00	0.00	0.00	-0.04	-0.21	0.22	0.10	-0.15	0.02
14	1	0.00	0.00	0.00	-0.06	-0.29	0.04	0.13	-0.17	-0.03
15	6	0.00	0.00	0.00	0.00	0.05	-0.19	0.02	-0.12	-0.10
16	1	0.00	0.00	0.00	0.03	0.18	-0.26	0.03	-0.05	-0.13
17	1	0.00	0.00	0.00	0.00	0.05	-0.14	0.03	-0.16	-0.05
18	1	0.00	0.00	0.00	-0.02	-0.07	-0.29	-0.04	-0.15	-0.15
19	6	0.00	0.00	0.00	0.00	0.19	0.17	0.09	-0.06	0.01
20	1	0.00	0.00	0.00	0.00	0.21	0.21	0.10	-0.09	0.00
21	1	0.00	0.00	0.00	0.03	0.30	0.11	0.07	0.00	-0.01
22	1	0.00	0.00	-0.01	-0.03	0.16	0.28	0.13	-0.05	0.05
23	1	0.08	0.44	0.89	-0.02	-0.05	-0.08	0.19	0.01	-0.04
24	17	0.01	0.02	0.00	0.04	0.00	-0.12	-0.36	0.01	0.06
25	1	0.00	-0.01	0.01	-0.02	-0.04	-0.01	0.15	0.15	-0.07

Total free energy in solution:
with all non electrostatic terms (a.u.) = -1404.497414

III.7. Cartesian coordinates, three lower frequencies and PCM energy for III-B



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.072396	-0.522285	-0.144372
2	6	0	-0.097989	-0.268009	1.320659
3	6	0	0.939382	0.258253	2.010416
4	6	0	2.236613	0.535333	1.417799
5	6	0	2.687548	0.098605	0.206827
6	1	0	-1.027713	-0.480631	1.847070
7	1	0	0.818768	0.479916	3.068420
8	1	0	2.912759	1.120622	2.043785

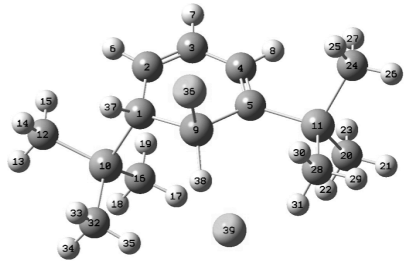
9	15	0	1.593362	-0.872252	-0.897488
10	14	0	-0.964348	0.919210	-1.117490
11	14	0	4.445407	0.469858	-0.408184
12	6	0	-2.640634	1.198827	-0.281848
13	1	0	-3.229371	1.928250	-0.853285
14	1	0	-3.228596	0.273801	-0.227398
15	1	0	-2.530542	1.589188	0.736805
16	6	0	0.042182	2.517183	-1.079802
17	1	0	0.968320	2.431686	-1.659394
18	1	0	-0.544318	3.340124	-1.509213
19	1	0	0.312131	2.799798	-0.055634
20	6	0	4.355290	1.647190	-1.892555
21	1	0	5.360405	1.866970	-2.276048
22	1	0	3.776771	1.208188	-2.714882
23	1	0	3.885483	2.601581	-1.623793
24	6	0	5.444162	1.285602	0.980256
25	1	0	5.522174	0.639290	1.863250
26	1	0	6.465079	1.488717	0.631511
27	1	0	5.013691	2.243350	1.298466
28	6	0	5.290224	-1.135679	-0.944940
29	1	0	6.309046	-0.929754	-1.299048
30	1	0	5.357207	-1.851723	-0.117553
31	1	0	4.749383	-1.629684	-1.760905
32	6	0	-1.235163	0.341592	-2.897796
33	1	0	-1.828763	-0.580545	-2.936121
34	1	0	-1.778534	1.107326	-3.466829
35	1	0	-0.288182	0.149594	-3.414830
36	17	0	1.972695	-2.879592	-0.157623
37	1	0	-0.711396	-1.382300	-0.394185

		1			2			3		
		A			A			A		
Frequencies --		18.2523			34.2644			41.9391		
Red. masses --		3.0835			4.1543			3.3313		
Frc consts --		0.0006			0.0029			0.0035		
IR Inten --		0.0927			0.2792			0.0285		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	0.00	0.01	0.00	-0.03	-0.01	-0.01	-0.04	-0.01
2	6	0.00	0.04	0.01	-0.01	-0.04	-0.01	-0.02	-0.07	-0.01
3	6	0.00	0.05	0.00	-0.01	-0.05	0.00	-0.03	-0.09	0.01
4	6	0.00	0.03	0.00	-0.02	-0.03	-0.01	-0.03	-0.06	0.02
5	6	0.00	0.01	0.00	-0.02	-0.03	-0.01	-0.02	-0.03	0.01
6	1	0.00	0.05	0.01	-0.02	-0.04	-0.01	-0.03	-0.08	-0.02
7	1	-0.01	0.07	-0.01	-0.01	-0.05	0.00	-0.04	-0.11	0.02
8	1	0.00	0.04	-0.01	-0.03	-0.01	-0.02	-0.04	-0.06	0.03
9	15	0.00	-0.01	0.02	-0.01	-0.08	0.02	0.00	-0.04	0.00
10	14	0.00	-0.02	-0.03	0.07	0.03	0.00	0.06	0.01	-0.01
11	14	0.00	0.01	-0.01	-0.05	0.03	-0.06	-0.04	0.04	0.01
12	6	0.00	0.00	-0.04	0.00	-0.03	-0.11	0.13	0.20	0.07
13	1	0.00	-0.01	-0.06	0.05	0.01	-0.10	0.16	0.23	0.07
14	1	0.00	0.00	-0.02	0.00	-0.04	-0.22	0.05	0.25	0.13
15	1	0.00	0.02	-0.05	-0.08	-0.11	-0.07	0.22	0.22	0.05
16	6	0.00	-0.02	-0.06	0.06	0.04	0.19	0.20	-0.07	-0.13
17	1	0.01	-0.04	-0.05	0.10	0.09	0.25	0.16	-0.18	-0.17
18	1	0.01	-0.03	-0.09	0.08	0.06	0.21	0.24	-0.04	-0.14
19	1	-0.01	0.01	-0.07	-0.02	-0.04	0.23	0.27	-0.05	-0.15
20	6	-0.01	0.18	0.13	-0.14	0.02	-0.05	-0.10	0.05	0.02
21	1	-0.01	0.19	0.12	-0.16	0.06	-0.09	-0.11	0.10	0.02
22	1	-0.05	0.30	0.10	-0.15	0.00	-0.04	-0.08	0.04	0.01
23	1	0.03	0.17	0.26	-0.16	0.01	-0.04	-0.15	0.03	0.03
24	6	0.07	-0.19	0.05	-0.04	0.06	-0.09	-0.07	0.08	0.00
25	1	0.05	-0.29	-0.01	0.01	0.07	-0.09	-0.03	0.08	0.00
26	1	0.08	-0.21	0.06	-0.05	0.09	-0.12	-0.08	0.14	0.00
27	1	0.13	-0.20	0.16	-0.06	0.05	-0.08	-0.12	0.06	0.02
28	6	-0.09	0.04	-0.22	-0.02	0.05	-0.08	0.02	0.08	-0.01
29	1	-0.09	0.04	-0.22	-0.04	0.08	-0.12	0.00	0.13	-0.03
30	1	-0.10	-0.08	-0.32	0.03	0.05	-0.09	0.06	0.08	-0.02

31	1	-0.13	0.17	-0.28	-0.04	0.03	-0.06	0.03	0.06	-0.01
32	6	0.01	-0.07	-0.01	0.22	0.16	-0.06	-0.09	-0.04	0.03
33	1	0.01	-0.07	0.01	0.26	0.14	-0.17	-0.21	0.04	0.09
34	1	0.01	-0.08	-0.03	0.22	0.18	-0.03	-0.01	0.01	0.01
35	1	0.01	-0.08	0.00	0.26	0.23	-0.01	-0.13	-0.19	0.00
36	17	0.00	0.00	0.07	-0.02	-0.04	0.12	0.00	-0.04	0.01
37	1	0.00	0.00	0.03	-0.04	0.00	-0.03	-0.02	-0.02	-0.04

Total free energy in solution:
 with all non electrostatic terms (a.u.) = -1813.252416

III.8. Cartesian coordinates, three lower frequencies and PCM energy for III-BTSIII-D



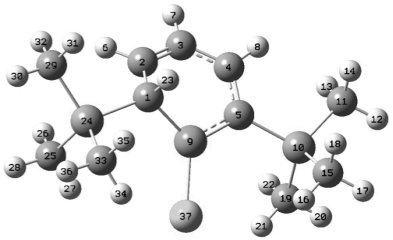
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.592107	-1.014699	0.008511
2	6	0	-1.442390	-1.670898	1.344725
3	6	0	-0.351271	-1.601901	2.138659
4	6	0	0.892138	-0.937959	1.778008
5	6	0	1.238319	-0.407341	0.569290
6	1	0	-2.320351	-2.201677	1.705784
7	1	0	-0.389648	-2.068400	3.119458
8	1	0	1.626413	-0.872254	2.581785
9	15	0	0.026279	-0.613407	-0.709558
10	14	0	-3.009543	0.383993	0.103023
11	14	0	2.966112	0.383339	0.264332
12	6	0	-4.548400	-0.650270	0.512517
13	1	0	-5.430209	0.003841	0.492458
14	1	0	-4.725490	-1.450581	-0.217570
15	1	0	-4.509865	-1.101772	1.511067
16	6	0	-2.685333	1.620339	1.474828
17	1	0	-1.795537	2.218987	1.255332
18	1	0	-3.543599	2.300659	1.558220
19	1	0	-2.558855	1.125311	2.445318
20	6	0	3.108291	1.938530	1.315975
21	1	0	4.103275	2.388673	1.201438
22	1	0	2.353763	2.667255	1.001655
23	1	0	2.961294	1.724684	2.382295
24	6	0	4.227497	-0.912904	0.837469
25	1	0	4.140141	-1.844166	0.264522
26	1	0	5.248205	-0.532001	0.700785
27	1	0	4.113968	-1.162175	1.900111
28	6	0	3.205699	0.737818	-1.570908
29	1	0	4.217741	1.131271	-1.734114
30	1	0	3.104469	-0.161421	-2.191557
31	1	0	2.493726	1.494561	-1.917894
32	6	0	-3.218882	1.131024	-1.610867

33	1	0	-3.329272	0.360950	-2.385628
34	1	0	-4.132556	1.740444	-1.626186
35	1	0	-2.376345	1.782808	-1.863137
36	17	0	0.574846	-2.326763	-1.811524
37	1	0	-2.065825	-1.713231	-0.695822
38	1	0	0.013209	0.430468	-1.647457
39	17	0	0.014203	2.491809	-0.725519

		1			2			3		
		A			A			A		
Frequencies --		-65.2298			29.4856			53.0617		
Red. masses --		9.2090			4.4144			3.1507		
Frc consts --		0.0231			0.0023			0.0052		
IR Inten --		13.7951			1.0011			0.2592		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	-0.09	0.09	0.01	-0.01	0.09	0.00	0.00	0.00
2	6	-0.01	-0.10	0.07	0.01	0.08	0.13	0.00	0.01	0.01
3	6	-0.01	-0.10	0.08	0.02	0.11	0.12	-0.01	0.02	0.01
4	6	-0.02	-0.09	0.08	0.03	0.06	0.06	-0.01	0.02	0.01
5	6	-0.02	-0.09	0.08	0.02	0.00	0.04	0.00	0.00	0.00
6	1	0.00	-0.12	0.06	0.01	0.11	0.18	-0.01	0.01	0.01
7	1	-0.01	-0.11	0.08	0.02	0.17	0.15	-0.01	0.03	0.01
8	1	-0.02	-0.09	0.09	0.05	0.06	0.04	-0.01	0.04	0.01
9	15	-0.02	-0.03	0.06	-0.01	0.02	0.06	0.00	-0.02	0.00
10	14	0.02	-0.05	0.05	-0.04	-0.05	-0.05	0.01	0.01	-0.01
11	14	-0.03	-0.06	0.07	0.03	-0.05	-0.04	-0.01	0.01	0.01
12	6	0.01	0.00	0.12	-0.04	-0.09	-0.13	0.01	0.04	0.05
13	1	0.02	0.02	0.09	-0.05	-0.11	-0.17	0.02	0.04	0.03
14	1	-0.01	-0.03	0.16	0.02	-0.08	-0.15	0.00	0.00	0.10
15	1	0.00	0.06	0.14	-0.08	-0.09	-0.14	0.02	0.09	0.08
16	6	0.09	0.01	-0.02	-0.16	0.00	-0.07	0.04	0.05	-0.05
17	1	0.06	0.03	-0.11	-0.16	0.01	-0.03	0.03	0.05	-0.08
18	1	0.09	0.00	0.00	-0.18	-0.02	-0.15	0.04	0.05	-0.06
19	1	0.17	0.06	-0.01	-0.21	0.03	-0.05	0.05	0.08	-0.04
20	6	-0.08	-0.03	0.04	0.13	-0.07	-0.02	-0.01	-0.11	0.20
21	1	-0.08	-0.02	0.04	0.13	-0.09	-0.08	-0.02	-0.08	0.24
22	1	-0.08	-0.05	0.01	0.12	-0.05	0.04	-0.02	-0.08	0.30
23	1	-0.09	-0.01	0.04	0.20	-0.08	-0.02	0.01	-0.25	0.18
24	6	0.00	-0.02	0.08	0.02	-0.11	-0.13	0.01	-0.06	-0.19
25	1	0.02	-0.03	0.09	-0.04	-0.09	-0.15	-0.01	0.02	-0.32
26	1	-0.01	0.00	0.08	0.03	-0.13	-0.17	0.00	-0.04	-0.16
27	1	0.01	-0.01	0.09	0.06	-0.13	-0.13	0.03	-0.21	-0.22
28	6	-0.03	-0.06	0.07	-0.05	-0.02	-0.04	-0.04	0.23	0.05
29	1	-0.03	-0.06	0.08	-0.05	-0.05	-0.09	-0.05	0.24	0.08
30	1	-0.02	-0.06	0.07	-0.11	0.00	-0.06	-0.05	0.30	-0.05
31	1	-0.03	-0.06	0.06	-0.05	0.01	0.01	-0.05	0.27	0.15
32	6	0.04	-0.12	0.02	0.08	-0.11	-0.09	-0.01	-0.04	-0.03
33	1	-0.01	-0.15	0.06	0.15	-0.13	-0.07	-0.04	-0.07	0.00
34	1	0.07	-0.07	0.01	0.07	-0.12	-0.18	0.00	-0.03	-0.04
35	1	0.07	-0.17	-0.02	0.09	-0.10	-0.04	0.00	-0.07	-0.07
36	17	0.00	0.15	-0.16	-0.02	0.08	-0.02	0.01	-0.05	0.04
37	1	-0.02	-0.06	0.08	0.04	-0.08	0.13	-0.01	0.00	0.01
38	1	-0.07	0.37	0.43	-0.04	0.10	0.14	0.01	-0.04	-0.02
39	17	0.04	0.21	-0.29	0.00	0.07	0.08	-0.01	-0.01	-0.06

Total free energy in solution:
 with all non electrostatic terms (a.u.) = -2274.078469

III.9. Cartesian coordinates, three lower frequencies and PCM energy for III-BTSIII-E



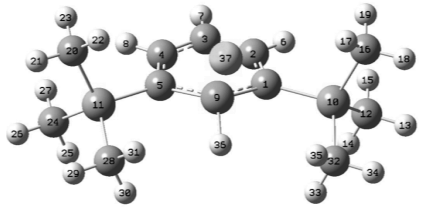
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.081015	-0.165327	-0.037677
2	6	0	0.031313	0.075201	1.465632
3	6	0	1.167415	-0.126770	2.198642
4	6	0	2.501752	-0.211425	1.673534
5	6	0	2.858553	0.243645	0.406540
6	1	0	-0.878365	0.363953	1.991671
7	1	0	1.074628	-0.101584	3.284560
8	1	0	3.292770	-0.539795	2.343547
9	15	0	1.477851	0.638892	-0.580731
10	14	0	4.664094	0.427119	-0.153437
11	6	0	5.777142	-0.305865	1.191298
12	1	0	6.827210	-0.227754	0.880531
13	1	0	5.677467	0.226324	2.144904
14	1	0	5.564238	-1.366583	1.370430
15	6	0	4.926511	-0.506186	-1.778278
16	1	0	4.297750	-0.105113	-2.582045
17	1	0	5.972025	-0.430616	-2.104829
18	1	0	4.685677	-1.570562	-1.666858
19	6	0	5.084167	2.258190	-0.384113
20	1	0	6.135643	2.377702	-0.677178
21	1	0	4.466885	2.723457	-1.161159
22	1	0	4.928993	2.819598	0.545400
23	1	0	-0.000617	-1.239706	-0.277919
24	14	0	-1.730868	0.424648	-0.833903
25	6	0	-1.959656	2.286515	-0.615707
26	1	0	-1.930685	2.574389	0.442159
27	1	0	-1.181497	2.857292	-1.135516
28	1	0	-2.930606	2.602274	-1.019154
29	6	0	-3.109629	-0.512981	0.064848
30	1	0	-4.081669	-0.286479	-0.392369
31	1	0	-2.963614	-1.598967	0.007567
32	1	0	-3.175128	-0.241454	1.125223
33	6	0	-1.733625	-0.057815	-2.661665
34	1	0	-0.964742	0.477658	-3.229890
35	1	0	-1.557352	-1.133303	-2.791273
36	1	0	-2.705294	0.172890	-3.117350
37	17	0	1.669398	1.804012	-2.277544

	1			2			3		
	A			A			A		
Frequencies --	-419.6971			28.2854			30.2141		
Red. masses --	18.4092			2.9083			4.6367		
Frc consts --	1.9105			0.0014			0.0025		
IR Inten --	2.1608			0.0081			0.2595		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
1 6	0.07	-0.19	-0.23	0.01	-0.01	-0.02	-0.02	-0.07	-0.03
2 6	0.08	-0.05	-0.13	0.00	-0.05	-0.01	0.00	-0.12	-0.02
3 6	0.03	-0.04	-0.06	0.00	-0.04	-0.01	0.00	-0.10	-0.03
4 6	0.05	-0.05	-0.05	0.00	0.00	0.00	0.01	-0.06	-0.02
5 6	0.03	-0.29	-0.13	0.00	0.02	0.00	0.00	-0.05	-0.02

6	1	-0.01	-0.27	-0.17	-0.01	-0.08	-0.01	-0.01	-0.17	-0.01
7	1	0.00	0.02	-0.07	-0.01	-0.06	-0.01	-0.01	-0.13	-0.03
8	1	0.08	0.25	0.07	0.00	0.00	0.00	0.01	-0.02	-0.01
9	15	-0.17	0.52	0.38	0.00	0.01	0.00	0.00	-0.10	-0.03
10	14	0.01	-0.03	-0.01	0.00	-0.01	0.00	0.00	0.06	0.02
11	6	0.01	0.00	0.00	0.01	0.15	0.08	0.02	0.14	0.05
12	1	0.01	0.00	0.01	0.01	0.14	0.08	0.02	0.21	0.07
13	1	0.01	0.00	-0.01	-0.02	0.25	0.03	-0.04	0.13	0.05
14	1	0.01	0.00	0.00	0.03	0.17	0.19	0.09	0.12	0.05
15	6	0.03	0.00	-0.02	0.01	-0.19	0.10	0.12	0.09	0.03
16	1	0.02	0.00	-0.01	-0.01	-0.30	0.07	0.10	0.04	0.01
17	1	0.02	-0.01	-0.04	0.00	-0.19	0.07	0.12	0.18	0.05
18	1	0.03	-0.01	-0.02	0.04	-0.18	0.23	0.20	0.07	0.02
19	6	-0.02	-0.01	0.00	-0.01	-0.03	-0.20	-0.13	0.10	0.05
20	1	-0.02	-0.03	0.01	0.00	-0.06	-0.20	-0.12	0.18	0.09
21	1	-0.01	-0.01	0.00	0.01	-0.12	-0.26	-0.13	0.05	0.02
22	1	-0.02	-0.01	0.01	-0.02	0.07	-0.27	-0.21	0.08	0.04
23	1	-0.04	-0.24	-0.14	0.01	-0.01	-0.05	-0.08	-0.06	-0.07
24	14	0.02	-0.02	-0.02	0.00	0.01	0.00	0.00	0.06	0.02
25	6	0.02	-0.02	0.01	-0.02	-0.01	0.13	0.14	0.08	0.07
26	1	0.02	-0.01	0.00	-0.03	-0.08	0.15	0.19	0.05	0.08
27	1	0.01	0.00	0.01	-0.03	0.03	0.17	0.17	0.03	0.07
28	1	0.01	-0.04	0.00	-0.03	0.01	0.14	0.15	0.16	0.11
29	6	0.01	0.00	0.00	0.01	-0.08	-0.07	-0.05	0.15	0.04
30	1	0.02	0.02	0.00	0.01	-0.04	-0.04	-0.04	0.21	0.05
31	1	-0.01	0.00	0.00	0.02	-0.07	-0.17	-0.12	0.14	0.04
32	1	0.01	0.00	0.00	0.02	-0.17	-0.04	-0.02	0.15	0.04
33	6	-0.02	0.00	-0.02	0.01	0.13	-0.03	-0.10	0.11	0.01
34	1	-0.02	0.00	-0.02	-0.01	0.18	0.00	-0.07	0.05	0.00
35	1	-0.02	0.00	-0.02	0.02	0.14	-0.11	-0.22	0.10	-0.02
36	1	-0.02	0.00	-0.03	0.00	0.15	-0.01	-0.09	0.22	0.05
37	17	0.03	-0.19	-0.08	-0.01	0.03	0.02	0.01	-0.15	-0.07

```
Total free energy in solution:
 with all non electrostatic terms            (a.u.) =   -1813.177209
```

III.10 Cartesian coordinates, three lower frequencies and PCM energy for III-C



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.028565	0.256636	-0.090246
2	6	0	0.029862	0.877760	1.169457
3	6	0	1.188655	1.202729	1.887072
4	6	0	2.476211	0.885099	1.435861
5	6	0	2.807212	0.265017	0.218173
6	1	0	-0.919844	1.092833	1.660007
7	1	0	1.080910	1.668424	2.862377
8	1	0	3.297190	1.105592	2.118911
9	15	0	1.493718	0.072698	-0.887923

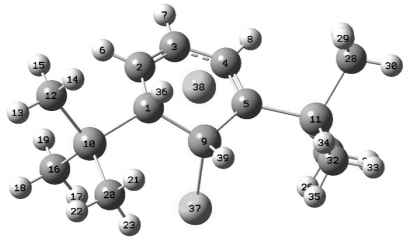
10	14	0	-1.677389	-0.138530	-0.938447
11	14	0	4.601401	-0.121983	-0.256053
12	6	0	-2.903909	-0.706807	0.388763
13	1	0	-3.863903	-0.973221	-0.072399
14	1	0	-2.535985	-1.587404	0.929203
15	1	0	-3.107326	0.077899	1.127863
16	6	0	-2.348886	1.400964	-1.810020
17	1	0	-1.646101	1.760809	-2.570540
18	1	0	-3.305924	1.187655	-2.304436
19	1	0	-2.514847	2.220337	-1.099357
20	6	0	5.466530	1.452589	-0.849419
21	1	0	6.510521	1.251485	-1.123877
22	1	0	4.958809	1.870223	-1.726783
23	1	0	5.468766	2.224567	-0.069702
24	6	0	5.485702	-0.805153	1.273577
25	1	0	4.999917	-1.715811	1.644568
26	1	0	6.526884	-1.055011	1.031270
27	1	0	5.509268	-0.080796	2.097084
28	6	0	4.623549	-1.419336	-1.635743
29	1	0	5.660122	-1.684039	-1.881515
30	1	0	4.112340	-2.344278	-1.339745
31	1	0	4.158449	-1.051867	-2.558861
32	6	0	-1.420589	-1.522817	-2.205667
33	1	0	-1.014837	-2.432659	-1.745426
34	1	0	-2.380956	-1.788811	-2.665936
35	1	0	-0.748073	-1.222207	-3.018692
36	1	0	1.583910	-1.075420	-1.679282
37	17	0	1.680280	1.418141	-2.666952

		1			2			3		
		A			A			A		
Frequencies --		19.9313			32.7746			37.6007		
Red. masses --		3.0336			3.3622			5.0542		
Frc consts --		0.0007			0.0021			0.0042		
IR Inten --		0.0645			0.1096			0.5510		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	0.01	0.00	0.00	0.02	0.00	0.00	-0.06	0.03
2	6	0.00	0.04	-0.02	0.01	0.08	-0.03	0.00	-0.07	0.04
3	6	0.00	0.06	-0.03	0.01	0.11	-0.05	0.00	-0.09	0.05
4	6	0.00	0.05	-0.02	0.01	0.08	-0.04	0.00	-0.07	0.04
5	6	0.00	0.01	0.00	0.00	0.02	-0.01	0.00	-0.06	0.03
6	1	0.00	0.06	-0.03	0.01	0.11	-0.04	0.00	-0.06	0.03
7	1	0.00	0.09	-0.04	0.01	0.16	-0.07	-0.01	-0.10	0.05
8	1	0.00	0.07	-0.02	0.01	0.11	-0.05	0.00	-0.05	0.03
9	15	0.00	-0.01	0.00	0.00	-0.01	0.00	0.00	-0.10	0.04
10	14	0.00	0.01	0.00	0.00	-0.01	0.02	-0.02	0.07	-0.01
11	14	0.00	-0.01	0.02	0.00	0.00	0.01	0.02	0.07	-0.01
12	6	0.06	-0.19	-0.03	0.03	-0.04	0.04	-0.09	0.12	-0.05
13	1	0.05	-0.15	-0.02	0.02	-0.05	0.06	-0.09	0.19	-0.08
14	1	0.10	-0.25	-0.16	0.06	-0.05	0.02	-0.16	0.09	-0.06
15	1	0.07	-0.29	0.09	0.04	-0.06	0.06	-0.05	0.12	-0.04
16	6	-0.09	0.08	0.19	-0.05	-0.02	0.04	0.12	0.14	0.03
17	1	-0.12	0.20	0.22	-0.07	0.00	0.04	0.15	0.10	0.04
18	1	-0.09	0.10	0.18	-0.05	-0.03	0.06	0.10	0.24	0.02
19	1	-0.12	-0.01	0.29	-0.05	-0.02	0.05	0.19	0.14	0.05
20	6	0.00	-0.04	-0.05	0.07	0.04	0.23	-0.11	0.15	0.02
21	1	0.00	-0.05	-0.04	0.08	0.05	0.25	-0.10	0.24	0.01
22	1	0.01	-0.07	-0.07	0.12	0.15	0.25	-0.15	0.13	0.04
23	1	0.01	0.00	-0.09	0.06	-0.04	0.31	-0.16	0.13	0.04
24	6	0.00	0.06	0.05	-0.08	-0.20	-0.03	0.09	0.10	-0.04
25	1	-0.01	0.08	0.09	-0.11	-0.23	-0.16	0.17	0.05	-0.06
26	1	0.00	0.04	0.06	-0.07	-0.18	-0.01	0.11	0.18	-0.06
27	1	0.00	0.09	0.02	-0.11	-0.29	0.06	0.05	0.07	-0.02
28	6	0.00	-0.07	0.08	0.01	0.15	-0.13	0.09	0.11	-0.04
29	1	0.00	-0.08	0.09	0.01	0.16	-0.13	0.10	0.19	-0.07
30	1	0.00	-0.06	0.12	-0.01	0.13	-0.25	0.16	0.06	-0.06
31	1	0.00	-0.11	0.06	0.04	0.27	-0.10	0.04	0.10	-0.02

32	6	0.03	0.16	-0.15	0.00	0.00	0.01	-0.09	0.09	-0.05
33	1	0.06	0.12	-0.26	0.02	0.01	0.00	-0.18	0.04	-0.06
34	1	0.03	0.18	-0.17	0.00	-0.01	0.02	-0.10	0.18	-0.09
35	1	0.01	0.27	-0.13	-0.01	0.02	0.00	-0.04	0.06	-0.01
36	1	0.00	-0.03	0.03	-0.01	-0.04	0.04	-0.01	-0.13	0.08
37	17	0.00	-0.06	-0.03	0.00	-0.08	-0.05	0.00	-0.20	-0.03

Total free energy in solution:
with all non electrostatic terms (a.u.) = -1813.243907

III.11. Cartesian coordinates, three lower frequencies and PCM energy for III-CTSIII-D



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.010360	-0.385778	-0.043209
2	6	0	-0.035760	-0.088587	1.402203
3	6	0	1.057834	0.111770	2.187561
4	6	0	2.413983	0.061457	1.701006
5	6	0	2.843871	-0.024307	0.397342
6	1	0	-1.012623	-0.102196	1.882297
7	1	0	0.919760	0.258574	3.254954
8	1	0	3.181583	0.070441	2.475844
9	15	0	1.555521	-0.013611	-0.803228
10	14	0	-1.664095	-0.056748	-1.022852
11	14	0	4.688490	-0.149384	-0.087685
12	6	0	-2.920759	-1.230788	-0.250538
13	1	0	-3.883143	-1.149259	-0.772207
14	1	0	-2.575024	-2.267632	-0.336365
15	1	0	-3.106715	-1.018215	0.809497
16	6	0	-2.184557	1.745873	-0.786963
17	1	0	-1.448234	2.441539	-1.205549
18	1	0	-3.141261	1.930436	-1.293062
19	1	0	-2.320115	1.997107	0.272373
20	6	0	-1.387549	-0.469336	-2.839251
21	1	0	-0.967282	-1.476675	-2.943504
22	1	0	-2.347780	-0.447847	-3.371268
23	1	0	-0.722761	0.244224	-3.340625
24	6	0	5.446329	1.583554	-0.079873
25	1	0	6.511505	1.543068	-0.342613
26	1	0	4.948742	2.243489	-0.800409
27	1	0	5.365825	2.050898	0.909502
28	6	0	5.537994	-1.247451	1.193355
29	1	0	5.083303	-2.244459	1.225674
30	1	0	6.598456	-1.370247	0.937902
31	1	0	5.496255	-0.823423	2.204167
32	6	0	4.806767	-0.922106	-1.806185
33	1	0	5.861285	-1.065675	-2.074583

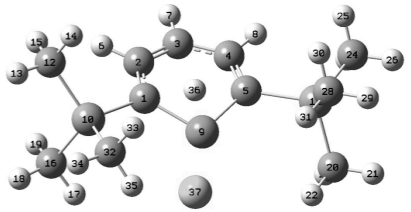
34	1	0	4.320576	-1.904553	-1.846392
35	1	0	4.364105	-0.289114	-2.585771
36	1	0	0.074033	-1.550377	-0.215326
37	17	0	1.620752	1.815140	-1.830968
38	17	0	0.618413	-3.254561	-1.030141
39	1	0	1.755574	-0.927426	-1.843266

	1	2	3
	A	A	A
Frequencies --	-32.2839	19.7035	28.0717
Red. masses --	10.8696	3.1253	5.6971
Frc consts --	0.0067	0.0007	0.0026
IR Inten --	11.7157	0.5453	3.4571

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.07	-0.04	-0.07	0.00	0.01	0.00	-0.01	-0.05	0.02
2	6	0.05	-0.17	-0.06	0.00	0.04	-0.01	0.00	-0.05	0.02
3	6	0.03	-0.20	-0.02	0.00	0.06	-0.01	0.00	-0.04	0.02
4	6	0.03	-0.10	0.00	0.00	0.04	-0.01	0.00	-0.01	0.02
5	6	0.04	0.00	-0.02	0.00	0.02	-0.01	0.00	-0.03	0.02
6	1	0.05	-0.26	-0.07	0.00	0.05	0.00	0.00	-0.05	0.02
7	1	0.01	-0.31	-0.01	0.00	0.08	-0.01	0.00	-0.03	0.02
8	1	0.03	-0.13	0.00	0.00	0.06	-0.01	0.00	0.03	0.02
9	15	0.05	0.06	-0.01	0.00	0.00	-0.01	0.01	-0.11	0.01
10	14	0.06	-0.05	-0.04	0.00	-0.02	-0.01	0.00	0.06	0.04
11	14	0.04	0.08	0.00	0.00	0.00	0.00	0.01	0.09	0.03
12	6	0.08	-0.08	-0.08	0.00	-0.01	0.02	-0.08	0.16	0.08
13	1	0.09	-0.11	-0.10	0.00	-0.02	0.02	-0.08	0.23	0.10
14	1	0.11	-0.07	-0.06	0.01	-0.01	0.04	-0.16	0.14	0.09
15	1	0.04	-0.08	-0.08	0.00	0.02	0.01	-0.04	0.19	0.08
16	6	0.03	-0.06	0.01	-0.01	-0.01	-0.04	0.14	0.10	0.03
17	1	0.02	-0.04	0.01	-0.01	-0.02	-0.06	0.17	0.04	-0.01
18	1	0.02	-0.07	0.02	-0.01	-0.03	-0.05	0.13	0.16	0.06
19	1	0.05	-0.09	0.01	-0.01	0.01	-0.05	0.20	0.13	0.03
20	6	0.06	0.02	-0.06	0.00	-0.05	0.00	-0.08	0.00	0.04
21	1	0.03	0.02	-0.10	0.00	-0.05	0.02	-0.13	-0.02	0.05
22	1	0.06	0.07	-0.06	0.00	-0.06	0.00	-0.09	0.04	0.07
23	1	0.07	0.03	-0.03	0.00	-0.06	-0.01	-0.05	-0.04	0.01
24	6	-0.01	0.11	0.00	0.06	-0.02	0.22	-0.09	0.13	0.10
25	1	-0.01	0.14	0.01	0.06	-0.02	0.22	-0.09	0.21	0.12
26	1	-0.03	0.09	0.01	0.08	0.08	0.29	-0.12	0.12	0.11
27	1	-0.03	0.10	0.01	0.06	-0.14	0.27	-0.14	0.10	0.11
28	6	0.09	0.10	-0.01	-0.06	-0.19	-0.13	0.07	0.10	0.01
29	1	0.12	0.09	-0.01	-0.07	-0.19	-0.29	0.14	0.07	-0.03
30	1	0.09	0.14	-0.02	-0.05	-0.16	-0.10	0.08	0.19	0.03
31	1	0.08	0.10	-0.01	-0.10	-0.34	-0.07	0.01	0.06	0.03
32	6	0.09	0.09	-0.01	0.00	0.21	-0.10	0.08	0.15	0.01
33	1	0.10	0.14	0.00	0.00	0.23	-0.11	0.09	0.24	0.01
34	1	0.14	0.07	-0.02	0.00	0.21	-0.21	0.16	0.11	-0.02
35	1	0.07	0.08	-0.01	0.00	0.30	-0.02	0.03	0.13	0.03
36	1	0.10	-0.11	-0.18	0.01	0.01	0.03	-0.07	-0.04	0.01
37	17	0.05	0.09	0.00	0.00	-0.01	-0.03	0.03	-0.18	-0.10
38	17	-0.41	-0.06	0.18	0.00	-0.01	0.07	-0.06	-0.05	-0.12
39	1	0.12	0.17	-0.09	0.00	-0.01	0.00	-0.01	-0.19	0.07

Total free energy in solution:
with all non electrostatic terms (a.u.) = -2274.077560

III.12. Cartesian coordinates, three lower frequencies and PCM energy for III-CTSIII-E



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.002072	-0.032235	0.013331
2	6	0	-0.020085	-0.295582	1.401711
3	6	0	1.120764	-0.421056	2.177340
4	6	0	2.451778	-0.396293	1.671862
5	6	0	2.791495	-0.130787	0.364923
6	1	0	-0.977683	-0.470501	1.892168
7	1	0	0.994834	-0.643128	3.235385
8	1	0	3.234060	-0.661693	2.383084
9	15	0	1.521343	0.464934	-0.803050
10	14	0	-1.633802	0.045383	-0.984291
11	14	0	4.595705	-0.242816	-0.255230
12	6	0	-2.755607	-1.372282	-0.421033
13	1	0	-3.712290	-1.332009	-0.957952
14	1	0	-2.303271	-2.351030	-0.622865
15	1	0	-2.983782	-1.323328	0.650745
16	6	0	-2.417842	1.717712	-0.586149
17	1	0	-1.727392	2.537799	-0.814036
18	1	0	-3.333001	1.862963	-1.175051
19	1	0	-2.685809	1.796509	0.474442
20	6	0	5.174631	1.453670	-0.844150
21	1	0	6.209045	1.394343	-1.208078
22	1	0	4.548630	1.836058	-1.658069
23	1	0	5.135036	2.193296	-0.036745
24	6	0	5.697125	-0.861797	1.154924
25	1	0	5.391489	-1.849304	1.522328
26	1	0	6.731576	-0.952490	0.798881
27	1	0	5.707175	-0.169247	2.005618
28	6	0	4.632199	-1.480673	-1.688782
29	1	0	5.647901	-1.562458	-2.097108
30	1	0	4.319582	-2.481402	-1.366201
31	1	0	3.971556	-1.169781	-2.507114
32	6	0	-1.276372	-0.103855	-2.831885
33	1	0	-0.781301	-1.050031	-3.081759
34	1	0	-2.219726	-0.066305	-3.392108
35	1	0	-0.643040	0.712857	-3.196092
36	1	0	1.135701	-1.009773	-1.052197
37	17	0	1.657492	2.789658	-0.153114

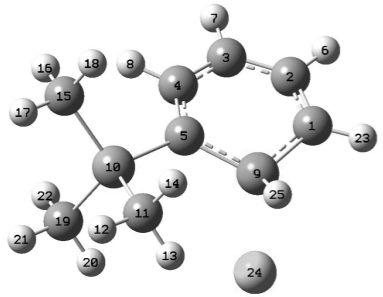
	1	2	3
	A	A	A
Frequencies --	-844.9146	17.3992	21.8088
Red. masses --	1.1151	3.0810	3.2753
Frc consts --	0.4690	0.0005	0.0009
IR Inten --	39.6146	0.3165	0.4648

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	-0.03	0.04	0.04	0.00	0.01	0.01	0.00	-0.03	0.00
2	6	-0.01	0.02	-0.02	0.00	0.04	0.02	0.00	-0.07	-0.01
3	6	0.02	0.00	0.00	0.00	0.05	0.02	0.01	-0.09	-0.02
4	6	0.00	0.01	0.01	0.00	0.04	0.01	0.01	-0.06	-0.02
5	6	0.00	-0.01	-0.01	0.00	0.01	0.01	0.00	-0.02	-0.01

6	1	0.00	-0.02	0.00	0.00	0.05	0.02	0.01	-0.10	-0.02
7	1	0.01	-0.03	-0.01	0.01	0.08	0.02	0.01	-0.12	-0.03
8	1	0.00	0.02	0.01	0.00	0.05	0.02	0.01	-0.07	-0.03
9	15	-0.01	-0.04	0.01	0.00	-0.01	0.00	0.00	0.01	0.01
10	14	0.00	0.00	0.00	0.00	-0.02	0.01	0.00	0.01	-0.01
11	14	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.03	-0.02
12	6	0.00	0.00	0.00	-0.01	0.01	0.07	-0.11	0.15	0.11
13	1	0.00	0.00	0.00	-0.01	-0.01	0.07	-0.10	0.18	0.09
14	1	0.00	0.00	0.00	-0.01	0.00	0.10	-0.19	0.09	0.21
15	1	0.00	0.00	0.00	-0.01	0.05	0.07	-0.13	0.27	0.10
16	6	0.00	0.00	0.00	0.01	0.00	-0.05	0.14	0.11	-0.17
17	1	0.00	0.00	0.00	0.01	-0.02	-0.08	0.21	0.03	-0.23
18	1	0.00	0.01	0.00	0.01	-0.02	-0.05	0.16	0.13	-0.20
19	1	0.00	0.00	0.00	0.02	0.04	-0.05	0.12	0.22	-0.18
20	6	0.00	0.00	0.00	0.08	0.05	0.21	-0.04	0.04	-0.03
21	1	0.00	0.00	0.00	0.07	0.05	0.20	-0.04	0.07	-0.02
22	1	0.00	0.00	0.00	0.09	0.18	0.27	-0.05	0.01	-0.03
23	1	0.00	0.00	0.00	0.12	-0.05	0.31	-0.07	0.05	-0.03
24	6	0.00	0.00	0.00	-0.04	-0.20	-0.05	0.02	0.06	-0.02
25	1	0.00	0.00	0.00	-0.10	-0.22	-0.15	0.05	0.05	-0.01
26	1	0.00	0.00	0.00	-0.04	-0.23	-0.05	0.03	0.09	-0.02
27	1	0.00	0.00	0.00	0.00	-0.29	0.02	0.00	0.06	-0.02
28	6	0.00	0.00	0.00	-0.03	0.17	-0.13	0.03	0.02	-0.01
29	1	0.00	0.00	0.00	-0.03	0.18	-0.13	0.03	0.05	-0.02
30	1	0.00	0.00	0.00	-0.07	0.14	-0.25	0.05	0.02	-0.01
31	1	0.00	0.00	0.00	-0.01	0.29	-0.11	0.02	0.00	-0.01
32	6	0.00	0.00	0.00	-0.01	-0.10	0.02	0.00	-0.20	0.00
33	1	0.00	0.00	0.00	-0.01	-0.11	0.05	-0.09	-0.27	0.10
34	1	0.00	0.00	0.00	-0.01	-0.11	0.02	0.01	-0.17	-0.01
35	1	0.00	0.00	0.00	0.00	-0.12	-0.02	0.08	-0.30	-0.07
36	1	0.67	0.15	-0.72	0.00	-0.02	0.04	0.01	0.01	-0.03
37	17	0.00	0.01	0.00	0.00	0.00	-0.07	-0.02	-0.01	0.09

Total free energy in solution:
 with all non electrostatic terms (a.u.) = -1813.185850

III.13. Cartesian coordinates, three lower frequencies and PCM energy for III-Cb



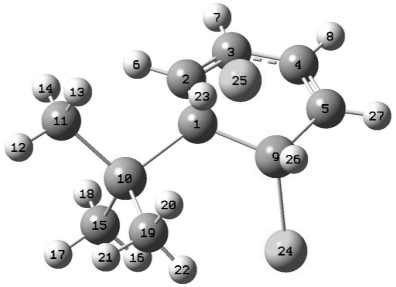
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.177216	0.733430	0.437992
2	6	0	0.098372	-0.222575	1.447372
3	6	0	1.164759	-1.032522	1.864798
4	6	0	2.450063	-0.921596	1.323102
5	6	0	2.865442	-0.057451	0.290694

6	1	0	-0.852568	-0.318461	1.969454
7	1	0	0.999716	-1.738515	2.672995
8	1	0	3.219759	-1.545788	1.777965
9	15	0	1.607483	0.802318	-0.522171
10	14	0	4.663529	-0.022860	-0.310288
11	6	0	4.986424	1.595361	-1.240082
12	1	0	6.037978	1.640417	-1.551902
13	1	0	4.379069	1.684086	-2.149429
14	1	0	4.794893	2.475649	-0.613227
15	6	0	5.798115	-0.120108	1.203021
16	1	0	5.661223	-1.050544	1.767873
17	1	0	6.849726	-0.083005	0.890073
18	1	0	5.623311	0.716075	1.890832
19	6	0	4.995302	-1.491808	-1.455862
20	1	0	4.341278	-1.460237	-2.335204
21	1	0	6.035845	-1.491487	-1.806638
22	1	0	4.815754	-2.445490	-0.943865
23	1	0	-0.685478	1.333125	0.164727
24	17	0	1.271800	0.118373	-2.608655
25	1	0	1.949081	2.095526	-0.931254

		1			2			3		
		A			A			A		
Frequencies --		20.1310			60.9452			99.7147		
Red. masses --		3.5228			5.7210			4.5193		
Frc consts --		0.0008			0.0125			0.0265		
IR Inten --		0.1920			1.2633			0.6059		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	-0.01	0.01	-0.03	0.09	0.12	0.03	0.07	0.19	0.07
2	6	0.00	0.06	0.02	0.06	0.10	0.01	-0.03	0.12	-0.01
3	6	0.01	0.09	0.06	0.01	-0.02	-0.08	-0.13	-0.06	-0.10
4	6	0.01	0.08	0.05	-0.01	-0.09	-0.12	-0.10	-0.14	-0.08
5	6	0.00	0.03	0.01	0.02	-0.07	-0.10	-0.02	-0.09	0.01
6	1	0.00	0.08	0.02	0.08	0.18	0.07	-0.03	0.19	0.01
7	1	0.01	0.13	0.09	-0.01	-0.03	-0.10	-0.21	-0.12	-0.17
8	1	0.01	0.11	0.08	-0.03	-0.15	-0.16	-0.17	-0.25	-0.12
9	15	-0.01	-0.02	-0.03	0.04	-0.01	-0.06	0.05	0.04	0.04
10	14	0.00	0.02	0.00	0.06	-0.01	0.03	-0.03	-0.01	-0.03
11	6	0.06	0.12	0.19	0.08	0.02	0.09	-0.20	0.03	-0.01
12	1	0.06	0.12	0.20	0.11	0.07	0.19	-0.20	0.16	0.01
13	1	0.07	0.24	0.19	0.16	0.01	0.03	-0.20	-0.03	-0.02
14	1	0.08	0.05	0.29	-0.01	0.00	0.08	-0.31	0.01	-0.01
15	6	0.00	-0.20	-0.02	-0.08	0.01	0.14	0.02	0.05	-0.06
16	1	-0.01	-0.28	-0.14	-0.08	-0.01	0.10	0.03	0.08	-0.02
17	1	0.00	-0.17	-0.02	-0.05	0.08	0.24	0.01	0.04	-0.09
18	1	0.01	-0.29	0.10	-0.19	-0.02	0.15	0.03	0.08	-0.09
19	6	-0.06	0.14	-0.18	0.25	0.03	0.03	0.06	0.05	-0.08
20	1	-0.08	0.25	-0.16	0.36	0.02	-0.05	0.01	0.01	-0.04
21	1	-0.07	0.17	-0.20	0.30	0.09	0.16	0.04	0.19	-0.14
22	1	-0.06	0.09	-0.28	0.23	0.01	-0.01	0.21	0.01	-0.11
23	1	-0.01	-0.01	-0.06	0.13	0.20	0.09	0.15	0.34	0.14
24	17	0.01	-0.12	0.00	-0.26	-0.03	0.00	0.11	-0.10	0.09
25	1	-0.02	-0.04	-0.09	0.12	-0.05	-0.10	0.14	0.01	0.01

Total free energy in solution:
 with all non electrostatic terms (a.u.) = -1404.511790

III.14. Cartesian coordinates, three lower frequencies and PCM energy for III-CbTSIII-Eb



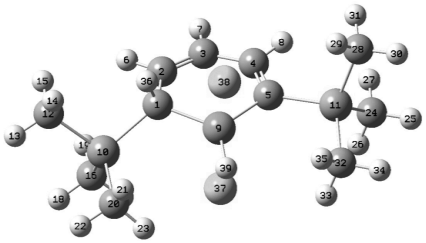
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.008907	-0.050127	-0.013655
2	6	0	-0.007650	-0.060355	1.465617
3	6	0	1.077648	-0.019596	2.283450
4	6	0	2.435042	0.069348	1.805438
5	6	0	2.819482	0.238135	0.507847
6	1	0	-0.986661	-0.170032	1.928281
7	1	0	0.931634	-0.091540	3.357090
8	1	0	3.223854	-0.014525	2.551624
9	15	0	1.582715	0.406155	-0.730748
10	14	0	-1.643414	0.573931	-0.859148
11	6	0	-2.952768	-0.667474	-0.312015
12	1	0	-3.917290	-0.420872	-0.774445
13	1	0	-2.675874	-1.679329	-0.630954
14	1	0	-3.108228	-0.680632	0.773631
15	6	0	-2.039753	2.311601	-0.229374
16	1	0	-1.265932	3.034156	-0.513312
17	1	0	-2.989108	2.658206	-0.658248
18	1	0	-2.142878	2.340112	0.862402
19	6	0	-1.434456	0.537012	-2.728934
20	1	0	-1.071968	-0.444831	-3.055623
21	1	0	-2.406888	0.715516	-3.206716
22	1	0	-0.745185	1.305628	-3.097155
23	1	0	0.023079	-1.134032	-0.430802
24	17	0	1.717340	2.341997	-1.497692
25	17	0	0.581348	-2.590477	-1.758595
26	1	0	1.761600	-0.422396	-1.855847
27	1	0	3.864996	0.304767	0.223375

	1			2			3		
	A			A			A		
Frequencies --	-54.6237			41.3924			50.7800		
Red. masses --	8.0423			6.0397			3.6650		
Frc consts --	0.0141			0.0061			0.0056		
IR Inten --	11.1707			3.5221			1.0060		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
1 6	-0.09	0.02	0.10	0.05	-0.02	0.04	-0.02	0.06	0.02
2 6	-0.05	0.18	0.12	0.00	0.02	0.03	0.02	0.17	0.03
3 6	-0.02	0.18	0.07	-0.04	0.12	0.07	0.06	0.12	-0.02
4 6	-0.02	0.03	0.02	-0.03	0.19	0.12	0.05	-0.07	-0.08
5 6	-0.04	-0.10	0.00	0.01	0.14	0.13	0.01	-0.15	-0.10
6 1	-0.05	0.32	0.17	-0.01	-0.02	0.00	0.03	0.31	0.08
7 1	0.01	0.32	0.08	-0.07	0.16	0.07	0.09	0.21	-0.01
8 1	-0.01	0.02	0.01	-0.05	0.29	0.16	0.07	-0.14	-0.11
9 15	-0.06	-0.13	-0.01	0.06	-0.02	0.06	-0.03	-0.02	-0.04
10 14	-0.05	0.05	0.06	0.03	-0.04	0.02	-0.03	0.00	-0.01
11 6	-0.09	0.09	0.07	0.09	-0.15	-0.09	0.04	-0.13	-0.14

12	1	-0.09	0.13	0.11	0.08	-0.16	-0.07	0.02	-0.15	-0.10
13	1	-0.14	0.08	0.03	0.15	-0.11	-0.19	0.11	-0.08	-0.25
14	1	-0.04	0.06	0.07	0.09	-0.26	-0.10	0.06	-0.26	-0.14
15	6	-0.02	0.07	0.02	-0.04	-0.11	0.15	-0.17	-0.06	0.06
16	1	0.01	0.04	0.03	-0.05	-0.06	0.23	-0.19	0.00	0.14
17	1	0.01	0.10	-0.01	-0.03	-0.10	0.16	-0.16	-0.10	0.03
18	1	-0.04	0.09	0.02	-0.06	-0.19	0.15	-0.23	-0.13	0.06
19	6	-0.04	0.00	0.06	0.05	0.12	0.02	0.05	0.12	-0.01
20	1	-0.03	-0.01	0.09	0.10	0.17	-0.06	0.12	0.16	-0.05
21	1	-0.04	-0.02	0.05	0.03	0.10	0.04	0.06	0.09	-0.04
22	1	-0.04	-0.01	0.04	0.00	0.19	0.08	0.02	0.19	0.07
23	1	-0.15	0.04	0.26	0.02	-0.02	0.02	-0.03	0.04	0.11
24	17	-0.01	-0.16	-0.03	0.04	-0.10	-0.13	0.05	0.01	0.06
25	17	0.25	0.06	-0.20	-0.16	0.05	-0.12	-0.01	-0.01	0.08
26	1	-0.24	-0.36	0.09	0.10	-0.13	0.14	-0.13	-0.01	-0.07
27	1	-0.04	-0.21	-0.03	0.02	0.19	0.17	0.01	-0.28	-0.15

Total free energy in solution:
with all non electrostatic terms (a.u.) = -1865.347194

III.15. Cartesian coordinates, three lower frequencies and PCM energy for III-D



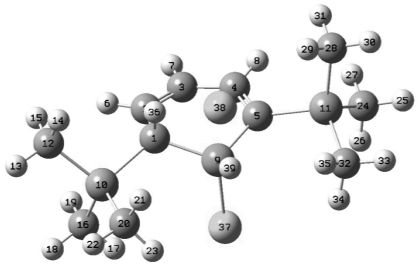
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.506363	0.396298	0.686310
2	6	0	1.284216	-0.381075	1.960482
3	6	0	0.113012	-0.854539	2.435427
4	6	0	-1.195304	-0.730660	1.796263
5	6	0	-1.473012	-0.233300	0.564771
6	1	0	2.173936	-0.524635	2.572045
7	1	0	0.126670	-1.370196	3.392659
8	1	0	-2.032126	-1.095252	2.392657
9	15	0	-0.020680	0.323702	-0.333860
10	14	0	3.220635	0.024552	-0.182349
11	14	0	-3.232610	-0.146015	-0.170878
12	6	0	4.428739	1.137800	0.764137
13	1	0	5.451366	0.991587	0.392831
14	1	0	4.183031	2.200505	0.644599
15	1	0	4.441479	0.918185	1.839549
16	6	0	3.764955	-1.769595	0.000580
17	1	0	3.082845	-2.454870	-0.509829
18	1	0	4.767156	-1.892492	-0.431572
19	1	0	3.824369	-2.071115	1.053425
20	6	0	3.147758	0.572687	-1.988031
21	1	0	2.775699	1.600125	-2.090247
22	1	0	4.156812	0.549208	-2.420086
23	1	0	2.515871	-0.088250	-2.591230

24	6	0	-4.049290	-1.824714	0.131749
25	1	0	-5.066516	-1.834988	-0.281052
26	1	0	-3.481275	-2.631526	-0.345931
27	1	0	-4.128426	-2.058219	1.200750
28	6	0	-4.197286	1.223690	0.701123
29	1	0	-3.707860	2.193814	0.561299
30	1	0	-5.218085	1.291295	0.302356
31	1	0	-4.271755	1.039078	1.779990
32	6	0	-3.113235	0.201203	-2.024188
33	1	0	-2.511964	-0.553845	-2.545090
34	1	0	-4.116671	0.185539	-2.469083
35	1	0	-2.684419	1.189916	-2.228091
36	1	0	1.609258	1.455094	0.962054
37	17	0	0.377040	-1.807341	-1.142772
38	17	0	-0.534461	2.555375	-0.017198
39	1	0	-0.036889	0.662633	-1.681153

	1			2			3		
	A			A			A		
Frequencies --	21.6705			28.2454			43.9447		
Red. masses --	3.4191			3.9947			3.1580		
Frc consts --	0.0009			0.0019			0.0036		
IR Inten --	0.0608			0.1533			0.2079		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
1 6	-0.01	-0.03	-0.05	-0.01	-0.02	-0.03	0.01	0.01	-0.03
2 6	-0.01	-0.11	-0.05	-0.02	-0.07	-0.03	0.00	-0.03	-0.03
3 6	-0.02	-0.12	-0.04	-0.03	-0.06	-0.02	-0.01	-0.06	-0.02
4 6	-0.02	-0.07	-0.02	-0.02	-0.02	-0.01	-0.01	-0.05	-0.02
5 6	-0.01	-0.03	-0.01	-0.01	-0.02	0.00	0.00	0.00	-0.01
6 1	-0.02	-0.16	-0.06	-0.02	-0.10	-0.04	-0.01	-0.05	-0.03
7 1	-0.03	-0.18	-0.04	-0.04	-0.09	-0.03	-0.01	-0.09	-0.02
8 1	-0.02	-0.07	-0.02	-0.03	0.01	0.00	-0.01	-0.08	-0.02
9 15	0.00	-0.03	-0.02	0.00	-0.07	-0.02	0.01	0.05	-0.01
10 14	0.00	0.05	0.02	0.01	0.04	0.01	-0.02	-0.01	0.00
11 14	0.00	0.04	0.01	-0.01	0.06	0.02	0.01	-0.01	0.03
12 6	-0.03	0.09	0.00	-0.05	0.11	0.09	-0.04	0.03	0.21
13 1	-0.02	0.13	0.03	-0.04	0.15	0.11	-0.05	0.01	0.21
14 1	-0.06	0.10	-0.04	-0.11	0.09	0.10	-0.10	-0.04	0.29
15 1	-0.02	0.05	-0.01	-0.04	0.15	0.10	0.00	0.14	0.26
16 6	0.06	0.02	0.10	0.11	0.08	0.00	0.06	0.09	-0.12
17 1	0.06	0.02	0.09	0.10	0.09	-0.12	0.01	0.15	-0.38
18 1	0.04	0.04	0.17	0.05	0.05	0.08	-0.07	-0.05	0.00
19 1	0.12	-0.02	0.11	0.23	0.12	0.04	0.30	0.21	-0.03
20 6	-0.03	0.11	0.03	-0.04	-0.02	-0.01	-0.10	-0.19	-0.05
21 1	-0.08	0.12	-0.02	-0.12	-0.05	-0.01	-0.15	-0.25	0.02
22 1	-0.03	0.16	0.07	-0.04	0.03	0.01	-0.11	-0.20	-0.05
23 1	0.00	0.09	0.04	0.00	-0.07	-0.06	-0.08	-0.22	-0.16
24 6	-0.08	0.19	-0.08	-0.05	-0.03	0.13	-0.01	0.00	0.03
25 1	-0.08	0.23	-0.07	-0.05	0.01	0.15	-0.01	0.00	0.05
26 1	-0.14	0.16	-0.19	-0.08	-0.04	0.22	-0.01	0.00	0.01
27 1	-0.09	0.28	-0.06	-0.05	-0.13	0.10	-0.04	0.02	0.03
28 6	0.06	0.08	0.19	0.05	0.06	-0.15	-0.01	-0.01	0.07
29 1	0.10	0.00	0.24	0.07	0.11	-0.22	0.00	-0.02	0.07
30 1	0.07	0.10	0.21	0.05	0.12	-0.15	0.00	-0.03	0.10
31 1	0.06	0.17	0.22	0.06	-0.04	-0.19	-0.04	0.00	0.08
32 6	0.00	-0.12	-0.04	-0.01	0.23	0.08	0.05	-0.04	0.02
33 1	-0.02	-0.15	-0.14	-0.06	0.23	0.17	0.07	-0.04	0.00
34 1	0.00	-0.12	-0.04	-0.01	0.30	0.09	0.06	-0.06	0.04
35 1	0.02	-0.20	0.02	0.03	0.28	0.01	0.05	-0.05	0.02
36 1	-0.03	0.00	-0.11	-0.05	-0.01	-0.06	0.03	0.01	-0.06
37 17	0.02	-0.03	-0.02	0.04	-0.05	-0.09	0.00	0.02	0.04
38 17	0.02	-0.04	0.00	-0.01	-0.09	0.06	0.02	0.06	-0.09
39 1	0.00	-0.04	-0.02	0.01	-0.11	-0.03	0.02	0.07	0.00

Total free energy in solution:
with all non electrostatic terms (a.u.) = -2274.079080

III.16. Cartesian coordinates, three lower frequencies and PCM energy for III-DTSIII-E



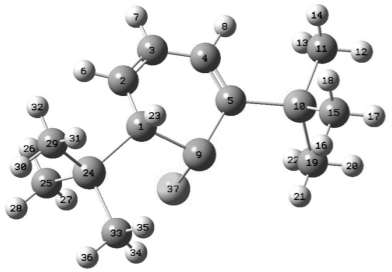
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.125880	0.284043	0.055029
2	6	0	0.028255	0.154523	1.548141
3	6	0	1.085966	0.115996	2.388881
4	6	0	2.479463	0.141251	1.958567
5	6	0	2.963288	0.445675	0.720475
6	1	0	-0.969734	0.035496	1.966060
7	1	0	0.905654	-0.015693	3.452663
8	1	0	3.199005	-0.150258	2.725308
9	15	0	1.723089	0.967396	-0.446445
10	14	0	-1.469181	0.956899	-0.846912
11	14	0	4.809018	0.269493	0.227806
12	6	0	-2.728005	-0.441886	-0.681446
13	1	0	-3.682895	-0.148968	-1.136494
14	1	0	-2.380871	-1.348382	-1.191855
15	1	0	-2.932942	-0.701976	0.364643
16	6	0	-2.105994	2.517123	0.006192
17	1	0	-1.385598	3.340195	-0.050803
18	1	0	-3.032988	2.851363	-0.477906
19	1	0	-2.334782	2.343406	1.064889
20	6	0	-1.042645	1.264880	-2.655697
21	1	0	-0.531623	0.400365	-3.096991
22	1	0	-1.961240	1.442014	-3.230073
23	1	0	-0.401803	2.144887	-2.788825
24	6	0	5.834761	1.092318	1.590655
25	1	0	6.905372	0.993869	1.368712
26	1	0	5.608906	2.161962	1.678157
27	1	0	5.664414	0.632034	2.572039
28	6	0	5.195724	-1.569726	0.102532
29	1	0	4.547107	-2.038082	-0.647162
30	1	0	6.241268	-1.726671	-0.193768
31	1	0	5.038552	-2.083482	1.059224
32	6	0	5.083869	1.132008	-1.427889
33	1	0	6.150761	1.101500	-1.684459
34	1	0	4.783358	2.187076	-1.413405
35	1	0	4.543111	0.622231	-2.234451
36	1	0	0.224298	-0.728755	-0.389576
37	17	0	1.649708	3.059701	-0.340079
38	17	0	1.967449	-1.535586	-2.238024
39	1	0	1.999778	0.561833	-1.775423

	1	2	3
	A	A	A
Frequencies --	-112.2930	22.4142	35.9000

Red. masses --		5.5573			3.2000			4.8737		
Frc consts --		0.0413			0.0009			0.0037		
IR Inten --		8.8049			0.8257			0.8261		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	0.01	0.12	0.01	0.00	0.01	-0.02	-0.04	-0.04
2	6	-0.02	0.04	0.11	0.01	0.04	0.01	-0.02	-0.12	-0.04
3	6	-0.02	0.02	0.10	0.01	0.06	0.01	-0.02	-0.16	-0.04
4	6	-0.02	0.01	0.10	0.01	0.05	0.01	-0.02	-0.11	-0.03
5	6	-0.02	0.04	0.11	0.01	0.02	0.00	-0.01	-0.06	-0.01
6	1	-0.02	0.09	0.12	0.01	0.04	0.01	-0.02	-0.14	-0.05
7	1	-0.01	0.04	0.11	0.01	0.08	0.01	-0.03	-0.22	-0.05
8	1	-0.02	-0.02	0.10	0.01	0.07	0.02	-0.02	-0.10	-0.03
9	15	0.00	-0.03	0.04	0.01	-0.01	-0.01	0.00	-0.07	-0.03
10	14	0.02	-0.02	0.05	0.00	-0.02	-0.01	-0.01	0.08	0.03
11	14	-0.03	0.02	0.06	0.01	0.01	0.01	0.01	0.08	0.02
12	6	0.00	-0.01	0.03	0.01	-0.01	0.03	-0.09	0.15	0.02
13	1	0.01	0.00	0.02	0.00	-0.03	0.03	-0.08	0.22	0.04
14	1	0.00	-0.01	0.04	0.01	-0.03	0.05	-0.16	0.14	0.00
15	1	-0.02	0.00	0.03	0.01	0.01	0.04	-0.10	0.14	0.02
16	6	0.01	0.00	0.02	0.01	0.00	-0.04	0.09	0.09	0.09
17	1	0.02	-0.01	0.02	0.01	0.00	-0.07	0.12	0.06	0.07
18	1	0.02	0.00	0.00	0.00	-0.01	-0.05	0.09	0.14	0.13
19	1	-0.02	0.02	0.02	0.01	0.03	-0.04	0.13	0.08	0.09
20	6	0.03	-0.03	0.05	0.00	-0.06	-0.02	-0.04	0.10	0.02
21	1	0.01	-0.03	0.05	0.00	-0.07	0.01	-0.12	0.08	-0.02
22	1	0.03	-0.01	0.06	0.00	-0.08	-0.02	-0.05	0.18	0.06
23	1	0.04	-0.04	0.05	0.00	-0.06	-0.04	0.01	0.06	0.03
24	6	0.02	0.00	0.04	0.02	-0.18	0.12	-0.08	0.14	0.06
25	1	0.01	-0.01	0.01	0.01	-0.18	0.11	-0.07	0.22	0.08
26	1	0.04	0.01	0.04	0.04	-0.19	0.25	-0.17	0.12	0.06
27	1	0.03	0.01	0.04	0.01	-0.30	0.06	-0.07	0.12	0.05
28	6	-0.04	0.02	0.03	-0.03	0.02	-0.22	0.15	0.11	0.00
29	1	-0.04	0.03	0.03	-0.06	0.12	-0.27	0.18	0.07	0.00
30	1	-0.04	0.03	0.02	-0.04	0.04	-0.26	0.16	0.20	-0.01
31	1	-0.03	0.00	0.03	-0.02	-0.09	-0.28	0.20	0.08	0.00
32	6	-0.04	0.01	0.05	0.05	0.21	0.11	-0.01	0.12	0.04
33	1	-0.04	-0.01	0.05	0.05	0.21	0.12	-0.01	0.18	0.06
34	1	-0.03	0.02	0.05	0.08	0.22	0.24	-0.07	0.10	0.05
35	1	-0.05	0.02	0.06	0.05	0.32	0.04	0.03	0.10	0.02
36	1	0.01	0.00	0.14	0.01	0.00	0.03	-0.07	-0.02	-0.09
37	17	0.04	-0.03	-0.16	0.00	0.00	-0.04	0.05	-0.07	-0.09
38	17	0.01	0.02	-0.27	-0.05	-0.04	0.04	-0.01	-0.12	0.04
39	1	-0.06	-0.82	0.14	0.00	-0.01	0.00	0.00	-0.12	-0.02

Total free energy in solution:
with all non electrostatic terms (a.u.) = -2274.078734

III.17. Cartesian coordinates, three lower frequencies and PCM energy for III-E



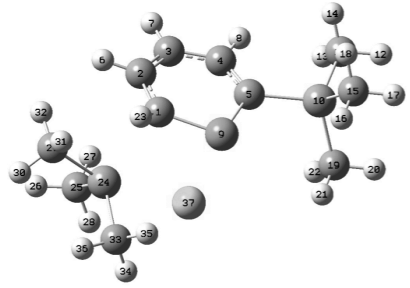
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.444117	0.951178	0.435711
2	6	0	0.802454	1.979191	1.468030
3	6	0	2.036792	2.119861	1.995927
4	6	0	3.181279	1.306799	1.615042
5	6	0	3.279421	0.507671	0.516331
6	1	0	0.010104	2.632104	1.834587
7	1	0	2.199079	2.866840	2.770306
8	1	0	4.042224	1.385579	2.281299
9	15	0	1.849387	0.311663	-0.614702
10	14	0	4.851646	-0.485367	0.125807
11	6	0	6.232995	0.024843	1.318506
12	1	0	7.150198	-0.529833	1.081416
13	1	0	6.467752	1.093797	1.242905
14	1	0	5.982952	-0.194175	2.364141
15	6	0	4.485875	-2.333308	0.340560
16	1	0	3.680801	-2.661137	-0.328532
17	1	0	5.374865	-2.935326	0.110479
18	1	0	4.181535	-2.566027	1.368727
19	6	0	5.395183	-0.163250	-1.657567
20	1	0	6.292599	-0.750943	-1.892103
21	1	0	4.618410	-0.442686	-2.379289
22	1	0	5.630285	0.894612	-1.823215
23	1	0	0.168394	0.017965	0.968583
24	14	0	-1.188708	1.362873	-0.525978
25	6	0	-1.204056	3.157761	-1.113228
26	1	0	-1.103425	3.861359	-0.277604
27	1	0	-0.389907	3.356921	-1.817325
28	1	0	-2.153806	3.379887	-1.617538
29	6	0	-2.601840	1.099797	0.712275
30	1	0	-3.566338	1.353811	0.253520
31	1	0	-2.660416	0.055412	1.044787
32	1	0	-2.492290	1.727019	1.606221
33	6	0	-1.398534	0.172792	-1.979343
34	1	0	-0.640165	0.335336	-2.753584
35	1	0	-1.331933	-0.875359	-1.662209
36	1	0	-2.383631	0.316309	-2.442619
37	17	0	2.227660	1.970340	-1.955156

		1			2			3		
		A			A			A		
Frequencies --		23.8983			33.2416			39.8345		
Red. masses --		3.0016			6.2683			3.1957		
Frc consts --		0.0010			0.0041			0.0030		
IR Inten --		0.0249			0.5768			0.1008		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	-0.01	-0.03	0.00	-0.04	-0.04	0.05	0.02	0.03	0.01
2	6	-0.02	-0.06	0.03	-0.03	-0.05	0.05	0.04	0.07	-0.03

3	6	-0.03	-0.06	0.04	-0.02	-0.03	0.03	0.05	0.10	-0.07
4	6	-0.02	-0.04	0.02	-0.01	0.00	0.01	0.04	0.09	-0.05
5	6	-0.01	-0.02	0.01	-0.02	-0.03	0.02	0.02	0.04	-0.02
6	1	-0.03	-0.07	0.05	-0.03	-0.06	0.07	0.04	0.07	-0.04
7	1	-0.04	-0.08	0.06	-0.02	-0.03	0.03	0.06	0.14	-0.10
8	1	-0.02	-0.04	0.02	0.01	0.04	-0.02	0.05	0.11	-0.07
9	15	0.00	-0.01	0.00	-0.05	-0.12	0.08	0.00	0.01	0.01
10	14	0.00	0.00	0.00	0.04	0.06	-0.01	-0.01	-0.02	0.02
11	6	0.06	0.16	-0.14	-0.01	0.07	0.04	-0.01	-0.07	0.04
12	1	0.08	0.19	-0.17	0.02	0.12	0.02	-0.04	-0.12	0.08
13	1	0.00	0.17	-0.24	-0.05	0.08	0.10	0.05	-0.08	0.03
14	1	0.16	0.22	-0.11	-0.01	0.00	0.02	-0.05	-0.04	0.04
15	6	0.07	0.01	0.19	0.13	0.03	-0.11	-0.09	0.00	0.03
16	1	0.05	-0.08	0.26	0.16	0.02	-0.15	-0.09	0.03	0.02
17	1	0.08	0.01	0.19	0.17	0.10	-0.13	-0.11	-0.04	0.05
18	1	0.14	0.09	0.22	0.13	-0.04	-0.13	-0.12	0.02	0.03
19	6	-0.13	-0.15	-0.07	0.05	0.19	0.02	0.04	-0.05	0.03
20	1	-0.12	-0.14	-0.07	0.10	0.25	0.01	0.02	-0.10	0.04
21	1	-0.16	-0.25	0.01	0.09	0.18	-0.01	0.04	-0.02	0.01
22	1	-0.18	-0.15	-0.19	-0.01	0.21	0.08	0.09	-0.07	0.03
23	1	-0.03	-0.04	-0.03	-0.12	-0.01	0.04	0.04	0.04	0.05
24	14	0.01	0.02	-0.02	0.01	0.08	0.00	0.01	-0.01	0.02
25	6	0.03	0.05	0.06	0.12	0.11	0.09	-0.09	0.04	0.18
26	1	-0.01	0.01	0.10	0.09	0.06	0.13	-0.25	-0.02	0.25
27	1	0.05	0.09	0.11	0.17	0.11	0.15	-0.02	0.18	0.29
28	1	0.05	0.07	0.04	0.16	0.17	0.04	-0.04	0.00	0.08
29	6	-0.02	-0.03	-0.06	-0.04	0.10	-0.06	0.00	-0.21	-0.03
30	1	-0.01	-0.01	-0.07	-0.01	0.17	-0.08	-0.01	-0.23	-0.02
31	1	-0.03	-0.05	-0.11	-0.11	0.08	-0.11	0.06	-0.25	-0.13
32	1	-0.03	-0.07	-0.03	-0.04	0.05	-0.03	-0.04	-0.29	0.03
33	6	0.03	0.09	-0.08	0.00	0.16	-0.07	0.11	0.11	-0.09
34	1	0.06	0.12	-0.06	0.04	0.15	-0.03	0.11	0.23	-0.06
35	1	0.02	0.08	-0.13	-0.08	0.14	-0.11	0.16	0.09	-0.19
36	1	0.05	0.12	-0.10	0.03	0.25	-0.10	0.11	0.10	-0.10
37	17	0.00	0.01	0.03	-0.07	-0.24	-0.08	-0.05	-0.02	-0.04

Total free energy in solution:
 with all non electrostatic terms (a.u.) = -1813.248014

III.18. Cartesian coordinates, three lower frequencies and PCM energy for III-ETSIII-G



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.184959	-0.757481	-0.128911
2	6	0	0.066519	-0.683093	1.285568

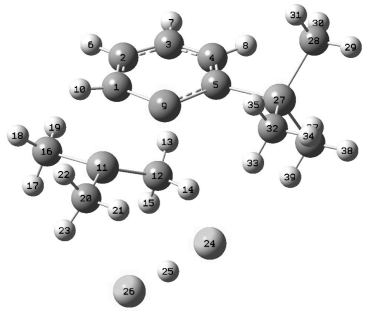
3	6	0	1.072819	-0.225480	2.118500
4	6	0	2.378142	0.052538	1.653151
5	6	0	2.814830	-0.011962	0.331016
6	1	0	-0.861919	-1.017998	1.744754
7	1	0	0.882182	-0.158460	3.186454
8	1	0	3.109005	0.303890	2.422697
9	15	0	1.694907	-0.352328	-0.987523
10	14	0	4.634056	0.321100	-0.125370
11	6	0	5.646570	0.548728	1.461252
12	1	0	6.701110	0.714195	1.204974
13	1	0	5.314258	1.417242	2.043567
14	1	0	5.603363	-0.333270	2.112549
15	6	0	5.310539	-1.159924	-1.095316
16	1	0	4.737507	-1.333973	-2.014453
17	1	0	6.356013	-0.990638	-1.384810
18	1	0	5.272716	-2.080896	-0.500166
19	6	0	4.753629	1.880582	-1.187990
20	1	0	5.796932	2.083637	-1.463945
21	1	0	4.173907	1.781773	-2.113392
22	1	0	4.365352	2.757045	-0.655796
23	1	0	-0.458272	-1.467439	-0.647443
24	14	0	-1.514165	0.904250	-0.820481
25	6	0	-1.975131	2.392385	0.245992
26	1	0	-3.032755	2.341571	0.535506
27	1	0	-1.370655	2.413913	1.159674
28	1	0	-1.780114	3.326842	-0.288559
29	6	0	-2.799451	-0.416807	-0.291661
30	1	0	-3.780185	0.005403	-0.559677
31	1	0	-2.702044	-1.370316	-0.823633
32	1	0	-2.824015	-0.618355	0.784452
33	6	0	-1.699281	0.961709	-2.698429
34	1	0	-1.518865	1.973262	-3.073361
35	1	0	-0.969919	0.305988	-3.187691
36	1	0	-2.704582	0.629553	-2.988730
37	17	0	0.727572	2.158132	-1.193296

		1			2			3		
		A			A			A		
Frequencies --		-279.7018			24.4740			37.3722		
Red. masses --		12.1926			3.1537			4.1551		
Frc consts --		0.5620			0.0011			0.0034		
IR Inten --		35.6757			0.1648			1.0950		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	-0.28	0.35	-0.08	0.01	0.00	-0.04	0.01	0.04	0.06
2	6	-0.08	0.11	0.02	0.00	-0.04	-0.04	0.01	0.13	0.06
3	6	-0.05	-0.02	-0.01	0.00	-0.05	-0.02	0.02	0.17	0.03
4	6	-0.01	-0.03	-0.03	0.00	-0.03	-0.01	0.02	0.12	0.01
5	6	-0.02	0.04	0.00	0.00	0.00	-0.02	0.01	0.05	0.01
6	1	-0.07	0.08	0.04	0.01	-0.05	-0.05	0.02	0.15	0.09
7	1	0.01	-0.13	0.01	0.00	-0.07	-0.02	0.02	0.24	0.02
8	1	0.00	-0.15	-0.01	0.00	-0.05	-0.01	0.03	0.14	-0.01
9	15	-0.12	0.26	-0.04	0.00	0.04	-0.03	-0.01	0.03	0.04
10	14	0.00	0.00	0.00	0.01	-0.01	-0.01	0.02	-0.04	-0.03
11	6	-0.01	-0.01	0.00	-0.04	0.19	-0.01	0.07	-0.12	-0.05
12	1	-0.01	0.00	0.00	-0.04	0.21	0.00	0.08	-0.19	-0.07
13	1	-0.01	0.00	0.00	-0.09	0.24	-0.10	0.14	-0.11	-0.03
14	1	0.00	0.00	0.00	-0.01	0.26	0.08	0.03	-0.13	-0.06
15	6	-0.01	-0.01	0.00	0.06	-0.12	0.18	-0.09	-0.07	-0.06
16	1	-0.01	-0.01	0.00	0.09	-0.22	0.18	-0.12	-0.03	-0.05
17	1	-0.01	0.00	0.00	0.07	-0.14	0.20	-0.08	-0.13	-0.08
18	1	0.00	-0.01	0.00	0.04	-0.05	0.28	-0.13	-0.08	-0.07
19	6	0.00	-0.01	0.00	0.01	-0.14	-0.19	0.09	-0.04	-0.02
20	1	0.01	-0.01	0.01	0.01	-0.15	-0.18	0.09	-0.10	-0.05
21	1	0.01	0.00	0.00	0.04	-0.26	-0.20	0.05	0.01	0.00
22	1	0.00	-0.01	0.00	-0.03	-0.08	-0.31	0.17	-0.02	0.00
23	1	0.06	-0.09	0.06	0.01	0.01	-0.06	0.03	-0.01	0.11
24	14	0.01	-0.30	0.11	0.00	0.01	0.01	-0.01	-0.04	-0.04

25	6	0.14	-0.13	-0.01	-0.02	-0.04	0.08	-0.13	-0.11	0.00
26	1	0.13	-0.07	-0.03	-0.02	-0.06	0.07	-0.14	-0.18	-0.03
27	1	0.12	-0.01	0.00	-0.02	-0.08	0.08	-0.16	-0.10	0.02
28	1	0.15	-0.20	-0.14	-0.02	-0.02	0.12	-0.17	-0.08	0.04
29	6	-0.21	-0.07	0.01	0.01	-0.03	-0.06	0.03	-0.14	-0.17
30	1	-0.21	-0.08	0.01	0.00	-0.02	-0.03	0.01	-0.15	-0.13
31	1	-0.22	-0.09	0.02	0.01	0.00	-0.11	0.07	-0.07	-0.29
32	1	-0.22	-0.08	0.01	0.01	-0.09	-0.07	0.04	-0.27	-0.20
33	6	0.08	-0.05	0.08	0.00	0.09	0.01	0.07	0.03	-0.04
34	1	0.08	0.00	0.22	0.00	0.10	0.05	0.06	0.04	0.00
35	1	0.05	0.00	-0.03	-0.01	0.11	-0.02	0.10	0.06	-0.04
36	1	0.06	0.01	0.06	-0.01	0.10	0.00	0.09	0.01	-0.10
37	17	0.25	-0.02	-0.04	-0.01	0.04	0.06	-0.05	0.05	0.11

Total free energy in solution:
with all non electrostatic terms (a.u.) = -1813.204343

III.19. Cartesian coordinates, three lower frequencies and PCM energy for III-ETSIII-G'



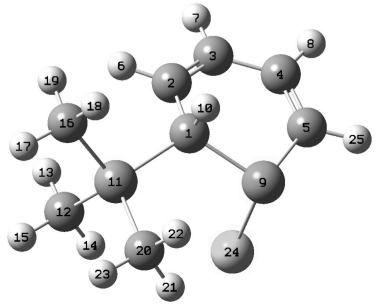
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.036389	0.027088	0.418854
2	6	0	0.143589	0.356022	1.789164
3	6	0	1.367378	0.559245	2.414888
4	6	0	2.597341	0.406505	1.749703
5	6	0	2.772833	0.018537	0.413139
6	1	0	-0.767153	0.461450	2.376595
7	1	0	1.379712	0.834221	3.466503
8	1	0	3.488482	0.601852	2.348350
9	15	0	1.416461	-0.334515	-0.636831
10	1	0	-0.942496	-0.304612	0.066870
11	14	0	-0.476405	2.187825	-0.623476
12	6	0	0.951160	3.233709	-0.051252
13	1	0	1.202378	3.009412	0.991045
14	1	0	1.828197	3.106715	-0.691128
15	1	0	0.638496	4.282071	-0.118952
16	6	0	-2.062408	2.540027	0.318004
17	1	0	-2.500373	3.446673	-0.124622
18	1	0	-2.804800	1.740601	0.218223
19	1	0	-1.891388	2.742843	1.380047
20	6	0	-0.820381	1.520136	-2.333146
21	1	0	0.097690	1.393253	-2.913331
22	1	0	-1.365477	0.569877	-2.278407
23	1	0	-1.447012	2.253099	-2.854215

24	17	0	2.542404	2.576834	-3.161314
25	1	0	1.307063	3.743565	-3.127002
26	17	0	0.163713	4.693538	-2.991605
27	14	0	4.554585	-0.113030	-0.311010
28	6	0	5.547291	-1.215142	0.870448
29	1	0	6.577597	-1.322784	0.507255
30	1	0	5.603732	-0.798953	1.884247
31	1	0	5.116208	-2.221240	0.944932
32	6	0	4.479844	-0.878744	-2.030035
33	1	0	3.916704	-0.244061	-2.724343
34	1	0	5.497522	-0.979210	-2.429597
35	1	0	4.028522	-1.878774	-2.028468
36	6	0	5.278242	1.627175	-0.371051
37	1	0	5.280582	2.110943	0.614042
38	1	0	6.317044	1.594157	-0.724988
39	1	0	4.707851	2.255629	-1.065605

		1			2			3		
		A			A			A		
Frequencies --		-117.5682			28.3323			37.6011		
Red. masses --		9.7767			4.4081			3.8525		
Frc consts --		0.0796			0.0021			0.0032		
IR Inten --		20.9854			0.1466			2.3863		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	-0.14	0.08	-0.02	-0.03	-0.06	0.01	0.01	0.00
2	6	0.00	-0.06	0.04	-0.05	-0.08	-0.05	0.02	0.03	0.00
3	6	0.01	-0.02	0.03	-0.06	-0.11	-0.01	0.02	0.04	-0.01
4	6	0.01	-0.01	0.03	-0.05	-0.09	0.01	0.02	0.02	-0.01
5	6	-0.01	-0.02	0.03	-0.02	-0.02	0.00	0.02	-0.01	0.00
6	1	0.01	-0.05	0.05	-0.06	-0.11	-0.06	0.02	0.04	0.00
7	1	0.01	0.02	0.02	-0.09	-0.16	0.00	0.02	0.06	-0.02
8	1	0.01	0.02	0.02	-0.06	-0.12	0.04	0.02	0.03	-0.02
9	15	-0.02	-0.06	0.06	0.00	0.02	-0.05	0.01	-0.02	0.01
10	1	-0.02	0.00	0.05	-0.01	-0.01	-0.10	0.01	0.00	0.01
11	14	0.02	0.26	-0.21	0.03	0.02	0.02	-0.01	-0.02	-0.01
12	6	0.12	-0.01	0.02	0.08	-0.05	0.00	-0.06	0.02	0.02
13	1	0.06	-0.24	-0.01	0.12	-0.10	-0.02	-0.09	0.05	0.03
14	1	0.13	0.02	0.04	0.05	-0.05	-0.04	-0.03	0.03	0.05
15	1	0.21	0.03	0.20	0.11	-0.03	0.06	-0.08	0.01	-0.02
16	6	0.05	0.15	-0.14	0.07	0.06	0.07	-0.05	-0.07	-0.06
17	1	-0.02	0.15	-0.08	0.08	0.08	0.09	-0.06	-0.08	-0.06
18	1	0.09	0.12	-0.15	0.04	0.09	0.09	-0.03	-0.09	-0.09
19	1	0.09	0.11	-0.14	0.11	0.05	0.07	-0.09	-0.08	-0.05
20	6	0.04	-0.08	-0.07	-0.05	0.06	0.02	0.06	-0.01	-0.03
21	1	0.02	-0.10	-0.09	-0.08	0.02	-0.01	0.08	0.02	0.00
22	1	0.14	-0.13	0.12	-0.11	0.09	0.02	0.08	-0.02	-0.06
23	1	-0.06	-0.22	-0.16	-0.03	0.10	0.04	0.06	-0.02	-0.04
24	17	-0.01	0.15	-0.12	-0.07	-0.10	-0.09	0.02	0.13	0.04
25	1	0.29	-0.35	0.04	0.01	-0.02	-0.01	-0.02	0.10	0.03
26	17	-0.07	-0.21	0.20	0.07	0.04	0.07	-0.05	0.06	0.01
27	14	-0.02	-0.01	0.02	0.00	0.04	0.02	0.01	-0.07	0.00
28	6	0.01	0.00	0.00	0.07	0.21	0.11	0.03	0.07	0.10
29	1	0.01	0.00	-0.01	0.08	0.24	0.12	0.02	0.02	0.09
30	1	0.01	-0.01	0.00	0.05	0.29	0.08	0.07	0.20	0.05
31	1	0.01	-0.01	0.00	0.14	0.18	0.20	0.03	0.08	0.25
32	6	-0.01	0.00	0.01	0.06	-0.10	0.08	-0.02	-0.26	0.08
33	1	-0.03	-0.03	0.01	0.04	-0.18	0.02	-0.02	-0.34	0.02
34	1	-0.01	0.02	0.01	0.07	-0.08	0.10	-0.03	-0.32	0.08
35	1	0.01	-0.01	0.02	0.11	-0.12	0.16	-0.03	-0.26	0.20
36	6	0.00	-0.01	0.02	-0.12	0.09	-0.11	0.01	-0.07	-0.21
37	1	0.01	-0.02	0.02	-0.17	0.17	-0.14	0.04	0.03	-0.26
38	1	-0.01	-0.01	0.01	-0.11	0.13	-0.08	0.00	-0.12	-0.24
39	1	0.00	0.01	0.03	-0.15	-0.01	-0.17	-0.01	-0.14	-0.26

Total free energy in solution:
with all non electrostatic terms (a.u.) = -2274.064392

III.20. Cartesian coordinates, three lower frequencies and PCM energy for III-Eb

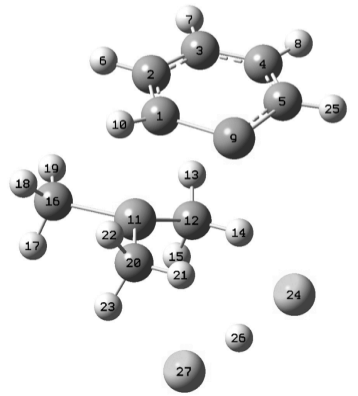


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.007646	-0.012299	-0.006947
2	6	0	-0.000710	-0.049880	1.494026
3	6	0	1.107194	-0.055840	2.265867
4	6	0	2.458306	0.033835	1.738269
5	6	0	2.766653	0.370599	0.463448
6	1	0	-0.968606	-0.111329	1.991800
7	1	0	0.999576	-0.131072	3.345649
8	1	0	3.270972	-0.146824	2.442149
9	15	0	1.539013	0.663173	-0.841400
10	1	0	0.058578	-1.060863	-0.365222
11	14	0	-1.677331	0.580053	-0.765581
12	6	0	-2.277464	2.171237	0.055526
13	1	0	-2.405906	2.049127	1.138102
14	1	0	-1.577221	2.996745	-0.107330
15	1	0	-3.250876	2.463033	-0.360396
16	6	0	-2.919989	-0.811437	-0.421950
17	1	0	-3.915684	-0.535317	-0.792744
18	1	0	-2.630285	-1.744524	-0.922091
19	1	0	-3.021472	-1.026640	0.649314
20	6	0	-1.493442	0.804864	-2.633008
21	1	0	-0.827316	1.638503	-2.882352
22	1	0	-1.096013	-0.096799	-3.115466
23	1	0	-2.472365	1.015794	-3.083291
24	17	0	1.339232	2.812154	-0.637445
25	1	0	3.809457	0.479201	0.170974

		1			2			3		
		A			A			A		
Frequencies --		38.5999			62.9284			95.3908		
Red. masses --		3.9300			3.7014			6.6582		
Frc consts --		0.0034			0.0086			0.0357		
IR Inten --		0.4350			0.0371			0.9970		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	-0.04	0.02	-0.03	0.07	0.06	0.01	-0.08	0.05
2	6	-0.01	-0.01	0.02	0.01	0.23	0.06	0.09	0.01	0.05
3	6	-0.03	0.06	0.04	0.05	0.17	0.01	0.12	0.11	0.01
4	6	-0.02	0.10	0.07	0.03	-0.05	-0.07	0.10	0.08	-0.06
5	6	0.00	0.04	0.06	0.00	-0.15	-0.10	0.04	-0.03	-0.10
6	1	-0.02	-0.04	0.01	0.03	0.41	0.11	0.11	-0.02	0.10
7	1	-0.04	0.08	0.04	0.10	0.30	0.02	0.17	0.18	0.02
8	1	-0.03	0.17	0.09	0.05	-0.13	-0.11	0.13	0.13	-0.08
9	15	0.02	-0.08	0.01	-0.05	-0.01	-0.03	-0.05	-0.08	-0.03
10	1	-0.03	-0.04	0.04	-0.01	0.03	0.17	-0.07	-0.09	0.09
11	14	0.01	0.02	0.03	-0.03	-0.02	-0.01	0.07	0.05	0.00
12	6	-0.01	-0.08	0.20	-0.14	-0.06	0.00	0.09	0.08	-0.06
13	1	-0.09	-0.22	0.18	-0.31	-0.12	-0.03	0.13	0.13	-0.05
14	1	0.01	-0.07	0.35	-0.10	-0.07	0.15	0.06	0.09	-0.12
15	1	0.02	0.00	0.17	-0.07	-0.02	-0.13	0.06	0.03	-0.03
16	6	0.03	-0.04	-0.17	0.04	-0.11	-0.10	-0.08	0.16	-0.09
17	1	0.02	0.01	-0.09	0.02	-0.14	-0.06	-0.02	0.25	-0.19
18	1	0.02	0.05	-0.33	0.09	-0.05	-0.18	-0.12	0.12	-0.04
19	1	0.07	-0.22	-0.20	0.07	-0.21	-0.12	-0.20	0.20	-0.09
20	6	0.03	0.24	0.06	0.03	0.04	0.01	0.24	0.00	0.00
21	1	0.03	0.27	0.16	-0.03	0.09	0.06	0.29	-0.03	0.04
22	1	0.04	0.30	-0.04	0.11	0.08	0.00	0.24	-0.02	0.06
23	1	0.03	0.28	0.08	0.03	-0.02	-0.02	0.28	0.03	-0.08
24	17	-0.02	-0.06	-0.15	0.08	-0.02	0.08	-0.26	-0.11	0.11
25	1	0.00	0.07	0.07	0.00	-0.30	-0.17	0.03	-0.07	-0.17

Total free energy in solution:
with all non electrostatic terms (a.u.) = -1404.517880

III.21. Cartesian coordinates, three lower frequencies and PCM energy for IIIEbTSIIIGb



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.149446	-1.012558	0.029859
2	6	0	-0.383529	-1.125815	1.420749
3	6	0	0.365284	-0.447256	2.373852
4	6	0	1.451262	0.377864	2.028307
5	6	0	1.892820	0.580845	0.724327
6	1	0	-1.191648	-1.772068	1.759641
7	1	0	0.114670	-0.566817	3.424343
8	1	0	1.982542	0.879385	2.835877
9	15	0	1.199566	-0.130638	-0.711603
10	1	0	-0.658431	-1.733183	-0.612317
11	14	0	-1.929186	0.578909	-0.661924
12	6	0	-1.529712	2.023790	0.439725
13	1	0	-1.331808	1.671897	1.458044

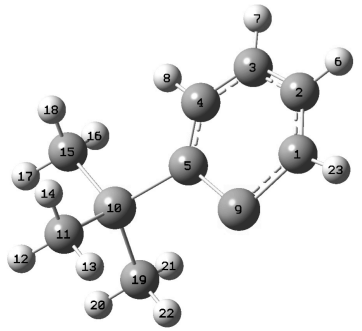
14	1	0	-0.686568	2.608768	0.065642
15	1	0	-2.409045	2.677480	0.457587
16	6	0	-3.416909	-0.391545	-0.051553
17	1	0	-4.311435	0.124390	-0.430780
18	1	0	-3.447641	-1.415129	-0.441153
19	1	0	-3.493005	-0.418599	1.040069
20	6	0	-1.665698	0.312597	-2.491845
21	1	0	-0.821675	0.889152	-2.878023
22	1	0	-1.525325	-0.754335	-2.705442
23	1	0	-2.569523	0.655516	-3.008089
24	17	0	0.511461	3.134524	-2.212103
25	1	0	2.746265	1.237423	0.567571
26	1	0	-1.131099	3.391636	-2.316256
27	17	0	-2.646040	3.493506	-2.334097

	1	2	3
	A	A	A
Frequencies --	-173.6425	33.9779	49.6457
Red. masses --	7.2338	6.1587	10.9568
Frc consts --	0.1285	0.0042	0.0159
IR Inten --	70.1854	4.2870	27.2260

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.10	-0.14	0.06	-0.05	-0.02	0.08	0.05	0.12	-0.15
2	6	0.04	-0.06	0.03	0.04	0.12	0.11	0.03	0.00	-0.16
3	6	0.02	-0.01	0.03	0.11	0.19	-0.01	-0.03	-0.03	-0.10
4	6	0.01	0.00	0.03	0.10	0.16	-0.15	-0.08	0.07	-0.01
5	6	0.01	-0.03	0.02	0.01	0.03	-0.20	-0.07	0.21	0.01
6	1	0.04	-0.05	0.04	0.05	0.16	0.22	0.07	-0.08	-0.23
7	1	-0.01	0.03	0.02	0.18	0.29	0.02	-0.04	-0.13	-0.11
8	1	-0.01	0.03	0.02	0.15	0.23	-0.23	-0.12	0.04	0.03
9	15	0.02	-0.09	0.04	-0.09	-0.10	-0.08	0.01	0.27	-0.06
10	1	-0.01	-0.04	0.04	-0.11	-0.06	0.18	0.11	0.14	-0.21
11	14	-0.16	0.23	-0.13	-0.06	-0.02	-0.03	-0.09	0.08	-0.03
12	6	0.06	0.02	0.05	-0.13	-0.05	0.03	-0.06	0.00	0.07
13	1	0.12	-0.15	-0.02	-0.20	-0.08	0.03	0.04	-0.11	0.01
14	1	0.06	0.03	0.08	-0.09	-0.05	0.10	-0.11	0.08	0.08
15	1	0.10	0.07	0.20	-0.12	-0.04	-0.02	-0.09	-0.05	0.22
16	6	-0.05	0.11	-0.07	-0.06	-0.07	-0.11	-0.06	0.07	0.02
17	1	-0.12	0.03	-0.03	-0.06	-0.06	-0.09	-0.09	0.05	0.04
18	1	0.03	0.11	-0.07	-0.04	-0.05	-0.18	-0.06	0.06	0.03
19	1	0.01	0.11	-0.06	-0.07	-0.15	-0.11	-0.03	0.07	0.02
20	6	0.06	-0.04	-0.05	0.02	0.00	-0.02	-0.14	-0.04	-0.03
21	1	0.07	-0.07	-0.06	-0.01	0.05	0.00	-0.14	-0.08	-0.10
22	1	0.12	-0.06	0.11	0.11	0.00	-0.01	-0.14	-0.06	0.06
23	1	0.10	-0.13	-0.16	0.01	-0.08	-0.05	-0.15	-0.09	-0.04
24	17	-0.07	0.13	-0.08	0.06	0.01	0.21	0.09	-0.29	0.06
25	1	-0.01	-0.01	0.01	0.00	0.02	-0.32	-0.11	0.27	0.08
26	1	0.68	-0.13	0.06	0.08	-0.01	0.10	0.13	-0.21	0.10
27	17	0.05	-0.18	0.10	0.07	-0.04	0.00	0.12	-0.15	0.14

Total free energy in solution:
with all non electrostatic terms (a.u.) = -1865.334327

III.22. Cartesian coordinates, three lower frequencies and PCM energy for IIIG



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.806767	-0.863555	0.000045
2	6	0	3.220024	0.468130	0.000041
3	6	0	2.321143	1.538638	-0.000017
4	6	0	0.930581	1.369627	-0.000087
5	6	0	0.269338	0.132244	-0.000116
6	1	0	4.286811	0.689108	0.000084
7	1	0	2.717453	2.551643	-0.000007
8	1	0	0.331612	2.280374	-0.000121
9	15	0	1.144715	-1.394323	-0.000070
10	14	0	-1.635910	0.049271	0.000009
11	6	0	-2.223410	-0.870830	1.547600
12	1	0	-3.318997	-0.939100	1.570761
13	1	0	-1.824697	-1.892122	1.580946
14	1	0	-1.899999	-0.359156	2.462637
15	6	0	-2.355117	1.803048	-0.000947
16	1	0	-2.055462	2.374027	-0.888653
17	1	0	-3.451709	1.752321	-0.000611
18	1	0	-2.055005	2.375254	0.885815
19	6	0	-2.223586	-0.872564	-1.546475
20	1	0	-3.319212	-0.940169	-1.569784
21	1	0	-1.899652	-0.362337	-2.462133
22	1	0	-1.825520	-1.894154	-1.578355
23	1	0	3.571939	-1.639068	0.000075

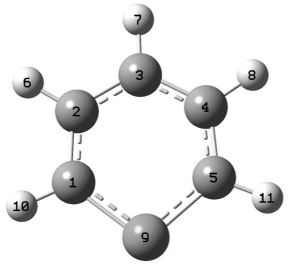
	1	2	3
	A	A	A
Frequencies --	13.3374	89.3009	119.9080
Red. masses --	4.1152	3.2692	3.4579
Frc consts --	0.0004	0.0154	0.0293
IR Inten --	0.3504	0.2338	0.1222

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	0.00	-0.09	0.00	0.00	0.16	0.08	0.08	0.00
2	6	0.00	0.00	0.08	0.00	0.00	0.20	-0.01	0.11	0.00
3	6	0.00	0.00	0.20	0.00	0.00	0.03	-0.10	0.04	0.00
4	6	0.00	0.00	0.16	0.00	0.00	-0.14	-0.08	-0.08	0.00
5	6	0.00	0.00	0.00	0.00	0.00	-0.16	0.00	-0.12	0.00
6	1	0.00	0.00	0.12	0.00	0.00	0.36	-0.03	0.19	0.00
7	1	0.00	0.00	0.33	0.00	0.00	0.05	-0.18	0.07	0.00
8	1	0.00	0.00	0.26	0.00	0.00	-0.23	-0.14	-0.12	0.00
9	15	0.00	0.00	-0.18	0.00	0.00	-0.05	0.12	-0.06	0.00
10	14	0.00	0.00	0.01	0.00	0.00	-0.05	-0.01	-0.04	0.00
11	6	0.01	0.17	0.11	0.20	-0.01	0.02	-0.17	0.05	-0.01
12	1	0.01	0.16	0.13	0.20	0.02	0.20	-0.18	0.22	-0.04
13	1	0.01	0.17	0.21	0.19	-0.01	-0.05	-0.33	-0.02	0.00

14	1	0.02	0.26	0.05	0.36	-0.02	-0.02	-0.11	-0.01	0.00
15	6	0.00	0.00	-0.18	0.00	0.00	0.05	0.21	0.06	0.00
16	1	0.03	-0.09	-0.23	-0.10	0.01	0.02	0.29	0.02	0.00
17	1	0.00	0.00	-0.21	0.00	0.00	0.17	0.21	0.21	0.00
18	1	-0.03	0.09	-0.23	0.10	-0.01	0.02	0.29	0.02	0.00
19	6	-0.01	-0.17	0.11	-0.20	0.01	0.02	-0.17	0.05	0.01
20	1	-0.01	-0.16	0.13	-0.20	-0.02	0.20	-0.18	0.22	0.04
21	1	-0.02	-0.26	0.05	-0.36	0.02	-0.02	-0.11	-0.01	0.00
22	1	-0.01	-0.17	0.22	-0.19	0.01	-0.05	-0.33	-0.02	0.00
23	1	0.00	0.00	-0.18	0.00	0.00	0.27	0.14	0.13	0.00

Total free energy in solution:
with all non electrostatic terms (a.u.) = -943.685793

III.23. Cartesian coordinates, three lower frequencies and PCM energy for IIIGb



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.130831	0.000078	0.019621
2	6	0	-0.019742	-0.000319	1.409809
3	6	0	1.208363	0.000152	2.080781
4	6	0	2.436278	0.001074	1.409502
5	6	0	2.547003	0.001610	0.019263
6	1	0	-0.930929	-0.001035	2.006907
7	1	0	1.208501	-0.000208	3.168100
8	1	0	3.347624	0.001387	2.006356
9	15	0	1.208016	0.001226	-1.103831
10	1	0	-1.131143	-0.000362	-0.411098
11	1	0	3.547225	0.002334	-0.411673

	1	2	3
	A	A	A
Frequencies --	300.7725	355.4157	467.7882
Red. masses --	4.0775	2.9322	9.7767
Frc consts --	0.2173	0.2182	1.2605
IR Inten --	0.3089	0.0000	4.4953

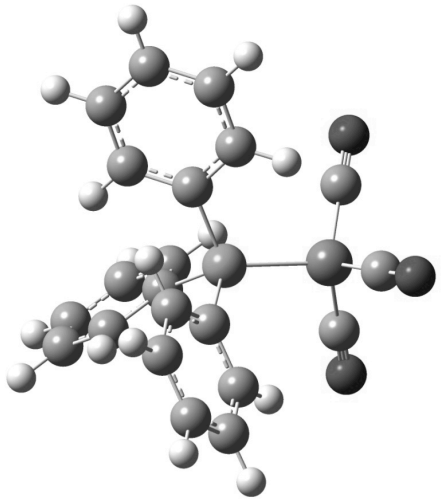
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	0.25	0.00	0.00	0.20	0.00	0.28	0.00	0.08
2	6	0.00	0.07	0.00	0.00	-0.21	0.00	0.16	0.00	0.15
3	6	0.00	-0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.41
4	6	0.00	0.07	0.00	0.00	0.21	0.00	-0.16	0.00	0.15
5	6	0.00	0.25	0.00	0.00	-0.20	0.00	-0.28	0.00	0.08
6	1	0.00	0.13	0.00	0.00	-0.50	0.00	0.01	0.00	-0.08
7	1	0.00	-0.60	0.00	0.00	0.00	0.00	0.00	0.00	0.41
8	1	0.00	0.13	0.00	0.00	0.50	0.00	-0.01	0.00	-0.08
9	15	0.00	-0.17	0.00	0.00	0.00	0.00	0.00	0.00	-0.37
10	1	0.00	0.43	0.00	0.00	0.40	0.00	0.18	0.00	0.31

11	1	0.00	0.43	0.00	0.00	-0.40	0.00	-0.18	0.00	0.31

Total free energy in solution:
with all non electrostatic terms (a.u.) = -534.956484

IV. OPTIMIZED STRUCTURES OF PART IV

IV.1. Cartesian coordinates, three lower frequencies, thermochemistry and CDA calculations for IV-A



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-.078934	-.050429	.047745
2	6	0	-.093004	-.048710	1.888449
3	6	0	1.138604	-.089286	2.557702
4	6	0	-1.273812	-.010577	2.641496
5	6	0	1.188168	-.104966	3.949420
6	1	0	2.061712	-.100075	1.983591
7	6	0	-1.221135	-.016455	4.035159
8	1	0	-2.236888	.030925	2.140523
9	6	0	.007623	-.066231	4.691279
10	1	0	2.150312	-.136795	4.454137
11	1	0	-2.144565	.020108	4.607734
12	1	0	.046003	-.068157	5.777623
13	6	0	-1.777409	.502409	-.394398
14	6	0	-2.832868	-.389805	-.623898
15	6	0	-2.016784	1.880140	-.498800
16	6	0	-4.102227	.089056	-.947765
17	1	0	-2.662804	-1.460633	-.555768
18	6	0	-3.287363	2.355939	-.812642

19	1	0	-1.200689	2.580758	-.340718
20	6	0	-4.332594	1.460597	-1.040049
21	1	0	-4.911465	-.613778	-1.129588
22	1	0	-3.458142	3.426625	-.889738
23	1	0	-5.322153	1.831283	-1.294962
24	6	0	-.087986	-1.839728	-.383919
25	6	0	.144095	-2.195277	-1.721049
26	6	0	-.307438	-2.851155	.559020
27	6	0	.143718	-3.532632	-2.107753
28	1	0	.332433	-1.420055	-2.459749
29	6	0	-.295792	-4.191235	.170863
30	1	0	-.482828	-2.593639	1.599385
31	6	0	-.073053	-4.534478	-1.161116
32	1	0	.323776	-3.792768	-3.147660
33	1	0	-.461006	-4.967110	.914254
34	1	0	-.062495	-5.579248	-1.461014
35	6	0	1.068755	1.526177	-2.567918
36	6	0	1.821787	2.611442	.093536
37	6	0	3.040249	.079226	-.885156
38	8	0	.749427	1.782503	-3.643691
39	8	0	1.981455	3.565020	.718095
40	8	0	3.978187	-.587745	-.885501
41	28	0	1.586824	1.132646	-.895722

	1	2	3
	A	A	A
Frequencies --	17.0483	18.7998	26.8268
Red. masses --	6.6078	5.3275	4.1505
Frc consts --	.0011	.0011	.0018
IR Inten --	.0564	.0894	.1331

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	15	.00	.00	.02	.00	-.01	-.01	.00	-.01	.02
2	6	.00	.01	.03	.00	.00	.02	.02	.00	.02
3	6	.04	.01	-.02	-.03	-.03	.10	-.04	-.04	.14
4	6	-.04	.00	.09	.04	.03	-.04	.10	.04	-.10
5	6	.03	.01	-.01	-.03	-.02	.13	-.02	-.03	.15
6	1	.07	.02	-.07	-.06	-.05	.14	-.10	-.07	.24
7	6	-.04	.00	.11	.04	.03	-.01	.12	.05	-.09
8	1	-.07	-.01	.14	.07	.05	-.10	.15	.06	-.19
9	6	-.01	.01	.05	.01	.01	.07	.06	.01	.03
10	1	.06	.02	-.05	-.06	-.04	.19	-.07	-.06	.25
11	1	-.08	-.01	.16	.08	.05	-.05	.18	.08	-.18
12	1	-.01	.00	.06	.01	.01	.09	.07	.02	.04
13	6	.01	.03	-.01	-.01	.00	-.01	-.01	-.01	.02
14	6	.11	-.10	.00	-.12	.15	-.05	-.01	-.01	.02
15	6	-.07	.19	-.05	.09	-.15	.03	-.01	-.01	.01
16	6	.12	-.08	-.03	-.14	.16	-.05	-.01	-.01	.02
17	1	.16	-.23	.02	-.19	.27	-.08	-.01	-.01	.02
18	6	-.05	.22	-.07	.07	-.14	.03	-.01	-.01	.02
19	1	-.14	.30	-.06	.17	-.27	.06	-.01	-.01	.01
20	6	.04	.08	-.07	-.04	.02	-.01	-.01	-.01	.02
21	1	.20	-.19	-.03	-.23	.28	-.08	-.01	-.01	.02
22	1	-.11	.35	-.10	.15	-.26	.07	-.01	-.01	.02
23	1	.05	.10	-.09	-.06	.02	.00	-.01	-.01	.02
24	6	-.01	-.02	.00	.01	-.03	-.02	-.01	.00	.02
25	6	.02	.01	.02	-.02	-.07	-.07	.08	.10	.12
26	6	-.05	-.05	-.03	.05	-.01	.03	-.13	-.09	-.10
27	6	.00	-.01	.01	-.02	-.09	-.08	.06	.10	.11
28	1	.05	.04	.05	-.05	-.09	-.10	.17	.18	.21
29	6	-.06	-.07	-.04	.05	-.03	.02	-.16	-.09	-.11
30	1	-.07	-.07	-.04	.08	.03	.07	-.20	-.17	-.18
31	6	-.03	-.04	-.02	.02	-.07	-.03	-.07	.01	-.01
32	1	.03	.01	.03	-.05	-.13	-.12	.13	.18	.19
33	1	-.09	-.10	-.06	.08	-.01	.05	-.26	-.16	-.21
34	1	-.04	-.06	-.03	.02	-.09	-.04	-.09	.01	-.02
35	6	-.03	-.05	.13	.03	.00	.10	.02	.00	-.04

36	6	.00	-.13	-.10	-.01	-.04	-.07	-.05	.00	-.03
37	6	.03	.12	-.04	-.02	.12	-.04	.04	.00	-.03
38	8	-.05	-.08	.20	.05	-.01	.18	.03	.01	-.05
39	8	.00	-.21	-.18	-.02	-.08	-.11	-.09	.01	-.03
40	8	.04	.20	-.07	-.03	.20	-.05	.08	.02	-.05
41	28	.00	-.01	.01	.00	.01	-.01	.00	-.01	-.02

HF=-1546.8856093

Sum of electronic and zero-point Energies= -1546.585086
Sum of electronic and thermal Energies= -1546.559657
Sum of electronic and thermal Enthalpies= -1546.558713
Sum of electronic and thermal Free Energies= -1546.645668

Electron donation between fragments (<0.001e for any omitted MO)

Alpha-spin MO	1->2	2->1
HOMO -69 (# 30)	0.000	-0.004
HOMO -66 (# 33)	-0.001	-0.002
HOMO -62 (# 37)	-0.011	0.000
HOMO -59 (# 40)	0.014	0.000
HOMO -58 (# 41)	0.002	0.000
HOMO -57 (# 42)	0.002	0.000
HOMO -53 (# 46)	0.023	-0.001
HOMO -52 (# 47)	0.001	0.000
HOMO -51 (# 48)	0.002	0.000
HOMO -47 (# 52)	0.008	-0.006
HOMO -46 (# 53)	0.006	-0.001
HOMO -45 (# 54)	0.000	0.002
HOMO -44 (# 55)	0.000	0.002
HOMO -43 (# 56)	0.004	0.000
HOMO -42 (# 57)	0.004	0.000
HOMO -41 (# 58)	0.009	0.000
HOMO -40 (# 59)	0.003	-0.001
HOMO -37 (# 62)	-0.008	-0.013
HOMO -34 (# 65)	0.006	0.001
HOMO -31 (# 68)	-0.008	-0.003
HOMO -30 (# 69)	0.001	-0.001
HOMO -29 (# 70)	0.001	-0.001
HOMO -27 (# 72)	0.004	-0.003
HOMO -26 (# 73)	0.004	-0.003
HOMO -25 (# 74)	0.002	0.000
HOMO -24 (# 75)	-0.001	-0.003
HOMO -23 (# 76)	-0.001	-0.003
HOMO -20 (# 79)	0.021	0.003
HOMO -19 (# 80)	0.004	0.000
HOMO -18 (# 81)	0.004	0.000
HOMO -17 (# 82)	0.006	0.000
HOMO -16 (# 83)	0.004	0.000
HOMO -15 (# 84)	0.001	0.000
HOMO -14 (# 85)	0.001	0.000
HOMO -13 (# 86)	0.001	0.001
HOMO -12 (# 87)	0.002	0.001
HOMO -11 (# 88)	0.080	0.012
HOMO -10 (# 89)	-0.001	0.008
HOMO -9 (# 90)	0.000	0.008
HOMO -8 (# 91)	0.003	-0.001
HOMO -7 (# 92)	0.003	-0.001
HOMO -6 (# 93)	0.001	0.000
HOMO -5 (# 94)	-0.006	-0.002
HOMO -4 (# 95)	0.002	0.000
HOMO -3 (# 96)	0.002	0.000

```
HOMO  -2 (# 97) -0.002  0.022
HOMO  -1 (# 98) -0.002  0.022
HOMO   0 (# 99)  0.130  0.007
------------------------------
Total over OMOs  0.321  0.036
==============================
TotalALPHA+BETA  0.643  0.073
```

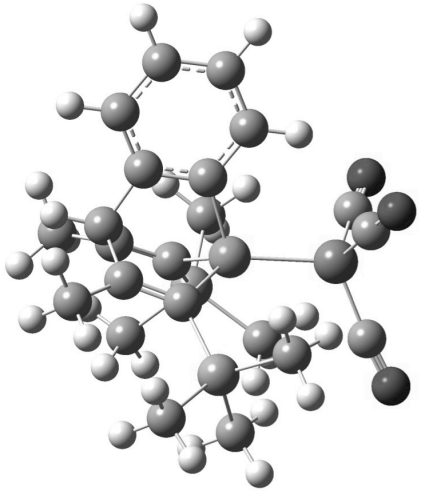
Repulsion and residue (Delta) terms between fragments

```
Alpha-spin MO    1<->2  Delta
HOMO -69 (# 30) -0.002  0.000
HOMO -66 (# 33) -0.002  0.000
HOMO -62 (# 37)  0.000  0.000
HOMO -59 (# 40)  0.002  0.000
HOMO -58 (# 41)  0.000  0.000
HOMO -57 (# 42)  0.000  0.000
HOMO -53 (# 46)  0.006 -0.001
HOMO -52 (# 47)  0.001  0.000
HOMO -51 (# 48)  0.001  0.000
HOMO -47 (# 52)  0.022  0.000
HOMO -46 (# 53) -0.013  0.000
HOMO -45 (# 54)  0.001  0.000
HOMO -44 (# 55)  0.001  0.000
HOMO -43 (# 56)  0.002  0.000
HOMO -42 (# 57)  0.002  0.000
HOMO -41 (# 58)  0.002  0.000
HOMO -40 (# 59)  0.039  0.000
HOMO -37 (# 62) -0.021 -0.001
HOMO -34 (# 65) -0.004  0.000
HOMO -31 (# 68) -0.009 -0.001
HOMO -30 (# 69)  0.004  0.000
HOMO -29 (# 70)  0.004  0.000
HOMO -27 (# 72)  0.005  0.000
HOMO -26 (# 73)  0.004  0.000
HOMO -25 (# 74) -0.007  0.000
HOMO -24 (# 75) -0.004  0.000
HOMO -23 (# 76) -0.006  0.000
HOMO -20 (# 79)  0.001 -0.002
HOMO -19 (# 80)  0.000  0.000
HOMO -18 (# 81)  0.000  0.000
HOMO -17 (# 82)  0.001  0.000
HOMO -16 (# 83)  0.002  0.000
HOMO -15 (# 84)  0.000  0.000
HOMO -14 (# 85)  0.000  0.000
HOMO -13 (# 86)  0.007  0.000
HOMO -12 (# 87)  0.006  0.000
HOMO -11 (# 88)  0.018 -0.009
HOMO -10 (# 89) -0.005  0.000
HOMO  -9 (# 90) -0.005  0.000
HOMO  -8 (# 91) -0.002 -0.001
HOMO  -7 (# 92) -0.001 -0.001
HOMO  -6 (# 93) -0.001 -0.001
HOMO  -5 (# 94) -0.016  0.000
HOMO  -4 (# 95)  0.001  0.000
HOMO  -3 (# 96)  0.000  0.000
HOMO  -2 (# 97) -0.035  0.001
HOMO  -1 (# 98) -0.035  0.001
HOMO   0 (# 99) -0.108 -0.007
------------------------------
```



```
Total over OMOs -0.142 -0.026
```

IV.2. Cartesian coordinates, three lower frequencies, thermochemistry and CDA calculations for IV-B



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	.711185	.258254	2.991561
2	6	0	3.037995	1.693896	2.394182
3	6	0	1.558012	.684792	4.019145
4	1	0	-.186290	-.305417	3.225226
5	6	0	2.713917	1.402141	3.722059
6	1	0	3.944156	2.248430	2.158729
7	1	0	1.310395	.453127	5.051764
8	1	0	3.370078	1.733974	4.522777
9	6	0	1.457521	-.683190	-.783809
10	6	0	.039512	1.751955	-.656452
11	6	0	2.540925	.123734	-.777544
12	6	0	1.275060	2.295115	-.680426
13	6	0	2.445776	1.494657	-.099026
14	1	0	3.380606	2.046710	-.239596
15	14	0	1.395399	-2.378531	-1.652047
16	14	0	-1.551826	2.379570	-1.483259
17	6	0	2.193576	1.265521	1.375204
18	6	0	1.026920	.554364	1.668761
19	15	0	.039582	.070484	.182220
20	6	0	2.168690	-3.694018	-.534970
21	1	0	3.204811	-3.447492	-.275000
22	1	0	1.609040	-3.803466	.400501
23	1	0	2.172696	-4.669757	-1.036885
24	6	0	2.316900	-2.333113	-3.315585
25	1	0	1.926417	-3.140125	-3.948630
26	1	0	2.146799	-1.390111	-3.847998
27	1	0	3.398452	-2.483791	-3.236682

28	6	0	-.366714	-2.881539	-2.091445
29	1	0	-1.001000	-3.018273	-1.213092
30	1	0	-.849324	-2.145497	-2.744567
31	1	0	-.333609	-3.833836	-2.636394
32	6	0	-1.422046	4.069612	-2.333866
33	1	0	-.672376	4.102431	-3.131780
34	1	0	-2.396950	4.263132	-2.801372
35	1	0	-1.233233	4.895846	-1.639270
36	6	0	-2.952560	2.540328	-.229896
37	1	0	-3.221024	1.579619	.216477
38	1	0	-2.679218	3.224442	.582249
39	1	0	-3.846031	2.945315	-.721798
40	6	0	-1.990029	1.150903	-2.852700
41	1	0	-2.950987	1.416235	-3.310865
42	1	0	-1.227872	1.169442	-3.641249
43	1	0	-2.071501	.122556	-2.490134
44	6	0	3.908951	-.183630	-1.315040
45	1	0	4.009185	-1.206330	-1.677119
46	1	0	4.174618	.499997	-2.133244
47	1	0	4.654368	-.031967	-.522319
48	6	0	1.689918	3.640717	-1.201814
49	1	0	.857039	4.248862	-1.547036
50	1	0	2.212681	4.195433	-.410310
51	1	0	2.405087	3.528863	-2.029002
52	28	0	-1.813591	-1.075185	.859244
53	6	0	-1.195867	-2.618620	1.532408
54	6	0	-2.592807	-.121028	2.170212
55	6	0	-3.035110	-1.375645	-.423420
56	8	0	-.841947	-3.614221	1.990903
57	8	0	-3.143946	.424273	3.021079
58	8	0	-3.877680	-1.607078	-1.172791

		1			2			3	
		A			A			A	
Frequencies --		3.1717			33.1211			37.4948	
Red. masses --		3.0205			4.7557			5.1727	
Frc consts --		.0000			.0031			.0043	
IR Inten --		.0106			.0289			.0063	
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	.03	-.03	-.01	-.04	.12	.00	.01	-.02	-.03
2	6	.01	.01	-.02	-.02	.08	-.03	.03	-.05	-.04
3	6	.04	-.03	-.02	-.06	.17	.00	.03	-.05	-.03
4	1	.04	-.05	-.01	-.05	.14	.02	.01	-.01	-.03
5	6	.03	-.01	-.02	-.04	.15	-.02	.04	-.06	-.04
6	1	.00	.02	-.02	-.01	.06	-.04	.03	-.05	-.04
7	1	.05	-.05	-.02	-.08	.23	.01	.04	-.05	-.03
8	1	.03	-.01	-.02	-.06	.19	-.02	.05	-.08	-.04
9	6	.02	.02	-.02	.00	-.03	.03	-.02	.00	-.04
10	6	-.01	.00	.00	.03	-.01	-.04	-.01	.02	.00
11	6	.00	.04	-.03	.01	-.05	.03	-.02	.00	-.05
12	6	-.02	.02	.00	.04	-.04	-.07	-.01	.01	-.01
13	6	-.01	.03	-.01	.02	-.03	-.02	-.01	-.01	-.03
14	1	-.02	.04	-.02	.03	-.04	-.03	-.01	-.01	-.04
15	14	.02	.00	.02	-.02	-.03	.02	.00	-.04	.04
16	14	-.02	-.01	.01	.01	.04	.03	-.03	.07	.06
17	6	.01	.01	-.02	.00	.03	-.02	.01	-.02	-.03
18	6	.02	-.01	-.01	-.01	.06	-.01	.01	-.02	-.03
19	15	.01	.00	-.01	.00	.01	.00	-.01	.00	-.02
20	6	-.14	.00	.13	-.09	-.07	.01	.02	.03	.11
21	1	-.15	-.05	.18	-.09	-.11	.04	.02	.06	.10
22	1	-.21	.06	.10	-.11	-.07	.00	.02	.08	.12
23	1	-.16	-.02	.16	-.11	-.06	-.01	.03	.00	.17
24	6	.18	-.13	.10	.03	-.03	.05	.01	-.12	.04
25	1	.07	-.03	.04	.01	.01	.01	.00	-.14	.07
26	1	.45	-.08	.11	.10	-.01	.07	.05	-.14	.00
27	1	.14	-.38	.22	.02	-.09	.08	.01	-.15	.06

28	6	.02	.10	-.11	-.03	.04	-.05	.02	-.09	.06
29	1	-.06	.21	-.15	-.05	.01	-.07	.03	-.12	.06
30	1	.13	.09	-.19	.01	.08	-.02	-.02	-.11	.06
31	1	-.01	.06	-.04	-.03	.06	-.09	.04	-.09	.06
32	6	-.04	-.01	.01	-.02	.08	.11	-.04	.13	.19
33	1	-.03	.00	.01	-.10	.10	.04	-.08	.18	.15
34	1	-.04	-.03	.00	-.06	.15	.23	-.07	.18	.25
35	1	-.06	-.01	.00	.09	.03	.15	.00	.07	.24
36	6	-.02	-.02	.01	.07	.00	.10	-.02	-.01	.08
37	1	-.02	-.02	.01	.09	-.01	.09	-.11	-.06	-.07
38	1	-.02	-.01	.01	.11	-.02	.10	.03	-.17	.20
39	1	-.02	-.02	.01	.04	.01	.16	.02	.15	.14
40	6	-.01	-.01	.01	-.06	.10	-.01	-.05	.15	.00
41	1	-.02	-.03	.02	-.06	.14	.03	-.05	.18	.01
42	1	-.02	.00	.00	-.08	.11	-.03	-.05	.17	.00
43	1	.01	-.02	.01	-.07	.09	-.04	-.06	.13	-.05
44	6	.00	.07	-.05	.02	-.09	.06	-.02	.01	-.07
45	1	.00	.09	-.11	.01	-.11	.11	-.03	.02	-.09
46	1	.00	.12	-.01	.04	-.14	.04	-.03	.03	-.06
47	1	.00	.02	-.04	.01	-.07	.07	-.01	-.01	-.07
48	6	-.04	.03	.02	.07	-.08	-.14	.00	.01	.00
49	1	-.05	.03	.04	.10	-.09	-.22	.00	.02	.02
50	1	-.04	.03	.02	.06	-.03	-.17	.02	-.01	.00
51	1	-.05	.05	.01	.10	-.15	-.11	-.01	.01	-.01
52	28	.01	-.01	-.01	.02	-.02	-.01	.00	.00	-.03
53	6	-.04	-.03	-.02	.04	-.03	-.06	.01	.05	.07
54	6	.04	.00	.01	-.02	-.12	.03	-.05	.04	-.08
55	6	-.02	.03	.01	.02	.01	-.02	.07	-.08	-.08
56	8	-.09	-.04	-.02	.06	-.04	-.08	.02	.09	.15
57	8	.06	.00	.02	-.06	-.20	.06	-.08	.06	-.12
58	8	-.04	.05	.02	.02	.04	-.03	.13	-.14	-.13

HF=-2172.357671

Sum of electronic and zero-point Energies= -2171.904992
Sum of electronic and thermal Energies= -2171.867604
Sum of electronic and thermal Enthalpies= -2171.866659
Sum of electronic and thermal Free Energies= -2171.976100

Electron donation between fragments (<0.001e for any omitted MO)

Alpha-spin MO	1->2	2->1
HOMO -94 (# 29)	0.002	0.000
HOMO -88 (# 35)	0.000	-0.006
HOMO -79 (# 44)	-0.001	-0.002
HOMO -75 (# 48)	-0.003	0.000
HOMO -74 (# 49)	0.002	0.000
HOMO -73 (# 50)	0.001	0.000
HOMO -72 (# 51)	0.009	0.000
HOMO -70 (# 53)	0.017	0.000
HOMO -69 (# 54)	0.008	0.000
HOMO -68 (# 55)	0.008	0.000
HOMO -67 (# 56)	0.003	0.000
HOMO -66 (# 57)	0.001	0.000
HOMO -65 (# 58)	0.004	0.000
HOMO -64 (# 59)	0.001	0.000
HOMO -63 (# 60)	0.006	0.000
HOMO -62 (# 61)	0.005	0.000
HOMO -61 (# 62)	0.007	0.000
HOMO -60 (# 63)	0.010	-0.001
HOMO -59 (# 64)	0.008	-0.001
HOMO -58 (# 65)	0.005	-0.003
HOMO -57 (# 66)	-0.001	0.003
HOMO -56 (# 67)	-0.002	0.002

```
 HOMO -55 (# 68)  0.002  0.000
 HOMO -54 (# 69)  0.002  0.000
 HOMO -53 (# 70)  0.001 -0.001
 HOMO -52 (# 71)  0.004 -0.001
 HOMO -51 (# 72)  0.002 -0.011
 HOMO -49 (# 74)  0.003  0.000
 HOMO -48 (# 75)  0.002 -0.001
 HOMO -47 (# 76)  0.000  0.003
 HOMO -45 (# 78)  0.000  0.001
 HOMO -44 (# 79)  0.001  0.002
 HOMO -43 (# 80) -0.001  0.001
 HOMO -42 (# 81)  0.002  0.001
 HOMO -40 (# 83)  0.004  0.001
 HOMO -39 (# 84)  0.001 -0.007
 HOMO -38 (# 85)  0.002 -0.003
 HOMO -36 (# 87)  0.002  0.000
 HOMO -35 (# 88)  0.003  0.000
 HOMO -34 (# 89)  0.003  0.001
 HOMO -33 (# 90)  0.002  0.000
 HOMO -32 (# 91)  0.001  0.000
 HOMO -31 (# 92)  0.002  0.000
 HOMO -30 (# 93)  0.005  0.001
 HOMO -29 (# 94)  0.005  0.000
 HOMO -28 (# 95)  0.003  0.000
 HOMO -27 (# 96)  0.008  0.000
 HOMO -26 (# 97)  0.001  0.000
 HOMO -25 (# 98)  0.002  0.000
 HOMO -24 (# 99)  0.003  0.000
 HOMO -21 (#102)  0.005  0.000
 HOMO -20 (#103)  0.003  0.000
 HOMO -18 (#105)  0.001  0.000
 HOMO -17 (#106)  0.011  0.001
 HOMO -15 (#108)  0.073  0.012
 HOMO -12 (#111)  0.005  0.000
 HOMO -11 (#112)  0.004  0.001
 HOMO -10 (#113)  0.004  0.000
 HOMO  -9 (#114)  0.003  0.001
 HOMO  -8 (#115) -0.003  0.006
 HOMO  -7 (#116) -0.004  0.004
 HOMO  -6 (#117)  0.001 -0.001
 HOMO  -4 (#119)  0.005  0.000
 HOMO  -3 (#120)  0.012  0.023
 HOMO  -2 (#121)  0.002  0.017
 HOMO  -1 (#122)  0.000  0.011
 HOMO   0 (#123)  0.124  0.012
 ----------------------------
 Total over OMOs  0.405  0.068
 ============================
 TotalALPHA+BETA  0.810  0.135
```

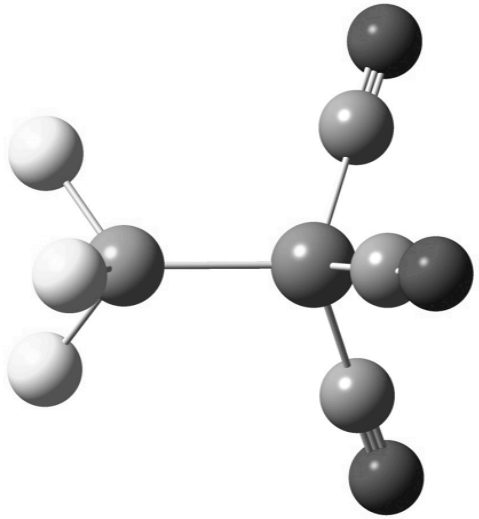
Repulsion and residue (Delta) terms between fragments

```
Alpha-spin MO    1<->2  Delta
 HOMO -94 (# 29)  0.000  0.000
 HOMO -88 (# 35) -0.002  0.000
 HOMO -79 (# 44) -0.003  0.000
 HOMO -75 (# 48)  0.000  0.000
 HOMO -74 (# 49)  0.000  0.000
 HOMO -73 (# 50)  0.000  0.000
 HOMO -72 (# 51)  0.002  0.000
 HOMO -70 (# 53)  0.002  0.000
```



```
 HOMO -69 (# 54)  0.001  0.000
 HOMO -68 (# 55)  0.000  0.000
 HOMO -67 (# 56)  0.001  0.000
 HOMO -66 (# 57)  0.000  0.000
 HOMO -65 (# 58)  0.001  0.000
 HOMO -64 (# 59)  0.000  0.000
 HOMO -63 (# 60)  0.001  0.000
 HOMO -62 (# 61)  0.001  0.000
 HOMO -61 (# 62)  0.002  0.000
 HOMO -60 (# 63)  0.016  0.000
 HOMO -59 (# 64)  0.011  0.000
 HOMO -58 (# 65) -0.009 -0.001
 HOMO -57 (# 66)  0.001  0.000
 HOMO -56 (# 67)  0.001 -0.001
 HOMO -55 (# 68)  0.000  0.000
 HOMO -54 (# 69)  0.003  0.000
 HOMO -53 (# 70)  0.000 -0.001
 HOMO -52 (# 71)  0.014  0.000
 HOMO -51 (# 72)  0.018  0.000
 HOMO -49 (# 74)  0.008  0.000
 HOMO -48 (# 75)  0.000  0.000
 HOMO -47 (# 76)  0.014  0.000
 HOMO -45 (# 78)  0.008  0.000
 HOMO -44 (# 79)  0.018  0.000
 HOMO -43 (# 80)  0.004  0.000
 HOMO -42 (# 81)  0.000  0.000
 HOMO -40 (# 83) -0.019  0.000
 HOMO -39 (# 84)  0.001 -0.001
 HOMO -38 (# 85) -0.001 -0.001
 HOMO -36 (# 87) -0.006  0.000
 HOMO -35 (# 88) -0.008  0.000
 HOMO -34 (# 89) -0.007  0.000
 HOMO -33 (# 90) -0.004  0.000
 HOMO -32 (# 91) -0.001  0.000
 HOMO -31 (# 92) -0.002  0.000
 HOMO -30 (# 93) -0.011  0.000
 HOMO -29 (# 94) -0.014  0.000
 HOMO -28 (# 95) -0.006  0.000
 HOMO -27 (# 96)  0.000  0.000
 HOMO -26 (# 97) -0.002  0.000
 HOMO -25 (# 98) -0.002  0.000
 HOMO -24 (# 99) -0.003  0.000
 HOMO -21 (#102) -0.006  0.000
 HOMO -20 (#103) -0.003  0.000
 HOMO -18 (#105)  0.000  0.000
 HOMO -17 (#106)  0.002 -0.001
 HOMO -15 (#108)  0.025 -0.013
 HOMO -12 (#111)  0.007 -0.001
 HOMO -11 (#112)  0.005  0.000
 HOMO -10 (#113)  0.001  0.000
 HOMO  -9 (#114)  0.007  0.000
 HOMO  -8 (#115) -0.016  0.000
 HOMO  -7 (#116) -0.013 -0.001
 HOMO  -6 (#117) -0.001  0.000
 HOMO  -4 (#119)  0.000  0.000
 HOMO  -3 (#120) -0.043 -0.002
 HOMO  -2 (#121) -0.026  0.000
 HOMO  -1 (#122) -0.025  0.000
 HOMO   0 (#123) -0.100 -0.009
 ----------------------------
      Total over OMOs -0.141 -0.041
```

IV.3. Cartesian coordinates, three lower frequencies, thermochemistry and CDA calculations for IV-C



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-.627195	.429112	-1.224908
2	6	0	-.780673	.211253	1.974463
3	6	0	1.887648	.649491	.754303
4	6	0	.553923	-1.993336	.508218
5	8	0	-1.446989	.462528	2.871092
6	8	0	.721495	-3.125764	.483839
7	8	0	2.895633	1.176824	.884584
8	28	0	.295792	-.199391	.574051
9	9	0	-.917412	-.635726	-2.368628
10	9	0	.078317	1.528879	-2.128866
11	9	0	-2.072101	1.088305	-1.173374

	1			2			3		
	A			A			A		
Frequencies --	10.0805			58.4856			59.4638		
Red. masses --	18.0835			16.0158			15.9981		
Frc consts --	.0011			.0323			.0333		
IR Inten --	.0000			.0296			.0293		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
1 15	.00	.00	.00	.00	.01	-.06	.00	-.06	.00
2 6	.00	-.14	-.02	.25	.01	-.03	-.02	.17	.03
3 6	.00	.05	.13	-.11	.07	.14	.22	.00	.08
4 6	.00	.09	-.11	-.14	-.10	.11	-.21	.04	-.09
5 8	.00	-.23	-.03	.57	.04	-.15	-.04	.38	.06
6 8	.00	.15	-.19	-.31	-.25	.20	-.47	.03	-.24
7 8	.01	.08	.21	-.24	.18	.29	.50	-.06	.21

8	28	.00	.00	.00	.00	.00	.06	.00	.05	.00
9	9	.00	-.33	.39	.11	.01	-.16	.15	-.16	-.01
10	9	-.01	-.17	-.48	.07	.01	-.17	-.17	-.16	-.01
11	9	.00	.50	.09	-.19	.01	-.16	.02	-.17	-.01

HF=-1151.7102687

Sum of electronic and zero-point Energies= -1151.675873
Sum of electronic and thermal Energies= -1151.662699
Sum of electronic and thermal Enthalpies= -1151.661755
Sum of electronic and thermal Free Energies= -1151.719083

Electron donation between fragments (<0.001e for any omitted MO)

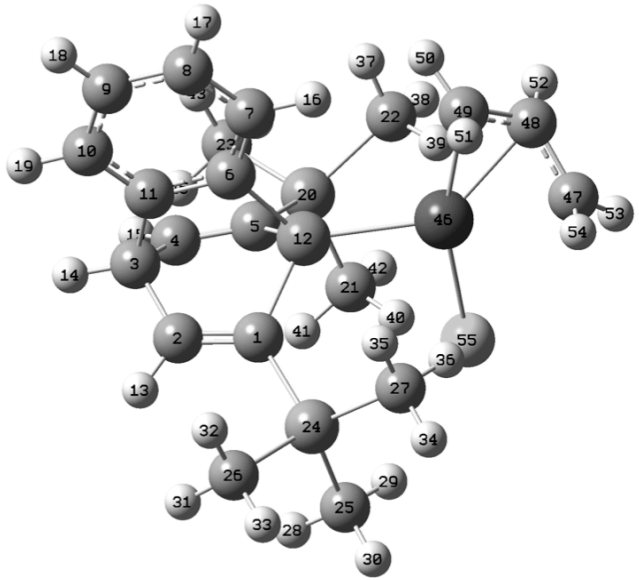
Alpha-spin MO	1->2	2->1
HOMO -40 (# 11)	0.001	0.000
HOMO -36 (# 15)	0.000	-0.003
HOMO -33 (# 18)	-0.001	-0.001
HOMO -32 (# 19)	0.047	-0.001
HOMO -31 (# 20)	0.005	0.000
HOMO -30 (# 21)	0.005	0.000
HOMO -26 (# 25)	0.036	-0.001
HOMO -25 (# 26)	0.001	-0.006
HOMO -22 (# 29)	0.004	0.000
HOMO -21 (# 30)	0.003	0.000
HOMO -20 (# 31)	0.012	0.000
HOMO -19 (# 32)	-0.004	-0.021
HOMO -18 (# 33)	0.004	-0.004
HOMO -17 (# 34)	0.004	-0.004
HOMO -14 (# 37)	-0.002	-0.003
HOMO -10 (# 41)	0.001	-0.001
HOMO -9 (# 42)	0.001	-0.001
HOMO -8 (# 43)	0.009	0.001
HOMO -7 (# 44)	0.009	0.001
HOMO -5 (# 46)	0.116	0.024
HOMO -4 (# 47)	-0.001	0.013
HOMO -3 (# 48)	-0.001	0.013
HOMO -2 (# 49)	-0.002	0.028
HOMO -1 (# 50)	-0.002	0.028
HOMO 0 (# 51)	0.114	0.008
Total over OMOs	0.360	0.068
TotalALPHA+BETA	0.721	0.136

Repulsion and residue (Delta) terms between fragments

Alpha-spin MO	1<->2	Delta
HOMO -40 (# 11)	0.000	0.000
HOMO -36 (# 15)	-0.001	0.000
HOMO -33 (# 18)	-0.002	0.000
HOMO -32 (# 19)	0.001	-0.002
HOMO -31 (# 20)	0.000	0.000
HOMO -30 (# 21)	0.000	0.000
HOMO -26 (# 25)	0.012	-0.001
HOMO -25 (# 26)	0.016	0.000
HOMO -22 (# 29)	0.002	0.000
HOMO -21 (# 30)	0.002	0.000
HOMO -20 (# 31)	0.013	0.000
HOMO -19 (# 32)	-0.026	-0.001
HOMO -18 (# 33)	0.000	-0.005

```
HOMO -17 (# 34)  0.000 -0.005
HOMO -14 (# 37) -0.005  0.000
HOMO -10 (# 41)  0.004  0.000
HOMO  -9 (# 42)  0.004  0.000
HOMO  -8 (# 43) -0.005  0.000
HOMO  -7 (# 44) -0.005  0.000
HOMO  -5 (# 46)  0.031 -0.035
HOMO  -4 (# 47) -0.006  0.001
HOMO  -3 (# 48) -0.006  0.001
HOMO  -2 (# 49) -0.011  0.004
HOMO  -1 (# 50) -0.011  0.004
HOMO   0 (# 51) -0.097 -0.010
------------------------------
Total over OMOs -0.081 -0.051
```

IV.4. Cartesian coordinates, three lower frequencies and thermochemistry for IV-D



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.001221	0.078597	-0.100531
2	6	0	-0.065030	0.191662	1.234202
3	6	0	1.201901	0.188787	2.082285

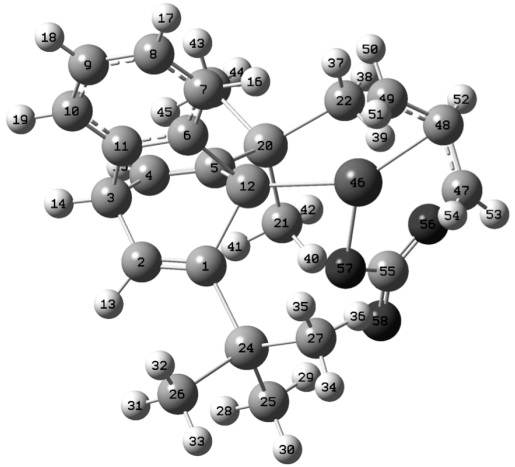
4	6	0	2.133879	1.282966	1.584435
5	6	0	2.506885	1.327129	0.297135
6	6	0	2.224661	-1.413641	0.493292
7	6	0	2.822759	-2.621806	0.154281
8	6	0	3.110234	-3.559569	1.151899
9	6	0	2.796076	-3.283936	2.479363
10	6	0	2.182707	-2.074316	2.821328
11	6	0	1.894659	-1.145282	1.828850
12	15	0	1.758943	-0.059167	-0.675740
13	1	0	-1.016184	0.247513	1.767739
14	1	0	0.971358	0.311678	3.146566
15	1	0	2.494679	2.003460	2.321521
16	1	0	3.058055	-2.839130	-0.884828
17	1	0	3.579129	-4.506764	0.886109
18	1	0	3.021515	-4.013737	3.256874
19	1	0	1.926496	-1.862563	3.860280
20	14	0	3.705023	2.666280	-0.353076
21	6	0	2.747950	4.155578	-1.063803
22	6	0	4.884020	1.929716	-1.662793
23	6	0	4.745232	3.255842	1.147820
24	14	0	-1.579097	-0.061280	-1.171774
25	6	0	-2.240526	1.655997	-1.675534
26	6	0	-2.903316	-0.910547	-0.069653
27	6	0	-1.257427	-1.178130	-2.686229
28	1	0	-2.453366	2.263023	-0.786287
29	1	0	-1.502421	2.177185	-2.293316
30	1	0	-3.170498	1.544527	-2.248826
31	1	0	-3.176800	-0.286948	0.791075
32	1	0	-2.550291	-1.880827	0.300703
33	1	0	-3.813556	-1.078712	-0.660386
34	1	0	-2.183270	-1.297588	-3.264252
35	1	0	-0.912993	-2.173160	-2.376163
36	1	0	-0.500298	-0.724833	-3.336881
37	1	0	5.487943	1.115601	-1.242677
38	1	0	5.559628	2.710156	-2.036254
39	1	0	4.305866	1.537421	-2.509364
40	1	0	2.131554	3.838984	-1.912653
41	1	0	2.093525	4.593962	-0.299759
42	1	0	3.451999	4.927586	-1.401811
43	1	0	5.257020	2.415873	1.633380
44	1	0	5.506541	3.968569	0.804282
45	1	0	4.125186	3.767473	1.895075
46	46	0	2.240746	-0.132755	-2.964413
47	6	0	2.655131	-0.478420	-5.093197
48	6	0	3.711890	-0.974725	-4.321260
49	6	0	3.430309	-1.904112	-3.287206
50	1	0	4.228891	-2.165341	-2.594546
51	1	0	2.667168	-2.670832	-3.439994
52	1	0	4.665758	-0.443400	-4.315612
53	1	0	2.791570	0.399659	-5.720788
54	1	0	1.780221	-1.095204	-5.307567
55	17	0	0.974819	1.847138	-3.358918

	1	2	3
	A	A	A
Frequencies --	21.4226	27.7221	39.6971
Red. masses --	4.4876	4.0424	4.1066
Frc consts --	0.0012	0.0018	0.0038
IR Inten --	1.7290	0.1134	0.0247

```
Sum of electronic and zero-point Energies=          -2282.363177
 Sum of electronic and thermal Energies=            -2282.330747
 Sum of electronic and thermal Enthalpies=          -2282.329803
 Sum of electronic and thermal Free Energies=       -2282.426702


HF=-2282.8103162
```

IV.5. Cartesian coordinates, three lower frequencies and thermochemistry for IV-E



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.112904	0.095001	-0.191726
2	6	0	0.356262	0.519255	1.056560
3	6	0	1.762709	0.434177	1.649232
4	6	0	2.722479	1.145865	0.698701
5	6	0	2.785788	0.796967	-0.594013
6	6	0	2.138232	-1.672741	0.434350
7	6	0	2.472378	-3.018670	0.333856
8	6	0	2.830475	-3.732076	1.483139
9	6	0	2.849223	-3.094849	2.721853
10	6	0	2.510497	-1.741117	2.824538
11	6	0	2.156071	-1.033829	1.680641
12	15	0	1.631973	-0.601859	-0.984839
13	1	0	-0.420942	0.952462	1.689790
14	1	0	1.799351	0.870478	2.655393

15	1	0	3.335286	1.946428	1.120295
16	1	0	2.450398	-3.502198	-0.642891
17	1	0	3.094451	-4.787645	1.408017
18	1	0	3.128277	-3.651231	3.617795
19	1	0	2.523274	-1.242943	3.795823
20	14	0	3.888978	1.730225	-1.848114
21	6	0	2.992161	3.307808	-2.440034
22	6	0	4.414581	0.620357	-3.300766
23	6	0	5.458765	2.267826	-0.863269
24	14	0	-1.607550	0.309820	-1.008272
25	6	0	-1.865844	2.039020	-1.766497
26	6	0	-2.839298	0.182885	0.483234
27	6	0	-2.093123	-1.129390	-2.166270
28	1	0	-1.706643	2.814371	-1.003880
29	1	0	-1.163445	2.195752	-2.601155
30	1	0	-2.898791	2.127703	-2.133909
31	1	0	-2.702826	1.003033	1.200833
32	1	0	-2.726015	-0.770087	1.016528
33	1	0	-3.867571	0.244215	0.100263
34	1	0	-3.159088	-1.050264	-2.421466
35	1	0	-1.919721	-2.102081	-1.686908
36	1	0	-1.490627	-1.061649	-3.076853
37	1	0	4.724096	-0.375680	-2.958790
38	1	0	5.252643	1.085707	-3.838544
39	1	0	3.558744	0.520806	-3.990734
40	1	0	2.069576	3.061351	-2.987517
41	1	0	2.737396	3.946279	-1.583240
42	1	0	3.649137	3.874707	-3.114267
43	1	0	5.981753	1.395618	-0.451034
44	1	0	6.145175	2.796487	-1.538556
45	1	0	5.208400	2.947565	-0.038174
46	46	0	1.418896	-1.398279	-3.113926
47	6	0	0.848454	-2.338517	-5.072871
48	6	0	2.119831	-2.736783	-4.655651
49	6	0	2.306384	-3.362415	-3.390587
50	1	0	3.323259	-3.561246	-3.050350
51	1	0	1.547949	-4.057603	-3.020483
52	1	0	2.984891	-2.293283	-5.153916
53	1	0	0.741476	-1.610400	-5.871927
54	1	0	-0.043398	-2.878115	-4.748251
55	6	0	0.828260	1.174621	-4.175569
56	8	0	1.698986	0.686283	-4.951426
57	8	0	0.397550	0.375620	-3.134759
58	8	0	0.302607	2.312608	-4.208766

```
1                      2                      3
                       A                      A                      A
 Frequencies --     31.6239                34.7157                43.4410
 Red. masses --      4.8152                 4.7137                 4.8374
 Frc consts  --      0.0028                 0.0033                 0.0054
 IR Inten    --      1.8358                 1.8436                 1.3708

Sum of electronic and zero-point Energies=          -2085.895235
 Sum of electronic and thermal Energies=            -2085.861087
 Sum of electronic and thermal Enthalpies=          -2085.860143
 Sum of electronic and thermal Free Energies=       -2085.959325


           HF=-2086.3568623
```

ANNEX 2: X-RAY DATA

I. X-RAY CRYSTAL STRUCTURES OF PART II

I.1. Crystallographic data for II-2

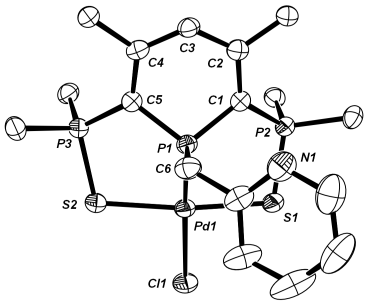


Table 1. Crystal data for pdspsn

Compound	pdspsn
Molecular formula	$C_{50}H_{40}Cl_{10}NP_3PdS_2$
Molecular weight	1272.76
Crystal habit	orange plate
Crystal dimensions(mm)	0.22x0.20x0.12
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	9.3110(10)
b(Å)	40.894(3)
c(Å)	14.6660(10)
α(°)	90.00
β(°)	103.8700(10)
γ(°)	90.00
V(Å^3)	5421.5(8)
Z	4
d(g-cm^{-3})	1.559
F000	2560
μ(cm^{-1})	1.037
Absorption corrections	multi-scan ; 0.8040 min, 0.8857 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite

T (K)	150.0(10)
Scan mode	phi and omega scans
Maximum θ	27.48
HKL ranges	-12 12 ; -53 48 ; -18 19
Reflections measured	19701
Unique data	11969
Rint	0.0216
Reflections used	9526
Criterion	>2sigma(I)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	627
Reflections / parameter	15
wR2	0.1457
R1	0.0479
Weights a, b	0.0856 ; 3.3180
GoF	1.050
difference peak / hole (e Å^{-3})	1.391(0.095) / -1.030(0.095)

Note: Three disordered CHCl3 molecules were found in the asymmetric unit. While it was possible to resolve this disorder for two of them, the third could not be and this solvent molecule was accounted for using the Platon SQUEEZE function.

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for pdspsn

atom	x	y	z	U(eq)
Pd(1)	11056(1)	3769(1)	5074(1)	30(1)
Cl(1)	13096(1)	3979(1)	4530(1)	43(1)
S(1)	11485(1)	4141(1)	6305(1)	35(1)
S(2)	10309(1)	3406(1)	3825(1)	39(1)
P(1)	9478(1)	3526(1)	5729(1)	27(1)
P(2)	9452(1)	4175(1)	6580(1)	29(1)
P(3)	8189(1)	3276(1)	3823(1)	31(1)
N(1)	10985(4)	3327(1)	8115(2)	46(1)
C(1)	8626(3)	3784(1)	6405(2)	29(1)
C(2)	7337(3)	3673(1)	6620(2)	29(1)
C(3)	6534(3)	3403(1)	6160(2)	29(1)
C(4)	6749(3)	3256(1)	5344(2)	29(1)
C(5)	7965(3)	3334(1)	4967(2)	30(1)
C(6)	10342(4)	3186(1)	6487(2)	36(1)
C(7)	11480(4)	3268(1)	7350(3)	39(1)
C(8)	12980(4)	3278(1)	7344(3)	57(1)
C(9)	13990(5)	3354(1)	8181(4)	73(2)
C(10)	13504(6)	3411(1)	8972(4)	69(1)
C(11)	12007(6)	3400(1)	8905(3)	62(1)
C(12)	8314(4)	4468(1)	5806(2)	33(1)
C(13)	8835(4)	4785(1)	5767(3)	41(1)
C(14)	7985(5)	5012(1)	5172(3)	51(1)
C(15)	6647(5)	4927(1)	4619(3)	57(1)
C(16)	6113(5)	4605(1)	4645(3)	60(1)
C(17)	6939(4)	4378(1)	5240(3)	42(1)
C(18)	9718(4)	4333(1)	7761(2)	33(1)
C(19)	10902(4)	4211(1)	8455(2)	43(1)

C(20)	11070(5)	4322(1)	9368(3)	53(1)
C(21)	10100(6)	4541(1)	9596(3)	58(1)
C(22)	8951(5)	4665(1)	8906(3)	50(1)
C(23)	8742(4)	4558(1)	7990(2)	39(1)
C(24)	6777(3)	3837(1)	7380(2)	32(1)
C(25)	7594(4)	3797(1)	8310(2)	40(1)
C(26)	7109(5)	3937(1)	9022(3)	52(1)
C(27)	5831(5)	4124(1)	8841(3)	57(1)
C(28)	5034(4)	4164(1)	7937(3)	53(1)
C(29)	5493(4)	4017(1)	7192(3)	40(1)
C(30)	5677(3)	2996(1)	4901(2)	31(1)
C(31)	6169(4)	2673(1)	4949(3)	41(1)
C(32)	5204(4)	2422(1)	4593(3)	49(1)
C(33)	3747(4)	2491(1)	4156(4)	58(1)
C(34)	3251(4)	2813(1)	4100(3)	56(1)
C(35)	4206(4)	3062(1)	4483(3)	44(1)
C(36)	7970(4)	2855(1)	3432(2)	39(1)
C(37)	9058(4)	2634(1)	3847(3)	47(1)
C(38)	8928(5)	2307(1)	3598(3)	60(1)
C(39)	7703(6)	2203(1)	2930(4)	66(1)
C(40)	6635(6)	2417(1)	2511(3)	64(1)
C(41)	6738(4)	2751(1)	2761(3)	48(1)
C(42)	6868(4)	3517(1)	2982(2)	35(1)
C(43)	5811(4)	3705(1)	3258(3)	41(1)
C(44)	4852(5)	3892(1)	2597(3)	55(1)
C(45)	4947(5)	3891(1)	1671(3)	63(1)
C(46)	5998(5)	3702(1)	1401(3)	58(1)
C(47)	6942(4)	3516(1)	2048(3)	49(1)
C(49)	10428(6)	4244(1)	2694(3)	65(1)
Cl(5)	9097(6)	4282(1)	3245(5)	65(1)
Cl(6)	11474(7)	4561(1)	2474(4)	73(1)
Cl(7)	10034(5)	3989(1)	1672(2)	66(1)
Cl(5A)	10970(10)	4647(2)	2365(5)	61(2)
Cl(6A)	9210(20)	4117(3)	1601(3)	107(4)
Cl(7A)	9030(10)	4389(3)	3365(8)	79(2)
C(50)	6349(8)	4762(2)	1858(5)	52(2)
Cl(8)	7384(2)	5109(1)	2227(2)	73(1)
Cl(9)	6824(4)	4608(1)	870(2)	118(1)
Cl(10)	4495(2)	4827(1)	1737(3)	111(1)
C(51)	5900(20)	4741(4)	1420(10)	52(2)
Cl(11)	7129(6)	5018(1)	1211(5)	111(2)
Cl(12)	4397(5)	4695(1)	455(3)	76(1)
Cl(13)	5110(10)	4876(2)	2361(4)	121(3)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for pdspsn

Pd(1)-P(1)	2.1783(8	Pd(1)-S(1)	2.3207(8)
Pd(1)-S(2)	2.332(1)	Pd(1)-Cl(1)	2.3894(8)
S(1)-P(2)	2.033(1)	S(2)-P(3)	2.043(1)
P(1)-C(5)	1.760(3)	P(1)-C(1)	1.761(3)
P(1)-C(6)	1.839(3)	P(2)-C(1)	1.767(3)
P(2)-C(12)	1.807(3)	P(2)-C(18)	1.809(3)
P(3)-C(5)	1.756(3)	P(3)-C(36)	1.810(3)
P(3)-C(42)	1.812(4)	N(1)-C(7)	1.334(5)
N(1)-C(11)	1.344(5)	C(1)-C(2)	1.388(4)
C(2)-C(3)	1.413(4)	C(2)-C(24)	1.496(4)
C(3)-C(4)	1.396(4)	C(4)-C(5)	1.411(4)
C(4)-C(30)	1.494(4)	C(6)-C(7)	1.480(5)
C(7)-C(8)	1.400(5)	C(8)-C(9)	1.390(7)
C(9)-C(10)	1.363(8)	C(10)-C(11)	1.375(7)
C(12)-C(13)	1.392(5)	C(12)-C(17)	1.397(5)

C(13)-C(14)	1.384(5)	C(14)-C(15)	1.359(6)
C(15)-C(16)	1.409(6)	C(16)-C(17)	1.376(5)
C(18)-C(23)	1.391(5)	C(18)-C(19)	1.400(5)
C(19)-C(20)	1.386(5)	C(20)-C(21)	1.371(7)
C(21)-C(22)	1.380(6)	C(22)-C(23)	1.381(5)
C(24)-C(29)	1.376(5)	C(24)-C(25)	1.403(5)
C(25)-C(26)	1.358(5)	C(26)-C(27)	1.385(6)
C(27)-C(28)	1.365(6)	C(28)-C(29)	1.399(5)
C(30)-C(35)	1.386(5)	C(30)-C(31)	1.396(5)
C(31)-C(32)	1.380(5)	C(32)-C(33)	1.383(6)
C(33)-C(34)	1.390(6)	C(34)-C(35)	1.379(5)
C(36)-C(37)	1.386(5)	C(36)-C(41)	1.387(5)
C(37)-C(38)	1.381(5)	C(38)-C(39)	1.380(7)
C(39)-C(40)	1.354(7)	C(40)-C(41)	1.413(6)
C(42)-C(43)	1.383(5)	C(42)-C(47)	1.388(5)
C(43)-C(44)	1.382(5)	C(44)-C(45)	1.382(6)
C(45)-C(46)	1.377(7)	C(46)-C(47)	1.359(6)
C(49)-Cl(5)	1.641(8)	C(49)-Cl(6)	1.699(7)
C(49)-Cl(7)	1.790(5)	C(49)-Cl(6A)	1.803(7)
C(49)-Cl(5A)	1.822(8)	C(49)-Cl(7A)	1.91(1)
C(50)-Cl(10)	1.713(8)	C(50)-Cl(8)	1.729(7)
C(50)-Cl(9)	1.731(7)	C(51)-Cl(11)	1.70(2)
C(51)-Cl(12)	1.75(2)	C(51)-Cl(13)	1.79(2)

P(1)-Pd(1)-S(1)	87.93(3)	P(1)-Pd(1)-S(2)	87.17(3)
S(1)-Pd(1)-S(2)	172.76(3)	P(1)-Pd(1)-Cl(1)	170.25(3)
S(1)-Pd(1)-Cl(1)	91.25(3)	S(2)-Pd(1)-Cl(1)	94.48(3)
P(2)-S(1)-Pd(1)	101.85(4)	P(3)-S(2)-Pd(1)	105.81(4)
C(5)-P(1)-C(1)	103.0(2)	C(5)-P(1)-C(6)	102.4(2)
C(1)-P(1)-C(6)	107.7(2)	C(5)-P(1)-Pd(1)	116.5(1)
C(1)-P(1)-Pd(1)	114.7(1)	C(6)-P(1)-Pd(1)	111.5(1)
C(1)-P(2)-C(12)	109.8(2)	C(1)-P(2)-C(18)	114.6(2)
C(12)-P(2)-C(18)	106.9(2)	C(1)-P(2)-S(1)	107.5(1)
C(12)-P(2)-S(1)	110.8(1)	C(18)-P(2)-S(1)	107.1(1)
C(5)-P(3)-C(36)	113.7(2)	C(5)-P(3)-C(42)	111.1(2)
C(36)-P(3)-C(42)	107.1(2)	C(5)-P(3)-S(2)	107.5(1)
C(36)-P(3)-S(2)	106.4(1)	C(42)-P(3)-S(2)	110.9(1)
C(7)-N(1)-C(11)	116.8(4)	C(2)-C(1)-P(1)	117.5(2)
C(2)-C(1)-P(2)	129.2(2)	P(1)-C(1)-P(2)	112.7(2)
C(1)-C(2)-C(3)	122.4(3)	C(1)-C(2)-C(24)	119.9(3)
C(3)-C(2)-C(24)	117.8(3)	C(4)-C(3)-C(2)	125.3(3)
C(3)-C(4)-C(5)	122.1(3)	C(3)-C(4)-C(30)	117.4(3)
C(5)-C(4)-C(30)	120.4(3)	C(4)-C(5)-P(3)	129.4(2)
C(4)-C(5)-P(1)	116.6(2)	P(3)-C(5)-P(1)	114.0(2)
C(7)-C(6)-P(1)	117.8(2)	N(1)-C(7)-C(8)	123.1(4)
N(1)-C(7)-C(6)	116.1(3)	C(8)-C(7)-C(6)	120.9(4)
C(9)-C(8)-C(7)	117.8(5)	C(10)-C(9)-C(8)	119.8(4)
C(9)-C(10)-C(11)	118.1(4)	N(1)-C(11)-C(10)	124.4(5)
C(13)-C(12)-C(17)	119.9(3)	C(13)-C(12)-P(2)	119.0(3)
C(17)-C(12)-P(2)	121.0(3)	C(14)-C(13)-C(12)	119.9(3)
C(15)-C(14)-C(13)	120.5(4)	C(14)-C(15)-C(16)	120.2(4)
C(17)-C(16)-C(15)	119.9(4)	C(16)-C(17)-C(12)	119.6(4)
C(23)-C(18)-C(19)	120.4(3)	C(23)-C(18)-P(2)	121.3(3)
C(19)-C(18)-P(2)	118.2(3)	C(20)-C(19)-C(18)	118.3(4)
C(21)-C(20)-C(19)	121.4(4)	C(20)-C(21)-C(22)	120.0(4)
C(21)-C(22)-C(23)	120.2(4)	C(22)-C(23)-C(18)	119.7(3)
C(29)-C(24)-C(25)	119.9(3)	C(29)-C(24)-C(2)	122.1(3)
C(25)-C(24)-C(2)	118.0(3)	C(26)-C(25)-C(24)	119.8(4)
C(25)-C(26)-C(27)	120.9(4)	C(28)-C(27)-C(26)	119.5(4)
C(27)-C(28)-C(29)	120.8(4)	C(24)-C(29)-C(28)	119.1(3)
C(35)-C(30)-C(31)	118.9(3)	C(35)-C(30)-C(4)	122.7(3)
C(31)-C(30)-C(4)	118.2(3)	C(32)-C(31)-C(30)	120.5(3)

C(31)-C(32)-C(33)	120.1(3)	C(32)-C(33)-C(34)	119.7(3)
C(35)-C(34)-C(33)	120.1(4)	C(34)-C(35)-C(30)	120.6(3)
C(37)-C(36)-C(41)	120.3(3)	C(37)-C(36)-P(3)	117.8(3)
C(41)-C(36)-P(3)	121.9(3)	C(38)-C(37)-C(36)	120.4(4)
C(39)-C(38)-C(37)	119.4(4)	C(40)-C(39)-C(38)	121.0(4)
C(39)-C(40)-C(41)	120.5(4)	C(36)-C(41)-C(40)	118.3(4)
C(43)-C(42)-C(47)	119.8(3)	C(43)-C(42)-P(3)	121.1(3)
C(47)-C(42)-P(3)	119.0(3)	C(44)-C(43)-C(42)	119.2(4)
C(45)-C(44)-C(43)	120.2(4)	C(46)-C(45)-C(44)	120.2(4)
C(47)-C(46)-C(45)	119.8(4)	C(46)-C(47)-C(42)	120.7(4)
Cl(5)-C(49)-Cl(6)	123.7(5)	Cl(5)-C(49)-Cl(7)	116.2(3)
Cl(6)-C(49)-Cl(7)	107.3(3)	Cl(5)-C(49)-Cl(6A)	94.4(5)
Cl(6)-C(49)-Cl(6A)	108.5(3)	Cl(7)-C(49)-Cl(6A)	29.5(4)
Cl(5)-C(49)-Cl(5A)	109.4(5)	Cl(6)-C(49)-Cl(5A)	18.5(2)
Cl(7)-C(49)-Cl(5A)	108.6(3)	Cl(6A)-C(49)-Cl(5A)	100.3(4)
Cl(5)-C(49)-Cl(7A)	13.0(4)	Cl(6)-C(49)-Cl(7A)	110.7(5)
Cl(7)-C(49)-Cl(7A)	125.8(4)	Cl(6A)-C(49)-Cl(7A)	100.8(6)
Cl(5A)-C(49)-Cl(7A)	97.0(5)	Cl(10)-C(50)-Cl(8)	112.1(4)
Cl(10)-C(50)-Cl(9)	115.0(4)	Cl(8)-C(50)-Cl(9)	109.0(4)
Cl(11)-C(51)-Cl(12)	112(1)	Cl(11)-C(51)-Cl(13)	111(1)
Cl(12)-C(51)-Cl(13)	105(1)		

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for pdspsn

atom	U11	U22	U33	U23	U13	U12
Pd(1)	24(1)	31(1)	36(1)	-2(1)	9(1)	-2(1)
Cl(1)	33(1)	49(1)	52(1)	-3(1)	18(1)	-9(1)
S(1)	27(1)	36(1)	44(1)	-8(1)	9(1)	-6(1)
S(2)	30(1)	46(1)	44(1)	-13(1)	16(1)	-7(1)
P(1)	23(1)	27(1)	31(1)	-1(1)	6(1)	-1(1)
P(2)	26(1)	29(1)	30(1)	-2(1)	6(1)	-2(1)
P(3)	28(1)	34(1)	33(1)	-6(1)	10(1)	-3(1)
N(1)	47(2)	44(2)	44(2)	5(1)	4(1)	0(1)
C(1)	27(1)	31(2)	29(2)	-2(1)	5(1)	-2(1)
C(2)	27(1)	31(2)	27(1)	4(1)	5(1)	2(1)
C(3)	25(1)	33(2)	30(2)	1(1)	8(1)	-4(1)
C(4)	24(1)	28(1)	34(2)	3(1)	5(1)	-2(1)
C(5)	28(2)	30(2)	32(2)	-3(1)	7(1)	-1(1)
C(6)	30(2)	33(2)	45(2)	3(1)	8(1)	2(1)
C(7)	33(2)	33(2)	46(2)	10(1)	3(1)	-3(1)
C(8)	32(2)	69(3)	67(3)	22(2)	3(2)	-2(2)
C(9)	36(2)	80(3)	92(4)	38(3)	-8(2)	-15(2)
C(10)	70(3)	54(3)	63(3)	13(2)	-22(2)	-15(2)
C(11)	81(3)	52(2)	44(2)	6(2)	-4(2)	1(2)
C(12)	33(2)	36(2)	32(2)	1(1)	10(1)	1(1)
C(13)	43(2)	37(2)	44(2)	2(2)	11(2)	-3(2)
C(14)	59(2)	36(2)	60(2)	10(2)	21(2)	0(2)
C(15)	49(2)	52(2)	71(3)	25(2)	15(2)	16(2)
C(16)	41(2)	63(3)	68(3)	20(2)	-2(2)	2(2)
C(17)	33(2)	41(2)	47(2)	6(2)	3(2)	-2(1)
C(18)	36(2)	32(2)	29(2)	-2(1)	5(1)	-9(1)
C(19)	44(2)	41(2)	40(2)	1(2)	2(2)	-6(2)
C(20)	60(2)	52(2)	36(2)	0(2)	-6(2)	-10(2)
C(21)	88(3)	52(2)	33(2)	-8(2)	12(2)	-22(2)
C(22)	68(3)	42(2)	46(2)	-11(2)	25(2)	-7(2)
C(23)	45(2)	38(2)	37(2)	-4(1)	12(2)	-2(2)
C(24)	29(2)	35(2)	33(2)	-3(1)	12(1)	-4(1)
C(25)	36(2)	48(2)	34(2)	1(1)	7(1)	-13(2)
C(26)	53(2)	72(3)	33(2)	-10(2)	14(2)	-21(2)
C(27)	55(2)	73(3)	48(2)	-29(2)	26(2)	-23(2)
C(28)	38(2)	58(2)	68(3)	-26(2)	22(2)	-3(2)

C(29)	34(2)	47(2)	39(2)	-10(2)	9(1)	-4(2)
C(30)	29(2)	30(2)	33(2)	-3(1)	9(1)	-4(1)
C(31)	35(2)	35(2)	53(2)	-2(2)	11(2)	-2(1)
C(32)	47(2)	29(2)	73(3)	-7(2)	15(2)	-4(2)
C(33)	39(2)	42(2)	92(3)	-21(2)	13(2)	-15(2)
C(34)	31(2)	46(2)	86(3)	-13(2)	3(2)	-6(2)
C(35)	28(2)	38(2)	64(2)	-4(2)	9(2)	-1(1)
C(36)	42(2)	37(2)	42(2)	-12(1)	18(2)	-4(1)
C(37)	42(2)	41(2)	61(2)	-13(2)	18(2)	-1(2)
C(38)	64(3)	42(2)	82(3)	-12(2)	28(2)	3(2)
C(39)	82(3)	41(2)	82(3)	-25(2)	32(3)	-9(2)
C(40)	73(3)	60(3)	60(3)	-26(2)	19(2)	-25(2)
C(41)	49(2)	46(2)	46(2)	-14(2)	9(2)	-9(2)
C(42)	32(2)	43(2)	32(2)	-2(1)	8(1)	-8(1)
C(43)	41(2)	46(2)	37(2)	5(2)	10(2)	5(2)
C(44)	48(2)	63(3)	52(2)	14(2)	9(2)	9(2)
C(45)	53(2)	81(3)	49(2)	25(2)	-1(2)	-7(2)
C(46)	62(3)	76(3)	35(2)	8(2)	12(2)	-8(2)
C(47)	49(2)	65(3)	36(2)	-2(2)	15(2)	-6(2)
C(49)	81(3)	62(3)	50(2)	6(2)	11(2)	-23(2)
Cl(5)	61(1)	64(3)	73(2)	12(2)	21(1)	15(2)
Cl(6)	84(3)	53(2)	79(2)	10(2)	16(2)	-19(2)
Cl(7)	82(2)	50(1)	71(1)	0(1)	27(1)	-4(1)
Cl(5A)	85(4)	47(3)	54(2)	-6(2)	24(3)	-25(2)
Cl(6A)	160(10)	97(5)	59(2)	-14(2)	8(3)	-58(6)
Cl(7A)	90(4)	71(5)	87(3)	8(4)	43(3)	4(4)
C(50)	64(5)	46(3)	45(4)	1(3)	10(3)	3(3)
Cl(8)	69(1)	47(1)	92(1)	-6(1)	3(1)	-7(1)
Cl(9)	161(3)	117(2)	88(2)	-44(2)	51(2)	-24(2)
Cl(10)	45(1)	109(2)	173(3)	4(2)	14(1)	10(1)
C(51)	64(5)	46(3)	45(4)	1(3)	10(3)	3(3)
Cl(11)	75(3)	100(4)	155(6)	30(4)	20(3)	-29(3)
Cl(12)	94(3)	62(2)	68(2)	-3(2)	11(2)	8(2)
Cl(13)	201(8)	110(4)	59(3)	-9(3)	48(4)	-26(5)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for pdspsn

atom	x	y	z	U(eq)
H(3)	5787	3313	6429	35
H(6A)	9546	3063	6675	43
H(6B)	10798	3037	6104	43
H(8)	13297	3235	6786	69
H(9)	15016	3366	8200	88
H(10)	14182	3457	9553	82
H(11)	11671	3447	9454	75
H(13)	9772	4846	6149	49
H(14)	8340	5229	5151	61
H(15)	6071	5084	4214	69
H(16)	5184	4545	4251	72
H(17)	6577	4162	5267	50
H(19)	11574	4058	8303	51
H(20)	11873	4243	9846	63
H(21)	10219	4609	10230	69
H(22)	8303	4823	9061	60
H(23)	7934	4639	7518	47
H(25)	8482	3673	8442	48
H(26)	7655	3907	9652	62

H(27)	5511	4224	9343	68
H(28)	4158	4292	7812	63
H(29)	4925	4041	6565	48
H(31)	7176	2625	5229	49
H(32)	5540	2202	4648	59
H(33)	3088	2320	3896	70
H(34)	2253	2861	3797	67
H(35)	3853	3281	4460	52
H(37)	9897	2707	4307	56
H(38)	9675	2156	3882	73
H(39)	7607	1979	2763	79
H(40)	5809	2341	2044	76
H(41)	5983	2901	2477	57
H(43)	5746	3705	3895	49
H(44)	4124	4023	2780	66
H(45)	4285	4020	1220	76
H(46)	6063	3701	763	69
H(47)	7661	3385	1859	59
H(49A)	11170	4110	3148	78
H(49B)	11224	4090	3015	78
H(50)	6660	4595	2365	63
H(51)	6397	4525	1591	63

I.2. Crystallographic data for II-4

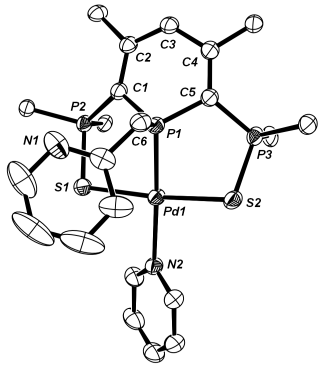


Table 1. Crystal data for pdp3s2n2

Compound	pdp3s2n2
Molecular formula	$C_{52}H_{42}N_2P_3PdS_2,BF_4$
Molecular weight	1283.85
Crystal habit	orange block
Crystal dimensions(mm)	0.20x0.20x0.16
Crystal system	triclinic
Space group	Pbar1
a(Å)	12.7870(10)

b(Å)	13.5470(10)
c(Å)	17.3590(10)
α(°)	111.8200(10)
β(°)	100.4000(10)
γ(°)	93.6300(10)
V(Å^3)	2717.6(3)
Z	2
d(g-cm^{-3})	1.569
F(000)	1296
μ(cm^{-1})	0.855
Absorption corrections	multi-scan ; 0.8475 min, 0.8753 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-17 17 ; -15 19 ; -24 24
Reflections measured	23605
Unique data	15786
Rint	0.0183
Reflections used	12722
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	586
Reflections / parameter	21
wR2	0.1527
R1	0.0466
Weights a, b	0.0957 ; 0.0829
GoF	1.115
difference peak / hole (e Å^{-3})	1.607(0.093) / -1.121(0.093)

Note: Two CHCL3 molecules revealed too disordered to be included in least-squares and were accounted for using the Platon SQUEEZE function. The data at hand do not permit to solve an eventual disorder in the BF4 anion.

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for pdp3s2n2

atom	x	y	z	U(eq)
Pd(1)	7484(1)	3687(1)	3369(1)	26(1)
S(1)	6450(1)	3629(1)	4320(1)	32(1)
S(2)	8383(1)	3607(1)	2294(1)	34(1)
P(1)	6389(1)	2273(1)	2407(1)	26(1)
P(2)	6047(1)	2021(1)	3953(1)	26(1)
P(3)	8276(1)	1995(1)	1635(1)	30(1)
N(2)	8448(2)	5136(2)	4290(1)	30(1)
C(1)	5819(2)	1417(2)	2835(1)	28(1)

C(2)	5466(2)	331(2)	2283(1)	28(1)
C(3)	5719(2)	-129(2)	1482(1)	30(1)
C(4)	6549(2)	325(2)	1218(1)	29(1)
C(5)	7012(2)	1396(2)	1642(1)	29(1)
C(6)	5330(2)	2743(2)	1816(1)	31(1)
C(7)	4983(2)	3742(2)	2387(2)	38(1)
N(1)	4164(2)	3617(2)	2735(2)	50(1)
C(8)	5562(3)	4739(2)	2580(2)	55(1)
C(9)	5344(4)	5641(3)	3158(3)	80(1)
C(10)	4493(5)	5539(4)	3540(2)	91(2)
C(11)	3916(4)	4520(4)	3303(2)	73(1)
C(12)	4908(2)	1910(2)	4419(1)	28(1)
C(13)	4061(2)	2472(2)	4274(2)	35(1)
C(14)	3190(2)	2437(2)	4642(2)	40(1)
C(15)	3162(2)	1858(2)	5148(2)	39(1)
C(16)	4001(2)	1315(2)	5296(2)	39(1)
C(17)	4887(2)	1339(2)	4931(2)	31(1)
C(18)	7111(2)	1481(2)	4438(1)	29(1)
C(19)	7567(2)	2023(2)	5304(2)	34(1)
C(20)	8391(2)	1629(2)	5699(2)	38(1)
C(21)	8746(2)	698(2)	5225(2)	39(1)
C(22)	8311(2)	165(2)	4368(2)	39(1)
C(23)	7489(2)	544(2)	3968(2)	33(1)
C(24)	4846(2)	-435(2)	2528(1)	32(1)
C(25)	3906(2)	-209(2)	2821(2)	37(1)
C(26)	3332(2)	-969(3)	3004(2)	47(1)
C(27)	3657(3)	-1960(3)	2878(2)	54(1)
C(28)	4572(3)	-2202(3)	2559(2)	60(1)
C(29)	5172(2)	-1438(2)	2402(2)	45(1)
C(30)	6941(2)	-424(2)	486(1)	33(1)
C(31)	7399(2)	-1297(2)	556(2)	46(1)
C(32)	7757(3)	-2009(3)	-128(2)	56(1)
C(33)	7636(2)	-1862(3)	-882(2)	53(1)
C(34)	7161(2)	-1005(3)	-963(2)	47(1)
C(35)	6804(2)	-290(2)	-273(2)	39(1)
C(36)	9359(2)	1478(2)	2121(1)	35(1)
C(37)	9159(2)	635(2)	2368(2)	38(1)
C(38)	10008(2)	267(3)	2765(2)	47(1)
C(39)	11049(2)	766(3)	2914(2)	54(1)
C(40)	11250(2)	1589(3)	2660(2)	52(1)
C(41)	10421(2)	1953(3)	2264(2)	42(1)
C(42)	8463(2)	1811(2)	584(1)	37(1)
C(43)	9259(2)	1269(2)	243(2)	39(1)
C(44)	9355(2)	1146(3)	-576(2)	45(1)
C(45)	8635(3)	1560(3)	-1041(2)	53(1)
C(46)	7848(3)	2088(3)	-698(2)	53(1)
C(47)	7762(2)	2231(3)	126(2)	44(1)
C(48)	8756(2)	5938(2)	4067(2)	37(1)
C(49)	9408(2)	6865(2)	4631(2)	48(1)
C(50)	9768(2)	6983(2)	5470(2)	49(1)
C(51)	9444(2)	6169(2)	5713(2)	45(1)
C(52)	8787(2)	5257(2)	5112(2)	36(1)
B(1)	8239(5)	-2602(5)	2553(3)	86(2)
F(1)	9212(2)	-2091(3)	3139(2)	112(1)
F(2)	7884(3)	-1800(4)	2317(3)	154(2)
F(3)	7444(3)	-2749(5)	2957(3)	159(2)
F(4)	8403(4)	-3413(7)	2000(5)	397(8)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for pdp3s2n2

Pd(1)-N(2)	2.140(2)	Pd(1)-P(1)	2.2040(6)
Pd(1)-S(1)	2.3126(6	Pd(1)-S(2)	2.3359(6)
S(1)-P(2)	2.0313(8	S(2)-P(3)	2.036(1)
P(1)-C(5)	1.771(2)	P(1)-C(1)	1.776(2)
P(1)-C(6)	1.841(2)	P(2)-C(1)	1.762(2)
P(2)-C(18)	1.808(2)	P(2)-C(12)	1.813(2)
P(3)-C(5)	1.767(2)	P(3)-C(36)	1.805(3)
P(3)-C(42)	1.809(2)	N(2)-C(48)	1.342(3)
N(2)-C(52)	1.357(3)	C(1)-C(2)	1.414(3)
C(2)-C(3)	1.404(3)	C(2)-C(24)	1.494(3)
C(3)-C(4)	1.420(3)	C(4)-C(5)	1.392(3)
C(4)-C(30)	1.493(3)	C(6)-C(7)	1.500(4)
C(7)-N(1)	1.332(4)	C(7)-C(8)	1.390(4)
N(1)-C(11)	1.354(4)	C(8)-C(9)	1.345(5)
C(9)-C(10)	1.397(7)	C(10)-C(11)	1.400(7)
C(12)-C(17)	1.380(3)	C(12)-C(13)	1.402(3)
C(13)-C(14)	1.386(3)	C(14)-C(15)	1.383(4)
C(15)-C(16)	1.378(4)	C(16)-C(17)	1.399(3)
C(18)-C(19)	1.395(3)	C(18)-C(23)	1.400(3)
C(19)-C(20)	1.396(3)	C(20)-C(21)	1.382(4)
C(21)-C(22)	1.378(4)	C(22)-C(23)	1.385(4)
C(24)-C(29)	1.396(4)	C(24)-C(25)	1.396(4)
C(25)-C(26)	1.390(4)	C(26)-C(27)	1.381(5)
C(27)-C(28)	1.389(5)	C(28)-C(29)	1.385(4)
C(30)-C(35)	1.379(3)	C(30)-C(31)	1.388(4)
C(31)-C(32)	1.397(4)	C(32)-C(33)	1.379(5)
C(33)-C(34)	1.385(5)	C(34)-C(35)	1.403(4)
C(36)-C(37)	1.386(4)	C(36)-C(41)	1.404(3)
C(37)-C(38)	1.398(4)	C(38)-C(39)	1.388(5)
C(39)-C(40)	1.368(5)	C(40)-C(41)	1.376(4)
C(42)-C(47)	1.379(4)	C(42)-C(43)	1.383(4)
C(43)-C(44)	1.397(3)	C(44)-C(45)	1.395(5)
C(45)-C(46)	1.367(5)	C(46)-C(47)	1.395(4)
C(48)-C(49)	1.375(4)	C(49)-C(50)	1.391(5)
C(50)-C(51)	1.384(5)	C(51)-C(52)	1.383(4)
B(1)-F(4)	1.221(6)	B(1)-F(2)	1.371(7)
B(1)-F(3)	1.379(7)	B(1)-F(1)	1.405(6)

N(2)-Pd(1)-P(1)	175.43(5)	N(2)-Pd(1)-S(1)	91.37(5)
P(1)-Pd(1)-S(1)	87.49(2)	N(2)-Pd(1)-S(2)	94.66(5)
P(1)-Pd(1)-S(2)	86.38(2)	S(1)-Pd(1)-S(2)	173.78(2)
P(2)-S(1)-Pd(1)	101.49(3)	P(3)-S(2)-Pd(1)	102.20(3)
C(5)-P(1)-C(1)	103.1(1)	C(5)-P(1)-C(6)	106.4(1)
C(1)-P(1)-C(6)	110.7(1)	C(5)-P(1)-Pd(1)	114.08(8)
C(1)-P(1)-Pd(1)	113.94(7)	C(6)-P(1)-Pd(1)	108.37(8)
C(1)-P(2)-C(18)	110.7(1)	C(1)-P(2)-C(12)	116.7(1)
C(18)-P(2)-C(12)	106.9(1)	C(1)-P(2)-S(1)	108.28(8)
C(18)-P(2)-S(1)	110.13(8)	C(12)-P(2)-S(1)	103.90(8)
C(5)-P(3)-C(36)	111.3(1)	C(5)-P(3)-C(42)	114.0(1)
C(36)-P(3)-C(42)	107.5(1)	C(5)-P(3)-S(2)	107.45(8)
C(36)-P(3)-S(2)	109.9(1)	C(42)-P(3)-S(2)	106.5(1)
C(48)-N(2)-C(52)	118.2(2)	C(48)-N(2)-Pd(1)	120.9(2)
C(52)-N(2)-Pd(1)	120.9(2)	C(2)-C(1)-P(2)	129.4(2)
C(2)-C(1)-P(1)	117.3(2)	P(2)-C(1)-P(1)	111.9(1)
C(3)-C(2)-C(1)	122.8(2)	C(3)-C(2)-C(24)	114.6(2)
C(1)-C(2)-C(24)	122.5(2)	C(2)-C(3)-C(4)	124.6(2)
C(5)-C(4)-C(3)	122.1(2)	C(5)-C(4)-C(30)	121.5(2)
C(3)-C(4)-C(30)	116.3(2)	C(4)-C(5)-P(3)	128.1(2)
C(4)-C(5)-P(1)	118.6(2)	P(3)-C(5)-P(1)	112.7(1)
C(7)-C(6)-P(1)	111.7(2)	N(1)-C(7)-C(8)	122.9(3)
N(1)-C(7)-C(6)	117.2(2)	C(8)-C(7)-C(6)	119.7(3)
C(7)-N(1)-C(11)	116.5(3)	C(9)-C(8)-C(7)	121.4(4)

C(8)-C(9)-C(10)	117.3(4)	C(9)-C(10)-C(11)	118.9(4)
N(1)-C(11)-C(10)	123.0(4)	C(17)-C(12)-C(13)	120.7(2)
C(17)-C(12)-P(2)	121.9(2)	C(13)-C(12)-P(2)	117.3(2)
C(14)-C(13)-C(12)	119.2(2)	C(15)-C(14)-C(13)	120.2(2)
C(16)-C(15)-C(14)	120.3(2)	C(15)-C(16)-C(17)	120.4(2)
C(12)-C(17)-C(16)	119.2(2)	C(19)-C(18)-C(23)	119.6(2)
C(19)-C(18)-P(2)	118.6(2)	C(23)-C(18)-P(2)	121.8(2)
C(18)-C(19)-C(20)	120.1(2)	C(21)-C(20)-C(19)	119.4(2)
C(22)-C(21)-C(20)	121.0(2)	C(21)-C(22)-C(23)	120.3(3)
C(22)-C(23)-C(18)	119.7(2)	C(29)-C(24)-C(25)	119.0(2)
C(29)-C(24)-C(2)	119.0(2)	C(25)-C(24)-C(2)	121.8(2)
C(26)-C(25)-C(24)	119.6(3)	C(27)-C(26)-C(25)	121.2(3)
C(26)-C(27)-C(28)	119.3(3)	C(29)-C(28)-C(27)	120.0(3)
C(28)-C(29)-C(24)	120.8(3)	C(35)-C(30)-C(31)	119.4(2)
C(35)-C(30)-C(4)	120.8(2)	C(31)-C(30)-C(4)	119.7(2)
C(30)-C(31)-C(32)	120.1(3)	C(33)-C(32)-C(31)	120.2(3)
C(32)-C(33)-C(34)	120.1(3)	C(33)-C(34)-C(35)	119.5(3)
C(30)-C(35)-C(34)	120.6(3)	C(37)-C(36)-C(41)	119.5(2)
C(37)-C(36)-P(3)	121.3(2)	C(41)-C(36)-P(3)	119.2(2)
C(36)-C(37)-C(38)	120.3(3)	C(39)-C(38)-C(37)	119.0(3)
C(40)-C(39)-C(38)	120.9(3)	C(39)-C(40)-C(41)	120.7(3)
C(40)-C(41)-C(36)	119.7(3)	C(47)-C(42)-C(43)	120.8(2)
C(47)-C(42)-P(3)	116.8(2)	C(43)-C(42)-P(3)	122.4(2)
C(42)-C(43)-C(44)	119.6(3)	C(45)-C(44)-C(43)	119.3(3)
C(46)-C(45)-C(44)	120.4(2)	C(45)-C(46)-C(47)	120.4(3)
C(42)-C(47)-C(46)	119.4(3)	N(2)-C(48)-C(49)	122.8(3)
C(48)-C(49)-C(50)	119.0(3)	C(51)-C(50)-C(49)	118.8(2)
C(52)-C(51)-C(50)	119.1(3)	N(2)-C(52)-C(51)	122.1(3)
F(4)-B(1)-F(2)	117.9(7)	F(4)-B(1)-F(3)	115.4(8)
F(2)-B(1)-F(3)	99.4(4)	F(4)-B(1)-F(1)	109.0(4)
F(2)-B(1)-F(1)	102.8(5)	F(3)-B(1)-F(1)	111.4(4)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for pdp3s2n2

atom	U11	U22	U33	U23	U13	U12
Pd(1)	26(1)	29(1)	22(1)	9(1)	3(1)	-2(1)
S(1)	37(1)	30(1)	26(1)	9(1)	10(1)	-1(1)
S(2)	36(1)	38(1)	26(1)	10(1)	7(1)	-8(1)
P(1)	25(1)	29(1)	21(1)	9(1)	3(1)	-1(1)
P(2)	25(1)	31(1)	23(1)	10(1)	6(1)	1(1)
P(3)	27(1)	40(1)	21(1)	10(1)	5(1)	-3(1)
N(2)	26(1)	32(1)	25(1)	8(1)	3(1)	-2(1)
C(1)	27(1)	31(1)	24(1)	10(1)	6(1)	-1(1)
C(2)	25(1)	32(1)	25(1)	11(1)	2(1)	-1(1)
C(3)	28(1)	32(1)	25(1)	8(1)	3(1)	-2(1)
C(4)	29(1)	35(1)	23(1)	11(1)	3(1)	1(1)
C(5)	28(1)	33(1)	23(1)	10(1)	5(1)	-1(1)
C(6)	32(1)	33(1)	25(1)	11(1)	1(1)	-1(1)
C(7)	45(1)	36(1)	31(1)	14(1)	-2(1)	11(1)
N(1)	61(2)	52(2)	38(1)	16(1)	12(1)	24(1)
C(8)	63(2)	37(2)	54(2)	19(1)	-14(1)	3(1)
C(9)	126(4)	35(2)	55(2)	12(2)	-27(2)	13(2)
C(10)	157(5)	55(2)	47(2)	8(2)	0(3)	64(3)
C(11)	104(3)	79(3)	51(2)	29(2)	27(2)	61(2)
C(12)	25(1)	32(1)	26(1)	9(1)	7(1)	1(1)
C(13)	28(1)	42(1)	37(1)	18(1)	7(1)	6(1)
C(14)	28(1)	45(2)	44(1)	15(1)	7(1)	8(1)
C(15)	31(1)	44(1)	42(1)	13(1)	16(1)	3(1)
C(16)	41(1)	41(1)	38(1)	17(1)	17(1)	4(1)
C(17)	29(1)	33(1)	33(1)	15(1)	9(1)	4(1)
C(18)	23(1)	35(1)	27(1)	12(1)	6(1)	-1(1)

C(19)	30(1)	45(1)	28(1)	14(1)	7(1)	5(1)
C(20)	27(1)	58(2)	31(1)	21(1)	6(1)	3(1)
C(21)	27(1)	54(2)	43(1)	26(1)	9(1)	9(1)
C(22)	33(1)	43(1)	44(1)	17(1)	12(1)	9(1)
C(23)	27(1)	39(1)	32(1)	12(1)	8(1)	2(1)
C(24)	34(1)	34(1)	23(1)	10(1)	1(1)	-6(1)
C(25)	37(1)	42(1)	28(1)	11(1)	7(1)	-9(1)
C(26)	44(1)	60(2)	31(1)	18(1)	6(1)	-15(1)
C(27)	60(2)	58(2)	48(2)	36(2)	-4(1)	-21(2)
C(28)	60(2)	50(2)	78(2)	44(2)	-5(2)	-8(1)
C(29)	43(1)	45(2)	52(2)	29(1)	4(1)	2(1)
C(30)	27(1)	40(1)	25(1)	6(1)	4(1)	-3(1)
C(31)	49(2)	47(2)	37(1)	10(1)	10(1)	8(1)
C(32)	52(2)	52(2)	49(2)	2(1)	13(1)	14(1)
C(33)	38(1)	60(2)	39(1)	-5(1)	14(1)	-6(1)
C(34)	44(1)	59(2)	24(1)	3(1)	9(1)	-13(1)
C(35)	37(1)	43(1)	26(1)	6(1)	2(1)	-9(1)
C(36)	32(1)	49(2)	21(1)	8(1)	7(1)	3(1)
C(37)	37(1)	48(2)	28(1)	13(1)	8(1)	8(1)
C(38)	47(2)	60(2)	32(1)	13(1)	6(1)	17(1)
C(39)	41(1)	83(2)	32(1)	12(1)	8(1)	25(2)
C(40)	33(1)	82(2)	30(1)	12(1)	6(1)	9(1)
C(41)	32(1)	62(2)	23(1)	10(1)	6(1)	2(1)
C(42)	38(1)	46(1)	21(1)	10(1)	5(1)	-7(1)
C(43)	36(1)	50(2)	23(1)	9(1)	6(1)	-7(1)
C(44)	48(2)	53(2)	27(1)	9(1)	13(1)	0(1)
C(45)	75(2)	59(2)	23(1)	14(1)	12(1)	-1(2)
C(46)	61(2)	67(2)	28(1)	21(1)	5(1)	4(2)
C(47)	41(1)	64(2)	27(1)	18(1)	7(1)	5(1)
C(48)	34(1)	34(1)	41(1)	12(1)	11(1)	1(1)
C(49)	37(1)	35(1)	64(2)	8(1)	19(1)	-2(1)
C(50)	30(1)	44(2)	50(2)	-6(1)	4(1)	-3(1)
C(51)	35(1)	49(2)	33(1)	-1(1)	-2(1)	7(1)
C(52)	30(1)	41(1)	29(1)	7(1)	2(1)	5(1)
B(1)	86(3)	105(4)	56(2)	15(3)	5(2)	62(3)
F(1)	91(2)	139(3)	80(2)	27(2)	-16(1)	45(2)
F(2)	106(2)	226(5)	186(4)	164(4)	-14(2)	14(3)
F(3)	115(3)	231(5)	167(4)	123(4)	30(3)	10(3)
F(4)	134(4)	380(10)	305(8)	-250(8)	-66(4)	134(5)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for pdp3s2n2

atom	x	y	z	U(eq)
H(3)	5307	-790.0001	1089	36
H(6A)	5600	2890	1363	38
H(6B)	4703	2170	1539	38
H(8)	6123	4785	2297	66
H(9)	5752	6320	3300	96
H(10)	4310	6151	3953	109
H(11)	3324	4458	3552	88
H(13)	4083	2872	3928	42
H(14)	2610	2813	4545	48
H(15)	2561	1834	5396	47
H(16)	3977	921	5647	46
H(17)	5467	967	5034	37
H(19)	7317	2662	5625	41
H(20)	8704	1997	6287	46

H(21)	9298	421	5495	46
H(22)	8575	-465	4049	47
H(23)	7184	170	3379	40
H(25)	3660	460	2894	45
H(26)	2703	-804	3220	56
H(27)	3259	-2471	3008	65
H(28)	4787	-2891	2449	72
H(29)	5813	-1597.9999	2206	54
H(31)	7469	-1410	1070	55
H(32)	8086	-2597	-74	67
H(33)	7878	-2349	-1347	63
H(34)	7077	-901	-1481	57
H(35)	6466	291	-331	47
H(37)	8443	304	2266	46
H(38)	9874	-315	2931	57
H(39)	11629	532	3195	65
H(40)	11969	1912	2759	62
H(41)	10568	2524	2089	50
H(43)	9737	983	563	46
H(44)	9904	784	-813	54
H(45)	8693	1474	-1599	63
H(46)	7357	2360	-1022	63
H(47)	7226	2614	368	53
H(48)	8512	5863	3495	45
H(49)	9611	7416	4451	57
H(50)	10228	7612	5870	59
H(51)	9670	6235	6284	54
H(52)	8567	4698	5279	43

I.3. Crystallographic data for II-6

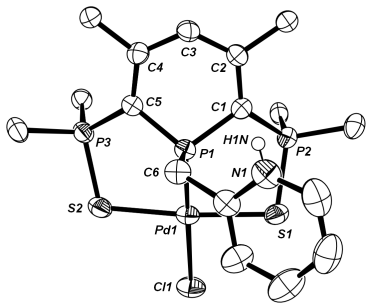


Table 1. Crystal data for mb128

Compound	mb128
Molecular formula	$C_{47}H_{38}ClNP_3PdS_2$,2(CH_2Cl_2),Cl
Molecular weight	1205.89
Crystal habit	orange plate
Crystal dimensions(mm)	0.23x0.16x0.05
Crystal system	triclinic

Space group	P-1
a(≈)	9.618(1)
b(≈)	13.260(1)
c(≈)	22.200(1)
α(∞)	82.918(1)
β(∞)	89.160(1)
γ(∞)	68.868(1)
V(≈^{3})	2619.4(4)
Z	2
d(g-cm^{-3})	1.529
F(000)	1220
μ(cm^{-1})	0.970
Absorption corrections	multi-scan ; 0.8077 min, 0.9531 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(≈)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	27.48
HKL ranges	-12 11 ; -17 17 ; -28 28
Reflections measured	21984
Unique data	11290
Rint	0.0280
Reflections used	8108
Criterion	I > 2σ(I)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	562
Reflections / parameter	14
wR2	0.1442
R1	0.0479
Weights a, b	0.0764 ; 0.7887
GoF	1.062
difference peak / hole (e ≈$^{-3}$)	1.201(0.089) / -0.918(0.089)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb128

atom	x	y	z	U(eq)
Pd(1)	7815(1)	5065(1)	1911(1)	34(1)
Cl(1)	9570(1)	5670(1)	1360(1)	49(1)
S(1)	7064(1)	6599(1)	2416(1)	42(1)
S(2)	8344(1)	3515(1)	1433(1)	41(1)
P(1)	6382(1)	4440(1)	2495(1)	30(1)
P(2)	4901(1)	6774(1)	2523(1)	32(1)
P(3)	6511(1)	3085(1)	1527(1)	33(1)
N(1)	7082(4)	4486(3)	4080(2)	44(1)
C(1)	4796(4)	5481(2)	2736(2)	31(1)
C(2)	3570(4)	5205(2)	2921(2)	31(1)

C(3)	3448(4)	4215(3)	2835(2)	34(1)
C(4)	4339(4)	3484(2)	2449(2)	31(1)
C(5)	5618(4)	3579(2)	2192(2)	32(1)
C(6)	7429(4)	3576(3)	3182(2)	37(1)
C(7)	7935(4)	4164(3)	3605(2)	37(1)
C(8)	9191(5)	4422(3)	3547(2)	49(1)
C(9)	9548(6)	5002(4)	3957(2)	62(1)
C(10)	8598(6)	5335(3)	4426(2)	62(1)
C(11)	7385(6)	5057(3)	4485(2)	58(1)
C(12)	4168(4)	7722(3)	3068(2)	38(1)
C(13)	5028(5)	7639(3)	3580(2)	53(1)
C(14)	4425(7)	8340(4)	4012(2)	70(1)
C(15)	3030(7)	9120(4)	3919(2)	71(2)
C(16)	2196(6)	9191(3)	3421(2)	57(1)
C(17)	2736(4)	8500(3)	2993(2)	43(1)
C(18)	3834(4)	7399(2)	1829(2)	34(1)
C(19)	4053(4)	8303(3)	1509(2)	43(1)
C(20)	3180(5)	8850(3)	999(2)	52(1)
C(21)	2100(5)	8505(3)	795(2)	49(1)
C(22)	1895(4)	7594(3)	1095(2)	46(1)
C(23)	2770(4)	7032(3)	1614(2)	37(1)
C(24)	2315(4)	6011(3)	3221(2)	34(1)
C(25)	2570(4)	6235(3)	3798(2)	39(1)
C(26)	1440(5)	6979(3)	4083(2)	45(1)
C(27)	58(5)	7505(3)	3796(2)	49(1)
C(28)	-209(4)	7287(3)	3228(2)	46(1)
C(29)	910(4)	6525(3)	2939(2)	40(1)
C(30)	3849(4)	2584(3)	2326(2)	33(1)
C(31)	2498(4)	2780(3)	2025(2)	41(1)
C(32)	2094(4)	1905(3)	1923(2)	48(1)
C(33)	2995(5)	854(3)	2129(2)	49(1)
C(34)	4311(5)	655(3)	2436(2)	49(1)
C(35)	4756(4)	1510(3)	2531(2)	43(1)
C(36)	5240(4)	3625(3)	878(2)	34(1)
C(37)	3760(4)	4270(3)	937(2)	36(1)
C(38)	2796(4)	4627(3)	437(2)	43(1)
C(39)	3309(5)	4357(3)	-129(2)	44(1)
C(40)	4801(5)	3738(3)	-192(2)	43(1)
C(41)	5771(4)	3369(3)	302(2)	39(1)
C(42)	7192(4)	1613(3)	1563(2)	41(1)
C(43)	6495(5)	1103(3)	1224(2)	54(1)
C(44)	7005(6)	-31(3)	1283(2)	70(1)
C(45)	8184(6)	-638(3)	1681(3)	76(2)
C(46)	8855(5)	-134(4)	2030(3)	76(2)
C(47)	8373(5)	988(3)	1960(2)	58(1)
C(48)	1681(7)	2368(4)	143(3)	83(2)
C(49)	2219(8)	9138(5)	5557(3)	109(2)
Cl(4)	3552(2)	1459(1)	51(1)	77(1)
Cl(3)	-511(2)	8362(1)	-322(1)	74(1)
Cl(5)	9265(3)	1365(1)	4466(1)	128(1)
Cl(6)	7754(3)	544(2)	3713(1)	168(1)
Cl(2)	5090(1)	6547(1)	5516(1)	64(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb128

Pd(1)-P(1)	2.184(1)	Pd(1)-S(2)	2.319(1)
Pd(1)-S(1)	2.323(1)	Pd(1)-Cl(1)	2.380(1)
S(1)-P(2)	2.023(1)	S(2)-P(3)	2.041(1)
P(1)-C(5)	1.762(3)	P(1)-C(1)	1.777(3)
P(1)-C(6)	1.853(3)	P(2)-C(1)	1.760(3)
P(2)-C(18)	1.798(4)	P(2)-C(12)	1.803(3)

P(3)-C(5)	1.771(3)	P(3)-C(36)	1.802(4)
P(3)-C(42)	1.812(3)	N(1)-C(7)	1.342(5)
N(1)-C(11)	1.342(6)	N(1)-H(1N)	0.77(5)
C(1)-C(2)	1.398(5)	C(2)-C(3)	1.396(5)
C(2)-C(24)	1.504(4)	C(3)-C(4)	1.410(4)
C(3)-H(3)	0.9500	C(4)-C(5)	1.390(5)
C(4)-C(30)	1.487(4)	C(6)-C(7)	1.481(5)
C(6)-H(6A)	0.9900	C(6)-H(6B)	0.9900
C(7)-C(8)	1.369(5)	C(8)-C(9)	1.383(6)
C(8)-H(8)	0.9500	C(9)-C(10)	1.382(7)
C(9)-H(9)	0.9500	C(10)-C(11)	1.344(7)
C(10)-H(10)	0.9500	C(11)-H(11)	0.9500
C(12)-C(13)	1.385(6)	C(12)-C(17)	1.389(5)
C(13)-C(14)	1.391(6)	C(13)-H(13)	0.9500
C(14)-C(15)	1.366(7)	C(14)-H(14)	0.9500
C(15)-C(16)	1.350(7)	C(15)-H(15)	0.9500
C(16)-C(17)	1.367(5)	C(16)-H(16)	0.9500
C(17)-H(17)	0.9500	C(18)-C(23)	1.394(5)
C(18)-C(19)	1.398(5)	C(19)-C(20)	1.379(5)
C(19)-H(19)	0.9500	C(20)-C(21)	1.379(6)
C(20)-H(20)	0.9500	C(21)-C(22)	1.383(6)
C(21)-H(21)	0.9500	C(22)-C(23)	1.398(5)
C(22)-H(22)	0.9500	C(23)-H(23)	0.9500
C(24)-C(29)	1.392(5)	C(24)-C(25)	1.396(5)
C(25)-C(26)	1.384(5)	C(25)-H(25)	0.9500
C(26)-C(27)	1.381(6)	C(26)-H(26)	0.9500
C(27)-C(28)	1.375(6)	C(27)-H(27)	0.9500
C(28)-C(29)	1.394(5)	C(28)-H(28)	0.9500
C(29)-H(29)	0.9500	C(30)-C(31)	1.393(5)
C(30)-C(35)	1.398(5)	C(31)-C(32)	1.394(5)
C(31)-H(31)	0.9500	C(32)-C(33)	1.373(5)
C(32)-H(32)	0.9500	C(33)-C(34)	1.369(6)
C(33)-H(33)	0.9500	C(34)-C(35)	1.386(5)
C(34)-H(34)	0.9500	C(35)-H(35)	0.9500
C(36)-C(37)	1.386(5)	C(36)-C(41)	1.404(5)
C(37)-C(38)	1.379(5)	C(37)-H(37)	0.9500
C(38)-C(39)	1.384(5)	C(38)-H(38)	0.9500
C(39)-C(40)	1.388(5)	C(39)-H(39)	0.9500
C(40)-C(41)	1.372(5)	C(40)-H(40)	0.9500
C(41)-H(41)	0.9500	C(42)-C(47)	1.388(5)
C(42)-C(43)	1.393(6)	C(43)-C(44)	1.393(6)
C(43)-H(43)	0.9500	C(44)-C(45)	1.383(7)
C(44)-H(44)	0.9500	C(45)-C(46)	1.384(8)
C(45)-H(45)	0.9500	C(46)-C(47)	1.378(6)
C(46)-H(46)	0.9500	C(47)-H(47)	0.9500
C(48)-Cl(3)#2	1.743(6)	C(48)-Cl(4)	1.794(6)
C(48)-H(48A)	0.9900	C(48)-H(48B)	0.9900
C(49)-Cl(6)#2	1.727(7)	C(49)-Cl(5)#2	1.783(8)
C(49)-H(49A)	0.9900	C(49)-H(49B)	0.9900
Cl(3)-C(48)#2	1.743(6)	Cl(5)-C(49)#2	1.784(8)
Cl(6)-C(49)#2	1.727(7)		

P(1)-Pd(1)-S(2)	86.55(3)	P(1)-Pd(1)-S(1)	88.39(3)
S(2)-Pd(1)-S(1)	174.37(3)	P(1)-Pd(1)-Cl(1)	173.92(4)
S(2)-Pd(1)-Cl(1)	94.45(3)	S(1)-Pd(1)-Cl(1)	90.84(3)
P(2)-S(1)-Pd(1)	98.70(4)	P(3)-S(2)-Pd(1)	106.00(4)
C(5)-P(1)-C(1)	103.5(2)	C(5)-P(1)-C(6)	102.7(2)
C(1)-P(1)-C(6)	107.9(2)	C(5)-P(1)-Pd(1)	117.2(1)
C(1)-P(1)-Pd(1)	113.5(1)	C(6)-P(1)-Pd(1)	111.1(1)
C(1)-P(2)-C(18)	109.8(2)	C(1)-P(2)-C(12)	114.4(2)
C(18)-P(2)-C(12)	106.0(2)	C(1)-P(2)-S(1)	108.8(1)
C(18)-P(2)-S(1)	110.5(1)	C(12)-P(2)-S(1)	107.2(1)

C(5)-P(3)-C(36)	110.4(2)	C(5)-P(3)-C(42)	113.9(2)
C(36)-P(3)-C(42)	106.8(2)	C(5)-P(3)-S(2)	107.4(1)
C(36)-P(3)-S(2)	112.3(1)	C(42)-P(3)-S(2)	106.1(1)
C(7)-N(1)-C(11)	123.4(4)	C(7)-N(1)-H(1N)	118(4)
C(11)-N(1)-H(1N)	118(4)	C(2)-C(1)-P(2)	129.5(2)
C(2)-C(1)-P(1)	117.8(2)	P(2)-C(1)-P(1)	110.8(2)
C(3)-C(2)-C(1)	122.8(3)	C(3)-C(2)-C(24)	118.3(3)
C(1)-C(2)-C(24)	118.9(3)	C(2)-C(3)-C(4)	125.1(3)
C(2)-C(3)-H(3)	117.4	C(4)-C(3)-H(3)	117.4
C(5)-C(4)-C(3)	122.9(3)	C(5)-C(4)-C(30)	120.3(3)
C(3)-C(4)-C(30)	116.8(3)	C(4)-C(5)-P(1)	117.7(2)
C(4)-C(5)-P(3)	129.2(3)	P(1)-C(5)-P(3)	112.6(2)
C(7)-C(6)-P(1)	114.8(2)	C(7)-C(6)-H(6A)	108.6
P(1)-C(6)-H(6A)	108.6	C(7)-C(6)-H(6B)	108.6
P(1)-C(6)-H(6B)	108.6	H(6A)-C(6)-H(6B)	107.5
N(1)-C(7)-C(8)	117.2(4)	N(1)-C(7)-C(6)	117.4(3)
C(8)-C(7)-C(6)	125.4(3)	C(7)-C(8)-C(9)	121.1(4)
C(7)-C(8)-H(8)	119.4	C(9)-C(8)-H(8)	119.4
C(10)-C(9)-C(8)	118.6(5)	C(10)-C(9)-H(9)	120.7
C(8)-C(9)-H(9)	120.7	C(11)-C(10)-C(9)	119.6(4)
C(11)-C(10)-H(10)	120.2	C(9)-C(10)-H(10)	120.2
N(1)-C(11)-C(10)	120.0(4)	N(1)-C(11)-H(11)	120.0
C(10)-C(11)-H(11)	120.0	C(13)-C(12)-C(17)	119.8(3)
C(13)-C(12)-P(2)	119.2(3)	C(17)-C(12)-P(2)	120.9(3)
C(12)-C(13)-C(14)	118.8(4)	C(12)-C(13)-H(13)	120.6
C(14)-C(13)-H(13)	120.6	C(15)-C(14)-C(13)	120.3(5)
C(15)-C(14)-H(14)	119.9	C(13)-C(14)-H(14)	119.9
C(16)-C(15)-C(14)	120.6(4)	C(16)-C(15)-H(15)	119.7
C(14)-C(15)-H(15)	119.7	C(15)-C(16)-C(17)	120.8(4)
C(15)-C(16)-H(16)	119.6	C(17)-C(16)-H(16)	119.6
C(16)-C(17)-C(12)	119.7(4)	C(16)-C(17)-H(17)	120.2
C(12)-C(17)-H(17)	120.2	C(23)-C(18)-C(19)	119.5(3)
C(23)-C(18)-P(2)	122.1(3)	C(19)-C(18)-P(2)	118.4(3)
C(20)-C(19)-C(18)	120.0(4)	C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0	C(21)-C(20)-C(19)	120.5(4)
C(21)-C(20)-H(20)	119.7	C(19)-C(20)-H(20)	119.7
C(20)-C(21)-C(22)	120.3(4)	C(20)-C(21)-H(21)	119.8
C(22)-C(21)-H(21)	119.8	C(21)-C(22)-C(23)	119.8(4)
C(21)-C(22)-H(22)	120.1	C(23)-C(22)-H(22)	120.1
C(18)-C(23)-C(22)	119.8(3)	C(18)-C(23)-H(23)	120.1
C(22)-C(23)-H(23)	120.1	C(29)-C(24)-C(25)	119.5(3)
C(29)-C(24)-C(2)	121.7(3)	C(25)-C(24)-C(2)	118.8(3)
C(26)-C(25)-C(24)	120.1(4)	C(26)-C(25)-H(25)	119.9
C(24)-C(25)-H(25)	119.9	C(27)-C(26)-C(25)	120.1(4)
C(27)-C(26)-H(26)	120.0	C(25)-C(26)-H(26)	120.0
C(28)-C(27)-C(26)	120.3(3)	C(28)-C(27)-H(27)	119.8
C(26)-C(27)-H(27)	119.8	C(27)-C(28)-C(29)	120.3(4)
C(27)-C(28)-H(28)	119.8	C(29)-C(28)-H(28)	119.8
C(24)-C(29)-C(28)	119.6(4)	C(24)-C(29)-H(29)	120.2
C(28)-C(29)-H(29)	120.2	C(31)-C(30)-C(35)	119.0(3)
C(31)-C(30)-C(4)	122.0(3)	C(35)-C(30)-C(4)	118.9(3)
C(30)-C(31)-C(32)	119.5(3)	C(30)-C(31)-H(31)	120.2
C(32)-C(31)-H(31)	120.2	C(33)-C(32)-C(31)	120.7(4)
C(33)-C(32)-H(32)	119.6	C(31)-C(32)-H(32)	119.6
C(34)-C(33)-C(32)	120.1(3)	C(34)-C(33)-H(33)	120.0
C(32)-C(33)-H(33)	120.0	C(33)-C(34)-C(35)	120.4(3)
C(33)-C(34)-H(34)	119.8	C(35)-C(34)-H(34)	119.8
C(34)-C(35)-C(30)	120.2(4)	C(34)-C(35)-H(35)	119.9
C(30)-C(35)-H(35)	119.9	C(37)-C(36)-C(41)	119.7(3)
C(37)-C(36)-P(3)	121.5(3)	C(41)-C(36)-P(3)	118.7(3)
C(38)-C(37)-C(36)	120.3(3)	C(38)-C(37)-H(37)	119.9
C(36)-C(37)-H(37)	119.9	C(37)-C(38)-C(39)	120.1(3)
C(37)-C(38)-H(38)	120.0	C(39)-C(38)-H(38)	120.0

C(38)-C(39)-C(40)	119.8(4)	C(38)-C(39)-H(39)	120.1
C(40)-C(39)-H(39)	120.1	C(41)-C(40)-C(39)	120.8(3)
C(41)-C(40)-H(40)	119.6	C(39)-C(40)-H(40)	119.6
C(40)-C(41)-C(36)	119.3(3)	C(40)-C(41)-H(41)	120.3
C(36)-C(41)-H(41)	120.3	C(47)-C(42)-C(43)	119.7(3)
C(47)-C(42)-P(3)	119.2(3)	C(43)-C(42)-P(3)	121.0(3)
C(44)-C(43)-C(42)	119.5(4)	C(44)-C(43)-H(43)	120.3
C(42)-C(43)-H(43)	120.3	C(45)-C(44)-C(43)	119.8(5)
C(45)-C(44)-H(44)	120.1	C(43)-C(44)-H(44)	120.1
C(44)-C(45)-C(46)	120.8(4)	C(44)-C(45)-H(45)	119.6
C(46)-C(45)-H(45)	119.6	C(47)-C(46)-C(45)	119.2(5)
C(47)-C(46)-H(46)	120.4	C(45)-C(46)-H(46)	120.4
C(46)-C(47)-C(42)	120.9(4)	C(46)-C(47)-H(47)	119.6
C(42)-C(47)-H(47)	119.6	Cl(3)#2-C(48)-Cl(4)	110.6(3)
Cl(3)#2-C(48)-H(48A)	109.5	Cl(4)-C(48)-H(48A)	109.5
Cl(3)#2-C(48)-H(48B)	109.5	Cl(4)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	108.1	Cl(6)#2-C(49)-Cl(5)#2	105.0(5)
Cl(6)#2-C(49)-H(49A)	110.8	Cl(5)#2-C(49)-H(49A)	110.8
Cl(6)#2-C(49)-H(49B)	110.8	Cl(5)#2-C(49)-H(49B)	110.8
H(49A)-C(49)-H(49B)	108.8		

Estimated standard deviations are given in the parenthesis.

Symmetry operators ::

1: x, y, z 2: -x, -y, -z

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb128

atom	U11	U22	U33	U23	U13	U12
Pd(1)	28(1)	38(1)	36(1)	-1(1)	2(1)	-13(1)
Cl(1)	37(1)	60(1)	53(1)	0(1)	9(1)	-24(1)
S(1)	34(1)	38(1)	58(1)	-6(1)	2(1)	-18(1)
S(2)	29(1)	48(1)	44(1)	-13(1)	7(1)	-12(1)
P(1)	27(1)	31(1)	31(1)	-5(1)	3(1)	-10(1)
P(2)	33(1)	29(1)	36(1)	-6(1)	2(1)	-13(1)
P(3)	29(1)	33(1)	34(1)	-8(1)	3(1)	-8(1)
N(1)	43(2)	46(2)	37(2)	1(1)	-3(2)	-10(1)
C(1)	31(2)	31(2)	32(2)	-6(1)	0(1)	-13(1)
C(2)	30(2)	32(2)	29(2)	-5(1)	4(1)	-9(1)
C(3)	34(2)	35(2)	34(2)	-5(1)	10(1)	-15(1)
C(4)	34(2)	27(2)	31(2)	1(1)	1(1)	-12(1)
C(5)	28(2)	32(2)	35(2)	-6(1)	3(1)	-10(1)
C(6)	36(2)	38(2)	34(2)	0(1)	-1(2)	-14(2)
C(7)	38(2)	38(2)	29(2)	3(1)	-2(2)	-9(2)
C(8)	56(2)	62(2)	36(2)	1(2)	-5(2)	-31(2)
C(9)	78(3)	68(3)	49(3)	10(2)	-21(2)	-41(3)
C(10)	86(4)	49(2)	46(3)	-5(2)	-22(2)	-20(2)
C(11)	66(3)	54(2)	39(2)	-7(2)	-7(2)	-3(2)
C(12)	51(2)	31(2)	37(2)	-6(1)	4(2)	-20(2)
C(13)	75(3)	44(2)	45(2)	-7(2)	-8(2)	-25(2)
C(14)	121(5)	62(3)	38(2)	-12(2)	-6(3)	-43(3)
C(15)	116(5)	55(3)	48(3)	-24(2)	20(3)	-34(3)
C(16)	77(3)	39(2)	54(3)	-17(2)	21(2)	-16(2)
C(17)	51(2)	36(2)	46(2)	-12(2)	7(2)	-18(2)
C(18)	37(2)	29(2)	35(2)	-10(1)	5(2)	-10(1)
C(19)	50(2)	38(2)	45(2)	-4(2)	1(2)	-23(2)
C(20)	65(3)	40(2)	47(2)	5(2)	-5(2)	-17(2)
C(21)	50(2)	44(2)	45(2)	0(2)	-8(2)	-11(2)
C(22)	43(2)	50(2)	42(2)	-8(2)	-1(2)	-14(2)
C(23)	39(2)	39(2)	33(2)	-7(1)	6(2)	-16(2)
C(24)	34(2)	32(2)	40(2)	-6(1)	5(2)	-15(1)

C(25)	45(2)	39(2)	36(2)	-8(2)	7(2)	-18(2)
C(26)	57(3)	39(2)	43(2)	-16(2)	15(2)	-18(2)
C(27)	45(2)	38(2)	65(3)	-19(2)	17(2)	-12(2)
C(28)	34(2)	42(2)	60(3)	-13(2)	6(2)	-10(2)
C(29)	38(2)	36(2)	45(2)	-7(2)	4(2)	-13(2)
C(30)	33(2)	32(2)	36(2)	-7(1)	5(1)	-15(1)
C(31)	37(2)	31(2)	54(2)	-4(2)	3(2)	-11(2)
C(32)	39(2)	45(2)	64(3)	-8(2)	-5(2)	-20(2)
C(33)	51(2)	34(2)	69(3)	-11(2)	-1(2)	-21(2)
C(34)	54(2)	27(2)	65(3)	-1(2)	-4(2)	-15(2)
C(35)	38(2)	37(2)	53(2)	-1(2)	-5(2)	-12(2)
C(36)	34(2)	34(2)	33(2)	-7(1)	4(1)	-12(1)
C(37)	33(2)	35(2)	36(2)	-3(1)	7(2)	-9(1)
C(38)	35(2)	47(2)	45(2)	-2(2)	6(2)	-13(2)
C(39)	50(2)	49(2)	34(2)	5(2)	-5(2)	-21(2)
C(40)	54(2)	49(2)	33(2)	-10(2)	6(2)	-24(2)
C(41)	41(2)	41(2)	35(2)	-9(2)	10(2)	-13(2)
C(42)	36(2)	35(2)	48(2)	-13(2)	6(2)	-4(2)
C(43)	63(3)	41(2)	58(3)	-13(2)	-6(2)	-15(2)
C(44)	98(4)	40(2)	73(3)	-19(2)	1(3)	-22(2)
C(45)	71(3)	32(2)	110(4)	-10(3)	16(3)	-1(2)
C(46)	50(3)	48(3)	110(4)	1(3)	-9(3)	2(2)
C(47)	42(2)	45(2)	79(3)	-10(2)	-12(2)	-6(2)
C(48)	109(5)	54(3)	84(4)	0(3)	-26(3)	-30(3)
C(49)	113(5)	90(4)	101(5)	-21(4)	-22(4)	-3(4)
Cl(4)	72(1)	76(1)	90(1)	-4(1)	-6(1)	-38(1)
Cl(3)	64(1)	74(1)	85(1)	-20(1)	-6(1)	-22(1)
Cl(5)	149(2)	86(1)	98(1)	1(1)	5(1)	14(1)
Cl(6)	218(3)	108(1)	90(1)	-30(1)	-56(1)	53(2)
Cl(2)	77(1)	50(1)	60(1)	-7(1)	27(1)	-18(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb128

atom	x	y	z	U(eq)
H(1N)	6470(50)	4250(40)	4150(20)	53
H(3)	2707	4018	3052	41
H(6A)	6788	3225	3403	44
H(6B)	8313	2990	3052	44
H(8)	9827	4198	3219	58
H(9)	10430	5168	3917	75
H(10)	8800	5757	4704	74
H(11)	6743	5265	4813	69
H(13)	6011	7113	3635	64
H(14)	4985	8276	4373	84
H(15)	2645	9617	4208	85
H(16)	1220	9728	3367	69
H(17)	2135	8551	2647	52
H(19)	4804	8541	1643	51
H(20)	3324	9470	785	62
H(21)	1495	8895	446	58
H(22)	1162	7350	949	55
H(23)	2640	6401	1819	44
H(25)	3521	5876	3996	47
H(26)	1615	7128	4477	54
H(27)	-713	8020	3991	59
H(28)	-1160	7657	3032	55
H(29)	713	6358	2552	47

H(31)	1856	3506	1891	49
H(32)	1185	2036	1709	57
H(33)	2706	264	2059	59
H(34)	4922	-72	2584	59
H(35)	5680	1364	2737	52
H(37)	3407	4466	1324	43
H(38)	1778	5059	480	52
H(39)	2642	4594	-473	53
H(40)	5156	3568	-582	52
H(41)	6791	2945	256	47
H(43)	5678	1525	955	65
H(44)	6542	-386	1051	84
H(45)	8539	-1411	1716	91
H(46)	9639	-556	2314	91
H(47)	8855	1337	2187	69
H(48A)	1671	2813	471	99
H(48B)	1311	2868	-237	99
H(49A)	3180	8576	5471	131
H(49B)	2030	9793	5256	131

I.4. Crystallographic data for II-11

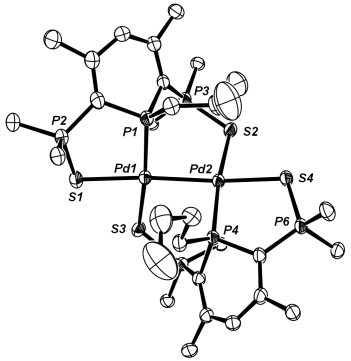


Table 1. Crystal data for mb122

Compound	mb122
Molecular formula	$C_{90}H_{80}P_6Pd_2S_4,C_4H_8O$
Molecular weight	1762.52
Crystal habit	red block
Crystal dimensions(mm)	0.22x0.20x0.16
Crystal system	triclinic
Space group	Pbar1
a(Å)	15.4760(10)
b(Å)	16.9140(10)
c(Å)	19.0940(10)
α(°)	67.3430(10)
β(°)	81.3850(10)

γ(°)	88.8490(10)
V(Å^3)	4556.4(5)
Z	2
d(g-cm^{-3})	1.285
F(000)	1816
μ(cm^{-1})	0.635
Absorption corrections	multi-scan ; 0.8728 min, 0.9052 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	27.48
HKL ranges	-20 20 ; -17 21 ; -22 24
Reflections measured	38721
Unique data	20337
Rint	0.0268
Reflections used	17311
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	921
Reflections / parameter	18
wR2	0.1426
R1	0.0446
Weights a, b	0.0796 ; 4.1503
GoF	1.093
difference peak / hole (e Å^{-3})	1.116(0.093) / -1.332(0.093)

Note: A cavity near 0,0,1/2 contains a very poorly resolved ether molecule that was accounted for using the Platon SQUEEZE function.

We were unable to determine wether the large thermal displacements observed for some carbon atoms of the phenyl ring defined by C16 to C21 are due to systematic errors or the result of a non resolved disorder.

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb122

atom	x	y	z	U(eq)
Pd(1)	3550(1)	326(1)	7274(1)	26(1)
Pd(2)	2793(1)	-937(1)	8464(1)	25(1)
S(1)	4324(1)	1398(1)	6111(1)	36(1)
S(2)	1960(1)	-131(1)	9082(1)	30(1)
S(3)	4927(1)	182(1)	7683(1)	30(1)
S(4)	1913(1)	-2123(1)	9411(1)	33(1)
P(1)	2237(1)	739(1)	6918(1)	27(1)
P(2)	3404(1)	1725(1)	5427(1)	34(1)
P(3)	1919(1)	1094(1)	8357(1)	25(1)

P(4)	3678(1)	-1806(1)	8081(1)	25(1)
P(5)	5123(1)	-972(1)	8473(1)	25(1)
P(6)	2426(1)	-3175(1)	9310(1)	29(1)
C(1)	2361(2)	1628(2)	5985(2)	34(1)
C(2)	1651(2)	2147(2)	5800(2)	37(1)
C(3)	909(2)	2085(2)	6353(2)	37(1)
C(4)	893(2)	1723(2)	7148(2)	31(1)
C(5)	1575(2)	1228(2)	7481(2)	27(1)
C(6)	1451(2)	29(2)	6780(2)	34(1)
C(7)	966(2)	-651(2)	7510(2)	41(1)
C(8)	175(3)	-1060(3)	7376(3)	60(1)
C(9)	357(4)	-1463(5)	6813(4)	101(2)
C(10)	3406(2)	1033(2)	4900(2)	38(1)
C(11)	2630(2)	710(2)	4811(2)	45(1)
C(12)	2635(3)	175(3)	4403(2)	52(1)
C(13)	3424(3)	-34(2)	4087(2)	52(1)
C(14)	4204(3)	278(2)	4181(2)	48(1)
C(15)	4197(2)	807(2)	4582(2)	44(1)
C(16)	3727(2)	2799(2)	4730(2)	46(1)
C(17)	3796(5)	3438(3)	4989(3)	90(2)
C(18)	4100(6)	4268(4)	4495(4)	122(3)
C(19)	4320(5)	4457(4)	3737(4)	100(2)
C(20)	4238(5)	3836(4)	3468(3)	104(3)
C(21)	3930(4)	2999(3)	3963(2)	81(2)
C(22)	1634(3)	2893(3)	5042(2)	59(1)
C(23)	1492(6)	3706(4)	5065(4)	108(2)
C(24)	1422(7)	4428(5)	4394(4)	139(4)
C(25)	1575(5)	4312(5)	3739(4)	112(3)
C(26)	1650(5)	3586(5)	3669(3)	103(2)
C(27)	1713(4)	2823(4)	4365(3)	81(2)
C(28)	107(2)	1899(2)	7614(2)	34(1)
C(29)	-191(3)	2728(3)	7427(3)	54(1)
C(30)	-913(3)	2887(3)	7862(3)	65(1)
C(31)	-1354(2)	2237(3)	8486(3)	58(1)
C(32)	-1088(2)	1409(3)	8667(2)	51(1)
C(33)	-356(2)	1237(2)	8234(2)	37(1)
C(34)	1264(2)	1647(2)	8886(2)	27(1)
C(35)	1331(2)	2535(2)	8611(2)	44(1)
C(36)	874(3)	2960(2)	9031(3)	56(1)
C(37)	348(2)	2516(2)	9716(2)	42(1)
C(38)	269(2)	1636(2)	9987(2)	37(1)
C(39)	726(2)	1198(2)	9573(2)	30(1)
C(40)	2968(2)	1658(2)	8152(2)	30(1)
C(41)	3443(2)	1488(2)	8754(2)	35(1)
C(42)	4220(2)	1943(2)	8650(2)	43(1)
C(43)	4520(2)	2576(3)	7943(3)	51(1)
C(44)	4051(3)	2759(3)	7351(2)	51(1)
C(45)	3270(2)	2304(2)	7441(2)	40(1)
C(46)	4814(2)	-1833(2)	8235(2)	27(1)
C(47)	5277(2)	-2539(2)	8214(2)	29(1)
C(48)	4851(2)	-3299(2)	8259(2)	31(1)
C(49)	3968(2)	-3515(2)	8511(2)	31(1)
C(50)	3363(2)	-2917(2)	8614(2)	29(1)
C(51)	3807(2)	-1696(2)	7079(2)	30(1)
C(52)	2955(2)	-1873(2)	6839(2)	40(1)
C(53)	3052(3)	-1757(3)	6003(2)	65(1)
C(54)	3593(4)	-2381(5)	5810(4)	110(2)
C(55)	6255(2)	-942(2)	8620(2)	28(1)
C(56)	6552(2)	-1561(2)	9253(2)	34(1)
C(57)	7407(2)	-1514(2)	9375(2)	42(1)
C(58)	7967(2)	-837(2)	8872(2)	44(1)
C(59)	7676(2)	-218(2)	8252(2)	43(1)
C(60)	6822(2)	-263(2)	8119(2)	35(1)

C(61)	4490(2)	-1158(2)	9409(2)	29(1)
C(62)	4301(2)	-464(2)	9617(2)	37(1)
C(63)	3838(2)	-592(2)	10332(2)	42(1)
C(64)	3571(2)	-1412(2)	10849(2)	40(1)
C(65)	3763(2)	-2108(2)	10649(2)	37(1)
C(66)	4226(2)	-1984(2)	9934(2)	32(1)
C(67)	6245(2)	-2568(2)	8155(2)	30(1)
C(68)	6637(2)	-3260(2)	8658(2)	43(1)
C(69)	7543(3)	-3293(3)	8596(3)	60(1)
C(70)	8064(3)	-2645(3)	8020(3)	60(1)
C(71)	7686(2)	-1969(3)	7509(3)	53(1)
C(72)	6779(2)	-1935(2)	7572(2)	37(1)
C(73)	3682(2)	-4414(2)	8650(2)	34(1)
C(74)	3097(3)	-4559(2)	8226(2)	46(1)
C(75)	2879(3)	-5382(2)	8298(3)	54(1)
C(76)	3248(3)	-6076(2)	8811(3)	58(1)
C(77)	3832(3)	-5949(2)	9241(3)	56(1)
C(78)	4044(3)	-5119(2)	9164(2)	46(1)
C(79)	2651(2)	-3870(2)	10256(2)	33(1)
C(80)	1946(2)	-4114(2)	10858(2)	43(1)
C(81)	2086(3)	-4578(3)	11606(2)	53(1)
C(82)	2910(3)	-4779(2)	11765(2)	51(1)
C(83)	3619(3)	-4537(2)	11177(2)	47(1)
C(84)	3485(2)	-4088(2)	10426(2)	38(1)
C(85)	1580(2)	-3758(2)	9112(2)	37(1)
C(86)	1095(2)	-3304(3)	8540(3)	52(1)
C(87)	467(3)	-3728(4)	8346(4)	73(1)
C(88)	302(3)	-4599(4)	8734(4)	77(2)
C(89)	765(4)	-5045(3)	9311(3)	73(2)
C(90)	1418(3)	-4636(2)	9498(2)	53(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb122

Pd(1)-P(1)	2.2515(8	Pd(1)-S(3)	2.3540(8)
Pd(1)-S(1)	2.4171(8	Pd(1)-Pd(2)	2.5815(3)
Pd(2)-P(4)	2.2396(7	Pd(2)-S(2)	2.3721(7)
Pd(2)-S(4)	2.3924(7	S(1)-P(2)	2.001(1)
S(2)-P(3)	2.006(1)	S(3)-P(5)	2.005(1)
S(4)-P(6)	2.000(1)	P(1)-C(5)	1.790(3)
P(1)-C(1)	1.822(3)	P(1)-C(6)	1.842(3)
P(2)-C(1)	1.768(3)	P(2)-C(10)	1.814(4)
P(2)-C(16)	1.816(4)	P(3)-C(5)	1.762(3)
P(3)-C(40)	1.812(3)	P(3)-C(34)	1.818(3)
P(4)-C(50)	1.794(3)	P(4)-C(46)	1.823(3)
P(4)-C(51)	1.831(3)	P(5)-C(46)	1.776(3)
P(5)-C(61)	1.819(3)	P(5)-C(55)	1.820(3)
P(6)-C(50)	1.749(3)	P(6)-C(79)	1.817(3)
P(6)-C(85)	1.821(3)	C(1)-C(2)	1.393(5)
C(2)-C(3)	1.414(4)	C(2)-C(22)	1.514(5)
C(3)-C(4)	1.398(4)	C(4)-C(5)	1.405(4)
C(4)-C(28)	1.490(4)	C(6)-C(7)	1.522(5)
C(7)-C(8)	1.518(5)	C(8)-C(9)	1.472(7)
C(10)-C(11)	1.389(5)	C(10)-C(15)	1.397(5)
C(11)-C(12)	1.402(6)	C(12)-C(13)	1.381(6)
C(13)-C(14)	1.388(6)	C(14)-C(15)	1.383(5)
C(16)-C(21)	1.358(5)	C(16)-C(17)	1.362(7)
C(17)-C(18)	1.399(7)	C(18)-C(19)	1.345(9)
C(19)-C(20)	1.350(9)	C(20)-C(21)	1.410(7)
C(22)-C(27)	1.329(6)	C(22)-C(23)	1.404(8)
C(23)-C(24)	1.406(8)	C(24)-C(25)	1.33(1)
C(25)-C(26)	1.29(1)	C(26)-C(27)	1.468(7)

C(28)-C(33)	1.388(5)	C(28)-C(29)	1.395(5)
C(29)-C(30)	1.377(5)	C(30)-C(31)	1.368(7)
C(31)-C(32)	1.376(6)	C(32)-C(33)	1.394(5)
C(34)-C(39)	1.385(4)	C(34)-C(35)	1.389(4)
C(35)-C(36)	1.384(5)	C(36)-C(37)	1.373(5)
C(37)-C(38)	1.377(5)	C(38)-C(39)	1.391(4)
C(40)-C(41)	1.391(5)	C(40)-C(45)	1.393(4)
C(41)-C(42)	1.388(5)	C(42)-C(43)	1.379(6)
C(43)-C(44)	1.366(6)	C(44)-C(45)	1.398(5)
C(46)-C(47)	1.391(4)	C(47)-C(48)	1.424(4)
C(47)-C(67)	1.487(4)	C(48)-C(49)	1.386(4)
C(49)-C(50)	1.414(4)	C(49)-C(73)	1.504(4)
C(51)-C(52)	1.529(4)	C(52)-C(53)	1.516(5)
C(53)-C(54)	1.457(8)	C(55)-C(56)	1.393(4)
C(55)-C(60)	1.396(4)	C(56)-C(57)	1.388(5)
C(57)-C(58)	1.387(5)	C(58)-C(59)	1.374(5)
C(59)-C(60)	1.391(5)	C(61)-C(62)	1.389(4)
C(61)-C(66)	1.395(4)	C(62)-C(63)	1.381(5)
C(63)-C(64)	1.383(5)	C(64)-C(65)	1.386(5)
C(65)-C(66)	1.382(4)	C(67)-C(72)	1.383(5)
C(67)-C(68)	1.394(4)	C(68)-C(69)	1.391(5)
C(69)-C(70)	1.379(7)	C(70)-C(71)	1.373(6)
C(71)-C(72)	1.393(5)	C(73)-C(74)	1.383(5)
C(73)-C(78)	1.391(5)	C(74)-C(75)	1.389(5)
C(75)-C(76)	1.384(6)	C(76)-C(77)	1.380(7)
C(77)-C(78)	1.396(5)	C(79)-C(84)	1.386(5)
C(79)-C(80)	1.399(4)	C(80)-C(81)	1.388(5)
C(81)-C(82)	1.362(6)	C(82)-C(83)	1.388(5)
C(83)-C(84)	1.385(5)	C(85)-C(86)	1.387(6)
C(85)-C(90)	1.388(5)	C(86)-C(87)	1.391(6)
C(87)-C(88)	1.378(8)	C(88)-C(89)	1.367(8)
C(89)-C(90)	1.397(7)		

P(1)-Pd(1)-S(3)	167.37(3)	P(1)-Pd(1)-S(1)	92.48(3)
S(3)-Pd(1)-S(1)	83.62(3)	P(1)-Pd(1)-Pd(2)	89.83(2)
S(3)-Pd(1)-Pd(2)	95.26(2)	S(1)-Pd(1)-Pd(2)	174.02(2)
P(4)-Pd(2)-S(2)	169.54(3)	P(4)-Pd(2)-S(4)	92.06(3)
S(2)-Pd(2)-S(4)	83.75(3)	P(4)-Pd(2)-Pd(1)	87.60(2)
S(2)-Pd(2)-Pd(1)	98.27(2)	S(4)-Pd(2)-Pd(1)	169.41(2)
P(2)-S(1)-Pd(1)	102.05(4)	P(3)-S(2)-Pd(2)	110.76(4)
P(5)-S(3)-Pd(1)	115.11(4)	P(6)-S(4)-Pd(2)	106.02(4)
C(5)-P(1)-C(1)	99.5(1)	C(5)-P(1)-C(6)	103.3(1)
C(1)-P(1)-C(6)	100.6(2)	C(5)-P(1)-Pd(1)	115.5(1)
C(1)-P(1)-Pd(1)	110.9(1)	C(6)-P(1)-Pd(1)	123.6(1)
C(1)-P(2)-C(10)	108.5(2)	C(1)-P(2)-C(16)	114.9(2)
C(10)-P(2)-C(16)	107.2(2)	C(1)-P(2)-S(1)	109.9(1)
C(10)-P(2)-S(1)	110.7(1)	C(16)-P(2)-S(1)	105.5(1)
C(5)-P(3)-C(40)	108.7(1)	C(5)-P(3)-C(34)	113.8(1)
C(40)-P(3)-C(34)	100.6(1)	C(5)-P(3)-S(2)	114.5(1)
C(40)-P(3)-S(2)	111.4(1)	C(34)-P(3)-S(2)	107.0(1)
C(50)-P(4)-C(46)	99.1(1)	C(50)-P(4)-C(51)	103.7(1)
C(46)-P(4)-C(51)	101.3(1)	C(50)-P(4)-Pd(2)	112.4(1)
C(46)-P(4)-Pd(2)	118.1(1)	C(51)-P(4)-Pd(2)	119.4(1)
C(46)-P(5)-C(61)	105.5(1)	C(46)-P(5)-C(55)	115.6(1)
C(61)-P(5)-C(55)	104.2(1)	C(46)-P(5)-S(3)	112.9(1)
C(61)-P(5)-S(3)	112.3(1)	C(55)-P(5)-S(3)	106.1(1)
C(50)-P(6)-C(79)	112.4(2)	C(50)-P(6)-C(85)	113.1(2)
C(79)-P(6)-C(85)	104.8(2)	C(50)-P(6)-S(4)	111.2(1)
C(79)-P(6)-S(4)	106.7(1)	C(85)-P(6)-S(4)	108.3(1)
C(2)-C(1)-P(2)	128.2(2)	C(2)-C(1)-P(1)	117.8(2)
P(2)-C(1)-P(1)	114.0(2)	C(1)-C(2)-C(3)	121.8(3)
C(1)-C(2)-C(22)	124.6(3)	C(3)-C(2)-C(22)	113.2(3)

C(4)-C(3)-C(2)	125.0(3)	C(3)-C(4)-C(5)	121.8(3)
C(3)-C(4)-C(28)	115.5(3)	C(5)-C(4)-C(28)	122.7(3)
C(4)-C(5)-P(3)	127.9(2)	C(4)-C(5)-P(1)	116.7(2)
P(3)-C(5)-P(1)	115.2(2)	C(7)-C(6)-P(1)	115.7(2)
C(8)-C(7)-C(6)	113.2(3)	C(9)-C(8)-C(7)	115.3(4)
C(11)-C(10)-C(15)	118.7(3)	C(11)-C(10)-P(2)	121.2(3)
C(15)-C(10)-P(2)	120.1(3)	C(10)-C(11)-C(12)	121.0(3)
C(13)-C(12)-C(11)	119.4(4)	C(12)-C(13)-C(14)	120.1(4)
C(15)-C(14)-C(13)	120.4(3)	C(14)-C(15)-C(10)	120.5(4)
C(21)-C(16)-C(17)	117.9(4)	C(21)-C(16)-P(2)	123.6(4)
C(17)-C(16)-P(2)	118.5(3)	C(16)-C(17)-C(18)	121.9(5)
C(19)-C(18)-C(17)	119.9(6)	C(18)-C(19)-C(20)	118.9(5)
C(19)-C(20)-C(21)	121.4(5)	C(16)-C(21)-C(20)	119.9(5)
C(27)-C(22)-C(23)	118.3(5)	C(27)-C(22)-C(2)	124.5(5)
C(23)-C(22)-C(2)	117.2(4)	C(22)-C(23)-C(24)	121.2(6)
C(25)-C(24)-C(23)	116.4(7)	C(26)-C(25)-C(24)	126.1(7)
C(25)-C(26)-C(27)	117.5(6)	C(22)-C(27)-C(26)	119.8(5)
C(33)-C(28)-C(29)	118.4(3)	C(33)-C(28)-C(4)	120.7(3)
C(29)-C(28)-C(4)	120.9(3)	C(30)-C(29)-C(28)	120.6(4)
C(31)-C(30)-C(29)	120.7(4)	C(30)-C(31)-C(32)	119.7(4)
C(31)-C(32)-C(33)	120.3(4)	C(28)-C(33)-C(32)	120.2(4)
C(39)-C(34)-C(35)	119.4(3)	C(39)-C(34)-P(3)	121.4(2)
C(35)-C(34)-P(3)	119.1(2)	C(36)-C(35)-C(34)	119.7(3)
C(37)-C(36)-C(35)	121.0(3)	C(36)-C(37)-C(38)	119.6(3)
C(37)-C(38)-C(39)	120.1(3)	C(34)-C(39)-C(38)	120.2(3)
C(41)-C(40)-C(45)	119.4(3)	C(41)-C(40)-P(3)	117.8(2)
C(45)-C(40)-P(3)	122.5(3)	C(42)-C(41)-C(40)	120.7(3)
C(43)-C(42)-C(41)	119.6(3)	C(44)-C(43)-C(42)	120.3(3)
C(43)-C(44)-C(45)	121.2(4)	C(40)-C(45)-C(44)	118.9(3)
C(47)-C(46)-P(5)	130.1(2)	C(47)-C(46)-P(4)	116.9(2)
P(5)-C(46)-P(4)	112.8(2)	C(46)-C(47)-C(48)	122.1(3)
C(46)-C(47)-C(67)	123.1(3)	C(48)-C(47)-C(67)	114.8(2)
C(49)-C(48)-C(47)	125.1(3)	C(48)-C(49)-C(50)	121.9(3)
C(48)-C(49)-C(73)	116.4(3)	C(50)-C(49)-C(73)	121.7(3)
C(49)-C(50)-P(6)	124.8(2)	C(49)-C(50)-P(4)	116.3(2)
P(6)-C(50)-P(4)	118.3(2)	C(52)-C(51)-P(4)	113.2(2)
C(53)-C(52)-C(51)	113.4(3)	C(54)-C(53)-C(52)	114.6(4)
C(56)-C(55)-C(60)	119.3(3)	C(56)-C(55)-P(5)	120.9(2)
C(60)-C(55)-P(5)	119.7(2)	C(57)-C(56)-C(55)	120.4(3)
C(58)-C(57)-C(56)	119.9(3)	C(59)-C(58)-C(57)	120.0(3)
C(58)-C(59)-C(60)	120.6(3)	C(59)-C(60)-C(55)	119.8(3)
C(62)-C(61)-C(66)	119.4(3)	C(62)-C(61)-P(5)	119.1(2)
C(66)-C(61)-P(5)	121.4(2)	C(63)-C(62)-C(61)	120.1(3)
C(62)-C(63)-C(64)	120.3(3)	C(63)-C(64)-C(65)	119.9(3)
C(66)-C(65)-C(64)	120.0(3)	C(65)-C(66)-C(61)	120.2(3)
C(72)-C(67)-C(68)	118.2(3)	C(72)-C(67)-C(47)	120.8(3)
C(68)-C(67)-C(47)	120.9(3)	C(69)-C(68)-C(67)	120.8(4)
C(70)-C(69)-C(68)	120.0(4)	C(71)-C(70)-C(69)	119.9(4)
C(70)-C(71)-C(72)	120.2(4)	C(67)-C(72)-C(71)	120.9(3)
C(74)-C(73)-C(78)	118.4(3)	C(74)-C(73)-C(49)	120.5(3)
C(78)-C(73)-C(49)	121.0(3)	C(73)-C(74)-C(75)	121.5(4)
C(76)-C(75)-C(74)	119.4(4)	C(77)-C(76)-C(75)	120.2(3)
C(76)-C(77)-C(78)	119.8(4)	C(73)-C(78)-C(77)	120.6(4)
C(84)-C(79)-C(80)	118.7(3)	C(84)-C(79)-P(6)	123.7(2)
C(80)-C(79)-P(6)	117.2(3)	C(81)-C(80)-C(79)	120.1(3)
C(82)-C(81)-C(80)	120.5(3)	C(81)-C(82)-C(83)	120.3(4)
C(84)-C(83)-C(82)	119.7(4)	C(83)-C(84)-C(79)	120.7(3)
C(86)-C(85)-C(90)	119.1(3)	C(86)-C(85)-P(6)	118.2(3)
C(90)-(85)-P(6)	122.7(3)	C(85)-C(86)-C(87)	120.2(4)
C(88)-C(87)-C(86)	120.5(5)	C(89)-C(88)-C(87)	119.3(4)
C(88)-C(89)-C(90)	121.0(4)	C(85)-C(90)-C(89)	119.7(5)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb122

atom	U11	U22	U33	U23	U13	U12
Pd(1)	26(1)	22(1)	25(1)	-6(1)	1(1)	-1(1)
Pd(2)	27(1)	18(1)	26(1)	-7(1)	3(1)	0(1)
S(1)	31(1)	38(1)	28(1)	-3(1)	1(1)	-3(1)
S(2)	37(1)	21(1)	26(1)	-7(1)	3(1)	4(1)
S(3)	31(1)	21(1)	34(1)	-5(1)	-5(1)	-1(1)
S(4)	33(1)	21(1)	37(1)	-9(1)	12(1)	-2(1)
P(1)	28(1)	26(1)	25(1)	-8(1)	2(1)	0(1)
P(2)	34(1)	36(1)	23(1)	-5(1)	3(1)	2(1)
P(3)	27(1)	20(1)	25(1)	-7(1)	1(1)	1(1)
P(4)	26(1)	20(1)	26(1)	-8(1)	3(1)	-2(1)
P(5)	27(1)	21(1)	27(1)	-8(1)	-1(1)	1(1)
P(6)	29(1)	20(1)	31(1)	-7(1)	6(1)	-3(1)
C(1)	34(2)	36(2)	27(2)	-9(1)	4(1)	-1(1)
C(2)	37(2)	39(2)	28(2)	-8(1)	-1(1)	0(1)
C(3)	31(2)	38(2)	33(2)	-6(1)	-4(1)	7(1)
C(4)	28(1)	28(2)	32(2)	-8(1)	1(1)	0(1)
C(5)	26(1)	25(1)	24(1)	-7(1)	2(1)	-2(1)
C(6)	34(2)	35(2)	33(2)	-14(1)	-3(1)	-1(1)
C(7)	38(2)	38(2)	46(2)	-18(2)	6(1)	-9(1)
C(8)	45(2)	57(3)	74(3)	-21(2)	-4(2)	-16(2)
C(9)	100(4)	113(5)	97(5)	-55(4)	12(4)	-51(4)
C(10)	38(2)	41(2)	25(2)	-7(1)	3(1)	3(1)
C(11)	47(2)	50(2)	32(2)	-11(2)	-1(1)	2(2)
C(12)	60(2)	57(2)	36(2)	-13(2)	-7(2)	-4(2)
C(13)	81(3)	38(2)	32(2)	-10(2)	0(2)	0(2)
C(14)	56(2)	37(2)	39(2)	-7(2)	10(2)	7(2)
C(15)	44(2)	38(2)	37(2)	-6(2)	5(1)	4(1)
C(16)	43(2)	47(2)	29(2)	2(2)	4(1)	5(2)
C(17)	156(6)	51(3)	46(3)	-3(2)	-3(3)	-49(3)
C(18)	217(9)	54(3)	66(4)	5(3)	-6(5)	-52(4)
C(19)	136(6)	50(3)	69(4)	8(3)	35(4)	-4(3)
C(20)	169(7)	66(3)	34(2)	10(2)	35(3)	26(4)
C(21)	139(5)	46(2)	35(2)	-2(2)	18(3)	35(3)
C(22)	47(2)	78(3)	32(2)	0(2)	-2(2)	14(2)
C(23)	195(8)	53(3)	56(3)	1(3)	-20(4)	6(4)
C(24)	250(10)	75(4)	61(4)	1(3)	-5(5)	16(6)
C(25)	151(7)	109(5)	53(3)	-15(3)	4(4)	41(5)
C(26)	139(6)	105(5)	40(3)	-12(3)	9(3)	40(4)
C(27)	97(4)	100(4)	47(3)	-26(3)	-23(3)	54(3)
C(28)	26(1)	39(2)	34(2)	-13(1)	-3(1)	2(1)
C(29)	43(2)	46(2)	66(3)	-20(2)	6(2)	7(2)
C(30)	47(2)	62(3)	94(4)	-42(3)	1(2)	16(2)
C(31)	29(2)	94(3)	67(3)	-49(3)	0(2)	9(2)
C(32)	30(2)	85(3)	38(2)	-27(2)	1(1)	-4(2)
C(33)	28(2)	48(2)	34(2)	-15(2)	-1(1)	-2(1)
C(34)	25(1)	28(1)	30(2)	-12(1)	-2(1)	2(1)
C(35)	46(2)	26(2)	52(2)	-14(2)	12(2)	-3(1)
C(36)	58(2)	29(2)	76(3)	-27(2)	21(2)	-4(2)
C(37)	36(2)	42(2)	56(2)	-31(2)	2(2)	3(1)
C(38)	28(2)	44(2)	38(2)	-19(2)	1(1)	5(1)
C(39)	29(1)	27(1)	34(2)	-12(1)	-3(1)	3(1)
C(40)	27(1)	25(1)	35(2)	-12(1)	3(1)	1(1)
C(41)	33(2)	34(2)	40(2)	-17(1)	-5(1)	3(1)
C(42)	36(2)	46(2)	56(2)	-28(2)	-11(2)	6(2)
C(43)	38(2)	57(2)	66(3)	-36(2)	5(2)	-13(2)
C(44)	50(2)	50(2)	46(2)	-17(2)	8(2)	-22(2)
C(45)	41(2)	38(2)	35(2)	-12(1)	3(1)	-8(1)
C(46)	30(1)	21(1)	26(1)	-8(1)	1(1)	-1(1)

C(47)	33(2)	24(1)	26(1)	-9(1)	2(1)	2(1)
C(48)	34(2)	24(1)	34(2)	-13(1)	4(1)	2(1)
C(49)	37(2)	20(1)	32(2)	-8(1)	5(1)	-2(1)
C(50)	31(2)	21(1)	31(2)	-9(1)	7(1)	-4(1)
C(51)	33(2)	26(1)	29(2)	-9(1)	2(1)	-3(1)
C(52)	38(2)	42(2)	41(2)	-18(2)	-5(1)	1(1)
C(53)	70(3)	82(3)	41(2)	-19(2)	-13(2)	-11(2)
C(54)	101(5)	171(7)	92(5)	-94(5)	10(4)	-24(5)
C(55)	27(1)	26(1)	32(2)	-13(1)	-3(1)	1(1)
C(56)	34(2)	30(2)	34(2)	-8(1)	-2(1)	2(1)
C(57)	39(2)	44(2)	39(2)	-11(2)	-12(1)	10(2)
C(58)	32(2)	53(2)	50(2)	-20(2)	-11(2)	3(2)
C(59)	32(2)	43(2)	47(2)	-12(2)	-2(1)	-5(1)
C(60)	32(2)	34(2)	33(2)	-9(1)	-3(1)	-1(1)
C(61)	29(1)	26(1)	29(2)	-10(1)	1(1)	2(1)
C(62)	42(2)	31(2)	39(2)	-17(1)	-3(1)	6(1)
C(63)	44(2)	44(2)	43(2)	-25(2)	-5(2)	10(2)
C(64)	36(2)	54(2)	30(2)	-19(2)	1(1)	3(2)
C(65)	35(2)	39(2)	31(2)	-9(1)	0(1)	-5(1)
C(66)	32(2)	27(1)	32(2)	-10(1)	0(1)	-1(1)
C(67)	33(2)	24(1)	35(2)	-15(1)	-2(1)	4(1)
C(68)	48(2)	29(2)	52(2)	-13(2)	-15(2)	8(1)
C(69)	55(2)	45(2)	91(3)	-30(2)	-35(2)	25(2)
C(70)	35(2)	57(2)	95(4)	-37(3)	-14(2)	11(2)
C(71)	32(2)	56(2)	71(3)	-27(2)	1(2)	3(2)
C(72)	33(2)	36(2)	38(2)	-11(1)	-1(1)	6(1)
C(73)	34(2)	23(1)	41(2)	-13(1)	9(1)	-2(1)
C(74)	57(2)	31(2)	52(2)	-20(2)	0(2)	-2(2)
C(75)	56(2)	41(2)	74(3)	-33(2)	-1(2)	-7(2)
C(76)	65(3)	25(2)	79(3)	-24(2)	19(2)	-8(2)
C(77)	68(3)	22(2)	68(3)	-14(2)	3(2)	1(2)
C(78)	53(2)	24(2)	56(2)	-13(2)	-2(2)	4(1)
C(79)	38(2)	22(1)	33(2)	-8(1)	5(1)	-1(1)
C(80)	41(2)	40(2)	36(2)	-5(2)	6(1)	0(1)
C(81)	57(2)	50(2)	33(2)	-3(2)	10(2)	1(2)
C(82)	66(3)	42(2)	32(2)	-3(2)	-2(2)	6(2)
C(83)	52(2)	33(2)	49(2)	-7(2)	-8(2)	13(2)
C(84)	41(2)	25(2)	41(2)	-9(1)	3(1)	3(1)
C(85)	33(2)	32(2)	45(2)	-19(2)	10(1)	-9(1)
C(86)	36(2)	45(2)	78(3)	-27(2)	-6(2)	-3(2)
C(87)	43(2)	84(4)	110(4)	-54(3)	-15(2)	-4(2)
C(88)	58(3)	92(4)	99(4)	-67(4)	24(3)	-40(3)
C(89)	94(4)	57(3)	71(3)	-42(3)	36(3)	-46(3)
C(90)	73(3)	34(2)	47(2)	-18(2)	14(2)	-19(2)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb122

atom	x	y	z	U(eq)
H(3)	381	2307	6170	44
H(6A)	1013	389	6484	41
H(6B)	1768	-262	6463	41
H(7A)	1374	-1103	7738	49
H(7B)	772	-386	7885	49
H(8A)	-97	-1500.9999	7873	73
H(8B)	-258	-615	7202	73
H(9A)	578	-1025	6307	152
H(9B)	-183	-1737	6786	152

H(9C)	796	-1896	6971	152
H(11)	2087	853	5029	54
H(12)	2101	-42	4344	63
H(13)	3434	-392	3806	63
H(14)	4745	127	3967	58
H(15)	4734	1018	4641	52
H(17)	3632	3316	5521	108
H(18)	4152	4697	4693	147
H(19)	4529	5019	3397	120
H(20)	4391	3967	2933	125
H(21)	3864	2575	3759	98
H(23)	1443	3768	5542	130
H(24)	1273	4969	4409	166
H(25)	1635	4811	3278	134
H(26)	1665	3545	3185	123
H(27)	1808	2281	4333	97
H(29)	106	3186	6995	65
H(30)	-1108	3456	7728	78
H(31)	-1841	2356	8792	70
H(32)	-1405	954	9089	61
H(33)	-175	665	8364	45
H(35)	1690	2851	8136	52
H(36)	924	3568	8844	67
H(37)	40	2815	10001	51
H(38)	-99	1326	10458	44
H(39)	670	591	9762	36
H(41)	3233	1055	9242	42
H(42)	4543	1821	9063	52
H(43)	5055	2885	7867	61
H(44)	4258	3204	6870	61
H(45)	2951	2433	7025	47
H(48)	5200	-3689	8104	37
H(51A)	4032	-1107	6743	36
H(51B)	4247	-2098	7000	36
H(52A)	2740	-2468	7165	48
H(52B)	2509	-1483.0001	6934	48
H(53A)	2463	-1791.0001	5871	78
H(53B)	3309	-1175	5681	78
H(54A)	4204	-2279	5841	166
H(54B)	3543	-2323	5287	166
H(54C)	3394	-2961	6172	166
H(56)	6166	-2019	9603	41
H(57)	7610	-1944	9802	50
H(58)	8552	-802	8958	53
H(59)	8061	244	7910	52
H(60)	6626	167	7688	42
H(62)	4490	99	9267	44
H(63)	3702	-115	10468	50
H(64)	3256	-1497	11341	48
H(65)	3577	-2671	11003	44
H(66)	4363	-2463	9801	38
H(68)	6282	-3714.9998	9049	51
H(69)	7803	-3761	8950	72
H(70)	8682	-2666.0002	7977	71
H(71)	8045	-1523	7111	64
H(72)	6524	-1470	7210	45
H(74)	2839	-4084	7878	55
H(75)	2481	-5468.9995	7999	65
H(76)	3098	-6642	8867	70
H(77)	4089	-6426	9589	67
H(78)	4440	-5033	9467	55
H(80)	1371	-3963	10754	51
H(81)	1603	-4756	12011	63

H(82)	3001	-5086	12280	61
H(83)	4193	-4679	11288	57
H(84)	3970	-3926.9998	10023	45
H(86)	1192	-2702.0002	8279	63
H(87)	150	-3416	7944	88
H(88)	-128	-4886	8602	92
H(89)	639	-5641.0005	9590	88
H(90)	1750	-4958	9886	64

I.5. Crystallographic data for II-12

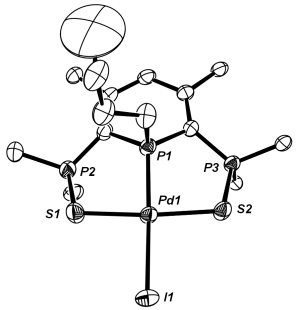


Table 1. Crystal data for mb403

Compound	mb403
Molecular formula	$C_{45}H_{39}IP_3PdS_2$
Molecular weight	970.09
Crystal habit	red block
Crystal dimensions(mm)	0.20x0.20x0.10
Crystal system	monoclinic
Space group	P 2_1/c
a(Å)	23.602(1)
b(Å)	10.447(1)
c(Å)	17.100(1)
α(°)	90.00
β(°)	104.234(1)
γ(°)	90.00
V(Å^3)	4086.9(5)
Z	4
d(g-cm^{-3})	1.577
F(000)	1940
μ(cm^{-1})	1.461
Absorption corrections	multi-scan ; 0.7588 min, 0.8677 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite

T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	28.70
HKL ranges	-31 20 ; -14 12 ; -22 23
Reflections measured	22733
Unique data	10307
Rint	0.0499
Reflections used	7112
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	478
Reflections / parameter	14
wR2	0.1360
R1	0.0455
Weights a, b	0.0694 ; 0.2882
GoF	1.040
difference peak / hole (e Å^{-3})	1.027(0.116) / -1.053(0.116)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb403

atom	x	y	z	U(eq)
I(1)	3049(1)	4502(1)	-2961(1)	45(1)
Pd(1)	2778(1)	4764(1)	-1529(1)	32(1)
S(1)	3706(1)	4186(1)	-776(1)	40(1)
S(2)	1831(1)	5390(1)	-2164(1)	46(1)
P(1)	2495(1)	4715(1)	-392(1)	30(1)
P(2)	3759(1)	5002(1)	322(1)	30(1)
P(3)	1628(1)	6531(1)	-1309(1)	36(1)
C(1)	3049(2)	5067(4)	489(2)	30(1)
C(2)	2873(2)	5512(3)	1166(2)	30(1)
C(3)	2300(2)	5970(4)	1112(2)	34(1)
C(4)	1874(2)	6232(4)	401(2)	31(1)
C(5)	1934(2)	5852(4)	-365(2)	32(1)
C(6A)	2215(2)	3156(4)	-230(3)	45(1)
C(7A)	1620(3)	2751(7)	-705(5)	52(2)
C(8A)	1306(4)	1571(7)	-455(6)	61(2)
C(9A)	1110(6)	1820(10)	290(10)	320(10)
C(6B)	2215(2)	3156(4)	-230(3)	45(1)
C(7B)	1974(5)	2910(10)	448(6)	52(2)
C(8B)	1722(5)	1570(10)	400(10)	61(2)
C(9B)	1110(6)	1820(10)	290(10)	320(10)
C(10)	3263(2)	5501(4)	1994(2)	33(1)
C(11)	3339(2)	6605(4)	2474(2)	42(1)
C(12)	3661(2)	6534(6)	3264(3)	54(1)
C(13)	3903(2)	5380(6)	3585(3)	59(2)
C(14)	3827(2)	4285(5)	3122(3)	53(1)
C(15)	3503(2)	4349(4)	2327(2)	38(1)
C(16)	1338(2)	6881(4)	512(2)	36(1)
C(17)	1368(2)	8075(5)	860(3)	50(1)
C(18)	875(2)	8602(6)	1028(3)	68(2)
C(19)	351(2)	7948(7)	849(4)	80(2)
C(20)	325(2)	6741(6)	511(4)	79(2)
C(21)	819(2)	6231(5)	342(3)	54(1)

C(22)	4067(2)	6592(4)	379(2)	31(1)
C(23)	4593(2)	6788(4)	152(2)	35(1)
C(24)	4875(2)	7957(4)	295(2)	39(1)
C(25)	4632(2)	8956(4)	638(2)	37(1)
C(26)	4100(2)	8780(4)	832(2)	37(1)
C(27)	3819(2)	7605(4)	707(2)	33(1)
C(28)	4287(2)	4058(4)	1043(2)	30(1)
C(29)	4159(2)	2770(4)	1153(2)	37(1)
C(30)	4543(2)	2032(4)	1700(2)	39(1)
C(31)	5066(2)	2544(4)	2144(2)	37(1)
C(32)	5200(2)	3800(4)	2033(2)	37(1)
C(33)	4810(2)	4576(4)	1494(2)	31(1)
C(34)	840(2)	6695(5)	-1551(3)	44(1)
C(35)	490(2)	5680(6)	-1872(3)	58(1)
C(36)	-125(2)	5782(7)	-2056(4)	79(2)
C(37)	-368(2)	6936(8)	-1904(4)	89(2)
C(38)	-29(2)	7943(6)	-1582(4)	77(2)
C(39)	589(2)	7851(5)	-1401(3)	56(1)
C(40)	1911(2)	8134(4)	-1360(3)	44(1)
C(41)	1707(2)	8866(5)	-2051(3)	56(1)
C(42)	1956(3)	10050(6)	-2107(4)	68(2)
C(43)	2403(3)	10504(5)	-1503(4)	71(2)
C(44)	2609(2)	9784(5)	-807(4)	66(2)
C(45)	2361(2)	8593(5)	-737(3)	49(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb403

I(1)-Pd(1)	2.6922(4	Pd(1)-P(1)	2.207(1)
Pd(1)-S(2)	2.325(1)	Pd(1)-S(1)	2.330(1)
S(1)-P(2)	2.037(1)	S(2)-P(3)	2.033(2)
P(1)-C(1)	1.774(4)	P(1)-C(5)	1.789(4)
P(1)-C(6A)	1.804(4)	P(2)-C(1)	1.769(4)
P(2)-C(22)	1.806(4)	P(2)-C(28)	1.814(4)
P(3)-C(5)	1.749(4)	P(3)-C(34)	1.811(4)
P(3)-C(40)	1.814(5)	C(1)-C(2)	1.403(5)
C(2)-C(3)	1.414(5)	C(2)-C(10)	1.488(5)
C(3)-C(4)	1.400(5)	C(3)-H(3)	0.9500
C(4)-C(5)	1.408(5)	C(4)-C(16)	1.488(5)
C(6A)-C(7A)	1.500(6)	C(6A)-H(6A)	0.9500
C(7A)-C(8A)	1.551(7)	C(7A)-H(7A1)	0.9900
C(7A)-H(7A2)	0.9900	C(8A)-C(9A)	1.48(1)
C(8A)-H(8A1)	0.9900	C(8A)-H(8A2)	0.9900
C(9A)-H(9A1)	0.9800	C(9A)-H(9A2)	0.9800
C(9A)-H(9A3)	0.9800	C(7B)-C(8B)	1.51(1)
C(7B)-H(7B1)	0.9900	C(7B)-H(7B2)	0.9900
C(8B)-H(8B1)	0.9900	C(8B)-H(8B2)	0.9900
C(10)-C(15)	1.391(6)	C(10)-C(11)	1.401(6)
C(11)-C(12)	1.381(6)	C(11)-H(11)	0.9500
C(12)-C(13)	1.388(7)	C(12)-H(12)	0.9500
C(13)-C(14)	1.378(7)	C(13)-H(13)	0.9500
C(14)-C(15)	1.387(6)	C(14)-H(14)	0.9500
C(15)-H(15)	0.9500	C(16)-C(21)	1.368(6)
C(16)-C(17)	1.377(6)	C(17)-C(18)	1.381(6)
C(17)-H(17)	0.9500	C(18)-C(19)	1.380(8)
C(18)-H(18)	0.9500	C(19)-C(20)	1.383(8)
C(19)-H(19)	0.9500	C(20)-C(21)	1.375(7)
C(20)-H(20)	0.9500	C(21)-H(21)	0.9500
C(22)-C(27)	1.392(5)	C(22)-C(23)	1.404(5)
C(23)-C(24)	1.383(6)	C(23)-H(23)	0.9500
C(24)-C(25)	1.387(6)	C(24)-H(24)	0.9500
C(25)-C(26)	1.388(5)	C(25)-H(25)	0.9500

C(26)-C(27)	1.386(6)	C(26)-H(26)	0.9500
C(27)-H(27)	0.9500	C(28)-C(33)	1.392(5)
C(28)-C(29)	1.402(5)	C(29)-C(30)	1.369(6)
C(29)-H(29)	0.9500	C(30)-C(31)	1.387(6)
C(30)-H(30)	0.9500	C(31)-C(32)	1.374(6)
C(31)-H(31)	0.9500	C(32)-C(33)	1.392(6)
C(32)-H(32)	0.9500	C(33)-H(33)	0.9500
C(34)-C(35)	1.372(7)	C(34)-C(39)	1.397(6)
C(35)-C(36)	1.412(7)	C(35)-H(35)	0.9500
C(36)-C(37)	1.39(1)	C(36)-H(36)	0.9500
C(37)-C(38)	1.36(1)	C(37)-H(37)	0.9500
C(38)-C(39)	1.417(6)	C(38)-H(38)	0.9500
C(39)-H(39)	0.9500	C(40)-C(45)	1.391(6)
C(40)-C(41)	1.391(6)	C(41)-C(42)	1.382(8)
C(41)-H(41)	0.9500	C(42)-C(43)	1.37(1)
C(42)-H(42)	0.9500	C(43)-C(44)	1.39(1)
C(43)-H(43)	0.9500	C(44)-C(45)	1.393(7)
C(44)-H(44)	0.9500	C(45)-H(45)	0.9500

P(1)-Pd(1)-S(2)	87.36(4)	P(1)-Pd(1)-S(1)	87.35(4)
S(2)-Pd(1)-S(1)	174.52(4)	P(1)-Pd(1)-I(1)	171.92(3)
S(2)-Pd(1)-I(1)	91.12(3)	S(1)-Pd(1)-I(1)	94.31(3)
P(2)-S(1)-Pd(1)	103.73(5)	P(3)-S(2)-Pd(1)	101.50(5)
C(1)-P(1)-C(5)	103.7(2)	C(1)-P(1)-C(6A)	106.2(2)
C(5)-P(1)-C(6A)	107.1(2)	C(1)-P(1)-Pd(1)	115.1(1)
C(5)-P(1)-Pd(1)	113.2(1)	C(6A)-P(1)-Pd(1)	110.9(2)
C(1)-P(2)-C(22)	109.8(2)	C(1)-P(2)-C(28)	115.5(2)
C(22)-P(2)-C(28)	105.3(2)	C(1)-P(2)-S(1)	108.6(1)
C(22)-P(2)-S(1)	111.6(1)	C(28)-P(2)-S(1)	106.0(1)
C(5)-P(3)-C(34)	114.7(2)	C(5)-P(3)-C(40)	110.2(2)
C(34)-P(3)-C(40)	105.8(2)	C(5)-P(3)-S(2)	108.0(1)
C(34)-P(3)-S(2)	107.6(2)	C(40)-P(3)-S(2)	110.6(1)
C(2)-C(1)-P(2)	129.2(3)	C(2)-C(1)-P(1)	117.6(3)
P(2)-C(1)-P(1)	112.6(2)	C(1)-C(2)-C(3)	122.1(3)
C(1)-C(2)-C(10)	122.8(3)	C(3)-C(2)-C(10)	115.1(3)
C(4)-C(3)-C(2)	126.4(3)	C(4)-C(3)-H(3)	116.8
C(2)-C(3)-H(3)	116.8	C(3)-C(4)-C(5)	122.5(3)
C(3)-C(4)-C(16)	115.5(3)	C(5)-C(4)-C(16)	121.9(3)
C(4)-C(5)-P(3)	129.2(3)	C(4)-C(5)-P(1)	117.0(3)
P(3)-C(5)-P(1)	112.7(2)	C(7A)-C(6A)-P(1)	120.1(4)
C(7A)-C(6A)-H(6A)	120.0	P(1)-C(6A)-H(6A)	120.0
C(6A)-C(7A)-C(8A)	121.5(6)	C(6A)-C(7A)-H(7A1)	107.0
C(8A)-C(7A)-H(7A1)	107.0	C(6A)-C(7A)-H(7A2)	107.0
C(8A)-C(7A)-H(7A2)	107.0	H(7A1)-C(7A)-H(7A2)	106.7
C(9A)-C(8A)-C(7A)	111.7(7)	C(9A)-C(8A)-H(8A1)	109.3
C(7A)-C(8A)-H(8A1)	109.3	C(9A)-C(8A)-H(8A2)	109.3
C(7A)-C(8A)-H(8A2)	109.3	H(8A1)-C(8A)-H(8A2)	107.9
C(8B)-C(7B)-H(7B1)	109.5	C(8B)-C(7B)-H(7B2)	109.5
H(7B1)-C(7B)-H(7B2)	108.1	C(7B)-C(8B)-H(8B1)	111.3
C(7B)-C(8B)-H(8B2)	111.3	H(8B1)-C(8B)-H(8B2)	109.2
C(15)-C(10)-C(11)	119.5(4)	C(15)-C(10)-C(2)	119.4(3)
C(11)-C(10)-C(2)	120.7(4)	C(12)-C(11)-C(10)	119.3(4)
C(12)-C(11)-H(11)	120.4	C(10)-C(11)-H(11)	120.4
C(11)-C(12)-C(13)	120.5(4)	C(11)-C(12)-H(12)	119.7
C(13)-C(12)-H(12)	119.7	C(14)-C(13)-C(12)	120.7(4)
C(14)-C(13)-H(13)	119.6	C(12)-C(13)-H(13)	119.6
C(13)-C(14)-C(15)	119.1(5)	C(13)-C(14)-H(14)	120.5
C(15)-C(14)-H(14)	120.5	C(14)-C(15)-C(10)	120.9(4)
C(14)-C(15)-H(15)	119.6	C(10)-C(15)-H(15)	119.6
C(21)-C(16)-C(17)	119.3(4)	C(21)-C(16)-C(4)	119.5(4)
C(17)-C(16)-C(4)	120.8(4)	C(16)-C(17)-C(18)	119.7(5)

C(16)-C(17)-H(17)	120.2	C(18)-C(17)-H(17)	120.2
C(19)-C(18)-C(17)	120.8(5)	C(19)-C(18)-H(18)	119.6
C(17)-C(18)-H(18)	119.6	C(18)-C(19)-C(20)	119.3(5)
C(18)-C(19)-H(19)	120.4	C(20)-C(19)-H(19)	120.4
C(21)-C(20)-C(19)	119.3(5)	C(21)-C(20)-H(20)	120.4
C(19)-C(20)-H(20)	120.4	C(16)-C(21)-C(20)	121.6(5)
C(16)-C(21)-H(21)	119.2	C(20)-C(21)-H(21)	119.2
C(27)-C(22)-C(23)	119.2(4)	C(27)-C(22)-P(2)	121.2(3)
C(23)-C(22)-P(2)	119.3(3)	C(24)-C(23)-C(22)	120.0(4)
C(24)-C(23)-H(23)	120.0	C(22)-C(23)-H(23)	120.0
C(23)-C(24)-C(25)	120.5(4)	C(23)-C(24)-H(24)	119.7
C(25)-C(24)-H(24)	119.7	C(24)-C(25)-C(26)	119.5(4)
C(24)-C(25)-H(25)	120.3	C(26)-C(25)-H(25)	120.3
C(27)-C(26)-C(25)	120.6(4)	C(27)-C(26)-H(26)	119.7
C(25)-C(26)-H(26)	119.7	C(26)-C(27)-C(22)	120.1(3)
C(26)-C(27)-H(27)	119.9	C(22)-C(27)-H(27)	119.9
C(33)-C(28)-C(29)	119.3(4)	C(33)-C(28)-P(2)	122.1(3)
C(29)-C(28)-P(2)	118.5(3)	C(30)-C(29)-C(28)	120.2(4)
C(30)-C(29)-H(29)	119.9	C(28)-C(29)-H(29)	119.9
C(29)-C(30)-C(31)	120.5(4)	C(29)-C(30)-H(30)	119.8
C(31)-C(30)-H(30)	119.8	C(32)-C(31)-C(30)	119.8(4)
C(32)-C(31)-H(31)	120.1	C(30)-C(31)-H(31)	120.1
C(31)-C(32)-C(33)	120.7(4)	C(31)-C(32)-H(32)	119.7
C(33)-C(32)-H(32)	119.7	C(32)-C(33)-C(28)	119.5(4)
C(32)-C(33)-H(33)	120.3	C(28)-C(33)-H(33)	120.3
C(35)-C(34)-C(39)	120.1(4)	C(35)-C(34)-P(3)	120.1(4)
C(39)-C(34)-P(3)	119.8(4)	C(34)-C(35)-C(36)	121.1(5)
C(34)-C(35)-H(35)	119.5	C(36)-C(35)-H(35)	119.5
C(37)-C(36)-C(35)	118.2(6)	C(37)-C(36)-H(36)	120.9
C(35)-C(36)-H(36)	120.9	C(38)-C(37)-C(36)	121.4(5)
C(38)-C(37)-H(37)	119.3	C(36)-C(37)-H(37)	119.3
C(37)-C(38)-C(39)	120.7(6)	C(37)-C(38)-H(38)	119.7
C(39)-C(38)-H(38)	119.7	C(34)-C(39)-C(38)	118.6(5)
C(34)-C(39)-H(39)	120.7	C(38)-C(39)-H(39)	120.7
C(45)-C(40)-C(41)	120.0(5)	C(45)-C(40)-P(3)	120.2(4)
C(41)-C(40)-P(3)	119.6(4)	C(42)-C(41)-C(40)	119.1(5)
C(42)-C(41)-H(41)	120.4	C(40)-C(41)-H(41)	120.4
C(43)-C(42)-C(41)	121.3(5)	C(43)-C(42)-H(42)	119.3
C(41)-C(42)-H(42)	119.3	C(42)-C(43)-C(44)	120.1(5)
C(42)-C(43)-H(43)	119.9	C(44)-C(43)-H(43)	119.9
C(43)-C(44)-C(45)	119.3(6)	C(43)-C(44)-H(44)	120.3
C(45)-C(44)-H(44)	120.3	C(40)-C(45)-C(44)	120.1(5)
C(40)-C(45)-H(45)	120.0	C(44)-C(45)-H(45)	120.0

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb403

atom	U11	U22	U33	U23	U13	U12
I(1)	53(1)	50(1)	38(1)	-4(1)	23(1)	1(1)
Pd(1)	31(1)	38(1)	29(1)	-7(1)	9(1)	2(1)
S(1)	32(1)	56(1)	33(1)	-15(1)	10(1)	7(1)
S(2)	42(1)	61(1)	31(1)	-8(1)	5(1)	16(1)
P(1)	27(1)	33(1)	31(1)	-6(1)	9(1)	1(1)
P(2)	27(1)	37(1)	29(1)	-5(1)	9(1)	2(1)
P(3)	31(1)	43(1)	34(1)	-3(1)	8(1)	6(1)
C(1)	26(2)	32(2)	32(2)	0(2)	9(2)	4(2)
C(2)	31(2)	29(2)	31(2)	-2(2)	11(2)	0(2)
C(3)	35(2)	40(2)	32(2)	-4(2)	17(2)	1(2)
C(4)	26(2)	30(2)	39(2)	-6(2)	14(2)	-3(2)
C(5)	27(2)	35(2)	35(2)	-2(2)	9(2)	4(2)
C(6A)	39(2)	31(2)	59(3)	-7(2)	5(2)	-4(2)
C(7A)	45(4)	40(4)	70(4)	-9(3)	15(3)	5(3)

C(8A)	48(4)	36(4)	101(6)	-10(4)	22(4)	1(3)
C(9A)	350(30)	170(10)	480(30)	140(20)	160(20)	-70(10)
C(6B)	39(2)	31(2)	59(3)	-7(2)	5(2)	-4(2)
C(7B)	45(4)	40(4)	70(4)	-9(3)	15(3)	5(3)
C(8B)	48(4)	36(4)	101(6)	-10(4)	22(4)	1(3)
C(9B)	350(30)	170(10)	480(30)	140(20)	160(20)	-70(10)
C(10)	29(2)	46(2)	28(2)	-4(2)	12(2)	-3(2)
C(11)	42(2)	48(3)	39(2)	-8(2)	16(2)	-7(2)
C(12)	44(3)	81(4)	40(2)	-24(3)	18(2)	-20(3)
C(13)	36(2)	111(5)	29(2)	-2(3)	7(2)	-2(3)
C(14)	42(3)	81(4)	38(2)	13(3)	14(2)	16(2)
C(15)	34(2)	49(3)	35(2)	-1(2)	13(2)	3(2)
C(16)	29(2)	45(2)	35(2)	-2(2)	13(2)	5(2)
C(17)	39(2)	53(3)	54(3)	-19(2)	3(2)	11(2)
C(18)	46(3)	74(4)	78(4)	-36(3)	5(3)	15(3)
C(19)	41(3)	112(5)	91(4)	-25(4)	25(3)	19(3)
C(20)	36(3)	94(5)	111(5)	-26(4)	30(3)	-13(3)
C(21)	34(2)	54(3)	78(3)	-10(3)	21(2)	-1(2)
C(22)	30(2)	38(2)	26(2)	6(2)	7(2)	8(2)
C(23)	39(2)	36(2)	34(2)	6(2)	18(2)	8(2)
C(24)	36(2)	45(2)	43(2)	9(2)	23(2)	4(2)
C(25)	38(2)	39(2)	37(2)	7(2)	14(2)	-2(2)
C(26)	40(2)	41(2)	33(2)	0(2)	14(2)	4(2)
C(27)	30(2)	40(2)	31(2)	0(2)	14(2)	0(2)
C(28)	31(2)	31(2)	31(2)	-4(2)	13(2)	6(2)
C(29)	33(2)	35(2)	42(2)	-8(2)	10(2)	-5(2)
C(30)	41(2)	33(2)	44(2)	2(2)	14(2)	5(2)
C(31)	39(2)	39(2)	36(2)	7(2)	13(2)	8(2)
C(32)	34(2)	45(2)	33(2)	2(2)	10(2)	1(2)
C(33)	32(2)	31(2)	32(2)	-3(2)	11(2)	-4(2)
C(34)	32(2)	57(3)	42(2)	2(2)	6(2)	8(2)
C(35)	38(2)	75(4)	59(3)	-12(3)	5(2)	3(2)
C(36)	41(3)	94(5)	94(4)	-20(4)	4(3)	-1(3)
C(37)	36(3)	123(6)	105(5)	-3(5)	10(3)	10(4)
C(38)	50(3)	80(4)	106(5)	8(4)	28(3)	24(3)
C(39)	41(3)	66(3)	62(3)	6(3)	15(2)	18(2)
C(40)	45(2)	50(3)	44(2)	-1(2)	23(2)	10(2)
C(41)	78(4)	49(3)	52(3)	3(2)	34(3)	17(3)
C(42)	105(5)	55(3)	64(4)	13(3)	57(4)	24(3)
C(43)	93(5)	44(3)	100(5)	2(3)	69(4)	8(3)
C(44)	57(3)	48(3)	102(5)	-18(3)	37(3)	-8(3)
C(45)	41(2)	50(3)	59(3)	2(2)	18(2)	4(2)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb403

atom	x	y	z	U(eq)
H(3)	2195	6114	1606	41
H(6A)	2445	2591	156	54
H(7A1)	1648	2602	-1266	62
H(7A2)	1357	3493	-721	62
H(8A1)	964	1349	-899	73
H(8A2)	1577	831	-366	73
H(9A1)	882	2611	225	486
H(9A2)	1451	1900	746	486
H(9A3)	866	1103	383	486
H(6B)	2228	2486	-601	54
H(7B1)	1663	3540	457	62

H(7B2)	2283	3001	954	62
H(8B1)	1801	1088	-58	73
H(8B2)	1881	1090	907	73
H(9B1)	1028	2715	134	486
H(9B2)	995	1643	790	486
H(9B3)	886	1261	-141	486
H(11)	3170	7394	2257	50
H(12)	3718	7280	3592	65
H(13)	4124	5344	4130	71
H(14)	3993	3497	3343	63
H(15)	3445	3596	2005	46
H(17)	1726	8534	983	60
H(18)	895	9426	1269	81
H(19)	11	8324	957	96
H(20)	-30	6269	396	94
H(21)	798	5406	102	65
H(23)	4755	6118	-99	42
H(24)	5237	8077	157	47
H(25)	4829	9754	740	45
H(26)	3926	9469	1051	45
H(27)	3456	7492	845	39
H(29)	3804	2408	847	44
H(30)	4451	1163	1777	47
H(31)	5331	2028	2524	45
H(32)	5563	4143	2327	44
H(33)	4899	5450	1434	37
H(35)	664	4897	-1971	70
H(36)	-366	5078	-2279	94
H(37)	-781.0001	7023	-2029.0001	107
H(38)	-207	8719	-1476	92
H(39)	827	8561	-1181	67
H(41)	1401	8557	-2480	68
H(42)	1813	10558	-2575	82
H(43)	2573	11313	-1559	85
H(44)	2916	10102	-382.0000	79
H(45)	2499	8093	-265	59

I.6. Crystallographic data for II-21

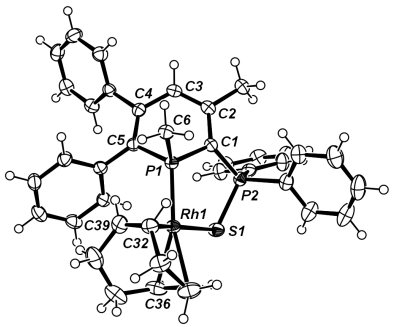


Table 1. Crystal data for mbx159

Compound	mbx159
Molecular formula	$C_{39}H_{39}P_2RhS$
Molecular weight	1409.22
Crystal habit	orange block
Crystal dimensions(mm)	0.40x0.24x0.20
Crystal system	triclinic
Space group	Pbar1
a(Å)	14.446(1)
b(Å)	14.881(1)
c(Å)	17.104(1)
α(°)	88.301(1)
β(°)	66.394(1)
γ(°)	78.842(1)
V(Å^3)	3300.8(4)
Z	2
d(g-cm^{-3})	1.418
F(000)	1456
μ(cm^{-1})	0.705
Absorption corrections	multi-scan ; 0.7658 min, 0.8719 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-20 18 ; -20 17 ; -24 19
Reflections measured	74673
Unique data	19225
Rint	0.0529
Reflections used	12640
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	779
Reflections / parameter	16
wR2	0.0858
R1	0.0346
Weights a, b	0.0424 ; 0.0000
GoF	0.922
difference peak / hole (e Å^{-3})	0.733(0.085) / -0.893(0.085)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mbx159

atom	x	y	z	U(eq)
Rh(1)	7433(1)	-306(1)	4627(1)	23(1)
S(1)	6983(1)	-609(1)	3503(1)	31(1)
P(1)	8281(1)	757(1)	3816(1)	22(1)
P(2)	8085(1)	-224(1)	2436(1)	24(1)

C(1)	8613(2)	606(1)	2706(1)	24(1)
C(2)	8994(2)	1337(1)	2190(1)	24(1)
C(3)	8816(2)	2198(1)	2551(1)	25(1)
C(4)	8042(2)	2520(1)	3394(1)	23(1)
C(5)	7629(2)	1949(1)	4021(1)	23(1)
C(6)	9470(2)	850(1)	3928(1)	27(1)
C(7)	9583(2)	1186(2)	1231(1)	31(1)
C(8)	7674(2)	3543(1)	3510(1)	24(1)
C(9)	8387(2)	4111(1)	3340(1)	30(1)
C(10)	8072(2)	5056(2)	3422(2)	37(1)
C(11)	7044(2)	5454(2)	3674(1)	34(1)
C(12)	6329(2)	4901(2)	3839(1)	32(1)
C(13)	6641(2)	3957(2)	3760(1)	28(1)
C(14)	6705(2)	2235(1)	4827(1)	24(1)
C(15)	5798(2)	1935(1)	4975(1)	29(1)
C(16)	4933(2)	2177(2)	5731(1)	33(1)
C(17)	4964(2)	2716(2)	6360(1)	35(1)
C(18)	5859(2)	3023(2)	6224(1)	34(1)
C(19)	6723(2)	2784(1)	5466(1)	30(1)
C(20)	7488(2)	212(1)	1713(1)	27(1)
C(21)	7840(2)	-129(2)	880(1)	35(1)
C(22)	7360(2)	237(2)	352(2)	42(1)
C(23)	6519(2)	951(2)	657(2)	38(1)
C(24)	6166(2)	1305(2)	1483(2)	40(1)
C(25)	6646(2)	942(2)	2013(1)	33(1)
C(26)	9004(2)	-1252(1)	1887(1)	31(1)
C(27)	10050(2)	-1285(2)	1609(1)	37(1)
C(28)	10752(2)	-2084(2)	1216(2)	47(1)
C(29)	10409(2)	-2847(2)	1104(2)	51(1)
C(30)	9371(2)	-2826(2)	1370(2)	51(1)
C(31)	8662(2)	-2028(2)	1766(2)	41(1)
C(32)	8221(2)	-473(2)	5467(1)	30(1)
C(33)	8194(2)	-1373(2)	5903(2)	39(1)
C(34)	7735(2)	-2044(2)	5589(2)	44(1)
C(35)	6969(2)	-1604(2)	5231(2)	36(1)
C(36)	6170(2)	-903(2)	5612(1)	39(1)
C(37)	5889(2)	-476(2)	6490(2)	54(1)
C(38)	6395(2)	319(2)	6488(2)	48(1)
C(39)	7422(2)	293(2)	5750(1)	34(1)
Rh(2)	2713(1)	5198(1)	98(1)	22(1)
S(2)	3340(1)	5590(1)	1087(1)	28(1)
P(3)	1827(1)	4268(1)	1069(1)	21(1)
P(4)	2306(1)	5308(1)	2247(1)	23(1)
C(40)	1630(2)	4521(1)	2133(1)	22(1)
C(41)	1255(2)	3854(1)	2740(1)	24(1)
C(42)	1368(2)	2966(1)	2477(1)	26(1)
C(43)	2060(2)	2559(1)	1635(1)	23(1)
C(44)	2423(2)	3061(1)	935(1)	23(1)
C(45)	550(2)	4218(1)	1115(1)	27(1)
C(46)	742(2)	4118(2)	3688(1)	31(1)
C(47)	2424(2)	1540(1)	1599(1)	25(1)
C(48)	1693(2)	982(1)	1928(1)	26(1)
C(49)	1996(2)	40(1)	1928(1)	31(1)
C(50)	3025(2)	-365(2)	1590(1)	33(1)
C(51)	3756(2)	175(2)	1266(1)	34(1)
C(52)	3457(2)	1119(2)	1271(1)	30(1)
C(53)	3258(2)	2691(1)	95(1)	24(1)
C(54)	4206(2)	2956(1)	-192(1)	29(1)
C(55)	4986(2)	2622(2)	-971(1)	35(1)
C(56)	4829(2)	2019(2)	-1484(1)	37(1)
C(57)	3892(2)	1748(2)	-1211(1)	36(1)
C(58)	3112(2)	2080(1)	-425(1)	30(1)
C(59)	2982(2)	4829(1)	2901(1)	26(1)

C(60)	2815(2)	5222(2)	3680(1)	36(1)
C(61)	3294(2)	4783(2)	4185(2)	44(1)
C(62)	3930(2)	3943(2)	3920(2)	43(1)
C(63)	4109(2)	3534(2)	3135(2)	44(1)
C(64)	3638(2)	3973(2)	2630(1)	36(1)
C(65)	1507(2)	6391(1)	2776(1)	28(1)
C(66)	446(2)	6522(2)	3028(1)	36(1)
C(67)	-186(2)	7356(2)	3401(2)	47(1)
C(68)	238(2)	8058(2)	3536(2)	53(1)
C(69)	1290(2)	7944(2)	3287(2)	48(1)
C(70)	1931(2)	7114(2)	2900(1)	38(1)
C(71)	4009(2)	5562(2)	-1053(1)	35(1)
C(72)	4098(2)	5062(2)	-1845(2)	55(1)
C(73)	3431(2)	4368(2)	-1689(1)	42(1)
C(74)	2469(2)	4528(2)	-875(1)	31(1)
C(75)	1767(2)	5363(1)	-608(1)	28(1)
C(76)	1847(2)	6201(2)	-1136(2)	35(1)
C(77)	2535(2)	6812(2)	-1045(2)	49(1)
C(78)	3322(2)	6348(2)	-720(1)	30(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mbx159

Rh(1)-C(39)	2.135(2)	Rh(1)-C(32)	2.145(2)
Rh(1)-C(36)	2.243(2)	Rh(1)-C(35)	2.252(2)
Rh(1)-P(1)	2.2778(5	Rh(1)-S(1)	2.3431(5)
S(1)-P(2)	2.0384(7	P(1)-C(1)	1.772(2)
P(1)-C(5)	1.812(2)	P(1)-C(6)	1.834(2)
P(2)-C(1)	1.732(2)	P(2)-C(20)	1.813(2)
P(2)-C(26)	1.813(2)	C(1)-C(2)	1.433(3)
C(2)-C(3)	1.372(3)	C(2)-C(7)	1.515(3)
C(3)-C(4)	1.450(3)	C(3)-H(3)	0.9500
C(4)-C(5)	1.363(3)	C(4)-C(8)	1.503(3)
C(5)-C(14)	1.484(3)	C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800	C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800	C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800	C(8)-C(13)	1.392(3)
C(8)-C(9)	1.393(3)	C(9)-C(10)	1.385(3)
C(9)-H(9)	0.9500	C(10)-C(11)	1.379(3)
C(10)-H(10)	0.9500	C(11)-C(12)	1.381(3)
C(11)-H(11)	0.9500	C(12)-C(13)	1.383(3)
C(12)-H(12)	0.9500	C(13)-H(13)	0.9500
C(14)-C(15)	1.391(3)	C(14)-C(19)	1.396(3)
C(15)-C(16)	1.387(3)	C(15)-H(15)	0.9500
C(16)-C(17)	1.380(3)	C(16)-H(16)	0.9500
C(17)-C(18)	1.384(3)	C(17)-H(17)	0.9500
C(18)-C(19)	1.387(3)	C(18)-H(18)	0.9500
C(19)-H(19)	0.9500	C(20)-C(21)	1.381(3)
C(20)-C(25)	1.395(3)	C(21)-C(22)	1.386(3)
C(21)-H(21)	0.9500	C(22)-C(23)	1.380(3)
C(22)-H(22)	0.9500	C(23)-C(24)	1.377(3)
C(23)-H(23)	0.9500	C(24)-C(25)	1.387(3)
C(24)-H(24)	0.9500	C(25)-H(25)	0.9500
C(26)-C(27)	1.382(3)	C(26)-C(31)	1.392(3)
C(27)-C(28)	1.388(3)	C(27)-H(27)	0.9500
C(28)-C(29)	1.370(4)	C(28)-H(28)	0.9500
C(29)-C(30)	1.376(4)	C(29)-H(29)	0.9500
C(30)-C(31)	1.393(3)	C(30)-H(30)	0.9500
C(31)-H(31)	0.9500	C(32)-C(39)	1.394(3)
C(32)-C(33)	1.513(3)	C(32)-H(32)	0.9501
C(33)-C(34)	1.515(3)	C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900	C(34)-C(35)	1.506(3)

C(34)-H(34A)	0.9900	C(34)-H(34B)	0.9900
C(35)-C(36)	1.348(3)	C(35)-H(35)	0.9499
C(36)-C(37)	1.514(3)	C(36)-H(36)	0.9499
C(37)-C(38)	1.505(4)	C(37)-H(37A)	0.9900
C(37)-H(37B)	0.9900	C(38)-C(39)	1.508(3)
C(38)-H(38A)	0.9900	C(38)-H(38B)	0.9900
C(39)-H(39)	0.9499	Rh(2)-C(75)	2.135(2)
Rh(2)-C(74)	2.143(2)	Rh(2)-C(71)	2.247(2)
Rh(2)-C(78)	2.261(2)	Rh(2)-P(3)	2.2713(5)
Rh(2)-S(2)	2.3475(5	S(2)-P(4)	2.0408(7)
P(3)-C(40)	1.766(2)	P(3)-C(44)	1.813(2)
P(3)-C(45)	1.831(2)	P(4)-C(40)	1.724(2)
P(4)-C(59)	1.809(2)	P(4)-C(65)	1.810(2)
C(40)-C(41)	1.433(3)	C(41)-C(42)	1.366(3)
C(41)-C(46)	1.516(3)	C(42)-C(43)	1.451(3)
C(42)-H(42)	0.9500	C(43)-C(44)	1.364(3)
C(43)-C(47)	1.501(3)	C(44)-C(53)	1.492(3)
C(45)-H(45A)	0.9800	C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800	C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800	C(46)-H(46C)	0.9800
C(47)-C(52)	1.387(3)	C(47)-C(48)	1.399(3)
C(48)-C(49)	1.386(3)	C(48)-H(48)	0.9500
C(49)-C(50)	1.376(3)	C(49)-H(49)	0.9500
C(50)-C(51)	1.379(3)	C(50)-H(50)	0.9500
C(51)-C(52)	1.387(3)	C(51)-H(51)	0.9500
C(52)-H(52)	0.9500	C(53)-C(54)	1.391(3)
C(53)-C(58)	1.391(3)	C(54)-C(55)	1.383(3)
C(54)-H(54)	0.9500	C(55)-C(56)	1.383(3)
C(55)-H(55)	0.9500	C(56)-C(57)	1.381(3)
C(56)-H(56)	0.9500	C(57)-C(58)	1.390(3)
C(57)-H(57)	0.9500	C(58)-H(58)	0.9500
C(59)-C(60)	1.382(3)	C(59)-C(64)	1.398(3)
C(60)-C(61)	1.386(3)	C(60)-H(60)	0.9500
C(61)-C(62)	1.368(4)	C(61)-H(61)	0.9500
C(62)-C(63)	1.395(3)	C(62)-H(62)	0.9500
C(63)-C(64)	1.380(3)	C(63)-H(63)	0.9500
C(64)-H(64)	0.9500	C(65)-C(66)	1.390(3)
C(65)-C(70)	1.396(3)	C(66)-C(67)	1.386(3)
C(66)-H(66)	0.9500	C(67)-C(68)	1.376(4)
C(67)-H(67)	0.9500	C(68)-C(69)	1.380(4)
C(68)-H(68)	0.9500	C(69)-C(70)	1.392(3)
C(69)-H(69)	0.9500	C(70)-H(70)	0.9500
C(71)-C(78)	1.347(3)	C(71)-C(72)	1.513(3)
C(71)-H(71)	0.9501	C(72)-C(73)	1.494(3)
C(72)-H(72A)	0.9900	C(72)-H(72B)	0.9900
C(73)-C(74)	1.506(3)	C(73)-H(73A)	0.9900
C(73)-H(73B)	0.9900	C(74)-C(75)	1.399(3)
C(74)-H(74)	0.9499	C(75)-C(76)	1.512(3)
C(75)-H(75)	0.9500	C(76)-C(77)	1.524(3)
C(76)-H(76A)	0.9900	C(76)-H(76B)	0.9900
C(77)-C(78)	1.502(3)	C(77)-H(77A)	0.9900
C(77)-H(77B)	0.9900	C(78)-H(78)	0.9500

C(39)-Rh(1)-C(32)	38.01(8)	C(39)-Rh(1)-C(36)	81.1(1)
C(32)-Rh(1)-C(36)	88.57(8)	C(39)-Rh(1)-C(35)	95.28(8)
C(32)-Rh(1)-C(35)	80.46(8)	C(36)-Rh(1)-C(35)	34.9(1)
C(39)-Rh(1)-P(1)	90.71(6)	C(32)-Rh(1)-P(1)	96.46(6)
C(36)-Rh(1)-P(1)	159.63(7)	C(35)-Rh(1)-P(1)	165.47(7)
C(39)-Rh(1)-S(1)	162.10(6)	C(32)-Rh(1)-S(1)	159.78(6)
C(36)-Rh(1)-S(1)	94.22(6)	C(35)-Rh(1)-S(1)	90.41(6)
P(1)-Rh(1)-S(1)	87.86(2)	P(2)-S(1)-Rh(1)	105.10(3)
C(1)-P(1)-C(5)	101.3(1)	C(1)-P(1)-C(6)	106.3(1)

C(5)-P(1)-C(6)	99.7(1)	C(1)-P(1)-Rh(1)	114.61(7)
C(5)-P(1)-Rh(1)	118.02(7)	C(6)-P(1)-Rh(1)	114.92(7)
C(1)-P(2)-C(20)	110.8(1)	C(1)-P(2)-C(26)	114.8(1)
C(20)-P(2)-C(26)	105.0(1)	C(1)-P(2)-S(1)	110.27(7)
C(20)-P(2)-S(1)	108.03(7)	C(26)-P(2)-S(1)	107.67(8)
C(2)-C(1)-P(2)	126.1(2)	C(2)-C(1)-P(1)	116.4(1)
P(2)-C(1)-P(1)	114.5(1)	C(3)-C(2)-C(1)	120.7(2)
C(3)-C(2)-C(7)	118.3(2)	C(1)-C(2)-C(7)	121.0(2)
C(2)-C(3)-C(4)	124.6(2)	C(2)-C(3)-H(3)	117.7
C(4)-C(3)-H(3)	117.7	C(5)-C(4)-C(3)	123.4(2)
C(5)-C(4)-C(8)	121.9(2)	C(3)-C(4)-C(8)	114.5(2)
C(4)-C(5)-C(14)	125.0(2)	C(4)-C(5)-P(1)	115.4(2)
C(14)-C(5)-P(1)	119.6(1)	P(1)-C(6)-H(6A)	109.5
P(1)-C(6)-H(6B)	109.5	H(6A)-C(6)-H(6B)	109.5
P(1)-C(6)-H(6C)	109.5	H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5	C(2)-C(7)-H(7A)	109.5
C(2)-C(7)-H(7B)	109.5	H(7A)-C(7)-H(7B)	109.5
C(2)-C(7)-H(7C)	109.5	H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5	C(13)-C(8)-C(9)	117.9(2)
C(13)-C(8)-C(4)	122.5(2)	C(9)-C(8)-C(4)	119.5(2)
C(10)-C(9)-C(8)	120.7(2)	C(10)-C(9)-H(9)	119.6
C(8)-C(9)-H(9)	119.6	C(11)-C(10)-C(9)	120.6(2)
C(11)-C(10)-H(10)	119.7	C(9)-C(10)-H(10)	119.7
C(10)-C(11)-C(12)	119.3(2)	C(10)-C(11)-H(11)	120.3
C(12)-C(11)-H(11)	120.3	C(11)-C(12)-C(13)	120.2(2)
C(11)-C(12)-H(12)	119.9	C(13)-C(12)-H(12)	119.9
C(12)-C(13)-C(8)	121.2(2)	C(12)-C(13)-H(13)	119.4
C(8)-C(13)-H(13)	119.4	C(15)-C(14)-C(19)	118.0(2)
C(15)-C(14)-C(5)	120.3(2)	C(19)-C(14)-C(5)	121.7(2)
C(16)-C(15)-C(14)	121.3(2)	C(16)-C(15)-H(15)	119.4
C(14)-C(15)-H(15)	119.4	C(17)-C(16)-C(15)	120.2(2)
C(17)-C(16)-H(16)	119.9	C(15)-C(16)-H(16)	119.9
C(16)-C(17)-C(18)	119.4(2)	C(16)-C(17)-H(17)	120.3
C(18)-C(17)-H(17)	120.3	C(17)-C(18)-C(19)	120.4(2)
C(17)-C(18)-H(18)	119.8	C(19)-C(18)-H(18)	119.8
C(18)-C(19)-C(14)	120.8(2)	C(18)-C(19)-H(19)	119.6
C(14)-C(19)-H(19)	119.6	C(21)-C(20)-C(25)	118.9(2)
C(21)-C(20)-P(2)	123.3(2)	C(25)-C(20)-P(2)	117.8(2)
C(20)-C(21)-C(22)	120.9(2)	C(20)-C(21)-H(21)	119.6
C(22)-C(21)-H(21)	119.6	C(23)-C(22)-C(21)	119.9(2)
C(23)-C(22)-H(22)	120.0	C(21)-C(22)-H(22)	120.0
C(24)-C(23)-C(22)	119.8(2)	C(24)-C(23)-H(23)	120.1
C(22)-C(23)-H(23)	120.1	C(23)-C(24)-C(25)	120.4(2)
C(23)-C(24)-H(24)	119.8	C(25)-C(24)-H(24)	119.8
C(24)-C(25)-C(20)	120.0(2)	C(24)-C(25)-H(25)	120.0
C(20)-C(25)-H(25)	120.0	C(27)-C(26)-C(31)	119.2(2)
C(27)-C(26)-P(2)	120.4(2)	C(31)-C(26)-P(2)	120.3(2)
C(26)-C(27)-C(28)	120.4(2)	C(26)-C(27)-H(27)	119.8
C(28)-C(27)-H(27)	119.8	C(29)-C(28)-C(27)	120.0(3)
C(29)-C(28)-H(28)	120.0	C(27)-C(28)-H(28)	120.0
C(28)-C(29)-C(30)	120.5(2)	C(28)-C(29)-H(29)	119.7
C(30)-C(29)-H(29)	119.7	C(29)-C(30)-C(31)	119.8(2)
C(29)-C(30)-H(30)	120.1	C(31)-C(30)-H(30)	120.1
C(26)-C(31)-C(30)	120.0(2)	C(26)-C(31)-H(31)	120.0
C(30)-C(31)-H(31)	120.0	C(39)-C(32)-C(33)	123.9(2)
C(39)-C(32)-Rh(1)	70.6(1)	C(33)-C(32)-Rh(1)	114.0(1)
C(39)-C(32)-H(32)	118.1	C(33)-C(32)-H(32)	118.0
Rh(1)-C(32)-H(32)	85.5	C(32)-C(33)-C(34)	114.6(2)
C(32)-C(33)-H(33A)	108.6	C(34)-C(33)-H(33A)	108.6
C(32)-C(33)-H(33B)	108.6	C(34)-C(33)-H(33B)	108.6
H(33A)-C(33)-H(33B)	107.6	C(35)-C(34)-C(33)	114.5(2)
C(35)-C(34)-H(34A)	108.6	C(33)-C(34)-H(34A)	108.6
C(35)-C(34)-H(34B)	108.6	C(33)-C(34)-H(34B)	108.6

H(34A)-C(34)-H(34B)	107.6	C(36)-C(35)-C(34)	125.6(2)
C(36)-C(35)-Rh(1)	72.2(1)	C(34)-C(35)-Rh(1)	108.3(1)
C(36)-C(35)-H(35)	117.1	C(34)-C(35)-H(35)	117.3
Rh(1)-C(35)-H(35)	89.5	C(35)-C(36)-C(37)	124.1(2)
C(35)-C(36)-Rh(1)	72.9(1)	C(37)-C(36)-Rh(1)	110.2(2)
C(35)-C(36)-H(36)	118.0	C(37)-C(36)-H(36)	117.9
Rh(1)-C(36)-H(36)	86.9	C(38)-C(37)-C(36)	114.3(2)
C(38)-C(37)-H(37A)	108.7	C(36)-C(37)-H(37A)	108.7
C(38)-C(37)-H(37B)	108.7	C(36)-C(37)-H(37B)	108.7
H(37A)-C(37)-H(37B)	107.6	C(37)-C(38)-C(39)	115.1(2)
C(37)-C(38)-H(38A)	108.5	C(39)-C(38)-H(38A)	108.5
C(37)-C(38)-H(38B)	108.5	C(39)-C(38)-H(38B)	108.5
H(38A)-C(38)-H(38B)	107.5	C(32)-C(39)-C(38)	124.9(2)
C(32)-C(39)-Rh(1)	71.4(1)	C(38)-C(39)-Rh(1)	110.2(2)
C(32)-C(39)-H(39)	117.5	C(38)-C(39)-H(39)	117.6
Rh(1)-C(39)-H(39)	88.2	C(75)-Rh(2)-C(74)	38.17(8)
C(75)-Rh(2)-C(71)	89.58(8)	C(74)-Rh(2)-C(71)	81.19(8)
C(75)-Rh(2)-C(78)	80.88(8)	C(74)-Rh(2)-C(78)	94.84(8)
C(71)-Rh(2)-C(78)	34.76(8)	C(75)-Rh(2)-P(3)	96.20(6)
C(74)-Rh(2)-P(3)	89.47(6)	C(71)-Rh(2)-P(3)	156.71(6)
C(78)-Rh(2)-P(3)	168.53(6)	C(75)-Rh(2)-S(2)	157.17(6)
C(74)-Rh(2)-S(2)	164.64(6)	C(71)-Rh(2)-S(2)	95.02(6)
C(78)-Rh(2)-S(2)	90.22(6)	P(3)-Rh(2)-S(2)	88.36(2)
P(4)-S(2)-Rh(2)	104.98(3)	C(40)-P(3)-C(44)	101.2(1)
C(40)-P(3)-C(45)	105.2(1)	C(44)-P(3)-C(45)	101.3(1)
C(40)-P(3)-Rh(2)	114.64(7)	C(44)-P(3)-Rh(2)	116.39(7)
C(45)-P(3)-Rh(2)	116.10(7)	C(40)-P(4)-C(59)	108.1(1)
C(40)-P(4)-C(65)	114.3(1)	C(59)-P(4)-C(65)	106.5(1)
C(40)-P(4)-S(2)	110.89(7)	C(59)-P(4)-S(2)	109.59(7)
C(65)-P(4)-S(2)	107.28(7)	C(41)-C(40)-P(4)	124.7(2)
C(41)-C(40)-P(3)	116.5(1)	P(4)-C(40)-P(3)	114.8(1)
C(42)-C(41)-C(40)	120.7(2)	C(42)-C(41)-C(46)	118.8(2)
C(40)-C(41)-C(46)	120.5(2)	C(41)-C(42)-C(43)	124.7(2)
C(41)-C(42)-H(42)	117.7	C(43)-C(42)-H(42)	117.7
C(44)-C(43)-C(42)	123.3(2)	C(44)-C(43)-C(47)	121.7(2)
C(42)-C(43)-C(47)	114.9(2)	C(43)-C(44)-C(53)	125.0(2)
C(43)-C(44)-P(3)	115.8(2)	C(53)-C(44)-P(3)	119.2(1)
P(3)-C(45)-H(45A)	109.5	P(3)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5	P(3)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5	H(45B)-C(45)-H(45C)	109.5
C(41)-C(46)-H(46A)	109.5	C(41)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5	C(41)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5	H(46B)-C(46)-H(46C)	109.5
C(52)-C(47)-C(48)	118.0(2)	C(52)-C(47)-C(43)	123.1(2)
C(48)-C(47)-C(43)	118.9(2)	C(49)-C(48)-C(47)	120.8(2)
C(49)-C(48)-H(48)	119.6	C(47)-C(48)-H(48)	119.6
C(50)-C(49)-C(48)	120.4(2)	C(50)-C(49)-H(49)	119.8
C(48)-C(49)-H(49)	119.8	C(49)-C(50)-C(51)	119.5(2)
C(49)-C(50)-H(50)	120.2	C(51)-C(50)-H(50)	120.2
C(50)-C(51)-C(52)	120.3(2)	C(50)-C(51)-H(51)	119.8
C(52)-C(51)-H(51)	119.8	C(47)-C(52)-C(51)	121.0(2)
C(47)-C(52)-H(52)	119.5	C(51)-C(52)-H(52)	119.5
C(54)-C(53)-C(58)	118.1(2)	C(54)-C(53)-C(44)	120.5(2)
C(58)-C(53)-C(44)	121.4(2)	C(55)-C(54)-C(53)	121.1(2)
C(55)-C(54)-H(54)	119.4	C(53)-C(54)-H(54)	119.4
C(56)-C(55)-C(54)	120.2(2)	C(56)-C(55)-H(55)	119.9
C(54)-C(55)-H(55)	119.9	C(57)-C(56)-C(55)	119.6(2)
C(57)-C(56)-H(56)	120.2	C(55)-C(56)-H(56)	120.2
C(56)-C(57)-C(58)	120.1(2)	C(56)-C(57)-H(57)	119.9
C(58)-C(57)-H(57)	119.9	C(57)-C(58)-C(53)	120.9(2)
C(57)-C(58)-H(58)	119.6	C(53)-C(58)-H(58)	119.6
C(60)-C(59)-C(64)	118.9(2)	C(60)-C(59)-P(4)	123.7(2)
C(64)-C(59)-P(4)	117.2(2)	C(59)-C(60)-C(61)	121.0(2)

C(59)-C(60)-H(60)	119.5	C(61)-C(60)-H(60)	119.5
C(62)-C(61)-C(60)	119.9(2)	C(62)-C(61)-H(61)	120.0
C(60)-C(61)-H(61)	120.0	C(61)-C(62)-C(63)	120.0(2)
C(61)-C(62)-H(62)	120.0	C(63)-C(62)-H(62)	120.0
C(64)-C(63)-C(62)	120.1(2)	C(64)-C(63)-H(63)	120.0
C(62)-C(63)-H(63)	120.0	C(63)-C(64)-C(59)	120.1(2)
C(63)-C(64)-H(64)	119.9	C(59)-C(64)-H(64)	119.9
C(66)-C(65)-C(70)	119.0(2)	C(66)-C(65)-P(4)	119.1(2)
C(70)-C(65)-P(4)	121.8(2)	C(67)-C(66)-C(65)	120.8(2)
C(67)-C(66)-H(66)	119.6	C(65)-C(66)-H(66)	119.6
C(68)-C(67)-C(66)	119.7(2)	C(68)-C(67)-H(67)	120.1
C(66)-C(67)-H(67)	120.1	C(67)-C(68)-C(69)	120.5(2)
C(67)-C(68)-H(68)	119.8	C(69)-C(68)-H(68)	119.8
C(68)-C(69)-C(70)	120.1(2)	C(68)-C(69)-H(69)	119.9
C(70)-C(69)-H(69)	119.9	C(69)-C(70)-C(65)	119.9(2)
C(69)-C(70)-H(70)	120.1	C(65)-C(70)-H(70)	120.1
C(78)-C(71)-C(72)	122.3(2)	C(78)-C(71)-Rh(2)	73.2(1)
C(72)-C(71)-Rh(2)	109.8(2)	C(78)-C(71)-H(71)	118.9
C(72)-C(71)-H(71)	118.8	Rh(2)-C(71)-H(71)	87.0
C(73)-C(72)-C(71)	115.4(2)	C(73)-C(72)-H(72A)	108.4
C(71)-C(72)-H(72A)	108.4	C(73)-C(72)-H(72B)	108.4
C(71)-C(72)-H(72B)	108.4	H(72A)-C(72)-H(72B)	107.5
C(72)-C(73)-C(74)	115.6(2)	C(72)-C(73)-H(73A)	108.4
C(74)-C(73)-H(73A)	108.4	C(72)-C(73)-H(73B)	108.4
C(74)-C(73)-H(73B)	108.4	H(73A)-C(73)-H(73B)	107.4
C(75)-C(74)-C(73)	124.5(2)	C(75)-C(74)-Rh(2)	70.6(1)
C(73)-C(74)-Rh(2)	110.6(2)	C(75)-C(74)-H(74)	117.7
C(73)-C(74)-H(74)	117.8	Rh(2)-C(74)-H(74)	88.7
C(74)-C(75)-C(76)	123.8(2)	C(74)-C(75)-Rh(2)	71.2(1)
C(76)-C(75)-Rh(2)	113.8(1)	C(74)-C(75)-H(75)	118.1
C(76)-C(75)-H(75)	118.1	Rh(2)-C(75)-H(75)	85.0
C(75)-C(76)-C(77)	115.6(2)	C(75)-C(76)-H(76A)	108.4
C(77)-C(76)-H(76A)	108.4	C(75)-C(76)-H(76B)	108.4
C(77)-C(76)-H(76B)	108.4	H(76A)-C(76)-H(76B)	107.4
C(78)-C(77)-C(76)	114.8(2)	C(78)-C(77)-H(77A)	108.6
C(76)-C(77)-H(77A)	108.6	C(78)-C(77)-H(77B)	108.6
C(76)-C(77)-H(77B)	108.6	H(77A)-C(77)-H(77B)	107.5
C(71)-C(78)-C(77)	125.8(2)	C(71)-C(78)-Rh(2)	72.1(1)
C(77)-C(78)-Rh(2)	108.6(1)	C(71)-C(78)-H(78)	117.0
C(77)-C(78)-H(78)	117.1	Rh(2)-C(78)-H(78)	89.3

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mbx159

atom	U11	U22	U33	U23	U13	U12
Rh(1)	25(1)	25(1)	22(1)	5(1)	-11(1)	-7(1)
S(1)	35(1)	38(1)	27(1)	7(1)	-16(1)	-17(1)
P(1)	22(1)	23(1)	21(1)	3(1)	-10(1)	-5(1)
P(2)	27(1)	25(1)	22(1)	1(1)	-12(1)	-5(1)
C(1)	23(1)	25(1)	21(1)	1(1)	-7(1)	-4(1)
C(2)	20(1)	31(1)	23(1)	4(1)	-10(1)	-3(1)
C(3)	22(1)	27(1)	25(1)	7(1)	-9(1)	-7(1)
C(4)	22(1)	24(1)	26(1)	0(1)	-13(1)	-5(1)
C(5)	21(1)	24(1)	24(1)	0(1)	-9(1)	-5(1)
C(6)	25(1)	30(1)	27(1)	4(1)	-12(1)	-7(1)
C(7)	30(1)	35(1)	24(1)	1(1)	-8(1)	-6(1)
C(8)	26(1)	26(1)	19(1)	3(1)	-9(1)	-6(1)
C(9)	27(1)	31(1)	32(1)	2(1)	-11(1)	-5(1)
C(10)	40(1)	29(1)	43(1)	4(1)	-16(1)	-13(1)
C(11)	49(2)	23(1)	31(1)	2(1)	-19(1)	-2(1)
C(12)	32(1)	33(1)	27(1)	3(1)	-14(1)	2(1)
C(13)	27(1)	33(1)	26(1)	4(1)	-12(1)	-6(1)

C(14)	26(1)	21(1)	23(1)	5(1)	-10(1)	-3(1)
C(15)	30(1)	31(1)	27(1)	0(1)	-12(1)	-9(1)
C(16)	22(1)	39(1)	35(1)	4(1)	-6(1)	-8(1)
C(17)	29(1)	37(1)	26(1)	1(1)	-4(1)	2(1)
C(18)	40(1)	32(1)	26(1)	-4(1)	-10(1)	-4(1)
C(19)	29(1)	31(1)	32(1)	-2(1)	-13(1)	-7(1)
C(20)	29(1)	29(1)	26(1)	4(1)	-14(1)	-10(1)
C(21)	40(1)	36(1)	29(1)	-4(1)	-17(1)	1(1)
C(22)	56(2)	48(2)	27(1)	0(1)	-24(1)	-7(1)
C(23)	46(2)	41(1)	38(1)	9(1)	-29(1)	-10(1)
C(24)	34(1)	42(1)	41(1)	2(1)	-18(1)	4(1)
C(25)	34(1)	35(1)	28(1)	0(1)	-14(1)	0(1)
C(26)	38(1)	27(1)	29(1)	-1(1)	-18(1)	-1(1)
C(27)	38(1)	37(1)	34(1)	-3(1)	-15(1)	-1(1)
C(28)	41(2)	51(2)	43(2)	-6(1)	-16(1)	8(1)
C(29)	63(2)	38(2)	47(2)	-11(1)	-27(2)	16(1)
C(30)	70(2)	29(1)	63(2)	-9(1)	-42(2)	1(1)
C(31)	45(2)	31(1)	54(2)	-5(1)	-29(1)	-2(1)
C(32)	37(1)	36(1)	26(1)	9(1)	-18(1)	-14(1)
C(33)	44(2)	37(1)	43(1)	13(1)	-26(1)	-10(1)
C(34)	51(2)	37(1)	54(2)	21(1)	-30(1)	-17(1)
C(35)	45(2)	38(1)	38(1)	19(1)	-23(1)	-25(1)
C(36)	37(1)	54(2)	33(1)	20(1)	-16(1)	-22(1)
C(37)	38(2)	76(2)	36(2)	11(1)	-4(1)	-13(1)
C(38)	52(2)	56(2)	28(1)	1(1)	-15(1)	2(1)
C(39)	50(2)	34(1)	24(1)	6(1)	-22(1)	-6(1)
Rh(2)	21(1)	24(1)	21(1)	3(1)	-9(1)	-5(1)
S(2)	27(1)	36(1)	24(1)	4(1)	-11(1)	-13(1)
P(3)	20(1)	22(1)	21(1)	2(1)	-9(1)	-4(1)
P(4)	24(1)	25(1)	22(1)	1(1)	-11(1)	-5(1)
C(40)	23(1)	23(1)	22(1)	0(1)	-8(1)	-4(1)
C(41)	21(1)	30(1)	21(1)	1(1)	-10(1)	-3(1)
C(42)	22(1)	30(1)	23(1)	5(1)	-7(1)	-7(1)
C(43)	21(1)	24(1)	25(1)	1(1)	-11(1)	-3(1)
C(44)	22(1)	23(1)	24(1)	1(1)	-10(1)	-4(1)
C(45)	23(1)	31(1)	28(1)	5(1)	-12(1)	-9(1)
C(46)	32(1)	35(1)	23(1)	1(1)	-9(1)	-6(1)
C(47)	28(1)	25(1)	22(1)	2(1)	-11(1)	-3(1)
C(48)	26(1)	29(1)	23(1)	3(1)	-11(1)	-5(1)
C(49)	38(1)	29(1)	31(1)	4(1)	-18(1)	-11(1)
C(50)	45(1)	25(1)	29(1)	4(1)	-19(1)	-2(1)
C(51)	35(1)	32(1)	34(1)	4(1)	-17(1)	3(1)
C(52)	27(1)	33(1)	30(1)	8(1)	-12(1)	-7(1)
C(53)	25(1)	23(1)	22(1)	4(1)	-10(1)	1(1)
C(54)	30(1)	26(1)	30(1)	1(1)	-10(1)	-4(1)
C(55)	27(1)	33(1)	35(1)	4(1)	-5(1)	-3(1)
C(56)	36(1)	35(1)	26(1)	1(1)	-5(1)	8(1)
C(57)	43(1)	31(1)	31(1)	-7(1)	-15(1)	1(1)
C(58)	30(1)	29(1)	31(1)	1(1)	-13(1)	-5(1)
C(59)	23(1)	32(1)	28(1)	6(1)	-12(1)	-10(1)
C(60)	47(2)	34(1)	35(1)	5(1)	-25(1)	-10(1)
C(61)	62(2)	50(2)	37(1)	10(1)	-34(1)	-22(1)
C(62)	42(2)	55(2)	47(2)	24(1)	-32(1)	-20(1)
C(63)	33(1)	48(2)	48(2)	14(1)	-18(1)	-1(1)
C(64)	31(1)	43(1)	29(1)	3(1)	-10(1)	-1(1)
C(65)	33(1)	24(1)	27(1)	2(1)	-14(1)	-4(1)
C(66)	36(1)	35(1)	34(1)	1(1)	-12(1)	-2(1)
C(67)	43(2)	45(2)	40(2)	-2(1)	-9(1)	6(1)
C(68)	72(2)	33(2)	38(2)	-5(1)	-15(2)	10(1)
C(69)	79(2)	25(1)	44(2)	1(1)	-30(2)	-10(1)
C(70)	50(2)	33(1)	35(1)	3(1)	-22(1)	-8(1)
C(71)	28(1)	45(1)	27(1)	14(1)	-7(1)	-12(1)
C(72)	52(2)	58(2)	36(2)	-3(1)	3(1)	-13(1)

C(73)	47(2)	49(2)	28(1)	-3(1)	-18(1)	6(1)
C(74)	40(1)	33(1)	24(1)	5(1)	-18(1)	-6(1)
C(75)	28(1)	35(1)	23(1)	6(1)	-12(1)	-8(1)
C(76)	39(1)	33(1)	38(1)	9(1)	-23(1)	-6(1)
C(77)	48(2)	47(2)	62(2)	27(1)	-28(1)	-20(1)
C(78)	32(1)	34(1)	28(1)	11(1)	-12(1)	-15(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mbx159

atom	x	y	z	U(eq)
H(3)	9230	2613	2226	30
H(6A)	9966	268	3732	40
H(6B)	9315	990	4529	40
H(6C)	9764	1342	3581	40
H(7A)	9816	1749	991	46
H(7B)	9132	1027	977	46
H(7C)	10181	685	1104	46
H(9)	9098	3846	3165	36
H(10)	8568	5432	3304	44
H(11)	6831	6103	3734	41
H(12)	5621	5169	4005	38
H(13)	6142	3583	3877	34
H(15)	5770	1557	4550	34
H(16)	4319	1972	5816	40
H(17)	4375	2875	6882	41
H(18)	5881	3398	6652	41
H(19)	7334	2997	5381	36
H(21)	8420	-620	666	42
H(22)	7610	-4	-220	51
H(23)	6184	1198	297	45
H(24)	5590	1800	1690	47
H(25)	6400	1192	2581	39
H(27)	10290	-758	1685	44
H(28)	11470	-2102	1025	57
H(29)	10892	-3394	841	62
H(30)	9139	-3355	1283	61
H(31)	7944	-2013	1953	49
H(32)	8819	-427	4971	36
H(33A)	7789	-1243	6524	46
H(33B)	8906	-1667	5818	46
H(34A)	8302	-2467	5141	52
H(34B)	7391	-2415	6070	52
H(35)	7056	-1840	4691	43
H(36)	5757	-661	5310	47
H(37A)	5132	-263	6764	64
H(37B)	6082	-954	6842	64
H(38A)	6492	337	7027	57
H(38B)	5921	894	6480	57
H(39)	7531	840	5456	41
H(42)	965	2588	2874	31
H(45A)	244	3789	1542	40
H(45B)	615	4010	554	40
H(45C)	108	4830	1273	40
H(46A)	482	3596	4003	47
H(46B)	168	4640	3799	47
H(46C)	1246	4288	3876	47
H(48)	980	1253	2155	31

H(49)	1490	-329.0000	2161	37
H(50)	3230	-1013	1580	39
H(51)	4468	-101.0000	1039	41
H(52)	3969	1483	1046	36
H(54)	4321	3374	153	35
H(55)	5631	2807	-1154	42
H(56)	5363	1791	-2020.9999	45
H(57)	3780	1333	-1561	43
H(58)	2471	1887	-241	36
H(60)	2366	5802	3872	43
H(61)	3181	5066	4715	53
H(62)	4250	3637	4269	51
H(63)	4556	2952	2949	52
H(64)	3761	3693	2096	43
H(66)	151	6035	2945	44
H(67)	-908.9999	7443	3562	57
H(68)	-197	8625	3802	63
H(69)	1577	8433	3380	57
H(70)	2656	7039	2720	46
H(71)	4452	5313	-780	41
H(72A)	3925	5521	-2221	66
H(72B)	4825	4750	-2157	66
H(73A)	3845	3757	-1681	51
H(73B)	3227	4351	-2175	51
H(74)	2329	4027	-517	37
H(75)	1209	5407	-64	34
H(76A)	1145	6575	-976	42
H(76B)	2109	5996	-1745	42
H(77A)	2898	7051	-1609	59
H(77B)	2093	7343	-650	59
H(78)	3337	6634	-237	36

I.7. Crystallographic data for II-22

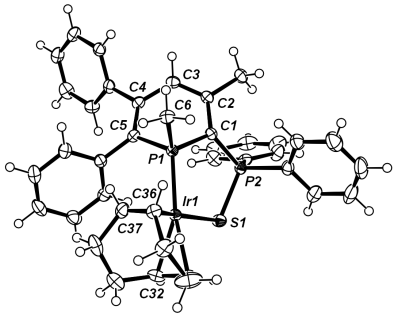


Table 1. Crystal data for mb111

Compound	mb111
Molecular formula	$C_{39}H_{39}IrP_2S$
Molecular weight	793.90
Crystal habit	orange block

Crystal dimensions(mm)	0.16x0.16x0.14
Crystal system	triclinic
Space group	Pbar1
a(Å)	14.4750(10)
b(Å)	14.8430(10)
c(Å)	17.0890(10)
α(°)	88.4450(10)
β(°)	66.5480(10)
γ(°)	79.0370(10)
V(Å^3)	3302.0(4)
Z	4
d(g-cm^{-3})	1.597
F(000)	1584
μ(cm^{-1})	4.231
Absorption corrections	multi-scan ; 0.5509 min, 0.5889 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-20 20 ; -20 18 ; -24 23
Reflections measured	40092
Unique data	19250
Rint	0.0245
Reflections used	15826
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	804
Reflections / parameter	19
wR2	0.0606
R1	0.0267
Weights a, b	0.0215 ; 0.0000
GoF	1.031
difference peak / hole (e Å^{-3})	1.486(0.112) / -1.333(0.112)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb111

atom	x	y	z	U(eq)
Ir(1)	7282(1)	4806(1)	9900(1)	17(1)
S(1)	6673(1)	4389(1)	8917(1)	24(1)
P(1)	8176(1)	5742(1)	8931(1)	17(1)
P(2)	7700(1)	4687(1)	7752(1)	19(1)
C(1)	8372(2)	5477(2)	7872(1)	19(1)
C(2)	8742(2)	6148(2)	7261(1)	20(1)
C(3)	8625(2)	7039(2)	7520(1)	21(1)
C(4)	7933(2)	7451(2)	8359(1)	20(1)
C(5)	7585(2)	6948(2)	9064(1)	19(1)

C(6)	9447(2)	5785(2)	8893(2)	23(1)
C(7)	7017(2)	5171(2)	7104(1)	22(1)
C(8)	6368(2)	6022(2)	7377(2)	31(1)
C(9)	5883(2)	6465(2)	6882(2)	40(1)
C(10)	6050(2)	6067(2)	6104(2)	39(1)
C(11)	6686(2)	5230(2)	5832(2)	41(1)
C(12)	7177(2)	4780(2)	6324(2)	32(1)
C(13)	8493(2)	3600(2)	7220(1)	24(1)
C(14)	8070(2)	2879(2)	7086(2)	33(1)
C(15)	8705(3)	2055(2)	6700(2)	43(1)
C(16)	9748(3)	1929(2)	6467(2)	46(1)
C(17)	10168(2)	2631(2)	6614(2)	44(1)
C(18)	9545(2)	3464(2)	6988(2)	30(1)
C(19)	9250(2)	5879(2)	6311(1)	27(1)
C(20)	7583(2)	8468(2)	8387(1)	21(1)
C(21)	8307(2)	9028(2)	8052(1)	23(1)
C(22)	8008(2)	9967(2)	8049(2)	27(1)
C(23)	6978(2)	10375(2)	8391(2)	28(1)
C(24)	6251(2)	9835(2)	8724(2)	31(1)
C(25)	6547(2)	8885(2)	8722(1)	25(1)
C(26)	6753(2)	7327(2)	9901(1)	21(1)
C(27)	6912(2)	7935(2)	10421(2)	27(1)
C(28)	6140(2)	8272(2)	11202(2)	32(1)
C(29)	5209(2)	8009(2)	11475(2)	33(1)
C(30)	5032(2)	7408(2)	10968(2)	31(1)
C(31)	5806(2)	7062(2)	10188(2)	25(1)
C(32)	5985(2)	4472(2)	11018(2)	30(1)
C(33)	6688(2)	3673(2)	10712(2)	28(1)
C(34)	7423(2)	3222(2)	11097(2)	50(1)
C(35)	8132(2)	3824(2)	11153(2)	31(1)
C(36)	8207(2)	4654(2)	10616(2)	24(1)
C(37)	7496(2)	5494(2)	10872(2)	26(1)
C(38)	6546(2)	5637(2)	11707(2)	38(1)
C(39)	5845(3)	4992(3)	11822(2)	60(1)
Ir(2)	12553(1)	10318(1)	5404(1)	19(1)
S(2)	12965(1)	10640(1)	6538(1)	26(1)
P(3)	11706(1)	9232(1)	6196(1)	17(1)
P(4)	11873(1)	10218(1)	7597(1)	20(1)
C(40)	11365(2)	9379(2)	7308(1)	20(1)
C(41)	10994(2)	8637(2)	7814(1)	21(1)
C(42)	11180(2)	7776(2)	7451(1)	21(1)
C(43)	11960(2)	7460(2)	6607(1)	19(1)
C(44)	12364(2)	8047(2)	5990(1)	19(1)
C(45)	10532(2)	9134(2)	6065(2)	24(1)
C(46)	12483(2)	9776(2)	8312(1)	22(1)
C(47)	13330(2)	9064(2)	8004(2)	30(1)
C(48)	13822(2)	8707(2)	8522(2)	37(1)
C(49)	13471(2)	9051(2)	9357(2)	34(1)
C(50)	12626(2)	9743(2)	9668(2)	37(1)
C(51)	12126(2)	10110(2)	9150(2)	31(1)
C(52)	10953(2)	11238(2)	8150(2)	26(1)
C(53)	11286(2)	12021(2)	8282(2)	36(1)
C(54)	10582(3)	12811(2)	8679(2)	46(1)
C(55)	9545(3)	12832(2)	8942(2)	47(1)
C(56)	9206(2)	12061(2)	8819(2)	42(1)
C(57)	9913(2)	11264(2)	8420(2)	33(1)
C(58)	10403(2)	8787(2)	8778(1)	27(1)
C(59)	12328(2)	6443(2)	6486(1)	20(1)
C(60)	11616(2)	5869(2)	6647(2)	26(1)
C(61)	11936(2)	4928(2)	6561(2)	33(1)
C(62)	12965(2)	4529(2)	6312(2)	31(1)
C(63)	13670(2)	5089(2)	6157(2)	29(1)
C(64)	13357(2)	6038(2)	6242(1)	24(1)

C(65)	13283(2)	7762(2)	5180(1)	20(1)
C(66)	13272(2)	7219(2)	4533(1)	27(1)
C(67)	14130(2)	6989(2)	3780(2)	30(1)
C(68)	15021(2)	7293(2)	3650(2)	31(1)
C(69)	15053(2)	7826(2)	4280(2)	31(1)
C(70)	14189(2)	8064(2)	5042(2)	26(1)
C(71)	11796(2)	10478(2)	4549(2)	27(1)
C(72)	12621(2)	9712(2)	4265(2)	32(1)
C(73)	13630(2)	9727(2)	3523(2)	45(1)
C(74)	14133(3)	10511(3)	3568(2)	56(1)
C(75)	13802(2)	10917(2)	4468(2)	34(1)
C(76)	12977(2)	11615(2)	4831(2)	31(1)
C(77)	12263(2)	12053(2)	4421(2)	45(1)
C(78)	11815(2)	11372(2)	4109(2)	36(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb111

Ir(1)-C(36)	2.124(2)	Ir(1)-C(37)	2.125(2)
Ir(1)-C(32)	2.206(2)	Ir(1)-C(33)	2.229(3)
Ir(1)-P(1)	2.2808(6	Ir(1)-S(1)	2.3301(6)
S(1)-P(2)	2.0530(8	P(1)-C(1)	1.760(2)
P(1)-C(5)	1.809(3)	P(1)-C(6)	1.827(2)
P(2)-C(1)	1.724(2)	P(2)-C(7)	1.811(2)
P(2)-C(13)	1.815(3)	C(1)-C(2)	1.439(3)
C(2)-C(3)	1.364(3)	C(2)-C(19)	1.519(3)
C(3)-C(4)	1.451(3)	C(3)-H(3)	0.9500
C(4)-C(5)	1.368(3)	C(4)-C(20)	1.495(3)
C(5)-C(26)	1.493(3)	C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800	C(6)-H(6C)	0.9800
C(7)-C(12)	1.382(3)	C(7)-C(8)	1.389(4)
C(8)-C(9)	1.381(3)	C(8)-H(8)	0.9500
C(9)-C(10)	1.381(4)	C(9)-H(9)	0.9500
C(10)-C(11)	1.365(4)	C(10)-H(10)	0.9500
C(11)-C(12)	1.388(4)	C(11)-H(11)	0.9500
C(12)-H(12)	0.9500	C(13)-C(18)	1.386(3)
C(13)-C(14)	1.395(3)	C(14)-C(15)	1.382(4)
C(14)-H(14)	0.9500	C(15)-C(16)	1.374(4)
C(15)-H(15)	0.9500	C(16)-C(17)	1.377(4)
C(16)-H(16)	0.9500	C(17)-C(18)	1.382(4)
C(17)-H(17)	0.9500	C(18)-H(18)	0.9500
C(19)-H(19A)	0.9800	C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800	C(20)-C(25)	1.393(3)
C(20)-C(21)	1.395(3)	C(21)-C(22)	1.379(3)
C(21)-H(21)	0.9500	C(22)-C(23)	1.384(4)
C(22)-H(22)	0.9500	C(23)-C(24)	1.376(4)
C(23)-H(23)	0.9500	C(24)-C(25)	1.394(4)
C(24)-H(24)	0.9500	C(25)-H(25)	0.9500
C(26)-C(31)	1.392(3)	C(26)-C(27)	1.393(3)
C(27)-C(28)	1.384(3)	C(27)-H(27)	0.9500
C(28)-C(29)	1.370(4)	C(28)-H(28)	0.9500
C(29)-C(30)	1.385(4)	C(29)-H(29)	0.9500
C(30)-C(31)	1.387(3)	C(30)-H(30)	0.9500
C(31)-H(31)	0.9500	C(32)-C(33)	1.367(4)
C(32)-C(39)	1.516(4)	C(32)-H(32)	0.99(3)
C(33)-C(34)	1.508(4)	C(33)-H(33)	0.97(2)
C(34)-C(35)	1.514(4)	C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900	C(35)-C(36)	1.511(4)
C(35)-H(35A)	0.9900	C(35)-H(35B)	0.9900
C(36)-C(37)	1.411(4)	C(36)-H(36)	0.97(3)
C(37)-C(38)	1.521(4)	C(37)-H(37)	0.83(3)
C(38)-C(39)	1.478(4)	C(38)-H(38A)	0.9900

C(38)-H(38B)	0.9900	C(39)-H(39A)	0.9900
C(39)-H(39B)	0.9900	Ir(2)-C(72)	2.126(2)
Ir(2)-C(71)	2.132(2)	Ir(2)-C(75)	2.203(3)
Ir(2)-C(76)	2.216(3)	Ir(2)-P(3)	2.2897(6)
Ir(2)-S(2)	2.3275(6	S(2)-P(4)	2.050(1)
P(3)-C(40)	1.773(2)	P(3)-C(44)	1.805(3)
P(3)-C(45)	1.831(2)	P(4)-C(40)	1.732(2)
P(4)-C(52)	1.808(3)	P(4)-C(46)	1.817(2)
C(40)-C(41)	1.433(3)	C(41)-C(42)	1.368(3)
C(41)-C(58)	1.523(3)	C(42)-C(43)	1.453(3)
C(42)-H(42)	0.9500	C(43)-C(44)	1.367(3)
C(43)-C(59)	1.493(3)	C(44)-C(65)	1.489(3)
C(45)-H(45A)	0.9800	C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800	C(46)-C(51)	1.384(3)
C(46)-C(47)	1.386(4)	C(47)-C(48)	1.380(4)
C(47)-H(47)	0.9500	C(48)-C(49)	1.385(4)
C(48)-H(48)	0.9500	C(49)-C(50)	1.367(4)
C(49)-H(49)	0.9500	C(50)-C(51)	1.392(3)
C(50)-H(50)	0.9500	C(51)-H(51)	0.9500
C(52)-C(57)	1.380(3)	C(52)-C(53)	1.396(3)
C(53)-C(54)	1.382(4)	C(53)-H(53)	0.9500
C(54)-C(55)	1.380(4)	C(54)-H(54)	0.9500
C(55)-C(56)	1.381(4)	C(55)-H(55)	0.9500
C(56)-C(57)	1.392(4)	C(56)-H(56)	0.9500
C(57)-H(57)	0.9500	C(58)-H(58A)	0.9800
C(58)-H(58B)	0.9800	C(58)-H(58C)	0.9800
C(59)-C(64)	1.390(3)	C(59)-C(60)	1.399(3)
C(60)-C(61)	1.377(4)	C(60)-H(60)	0.9500
C(61)-C(62)	1.387(4)	C(61)-H(61)	0.9500
C(62)-C(63)	1.378(4)	C(62)-H(62)	0.9500
C(63)-C(64)	1.388(4)	C(63)-H(63)	0.9500
C(64)-H(64)	0.9500	C(65)-C(66)	1.392(3)
C(65)-C(70)	1.396(3)	C(66)-C(67)	1.381(3)
C(66)-H(66)	0.9500	C(67)-C(68)	1.380(4)
C(67)-H(67)	0.9500	C(68)-C(69)	1.375(3)
C(68)-H(68)	0.9500	C(69)-C(70)	1.395(3)
C(69)-H(69)	0.9500	C(70)-H(70)	0.9500
C(71)-C(72)	1.417(4)	C(71)-C(78)	1.507(4)
C(71)-H(71)	1.00(3)	C(72)-C(73)	1.509(4)
C(72)-H(72)	0.97(3)	C(73)-C(74)	1.504(4)
C(73)-H(73A)	0.9900	C(73)-H(73B)	0.9900
C(74)-C(75)	1.519(4)	C(74)-H(74A)	0.9900
C(74)-H(74B)	0.9900	C(75)-C(76)	1.363(4)
C(75)-H(75)	0.93(3)	C(76)-C(77)	1.510(4)
C(76)-H(76)	1.02(3)	C(77)-C(78)	1.509(4)
C(77)-H(77A)	0.9900	C(77)-H(77B)	0.9900
C(78)-H(78A)	0.9900	C(78)-H(78B)	0.9900

C(36)-Ir(1)-C(37)	38.8(1)	C(36)-Ir(1)-C(32)	90.5(1)
C(37)-Ir(1)-C(32)	81.2(1)	C(36)-Ir(1)-C(33)	80.4(1)
C(37)-Ir(1)-C(33)	94.6(1)	C(32)-Ir(1)-C(33)	35.9(1)
C(36)-Ir(1)-P(1)	95.96(7)	C(37)-Ir(1)-P(1)	89.16(7)
C(32)-Ir(1)-P(1)	155.64(8)	C(33)-Ir(1)-P(1)	168.43(8)
C(36)-Ir(1)-S(1)	156.86(8)	C(37)-Ir(1)-S(1)	164.28(8)
C(32)-Ir(1)-S(1)	94.11(7)	C(33)-Ir(1)-S(1)	90.10(7)
P(1)-Ir(1)-S(1)	89.15(2)	P(2)-S(1)-Ir(1)	104.89(3)
C(1)-P(1)-C(5)	101.7(1)	C(1)-P(1)-C(6)	105.4(1)
C(5)-P(1)-C(6)	101.7(1)	C(1)-P(1)-Ir(1)	113.94(8)
C(5)-P(1)-Ir(1)	116.30(8)	C(6)-P(1)-Ir(1)	116.02(8)
C(1)-P(2)-C(7)	108.2(1)	C(1)-P(2)-C(13)	114.6(1)
C(7)-P(2)-C(13)	106.7(1)	C(1)-P(2)-S(1)	110.87(8)
C(7)-P(2)-S(1)	109.62(8)	C(13)-P(2)-S(1)	106.7(1)

C(2)-C(1)-P(2)	124.1(2)	C(2)-C(1)-P(1)	116.4(2)
P(2)-C(1)-P(1)	115.4(1)	C(3)-C(2)-C(1)	120.8(2)
C(3)-C(2)-C(19)	118.8(2)	C(1)-C(2)-C(19)	120.4(2)
C(2)-C(3)-C(4)	124.7(2)	C(2)-C(3)-H(3)	117.7
C(4)-C(3)-H(3)	117.7	C(5)-C(4)-C(3)	123.0(2)
C(5)-C(4)-C(20)	122.3(2)	C(3)-C(4)-C(20)	114.7(2)
C(4)-C(5)-C(26)	124.3(2)	C(4)-C(5)-P(1)	116.0(2)
C(26)-C(5)-P(1)	119.7(2)	P(1)-C(6)-H(6A)	109.5
P(1)-C(6)-H(6B)	109.5	H(6A)-C(6)-H(6B)	109.5
P(1)-C(6)-H(6C)	109.5	H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5	C(12)-C(7)-C(8)	118.9(2)
C(12)-C(7)-P(2)	123.5(2)	C(8)-C(7)-P(2)	117.3(2)
C(9)-C(8)-C(7)	120.5(2)	C(9)-C(8)-H(8)	119.7
C(7)-C(8)-H(8)	119.7	C(8)-C(9)-C(10)	120.1(3)
C(8)-C(9)-H(9)	119.9	C(10)-C(9)-H(9)	119.9
C(11)-C(10)-C(9)	119.7(3)	C(11)-C(10)-H(10)	120.2
C(9)-C(10)-H(10)	120.2	C(10)-C(11)-C(12)	120.7(3)
C(10)-C(11)-H(11)	119.7	C(12)-C(11)-H(11)	119.7
C(7)-C(12)-C(11)	120.2(3)	C(7)-C(12)-H(12)	119.9
C(11)-C(12)-H(12)	119.9	C(18)-C(13)-C(14)	119.1(2)
C(18)-C(13)-P(2)	118.8(2)	C(14)-C(13)-P(2)	121.9(2)
C(15)-C(14)-C(13)	119.7(3)	C(15)-C(14)-H(14)	120.1
C(13)-C(14)-H(14)	120.1	C(16)-C(15)-C(14)	120.7(3)
C(16)-C(15)-H(15)	119.7	C(14)-C(15)-H(15)	119.7
C(15)-C(16)-C(17)	119.9(3)	C(15)-C(16)-H(16)	120.1
C(17)-C(16)-H(16)	120.1	C(16)-C(17)-C(18)	120.1(3)
C(16)-C(17)-H(17)	119.9	C(18)-C(17)-H(17)	119.9
C(17)-C(18)-C(13)	120.5(3)	C(17)-C(18)-H(18)	119.8
C(13)-C(18)-H(18)	119.8	C(2)-C(19)-H(19A)	109.5
C(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
C(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(25)-C(20)-C(21)	118.1(2)
C(25)-C(20)-C(4)	122.2(2)	C(21)-C(20)-C(4)	119.6(2)
C(22)-C(21)-C(20)	121.0(2)	C(22)-C(21)-H(21)	119.5
C(20)-C(21)-H(21)	119.5	C(21)-C(22)-C(23)	120.4(2)
C(21)-C(22)-H(22)	119.8	C(23)-C(22)-H(22)	119.8
C(24)-C(23)-C(22)	119.5(3)	C(24)-C(23)-H(23)	120.2
C(22)-C(23)-H(23)	120.2	C(23)-C(24)-C(25)	120.4(3)
C(23)-C(24)-H(24)	119.8	C(25)-C(24)-H(24)	119.8
C(20)-C(25)-C(24)	120.6(2)	C(20)-C(25)-H(25)	119.7
C(24)-C(25)-H(25)	119.7	C(31)-C(26)-C(27)	118.5(2)
C(31)-C(26)-C(5)	120.4(2)	C(27)-C(26)-C(5)	121.1(2)
C(28)-C(27)-C(26)	120.7(2)	C(28)-C(27)-H(27)	119.7
C(26)-C(27)-H(27)	119.7	C(29)-C(28)-C(27)	120.3(2)
C(29)-C(28)-H(28)	119.9	C(27)-C(28)-H(28)	119.9
C(28)-C(29)-C(30)	120.1(2)	C(28)-C(29)-H(29)	119.9
C(30)-C(29)-H(29)	119.9	C(29)-C(30)-C(31)	119.8(2)
C(29)-C(30)-H(30)	120.1	C(31)-C(30)-H(30)	120.1
C(30)-C(31)-C(26)	120.6(2)	C(30)-C(31)-H(31)	119.7
C(26)-C(31)-H(31)	119.7	C(33)-C(32)-C(39)	122.0(3)
C(33)-C(32)-Ir(1)	72.9(2)	C(39)-C(32)-Ir(1)	111.1(2)
C(33)-C(32)-H(32)	118(2)	C(39)-C(32)-H(32)	117(2)
Ir(1)-C(32)-H(32)	104(2)	C(32)-C(33)-C(34)	125.5(3)
C(32)-C(33)-Ir(1)	71.2(2)	C(34)-C(33)-Ir(1)	110.9(2)
C(32)-C(33)-H(33)	120(2)	C(34)-C(33)-H(33)	112(2)
Ir(1)-C(33)-H(33)	103(2)	C(33)-C(34)-C(35)	114.0(2)
C(33)-C(34)-H(34A)	108.7	C(35)-C(34)-H(34A)	108.7
C(33)-C(34)-H(34B)	108.7	C(35)-C(34)-H(34B)	108.7
H(34A)-C(34)-H(34B)	107.6	C(36)-C(35)-C(34)	115.8(2)
C(36)-C(35)-H(35A)	108.3	C(34)-C(35)-H(35A)	108.3
C(36)-C(35)-H(35B)	108.3	C(34)-C(35)-H(35B)	108.3
H(35A)-C(35)-H(35B)	107.4	C(37)-C(36)-C(35)	123.8(2)
C(37)-C(36)-Ir(1)	70.6(1)	C(35)-C(36)-Ir(1)	114.5(2)

C(37)-C(36)-H(36)	114(2)	C(35)-C(36)-H(36)	118(2)
Ir(1)-C(36)-H(36)	104(1)	C(36)-C(37)-C(38)	122.8(3)
C(36)-C(37)-Ir(1)	70.6(1)	C(38)-C(37)-Ir(1)	112.2(2)
C(36)-C(37)-H(37)	115(2)	C(38)-C(37)-H(37)	112(2)
Ir(1)-C(37)-H(37)	119(2)	C(39)-C(38)-C(37)	115.3(2)
C(39)-C(38)-H(38A)	108.4	C(37)-C(38)-H(38A)	108.4
C(39)-C(38)-H(38B)	108.4	C(37)-C(38)-H(38B)	108.4
H(38A)-C(38)-H(38B)	107.5	C(38)-C(39)-C(32)	115.9(2)
C(38)-C(39)-H(39A)	108.3	C(32)-C(39)-H(39A)	108.3
C(38)-C(39)-H(39B)	108.3	C(32)-C(39)-H(39B)	108.3
H(39A)-C(39)-H(39B)	107.4	C(72)-Ir(2)-C(71)	38.9(1)
C(72)-Ir(2)-C(75)	81.0(1)	C(71)-Ir(2)-C(75)	89.2(1)
C(72)-Ir(2)-C(76)	95.2(1)	C(71)-Ir(2)-C(76)	79.9(1)
C(75)-Ir(2)-C(76)	35.9(1)	C(72)-Ir(2)-P(3)	90.83(8)
C(71)-Ir(2)-P(3)	96.36(8)	C(75)-Ir(2)-P(3)	159.3(1)
C(76)-Ir(2)-P(3)	164.75(8)	C(72)-Ir(2)-S(2)	161.62(8)
C(71)-Ir(2)-S(2)	159.25(8)	C(75)-Ir(2)-S(2)	93.26(7)
C(76)-Ir(2)-S(2)	90.08(7)	P(3)-Ir(2)-S(2)	88.58(2)
P(4)-S(2)-Ir(2)	105.16(3)	C(40)-P(3)-C(44)	101.2(1)
C(40)-P(3)-C(45)	106.6(1)	C(44)-P(3)-C(45)	100.0(1)
C(40)-P(3)-Ir(2)	114.07(8)	C(44)-P(3)-Ir(2)	118.08(8)
C(45)-P(3)-Ir(2)	114.97(8)	C(40)-P(4)-C(52)	115.3(1)
C(40)-P(4)-C(46)	110.7(1)	C(52)-P(4)-C(46)	105.4(1)
C(40)-P(4)-S(2)	110.45(8)	C(52)-P(4)-S(2)	106.9(1)
C(46)-P(4)-S(2)	107.69(8)	C(41)-C(40)-P(4)	126.0(2)
C(41)-C(40)-P(3)	116.2(2)	P(4)-C(40)-P(3)	114.8(1)
C(42)-C(41)-C(40)	121.2(2)	C(42)-C(41)-C(58)	118.4(2)
C(40)-C(41)-C(58)	120.4(2)	C(41)-C(42)-C(43)	124.4(2)
C(41)-C(42)-H(42)	117.8	C(43)-C(42)-H(42)	117.8
C(44)-C(43)-C(42)	122.9(2)	C(44)-C(43)-C(59)	122.5(2)
C(42)-C(43)-C(59)	114.5(2)	C(43)-C(44)-C(65)	124.2(2)
C(43)-C(44)-P(3)	116.0(2)	C(65)-C(44)-P(3)	119.8(2)
P(3)-C(45)-H(45A)	109.5	P(3)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5	P(3)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5	H(45B)-C(45)-H(45C)	109.5
C(51)-C(46)-C(47)	119.1(2)	C(51)-C(46)-P(4)	122.7(2)
C(47)-C(46)-P(4)	118.2(2)	C(48)-C(47)-C(46)	120.4(2)
C(48)-C(47)-H(47)	119.8	C(46)-C(47)-H(47)	119.8
C(47)-C(48)-C(49)	120.4(3)	C(47)-C(48)-H(48)	119.8
C(49)-C(48)-H(48)	119.8	C(50)-C(49)-C(48)	119.5(2)
C(50)-C(49)-H(49)	120.2	C(48)-C(49)-H(49)	120.2
C(49)-C(50)-C(51)	120.6(2)	C(49)-C(50)-H(50)	119.7
C(51)-C(50)-H(50)	119.7	C(46)-C(51)-C(50)	120.1(3)
C(46)-C(51)-H(51)	120.0	C(50)-C(51)-H(51)	120.0
C(57)-C(52)-C(53)	119.1(2)	C(57)-C(52)-P(4)	120.5(2)
C(53)-C(52)-P(4)	120.4(2)	C(54)-C(53)-C(52)	120.3(3)
C(54)-C(53)-H(53)	119.8	C(52)-C(53)-H(53)	119.8
C(55)-C(54)-C(53)	120.1(3)	C(55)-C(54)-H(54)	119.9
C(53)-C(54)-H(54)	119.9	C(54)-C(55)-C(56)	120.1(3)
C(54)-C(55)-H(55)	120.0	C(56)-C(55)-H(55)	120.0
C(55)-C(56)-C(57)	119.9(3)	C(55)-C(56)-H(56)	120.1
C(57)-C(56)-H(56)	120.1	C(52)-C(57)-C(56)	120.5(3)
C(52)-C(57)-H(57)	119.8	C(56)-C(57)-H(57)	119.8
C(41)-C(58)-H(58A)	109.5	C(41)-C(58)-H(58B)	109.5
H(58A)-C(58)-H(58B)	109.5	C(41)-C(58)-H(58C)	109.5
H(58A)-C(58)-H(58C)	109.5	H(58B)-C(58)-H(58C)	109.5
C(64)-C(59)-C(60)	118.2(2)	C(64)-C(59)-C(43)	122.3(2)
C(60)-C(59)-C(43)	119.4(2)	C(61)-C(60)-C(59)	120.4(2)
C(61)-C(60)-H(60)	119.8	C(59)-C(60)-H(60)	119.8
C(60)-C(61)-C(62)	121.0(3)	C(60)-C(61)-H(61)	119.5
C(62)-C(61)-H(61)	119.5	C(63)-C(62)-C(61)	119.0(3)
C(63)-C(62)-H(62)	120.5	C(61)-C(62)-H(62)	120.5
C(62)-C(63)-C(64)	120.5(3)	C(62)-C(63)-H(63)	119.7

C(64)-C(63)-H(63)	119.7	C(63)-C(64)-C(59)	120.9(2)
C(63)-C(64)-H(64)	119.6	C(59)-C(64)-H(64)	119.6
C(66)-C(65)-C(70)	117.9(2)	C(66)-C(65)-C(44)	122.5(2)
C(70)-C(65)-C(44)	119.6(2)	C(67)-C(66)-C(65)	121.0(2)
C(67)-C(66)-H(66)	119.5	C(65)-C(66)-H(66)	119.5
C(68)-C(67)-C(66)	120.7(2)	C(68)-C(67)-H(67)	119.6
C(66)-C(67)-H(67)	119.6	C(69)-C(68)-C(67)	119.5(2)
C(69)-C(68)-H(68)	120.3	C(67)-C(68)-H(68)	120.3
C(68)-C(69)-C(70)	120.2(2)	C(68)-C(69)-H(69)	119.9
C(70)-C(69)-H(69)	119.9	C(69)-C(70)-C(65)	120.8(2)
C(69)-C(70)-H(70)	119.6	C(65)-C(70)-H(70)	119.6
C(72)-C(71)-C(78)	123.3(3)	C(72)-C(71)-Ir(2)	70.3(1)
C(78)-C(71)-Ir(2)	115.1(2)	C(72)-C(71)-H(71)	116(2)
C(78)-C(71)-H(71)	115(2)	Ir(2)-C(71)-H(71)	107(1)
C(71)-C(72)-C(73)	123.4(3)	C(71)-C(72)-Ir(2)	70.8(1)
C(73)-C(72)-Ir(2)	111.8(2)	C(71)-C(72)-H(72)	107(2)
C(73)-C(72)-H(72)	119(2)	Ir(2)-C(72)-H(72)	115(2)
C(74)-C(73)-C(72)	114.9(2)	C(74)-C(73)-H(73A)	108.5
C(72)-C(73)-H(73A)	108.5	C(74)-C(73)-H(73B)	108.5
C(72)-C(73)-H(73B)	108.5	H(73A)-C(73)-H(73B)	107.5
C(73)-C(74)-C(75)	114.0(2)	C(73)-C(74)-H(74A)	108.8
C(75)-C(74)-H(74A)	108.8	C(73)-C(74)-H(74B)	108.8
C(75)-C(74)-H(74B)	108.8	H(74A)-C(74)-H(74B)	107.7
C(76)-C(75)-C(74)	122.9(3)	C(76)-C(75)-Ir(2)	72.6(2)
C(74)-C(75)-Ir(2)	111.8(2)	C(76)-C(75)-H(75)	123(2)
C(74)-C(75)-H(75)	112(2)	Ir(2)-C(75)-H(75)	102(2)
C(75)-C(76)-C(77)	125.3(3)	C(75)-C(76)-Ir(2)	71.5(2)
C(77)-C(76)-Ir(2)	110.6(2)	C(75)-C(76)-H(76)	120(2)
C(77)-C(76)-H(76)	112(2)	Ir(2)-C(76)-H(76)	103(2)
C(78)-C(77)-C(76)	113.7(3)	C(78)-C(77)-H(77A)	108.8
C(76)-C(77)-H(77A)	108.8	C(78)-C(77)-H(77B)	108.8
C(76)-C(77)-H(77B)	108.8	H(77A)-C(77)-H(77B)	107.7
C(71)-C(78)-C(77)	114.3(2)	C(71)-C(78)-H(78A)	108.7
C(77)-C(78)-H(78A)	108.7	C(71)-C(78)-H(78B)	108.7
C(77)-C(78)-H(78B)	108.7	H(78A)-C(78)-H(78B)	107.6

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb111

atom	U11	U22	U33	U23	U13	U12
Ir(1)	18(1)	18(1)	16(1)	3(1)	-8(1)	-4(1)
S(1)	25(1)	30(1)	21(1)	4(1)	-11(1)	-12(1)
P(1)	19(1)	18(1)	16(1)	2(1)	-9(1)	-4(1)
P(2)	22(1)	20(1)	17(1)	0(1)	-10(1)	-4(1)
C(1)	21(1)	21(1)	16(1)	1(1)	-7(1)	-5(1)
C(2)	20(1)	23(1)	18(1)	1(1)	-8(1)	-3(1)
C(3)	21(1)	25(1)	20(1)	6(1)	-9(1)	-6(1)
C(4)	23(1)	19(1)	22(1)	3(1)	-12(1)	-6(1)
C(5)	23(1)	18(1)	20(1)	3(1)	-12(1)	-5(1)
C(6)	22(1)	28(2)	25(1)	5(1)	-13(1)	-8(1)
C(7)	24(1)	25(1)	23(1)	5(1)	-13(1)	-10(1)
C(8)	30(2)	37(2)	27(1)	4(1)	-13(1)	-1(1)
C(9)	32(2)	45(2)	40(2)	14(1)	-16(1)	2(1)
C(10)	39(2)	50(2)	43(2)	24(2)	-29(1)	-21(2)
C(11)	61(2)	43(2)	37(2)	11(1)	-35(2)	-21(2)
C(12)	45(2)	29(2)	31(1)	3(1)	-24(1)	-9(1)
C(13)	32(1)	21(1)	21(1)	0(1)	-12(1)	-3(1)
C(14)	44(2)	26(2)	35(1)	2(1)	-21(1)	-9(1)
C(15)	75(2)	21(2)	41(2)	0(1)	-29(2)	-9(2)
C(16)	66(2)	25(2)	34(2)	-5(1)	-14(2)	10(2)
C(17)	42(2)	39(2)	38(2)	-1(1)	-9(1)	5(2)
C(18)	29(2)	27(2)	29(1)	-1(1)	-7(1)	-1(1)

C(19)	32(2)	29(2)	17(1)	1(1)	-8(1)	-7(1)
C(20)	29(1)	21(1)	16(1)	2(1)	-12(1)	-3(1)
C(21)	27(1)	23(1)	19(1)	2(1)	-10(1)	-5(1)
C(22)	40(2)	21(1)	27(1)	5(1)	-20(1)	-9(1)
C(23)	44(2)	19(1)	26(1)	5(1)	-20(1)	-4(1)
C(24)	33(2)	29(2)	28(1)	4(1)	-15(1)	6(1)
C(25)	26(1)	25(2)	27(1)	7(1)	-12(1)	-5(1)
C(26)	25(1)	17(1)	20(1)	2(1)	-8(1)	-1(1)
C(27)	30(1)	25(2)	27(1)	-1(1)	-14(1)	-4(1)
C(28)	38(2)	28(2)	27(1)	-6(1)	-14(1)	2(1)
C(29)	35(2)	31(2)	21(1)	-1(1)	-3(1)	6(1)
C(30)	25(1)	28(2)	31(1)	1(1)	-4(1)	-1(1)
C(31)	26(1)	20(1)	27(1)	1(1)	-9(1)	-4(1)
C(32)	23(1)	39(2)	24(1)	9(1)	-4(1)	-10(1)
C(33)	30(2)	27(2)	26(1)	11(1)	-9(1)	-12(1)
C(34)	44(2)	52(2)	67(2)	37(2)	-33(2)	-21(2)
C(35)	39(2)	28(2)	34(1)	9(1)	-23(1)	-4(1)
C(36)	28(1)	28(2)	23(1)	5(1)	-16(1)	-9(1)
C(37)	41(2)	24(2)	22(1)	3(1)	-19(1)	-10(1)
C(38)	44(2)	44(2)	22(1)	-8(1)	-13(1)	6(2)
C(39)	61(2)	56(3)	36(2)	-10(2)	12(2)	-18(2)
Ir(2)	22(1)	20(1)	17(1)	4(1)	-10(1)	-6(1)
S(2)	32(1)	32(1)	21(1)	5(1)	-14(1)	-16(1)
P(3)	20(1)	19(1)	16(1)	2(1)	-9(1)	-5(1)
P(4)	24(1)	20(1)	17(1)	0(1)	-10(1)	-5(1)
C(40)	23(1)	22(1)	16(1)	-1(1)	-8(1)	-4(1)
C(41)	20(1)	24(1)	19(1)	4(1)	-9(1)	-5(1)
C(42)	20(1)	24(1)	20(1)	5(1)	-9(1)	-6(1)
C(43)	21(1)	19(1)	19(1)	1(1)	-10(1)	-5(1)
C(44)	19(1)	21(1)	19(1)	1(1)	-9(1)	-5(1)
C(45)	26(1)	28(2)	25(1)	5(1)	-15(1)	-8(1)
C(46)	26(1)	24(1)	20(1)	3(1)	-13(1)	-9(1)
C(47)	30(2)	35(2)	24(1)	-2(1)	-12(1)	0(1)
C(48)	32(2)	37(2)	40(2)	-1(1)	-19(1)	6(1)
C(49)	43(2)	38(2)	34(1)	11(1)	-28(1)	-10(1)
C(50)	52(2)	41(2)	24(1)	1(1)	-23(1)	-8(2)
C(51)	38(2)	32(2)	25(1)	-4(1)	-17(1)	1(1)
C(52)	34(2)	22(1)	25(1)	-2(1)	-17(1)	1(1)
C(53)	42(2)	25(2)	49(2)	-5(1)	-27(1)	-1(1)
C(54)	62(2)	28(2)	54(2)	-12(2)	-33(2)	2(2)
C(55)	60(2)	34(2)	42(2)	-13(2)	-26(2)	19(2)
C(56)	34(2)	46(2)	37(2)	-5(2)	-13(1)	7(2)
C(57)	31(2)	31(2)	32(1)	-4(1)	-13(1)	2(1)
C(58)	28(1)	32(2)	19(1)	3(1)	-6(1)	-8(1)
C(59)	26(1)	22(1)	16(1)	4(1)	-10(1)	-6(1)
C(60)	26(1)	24(2)	30(1)	1(1)	-11(1)	-5(1)
C(61)	40(2)	25(2)	39(2)	3(1)	-19(1)	-12(1)
C(62)	45(2)	21(2)	29(1)	1(1)	-19(1)	-1(1)
C(63)	33(2)	27(2)	25(1)	4(1)	-15(1)	3(1)
C(64)	25(1)	27(2)	22(1)	6(1)	-12(1)	-7(1)
C(65)	22(1)	19(1)	18(1)	2(1)	-8(1)	-2(1)
C(66)	30(1)	29(2)	23(1)	0(1)	-11(1)	-9(1)
C(67)	36(2)	31(2)	22(1)	-5(1)	-11(1)	-4(1)
C(68)	32(2)	31(2)	21(1)	1(1)	-3(1)	1(1)
C(69)	23(1)	38(2)	29(1)	3(1)	-6(1)	-9(1)
C(70)	25(1)	29(2)	23(1)	-1(1)	-10(1)	-7(1)
C(71)	38(2)	29(2)	27(1)	7(1)	-25(1)	-12(1)
C(72)	50(2)	32(2)	21(1)	1(1)	-22(1)	-7(1)
C(73)	57(2)	52(2)	21(1)	0(1)	-12(1)	-6(2)
C(74)	40(2)	81(3)	32(2)	2(2)	1(1)	-14(2)
C(75)	33(2)	48(2)	30(1)	17(1)	-15(1)	-25(2)
C(76)	38(2)	29(2)	35(1)	15(1)	-20(1)	-17(1)
C(77)	50(2)	41(2)	59(2)	26(2)	-36(2)	-19(2)

C(78)	43(2)	31(2)	45(2)	15(1)	-30(1)	-12(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb111

atom	x	y	z	U(eq)
H(3)	9027	7417	7122	26
H(6A)	9881	5171	8740	35
H(6B)	9381	5998	9454	35
H(6C)	9759	6211	8464	35
H(8)	6256	6302	7909	38
H(9)	5434	7043	7077	48
H(10)	5723	6375	5759	46
H(11)	6793	4953	5299	49
H(12)	7623	4201	6126	38
H(14)	7349	2954	7260	39
H(15)	8419	1570	6595	52
H(16)	10178	1359	6205	56
H(17)	10888	2543	6457	52
H(18)	9839	3946	7088	36
H(19A)	9527	6395	5996	40
H(19B)	8743	5722	6121	40
H(19C)	9810	5346	6205	40
H(21)	9018	8759	7824	27
H(22)	8512	10336	7810	32
H(23)	6774	11023	8396	34
H(24)	5542	10112	8956	37
H(25)	6039	8518	8950	30
H(27)	7556	8120	10238	32
H(28)	6257	8688	11550	38
H(29)	4684	8239	12013	40
H(30)	4383	7233	11154	37
H(31)	5687	6639	9847	30
H(32)	5410(20)	4600(20)	10840(20)	36
H(33)	6620(20)	3260(20)	10320(20)	33
H(34A)	7844	2653	10750	60
H(34B)	7022	3043	11679	60
H(35A)	7896	4038	11756	38
H(35B)	8828	3441	10980	38
H(36)	8880(20)	4710(20)	10200(20)	29
H(37)	7750(20)	5960(20)	10760(20)	32
H(38A)	6771	5583	12185	46
H(38B)	6157	6271	11743	46
H(39A)	5130	5341	12079	71
H(39B)	5935	4538	12234	71
H(42)	10771	7356	7771	25
H(45A)	10231	8645	6414	36
H(45B)	10698	8985	5463	36
H(45C)	10039	9718	6250	36
H(47)	13573	8822	7433	36
H(48)	14405	8221	8305	44
H(49)	13815	8808	9710	41
H(50)	12378	9976	10242	44
H(51)	11539	10591	9372	38
H(53)	11999	12012	8098	44
H(54)	10814	13340	8772	55
H(55)	9064	13378	9208	57
H(56)	8491	12072	9006	50

H(57)	9679	10735	8333	39
H(58A)	10157	8226	9014	41
H(58B)	9816	9297	8905	41
H(58C)	10855	8933	9037	41
H(60)	10908	6130	6818	32
H(61)	11444	4547	6674	40
H(62)	13180	3880	6249	38
H(63)	14376	4823	5991	34
H(64)	13852	6415	6131	29
H(66)	12666	7003	4612	32
H(67)	14107	6617	3347	36
H(68)	15607	7135	3128	38
H(69)	15666	8033	4196	37
H(70)	14217	8436	5473	31
H(71)	11100(20)	10340(20)	4870(20)	32
H(72)	12320(20)	9170(20)	4340(20)	38
H(73A)	14109	9143	3489	54
H(73B)	13513	9757	2989	54
H(74A)	13973	11002	3212	67
H(74B)	14887	10292	3323	67
H(75)	14320(20)	10760(20)	4670(20)	41
H(76)	12910(20)	12000(20)	5340(20)	37
H(77A)	11694	12500	4840	54
H(77B)	12643	12397	3932	54
H(78A)	11104	11659	4192	43
H(78B)	12219	11239	3488	43

I.8. Crystallographic data for II-27

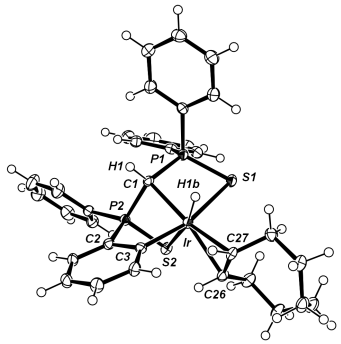


Table 1: Crystal data for xj296

Compound	xj296
Molecular formula	$C_{33}H_{35}IrP_2S_2$
Molecular weight	749.87
Crystal habit	yellow block
Crystal dimensions(mm)	0.20x0.20x0.10
Crystal system	triclinic

Space group	P -1
a(Å)	9.521(1)
b(Å)	11.397(1)
c(Å)	14.268(1)
α(°)	93.746(1)
β(°)	96.998(1)
γ(°)	104.701(1)
V(Å^3)	1478.9(2)
Z	2
d(g-cm^{-3})	1.684
F(000)	744
μ(cm^{-1})	4.785
Absorption corrections	multi-scan ; 0.4478 min, 0.6461 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.00
HKL ranges	-13 13 ; -14 16 ; -19 20
Reflections measured	17513
Unique data	8598
Rint	0.0417
Reflections used	7580
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	349
Reflections / parameter	21
wR2	0.0860
R1	0.0286
Weights a, b	0.0421 ; 0.0000
GoF	1.088
difference peak / hole (e Å^{-3})	1.140(0.277) / -2.890(0.277)

Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for xj296

atom	x	y	z	U(eq)
Ir(1)	1019(1)	7605(1)	2738(1)	15(1)
S(1)	-156(1)	9306(1)	3265(1)	19(1)
S(2)	979(1)	8460(1)	1119(1)	21(1)
P(1)	1883(1)	9661(1)	3953(1)	15(1)
P(2)	2717(1)	9664(1)	1878(1)	16(1)
C(1)	2849(4)	9222(3)	3053(2)	15(1)
C(2)	1949(4)	8475(3)	4712(2)	16(1)
C(3)	1467(4)	7360(3)	4128(2)	16(1)
C(4)	1392(4)	6301(4)	4591(3)	20(1)
C(5)	1755(4)	6381(4)	5577(3)	23(1)
C(6)	2185(4)	7484(4)	6120(3)	23(1)

C(7)	2289(4)	8557(3)	5693(2)	18(1)
C(8)	2583(4)	11151(3)	4586(2)	17(1)
C(9)	4004(4)	11510(4)	5088(3)	26(1)
C(10)	4566(5)	12686(4)	5521(3)	34(1)
C(11)	3728(5)	13524(4)	5447(3)	31(1)
C(12)	2315(5)	13163(4)	4952(3)	27(1)
C(13)	1750(4)	11993(4)	4526(3)	22(1)
C(14)	2629(4)	11234(3)	1861(2)	19(1)
C(15)	3533(4)	12128(4)	2553(3)	21(1)
C(16)	3486(5)	13337(4)	2540(3)	27(1)
C(17)	2557(5)	13667(4)	1849(3)	31(1)
C(18)	1653(5)	12779(4)	1153(3)	29(1)
C(19)	1669(4)	11561(4)	1166(3)	22(1)
C(20)	4426(4)	9573(3)	1468(2)	18(1)
C(21)	4441(4)	8717(4)	738(3)	24(1)
C(22)	5781(5)	8645(4)	471(3)	27(1)
C(23)	7079(4)	9408(4)	923(3)	25(1)
C(24)	7067(4)	10271(4)	1649(3)	28(1)
C(25)	5737(4)	10348(4)	1921(3)	26(1)
C(26)	-1237(4)	6406(3)	2580(3)	19(1)
C(27)	-322(4)	5722(3)	2285(3)	18(1)
C(28)	-443(4)	5239(4)	1267(3)	21(1)
C(29)	-1500(4)	3947(4)	1095(3)	27(1)
C(30)	-2997(4)	3842(4)	1409(3)	26(1)
C(31)	-3840(4)	4719(4)	996(3)	27(1)
C(32)	-3833(4)	5820(4)	1668(3)	27(1)
C(33)	-2365(4)	6801(4)	1924(3)	23(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table S1-3: Bond lengths (Å) and angles (°) for 2

Ir(1)-C(3)	2.030(3)	Ir(1)-C(1)	2.169(3)
Ir(1)-C(27)	2.209(4)	Ir(1)-C(26)	2.210(3)
Ir(1)-S(2)	2.564(1)	Ir(1)-S(1)	2.587(1)
Ir(1)-P(1)	2.704(1)	Ir(1)-P(2)	2.925(1)
Ir(1)-H(1B)	1.46(4)	S(1)-P(1)	1.996(1)
S(2)-P(2)	2.002(1)	P(1)-C(1)	1.785(3)
P(1)-C(2)	1.794(4)	P(1)-C(8)	1.796(4)
P(2)-C(1)	1.781(4)	P(2)-C(14)	1.814(4)
P(2)-C(20)	1.819(4)	C(1)-H(1A)	1.03(4)
C(2)-C(7)	1.389(5)	C(2)-C(3)	1.411(5)
C(3)-C(4)	1.404(5)	C(4)-C(5)	1.398(5)
C(4)-H(4)	0.9500	C(5)-C(6)	1.372(5)
C(5)-H(5)	0.9500	C(6)-C(7)	1.388(5)
C(6)-H(6)	0.9500	C(7)-H(7)	0.9500
C(8)-C(13)	1.392(5)	C(8)-C(9)	1.398(5)
C(9)-C(10)	1.383(6)	C(9)-H(9)	0.9500
C(10)-C(11)	1.393(6)	C(10)-H(10)	0.9500
C(11)-C(12)	1.388(6)	C(11)-H(11)	0.9500
C(12)-C(13)	1.373(5)	C(12)-H(12)	0.9500
C(13)-H(13)	0.9500	C(14)-C(19)	1.399(5)
C(14)-C(15)	1.404(5)	C(15)-C(16)	1.391(5)
C(15)-H(15)	0.9500	C(16)-C(17)	1.379(6)
C(16)-H(16)	0.9500	C(17)-C(18)	1.404(6)
C(17)-H(17)	0.9500	C(18)-C(19)	1.393(6)
C(18)-H(18)	0.9500	C(19)-H(19)	0.9500
C(20)-C(21)	1.385(5)	C(20)-C(25)	1.388(5)
C(21)-C(22)	1.394(5)	C(21)-H(21)	0.9500
C(22)-C(23)	1.374(6)	C(22)-H(22)	0.9500
C(23)-C(24)	1.384(6)	C(23)-H(23)	0.9500
C(24)-C(25)	1.390(5)	C(24)-H(24)	0.9500
C(25)-H(25)	0.9500	C(26)-C(27)	1.391(5)

C(26)-C(33)	1.513(5)	C(26)-H(26)	0.9476
C(27)-C(28)	1.500(5)	C(27)-H(27)	0.9498
C(28)-C(29)	1.544(5)	C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900	C(29)-C(30)	1.523(5)
C(29)-H(29A)	0.9967	C(29)-H(29B)	1.0161
C(30)-C(31)	1.536(6)	C(30)-H(64A)	0.9803
C(30)-H(64B)	0.9706	C(31)-C(32)	1.526(6)
C(31)-H(31A)	1.0128	C(31)-H(31B)	0.9978
C(32)-C(33)	1.538(5)	C(32)-H(62A)	0.9691
C(32)-H(62B)	1.0098	C(33)-H(33A)	1.0303
C(33)-H(33B)	0.9834		

C(3)-Ir(1)-C(1)	85.2(1)	C(3)-Ir(1)-C(27)	96.1(1)
C(1)-Ir(1)-C(27)	162.7(1)	C(3)-Ir(1)-C(26)	93.6(1)
C(1)-Ir(1)-C(26)	160.6(1)	C(27)-Ir(1)-C(26)	36.7(1)
C(3)-Ir(1)-S(2)	164.5(1)	C(1)-Ir(1)-S(2)	79.4(1)
C(27)-Ir(1)-S(2)	99.1(1)	C(26)-Ir(1)-S(2)	100.3(1)
C(3)-Ir(1)-S(1)	88.1(1)	C(1)-Ir(1)-S(1)	75.8(1)
C(27)-Ir(1)-S(1)	121.5(1)	C(26)-Ir(1)-S(1)	84.8(1)
S(2)-Ir(1)-S(1)	86.34(3)	C(3)-Ir(1)-P(1)	64.3(1)
C(1)-Ir(1)-P(1)	41.2(1)	C(27)-Ir(1)-P(1)	152.8(1)
C(26)-Ir(1)-P(1)	121.6(1)	S(2)-Ir(1)-P(1)	102.09(3)
S(1)-Ir(1)-P(1)	44.25(3)	C(3)-Ir(1)-P(2)	122.5(1)
C(1)-Ir(1)-P(2)	37.3(1)	C(27)-Ir(1)-P(2)	138.0(1)
C(26)-Ir(1)-P(2)	139.5(1)	S(2)-Ir(1)-P(2)	42.14(3)
S(1)-Ir(1)-P(2)	79.23(3)	P(1)-Ir(1)-P(2)	68.10(3)
C(3)-Ir(1)-H(1B)	95(2)	C(1)-Ir(1)-H(1B)	88(2)
C(27)-Ir(1)-H(1B)	75(2)	C(26)-Ir(1)-H(1B)	112(2)
S(2)-Ir(1)-H(1B)	87(2)	S(1)-Ir(1)-H(1B)	163(2)
P(1)-Ir(1)-H(1B)	123(2)	P(2)-Ir(1)-H(1B)	85(2)
P(1)-S(1)-Ir(1)	71.01(4)	P(2)-S(2)-Ir(1)	78.62(4)
C(1)-P(1)-C(2)	99.4(2)	C(1)-P(1)-C(8)	118.6(2)
C(2)-P(1)-C(8)	112.1(2)	C(1)-P(1)-S(1)	101.9(1)
C(2)-P(1)-S(1)	107.8(1)	C(8)-P(1)-S(1)	115.4(1)
C(1)-P(1)-Ir(1)	53.1(1)	C(2)-P(1)-Ir(1)	76.6(1)
C(8)-P(1)-Ir(1)	169.9(1)	S(1)-P(1)-Ir(1)	64.74(4)
C(1)-P(2)-C(14)	111.8(2)	C(1)-P(2)-C(20)	105.1(2)
C(14)-P(2)-C(20)	107.3(2)	C(1)-P(2)-S(2)	106.8(1)
C(14)-P(2)-S(2)	113.7(1)	C(20)-P(2)-S(2)	111.9(1)
C(1)-P(2)-Ir(1)	47.6(1)	C(14)-P(2)-Ir(1)	132.0(1)
C(20)-P(2)-Ir(1)	119.5(1)	S(2)-P(2)-Ir(1)	59.23(4)
P(2)-C(1)-P(1)	124.7(2)	P(2)-C(1)-Ir(1)	95.1(2)
P(1)-C(1)-Ir(1)	85.7(1)	P(2)-C(1)-H(1A)	118(2)
P(1)-C(1)-H(1A)	109(2)	Ir(1)-C(1)-H(1A)	120(2)
C(7)-C(2)-C(3)	123.6(3)	C(7)-C(2)-P(1)	129.4(3)
C(3)-C(2)-P(1)	106.8(2)	C(4)-C(3)-C(2)	116.1(3)
C(4)-C(3)-Ir(1)	131.6(3)	C(2)-C(3)-Ir(1)	112.2(2)
C(5)-C(4)-C(3)	120.4(3)	C(5)-C(4)-H(4)	119.8
C(3)-C(4)-H(4)	119.8	C(6)-C(5)-C(4)	121.6(4)
C(6)-C(5)-H(5)	119.2	C(4)-C(5)-H(5)	119.2
C(5)-C(6)-C(7)	120.1(3)	C(5)-C(6)-H(6)	119.9
C(7)-C(6)-H(6)	119.9	C(6)-C(7)-C(2)	118.2(3)
C(6)-C(7)-H(7)	120.9	C(2)-C(7)-H(7)	120.9
C(13)-C(8)-C(9)	119.2(3)	C(13)-C(8)-P(1)	120.0(3)
C(9)-C(8)-P(1)	120.6(3)	C(10)-C(9)-C(8)	120.1(4)
C(10)-C(9)-H(9)	119.9	C(8)-C(9)-H(9)	119.9
C(9)-C(10)-C(11)	120.2(4)	C(9)-C(10)-H(10)	119.9
C(11)-C(10)-H(10)	119.9	C(12)-C(11)-C(10)	119.5(4)
C(12)-C(11)-H(11)	120.3	C(10)-C(11)-H(11)	120.3
C(13)-C(12)-C(11)	120.5(4)	C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7	C(12)-C(13)-C(8)	120.5(4)
C(12)-C(13)-H(13)	119.8	C(8)-C(13)-H(13)	119.8

C(19)-C(14)-C(15)	119.8(4)	C(19)-C(14)-P(2)	120.6(3)
C(15)-C(14)-P(2)	119.6(3)	C(16)-C(15)-C(14)	120.0(4)
C(16)-C(15)-H(15)	120.0	C(14)-C(15)-H(15)	120.0
C(17)-C(16)-C(15)	120.4(4)	C(17)-C(16)-H(16)	119.8
C(15)-C(16)-H(16)	119.8	C(16)-C(17)-C(18)	119.9(4)
C(16)-C(17)-H(17)	120.1	C(18)-C(17)-H(17)	120.1
C(19)-C(18)-C(17)	120.4(4)	C(19)-C(18)-H(18)	119.8
C(17)-C(18)-H(18)	119.8	C(18)-C(19)-C(14)	119.5(4)
C(18)-C(19)-H(19)	120.3	C(14)-C(19)-H(19)	120.3
C(21)-C(20)-C(25)	119.7(3)	C(21)-C(20)-P(2)	121.1(3)
C(25)-C(20)-P(2)	119.2(3)	C(20)-C(21)-C(22)	119.3(4)
C(20)-C(21)-H(21)	120.4	C(22)-C(21)-H(21)	120.4
C(23)-C(22)-C(21)	121.0(4)	C(23)-C(22)-H(22)	119.5
C(21)-C(22)-H(22)	119.5	C(22)-C(23)-C(24)	119.9(4)
C(22)-C(23)-H(23)	120.1	C(24)-C(23)-H(23)	120.1
C(23)-C(24)-C(25)	119.6(4)	C(23)-C(24)-H(24)	120.2
C(25)-C(24)-H(24)	120.2	C(20)-C(25)-C(24)	120.6(4)
C(20)-C(25)-H(25)	119.7	C(24)-C(25)-H(25)	119.7
C(27)-C(26)-C(33)	124.6(3)	C(27)-C(26)-Ir(1)	71.6(2)
C(33)-C(26)-Ir(1)	115.2(2)	C(27)-C(26)-H(26)	117.6
C(33)-C(26)-H(26)	117.8	Ir(1)-C(26)-H(26)	82.9
C(26)-C(27)-C(28)	121.8(3)	C(26)-C(27)-Ir(1)	71.7(2)
C(28)-C(27)-Ir(1)	118.2(2)	C(26)-C(27)-H(27)	119.2
C(28)-C(27)-H(27)	119.1	Ir(1)-C(27)-H(27)	81.1
C(27)-C(28)-C(29)	109.4(3)	C(27)-C(28)-H(28A)	109.8
C(29)-C(28)-H(28A)	109.8	C(27)-C(28)-H(28B)	109.8
C(29)-C(28)-H(28B)	109.8	H(28A)-C(28)-H(28B)	108.2
C(30)-C(29)-C(28)	114.9(3)	C(30)-C(29)-H(29A)	108.2
C(28)-C(29)-H(29A)	110.8	C(30)-C(29)-H(29B)	106.2
C(28)-C(29)-H(29B)	111.1	H(29A)-C(29)-H(29B)	105.1
C(29)-C(30)-C(31)	115.4(3)	C(29)-C(30)-H(64A)	108.7
C(31)-C(30)-H(64A)	108.1	C(29)-C(30)-H(64B)	106.8
C(31)-C(30)-H(64B)	108.0	H(64A)-C(30)-H(64B)	109.7
C(32)-C(31)-C(30)	115.7(3)	C(32)-C(31)-H(31A)	106.6
C(30)-C(31)-H(31A)	110.6	C(32)-C(31)-H(31B)	107.5
C(30)-C(31)-H(31B)	110.5	H(31A)-C(31)-H(31B)	105.4
C(31)-C(32)-C(33)	116.6(3)	C(31)-C(32)-H(62A)	109.7
C(33)-C(32)-H(62A)	109.6	C(31)-C(32)-H(62B)	105.3
C(33)-C(32)-H(62B)	107.7	H(62A)-C(32)-H(62B)	107.5
C(26)-C(33)-C(32)	113.6(3)	C(26)-C(33)-H(33A)	105.3
C(32)-C(33)-H(33A)	110.3	C(26)-C(33)-H(33B)	108.7
C(32)-C(33)-H(33B)	112.9	H(33A)-C(33)-H(33B)	105.6

Table S1-4: Anisotropic displacement parameters for 2.

atom	U11	U22	U33	U23	U13	U12
Ir(1)	15(1)	14(1)	14(1)	1(1)	0(1)	2(1)
S(1)	17(1)	18(1)	21(1)	1(1)	-1(1)	4(1)
S(2)	19(1)	23(1)	16(1)	2(1)	-1(1)	-1(1)
P(1)	16(1)	14(1)	15(1)	1(1)	1(1)	3(1)
P(2)	16(1)	17(1)	14(1)	2(1)	1(1)	2(1)
C(1)	14(2)	14(2)	15(2)	3(1)	1(1)	0(1)
C(2)	15(2)	16(2)	17(2)	3(1)	2(1)	3(1)
C(3)	16(2)	17(2)	15(2)	4(1)	3(1)	4(1)
C(4)	22(2)	16(2)	20(2)	1(1)	-2(2)	3(1)
C(5)	29(2)	18(2)	21(2)	8(2)	-1(2)	2(2)
C(6)	27(2)	23(2)	16(2)	6(2)	-1(2)	2(2)
C(7)	20(2)	16(2)	15(2)	0(1)	0(1)	2(1)
C(8)	18(2)	15(2)	17(2)	1(1)	3(1)	3(1)
C(9)	23(2)	25(2)	29(2)	-1(2)	-1(2)	8(2)
C(10)	24(2)	32(3)	38(2)	-9(2)	-4(2)	2(2)

C(11)	36(2)	18(2)	35(2)	-6(2)	6(2)	1(2)
C(12)	36(2)	21(2)	28(2)	0(2)	6(2)	11(2)
C(13)	22(2)	21(2)	23(2)	-1(2)	3(2)	6(2)
C(14)	20(2)	19(2)	19(2)	4(1)	7(1)	6(1)
C(15)	21(2)	21(2)	21(2)	4(2)	4(2)	2(1)
C(16)	28(2)	22(2)	28(2)	1(2)	4(2)	2(2)
C(17)	37(2)	21(2)	39(2)	8(2)	9(2)	11(2)
C(18)	32(2)	32(2)	29(2)	12(2)	6(2)	17(2)
C(19)	23(2)	25(2)	20(2)	4(2)	4(2)	9(2)
C(20)	19(2)	21(2)	14(2)	4(1)	2(1)	4(1)
C(21)	23(2)	21(2)	23(2)	-2(2)	2(2)	3(2)
C(22)	29(2)	27(2)	26(2)	-2(2)	7(2)	9(2)
C(23)	24(2)	29(2)	26(2)	6(2)	7(2)	11(2)
C(24)	19(2)	37(3)	28(2)	-1(2)	1(2)	5(2)
C(25)	21(2)	30(2)	24(2)	-6(2)	1(2)	5(2)
C(26)	17(2)	15(2)	20(2)	1(1)	1(1)	-1(1)
C(27)	15(2)	15(2)	20(2)	0(1)	-2(1)	0(1)
C(28)	24(2)	20(2)	20(2)	-1(2)	4(2)	5(2)
C(29)	27(2)	23(2)	25(2)	-5(2)	-1(2)	1(2)
C(30)	29(2)	17(2)	25(2)	2(2)	-2(2)	-1(2)
C(31)	22(2)	29(2)	27(2)	7(2)	-5(2)	2(2)
C(32)	20(2)	24(2)	35(2)	2(2)	-5(2)	5(2)
C(33)	18(2)	18(2)	32(2)	4(2)	-1(2)	5(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 1-5: Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 2

atom	x	y	z	U(eq)
H(1B)	2040(40)	6950(40)	2430(30)	18
H(1A)	3850(40)	9150(40)	3370(30)	18
H(4)	1093	5525	4232	24
H(5)	1703	5655	5878	28
H(6)	2412	7513	6790	28
H(7)	2585	9326	6062	22
H(9)	4584	10944	5132	31
H(10)	5526	12923	5869	40
H(11)	4120	14337	5733	37
H(12)	1736	13729	4907	33
H(13)	782	11756	4187	26
H(15)	4176	11908	3031	25
H(16)	4098	13939	3010	32
H(17)	2528	14493	1844	37
H(18)	1027	13009	669	35
H(19)	1033	10957	707	26
H(21)	3550	8184	422	28
H(22)	5795	8061	-31	32
H(23)	7984	9342	739	30
H(24)	7961	10807	1958	34
H(25)	5727	10936	2422	31
H(26)	-1143	6644	3239	22
H(27)	394	5551	2741	21
H(28A)	537	5211	1117	26
H(28B)	-815	5784	847	26
H(29A)	-1052	3352	1417	32
H(29B)	-1697	3635	395	32
H(64A)	-2867	3987	2103	31

H(64B)	-3583.9998	3015	1208	31
H(31A)	-4906	4276	776	33
H(31B)	-3448	5034	417	33
H(62A)	-4197	5547	2244	33
H(62B)	-4563	6212	1330	33
H(33A)	-2518.9998	7562	2283	28
H(33B)	-1929	7088	1363	28

I.9. Crystallographic data for II-28

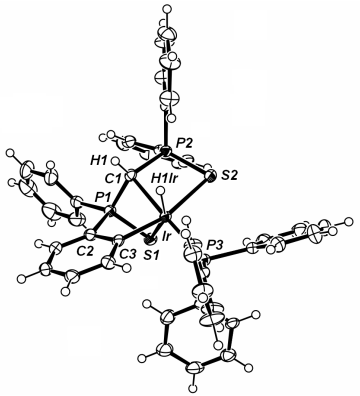


Table S2-1. Crystal data for 3

Compound	hh44
Molecular formula	$C_{43}H_{36}IrP_3S_2$, CH_2Cl_2
Molecular weight	986.87
Crystal habit	Colorless Plate
Crystal dimensions(mm)	0.28x0.26x0.20
Crystal system	monoclinic
Space group	C2/c
a(Å)	48.448(1)
b(Å)	13.092(1)
c(Å)	34.036(1)
α(°)	90.00
β(°)	132.767(1)
γ(°)	90.00
V(Å^3)	15848.5(13)
Z	16
d(g-cm^{-3})	1.654
F(000)	7840
μ(cm^{-1})	3.764
Absorption corrections	multi-scan ; 0.4188 min, 0.5198 max
Diffractometer	KappaCCD
X-ray source	MoKα

λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-68 49 ; 0 18 ; 0 47
Reflections measured	22642
Unique data	22642
Rint	0.0000
Reflections used	17503
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	889
Reflections / parameter	19
wR2	0.1404
R1	0.0551
Weights a, b	0.0269 ; 440.63
GoF	1.080
difference peak / hole (e Å^{-3})	3.435(0.198) / -2.174(0.198)

Table S2-2: Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3

atom	x	y	z	U(eq)
Ir(1)	2078(1)	4547(1)	410(1)	19(1)
S(1)	1420(1)	4484(1)	-557(1)	25(1)
S(2)	1771(1)	3869(1)	728(1)	26(1)
P(1)	1751(1)	3408(1)	-473(1)	22(1)
P(2)	1762(1)	2592(1)	394(1)	20(1)
P(3)	2137(1)	6198(1)	650(1)	21(1)
C(1)	1994(2)	2928(5)	172(3)	20(1)
C(2)	2127(2)	4045(5)	-364(3)	23(1)
C(3)	2306(2)	4697(5)	81(3)	22(1)
C(4)	2595(2)	5313(6)	209(3)	29(2)
C(5)	2694(2)	5266(6)	-90(3)	30(2)
C(6)	2508(2)	4613(6)	-531(3)	30(2)
C(7)	2220(2)	3999(6)	-669(3)	29(2)
C(8)	1521(2)	2533(6)	-1027(3)	28(2)
C(9)	1716(2)	1641(7)	-955(4)	38(2)
C(10)	1543(3)	952(7)	-1369(4)	46(2)
C(11)	1186(3)	1140(8)	-1854(4)	57(3)
C(12)	993(3)	2009(8)	-1936(4)	53(3)
C(13)	1161(3)	2717(7)	-1516(3)	41(2)
C(14)	1291(2)	2114(5)	-151(3)	23(1)
C(15)	1240(2)	1379(5)	-491(3)	28(2)
C(16)	882(2)	1048(6)	-941(3)	34(2)
C(17)	572(2)	1459(7)	-1051(3)	39(2)
C(18)	623(2)	2210(6)	-702(4)	39(2)
C(19)	982(2)	2540(6)	-263(3)	31(2)
C(20)	2019(2)	1579(5)	888(3)	21(1)
C(21)	1858(2)	660(6)	836(3)	35(2)
C(22)	2073(2)	-84(6)	1239(4)	40(2)
C(23)	2452(2)	114(7)	1689(4)	43(2)
C(24)	2608(2)	1032(7)	1741(3)	42(2)

C(25)	2396(2)	1777(6)	1345(3)	38(2)
C(26)	1833(2)	7102(5)	92(3)	24(1)
C(27)	1787(2)	6987(6)	-355(3)	36(2)
C(28)	1564(3)	7666(6)	-787(4)	41(2)
C(29)	1374(2)	8448(6)	-777(4)	39(2)
C(30)	1421(2)	8573(6)	-331(4)	34(2)
C(31)	1643(2)	7914(5)	99(3)	27(2)
C(32)	2607(2)	6782(5)	1074(3)	25(1)
C(33)	2653(2)	7801(6)	1051(4)	39(2)
C(34)	3022(2)	8221(6)	1398(4)	44(2)
C(35)	3332(2)	7619(6)	1765(3)	37(2)
C(36)	3280(2)	6598(6)	1782(3)	33(2)
C(37)	2921(2)	6173(6)	1441(3)	31(2)
C(38)	2016(2)	6449(5)	1046(3)	24(1)
C(39)	1651(2)	6190(6)	817(3)	30(2)
C(40)	1542(3)	6332(6)	1102(4)	39(2)
C(41)	1799(3)	6742(7)	1617(4)	42(2)
C(42)	2160(3)	6972(8)	1850(4)	47(2)
C(43)	2263(2)	6829(6)	1557(3)	34(2)
Ir(2)	737(1)	6956(1)	1284(1)	19(1)
S(3)	380(1)	6923(1)	1609(1)	25(1)
S(4)	1307(1)	6326(1)	2199(1)	28(1)
P(4)	182(1)	5813(1)	1069(1)	22(1)
P(5)	1009(1)	5024(1)	1901(1)	23(1)
P(6)	907(1)	8607(1)	1377(1)	21(1)
C(44)	591(2)	5324(5)	1237(3)	21(1)
C(45)	-39(2)	6402(5)	442(3)	24(1)
C(46)	222(2)	7049(5)	513(3)	23(1)
C(47)	92(2)	7591(5)	59(3)	27(1)
C(48)	-272(2)	7485(6)	-427(3)	35(2)
C(49)	-533(2)	6857(6)	-484(3)	35(2)
C(50)	-414(2)	6294(6)	-42(3)	29(2)
C(51)	-144(2)	4933(6)	978(3)	32(2)
C(52)	-284(2)	5074(7)	1218(4)	40(2)
C(53)	-535(3)	4380(10)	1136(5)	60(3)
C(54)	-647(3)	3540(10)	813(5)	76(4)
C(55)	-506(3)	3390(10)	566(5)	70(3)
C(56)	-255(3)	4082(7)	647(4)	45(2)
C(57)	920(2)	4526(5)	2302(3)	26(1)
C(58)	638(2)	3788(6)	2086(3)	32(2)
C(59)	568(3)	3404(6)	2391(4)	43(2)
C(60)	781(3)	3721(7)	2914(4)	50(2)
C(61)	1059(3)	4455(7)	3126(4)	52(3)
C(62)	1128(2)	4864(6)	2822(3)	34(2)
C(63)	1260(2)	4041(5)	1877(3)	25(1)
C(64)	1223(2)	2996(6)	1917(3)	35(2)
C(65)	1413(3)	2262(7)	1874(4)	44(2)
C(66)	1641(3)	2606(7)	1787(4)	45(2)
C(67)	1676(3)	3611(7)	1741(5)	52(3)
C(68)	1490(3)	4336(6)	1789(4)	40(2)
C(69)	657(2)	9540(5)	1447(3)	24(1)
C(70)	265(2)	9515(6)	1069(3)	36(2)
C(71)	67(2)	10236(7)	1088(4)	45(2)
C(72)	251(2)	10952(7)	1495(4)	40(2)
C(73)	636(2)	10960(6)	1878(4)	35(2)
C(74)	839(2)	10256(6)	1851(3)	30(2)
C(75)	871(2)	9179(5)	853(3)	24(1)
C(76)	770(2)	10195(5)	698(3)	30(2)
C(77)	786(2)	10609(6)	338(3)	34(2)
C(79)	1000(2)	9027(6)	283(3)	29(2)
C(80)	977(2)	8603(6)	637(3)	27(2)
C(81)	1401(2)	8874(5)	1967(3)	23(1)
C(82)	1537(2)	8622(5)	2472(3)	27(2)

C(83)	1910(2)	8776(5)	2928(3)	28(2)
C(84)	2160(2)	9186(6)	2900(3)	35(2)
C(85)	2028(2)	9446(7)	2399(3)	37(2)
C(86)	1649(2)	9297(6)	1936(3)	29(2)
C(778)	896(2)	10036(6)	127(3)	31(2)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table S2-3: Bond lengths (Å) and angles (°) for 3

Ir(1)-C(3)	2.047(6)	Ir(1)-C(1)	2.206(6)
Ir(1)-P(3)	2.259(2)	Ir(1)-S(2)	2.520(2)
Ir(1)-S(1)	2.599(2)	Ir(1)-P(1)	2.702(2)
Ir(1)-H(1IR)	1.70(1)	S(1)-P(1)	2.004(2)
S(2)-P(2)	2.005(2)	P(1)-C(1)	1.759(7)
P(1)-C(2)	1.797(7)	P(1)-C(8)	1.804(8)
P(2)-C(1)	1.783(6)	P(2)-C(14)	1.813(7)
P(2)-C(20)	1.816(7)	P(3)-C(38)	1.828(7)
P(3)-C(26)	1.837(7)	P(3)-C(32)	1.842(7)
C(1)-H(1)	1.0000	C(2)-C(7)	1.39(1)
C(2)-C(3)	1.41(1)	C(3)-C(4)	1.40(1)
C(4)-C(5)	1.39(1)	C(4)-H(4)	0.9500
C(5)-C(6)	1.40(1)	C(5)-H(5)	0.9500
C(6)-C(7)	1.38(1)	C(6)-H(6)	0.9500
C(7)-H(7)	0.9500	C(8)-C(13)	1.39(1)
C(8)-C(9)	1.41(1)	C(9)-C(10)	1.38(1)
C(9)-H(9)	0.9500	C(10)-C(11)	1.38(1)
C(10)-H(10)	0.9500	C(11)-C(12)	1.38(2)
C(11)-H(11)	0.9500	C(12)-C(13)	1.41(1)
C(12)-H(12)	0.9500	C(13)-H(13)	0.9500
C(14)-C(19)	1.39(1)	C(14)-C(15)	1.39(1)
C(15)-C(16)	1.39(1)	C(15)-H(15)	0.9500
C(16)-C(17)	1.39(1)	C(16)-H(16)	0.9500
C(17)-C(18)	1.43(1)	C(17)-H(17)	0.9500
C(18)-C(19)	1.38(1)	C(18)-H(18)	0.9500
C(19)-H(19)	0.9500	C(20)-C(21)	1.38(1)
C(20)-C(25)	1.40(1)	C(21)-C(22)	1.40(1)
C(21)-H(21)	0.9500	C(22)-C(23)	1.40(1)
C(22)-H(22)	0.9500	C(23)-C(24)	1.37(1)
C(23)-H(23)	0.9500	C(24)-C(25)	1.39(1)
C(24)-H(24)	0.9500	C(25)-H(25)	0.9500
C(26)-C(27)	1.39(1)	C(26)-C(31)	1.42(1)
C(27)-C(28)	1.40(1)	C(27)-H(27)	0.9500
C(28)-C(29)	1.39(1)	C(28)-H(28)	0.9500
C(29)-C(30)	1.38(1)	C(29)-H(29)	0.9500
C(30)-C(31)	1.38(1)	C(30)-H(30)	0.9500
C(31)-H(31)	0.9500	C(32)-C(33)	1.36(1)
C(32)-C(37)	1.39(1)	C(33)-C(34)	1.42(1)
C(33)-H(33)	0.9500	C(34)-C(35)	1.37(1)
C(34)-H(34)	0.9500	C(35)-C(36)	1.37(1)
C(35)-H(35)	0.9500	C(36)-C(37)	1.39(1)
C(36)-H(36)	0.9500	C(37)-H(37)	0.9500
C(38)-C(43)	1.37(1)	C(38)-C(39)	1.41(1)
C(39)-C(40)	1.39(1)	C(39)-H(39)	0.9500
C(40)-C(41)	1.39(1)	C(40)-H(40)	0.9500
C(41)-C(42)	1.38(1)	C(41)-H(41)	0.9500
C(42)-C(43)	1.40(1)	C(42)-H(42)	0.9500
C(43)-H(43)	0.9500	Ir(2)-C(46)	2.058(7)
Ir(2)-C(44)	2.222(6)	Ir(2)-P(6)	2.258(2)
Ir(2)-S(4)	2.515(2)	Ir(2)-S(3)	2.608(2)
Ir(2)-P(4)	2.708(2)	Ir(2)-H(2IR)	1.70(1)
S(3)-P(4)	2.003(2)	S(4)-P(5)	2.007(3)
P(4)-C(44)	1.768(6)	P(4)-C(45)	1.786(7)

P(4)-C(51)	1.803(8)	P(5)-C(44)	1.774(7)
P(5)-C(57)	1.809(7)	P(5)-C(63)	1.812(7)
P(6)-C(75)	1.830(7)	P(6)-C(81)	1.831(7)
P(6)-C(69)	1.846(7)	C(44)-H(44)	1.0000
C(45)-C(46)	1.40(1)	C(45)-C(50)	1.40(1)
C(46)-C(47)	1.40(1)	C(47)-C(48)	1.38(1)
C(47)-H(47)	0.9500	C(48)-C(49)	1.40(1)
C(48)-H(48)	0.9500	C(49)-C(50)	1.40(1)
C(49)-H(49)	0.9500	C(50)-H(50)	0.9500
C(51)-C(52)	1.38(1)	C(51)-C(56)	1.41(1)
C(52)-C(53)	1.39(1)	C(52)-H(52)	0.9500
C(53)-C(54)	1.38(2)	C(53)-H(53)	0.9500
C(54)-C(55)	1.41(2)	C(54)-H(54)	0.9500
C(55)-C(56)	1.38(1)	C(55)-H(55)	0.9500
C(56)-H(56)	0.9500	C(57)-C(62)	1.39(1)
C(57)-C(58)	1.41(1)	C(58)-C(59)	1.39(1)
C(58)-H(58)	0.9500	C(59)-C(60)	1.38(1)
C(59)-H(59)	0.9500	C(60)-C(61)	1.39(1)
C(60)-H(60)	0.9500	C(61)-C(62)	1.39(1)
C(61)-H(61)	0.9500	C(62)-H(62)	0.9500
C(63)-C(68)	1.39(1)	C(63)-C(64)	1.40(1)
C(64)-C(65)	1.40(1)	C(64)-H(64)	0.9500
C(65)-C(66)	1.40(1)	C(65)-H(65)	0.9500
C(66)-C(67)	1.35(1)	C(66)-H(66)	0.9500
C(67)-C(68)	1.39(1)	C(67)-H(67)	0.9500
C(68)-H(68)	0.9500	C(69)-C(74)	1.38(1)
C(69)-C(70)	1.39(1)	C(70)-C(71)	1.38(1)
C(70)-H(70)	0.9500	C(71)-C(72)	1.38(1)
C(71)-H(71)	0.9500	C(72)-C(73)	1.37(1)
C(72)-H(72)	0.9500	C(73)-C(74)	1.40(1)
C(73)-H(73)	0.9500	C(74)-H(74)	0.9500
C(75)-C(80)	1.37(1)	C(75)-C(76)	1.39(1)
C(76)-C(77)	1.39(1)	C(76)-H(76)	0.9500
C(77)-C(778)	1.37(1)	C(77)-H(77)	0.9500
C(79)-C(778)	1.38(1)	C(79)-C(80)	1.40(1)
C(79)-H(79)	0.9500	C(80)-H(80)	0.9500
C(81)-C(86)	1.39(1)	C(81)-C(82)	1.40(1)
C(82)-C(83)	1.38(1)	C(82)-H(82)	0.9500
C(83)-C(84)	1.39(1)	C(83)-H(83)	0.9500
C(84)-C(85)	1.40(1)	C(84)-H(84)	0.9500
C(85)-C(86)	1.40(1)	C(85)-H(85)	0.9500
C(86)-H(86)	0.9500	C(778)-H(778)	0.9500

C(3)-Ir(1)-C(1)	85.7(2)	C(3)-Ir(1)-P(3)	97.0(2)
C(1)-Ir(1)-P(3)	176.9(2)	C(3)-Ir(1)-S(2)	164.4(2)
C(1)-Ir(1)-S(2)	78.7(2)	P(3)-Ir(1)-S(2)	98.56(6)
C(3)-Ir(1)-S(1)	87.9(2)	C(1)-Ir(1)-S(1)	75.1(2)
P(3)-Ir(1)-S(1)	103.49(6)	S(2)-Ir(1)-S(1)	87.65(6)
C(3)-Ir(1)-P(1)	64.6(2)	C(1)-Ir(1)-P(1)	40.5(2)
P(3)-Ir(1)-P(1)	139.86(6)	S(2)-Ir(1)-P(1)	102.26(6)
S(1)-Ir(1)-P(1)	44.37(5)	C(3)-Ir(1)-H(1IR)	83(3)
C(1)-Ir(1)-H(1IR)	82(3)	P(3)-Ir(1)-H(1IR)	99(3)
S(2)-Ir(1)-H(1IR)	95(3)	S(1)-Ir(1)-H(1IR)	156(3)
P(1)-Ir(1)-H(1IR)	112(3)	P(1)-S(1)-Ir(1)	70.52(7)
P(2)-S(2)-Ir(1)	80.96(7)	C(1)-P(1)-C(2)	100.5(3)
C(1)-P(1)-C(8)	119.5(3)	C(2)-P(1)-C(8)	109.3(3)
C(1)-P(1)-S(1)	102.8(2)	C(2)-P(1)-S(1)	107.7(2)
C(8)-P(1)-S(1)	115.5(3)	C(1)-P(1)-Ir(1)	54.4(2)
C(2)-P(1)-Ir(1)	76.6(2)	C(8)-P(1)-Ir(1)	172.9(2)
S(1)-P(1)-Ir(1)	65.10(7)	C(1)-P(2)-C(14)	111.6(3)
C(1)-P(2)-C(20)	109.8(3)	C(14)-P(2)-C(20)	106.9(3)
C(1)-P(2)-S(2)	104.9(2)	C(14)-P(2)-S(2)	113.3(2)

C(20)-P(2)-S(2)	110.3(2)	C(38)-P(3)-C(26)	102.3(3)
C(38)-P(3)-C(32)	101.0(3)	C(26)-P(3)-C(32)	103.9(3)
C(38)-P(3)-Ir(1)	114.4(2)	C(26)-P(3)-Ir(1)	115.3(2)
C(32)-P(3)-Ir(1)	117.8(2)	P(1)-C(1)-P(2)	122.4(4)
P(1)-C(1)-Ir(1)	85.1(3)	P(2)-C(1)-Ir(1)	95.4(3)
P(1)-C(1)-H(1)	115.6	P(2)-C(1)-H(1)	115.6
Ir(1)-C(1)-H(1)	115.6	C(7)-C(2)-C(3)	123.7(6)
C(7)-C(2)-P(1)	128.7(6)	C(3)-C(2)-P(1)	107.5(5)
C(4)-C(3)-C(2)	115.9(6)	C(4)-C(3)-Ir(1)	132.8(6)
C(2)-C(3)-Ir(1)	111.3(4)	C(5)-C(4)-C(3)	121.0(7)
C(5)-C(4)-H(4)	119.5	C(3)-C(4)-H(4)	119.5
C(4)-C(5)-C(6)	121.2(7)	C(4)-C(5)-H(5)	119.4
C(6)-C(5)-H(5)	119.4	C(7)-C(6)-C(5)	119.3(7)
C(7)-C(6)-H(6)	120.3	C(5)-C(6)-H(6)	120.3
C(6)-C(7)-C(2)	118.9(7)	C(6)-C(7)-H(7)	120.6
C(2)-C(7)-H(7)	120.6	C(13)-C(8)-C(9)	119.9(7)
C(13)-C(8)-P(1)	121.6(6)	C(9)-C(8)-P(1)	118.5(6)
C(10)-C(9)-C(8)	119.5(8)	C(10)-C(9)-H(9)	120.2
C(8)-C(9)-H(9)	120.2	C(11)-C(10)-C(9)	120(1)
C(11)-C(10)-H(10)	119.8	C(9)-C(10)-H(10)	119.8
C(12)-C(11)-C(10)	121(1)	C(12)-C(11)-H(11)	119.4
C(10)-C(11)-H(11)	119.4	C(11)-C(12)-C(13)	120(1)
C(11)-C(12)-H(12)	120.2	C(13)-C(12)-H(12)	120.2
C(8)-C(13)-C(12)	119(1)	C(8)-C(13)-H(13)	120.3
C(12)-C(13)-H(13)	120.3	C(19)-C(14)-C(15)	120.0(7)
C(19)-C(14)-P(2)	121.0(6)	C(15)-C(14)-P(2)	118.6(5)
C(14)-C(15)-C(16)	121.0(7)	C(14)-C(15)-H(15)	119.5
C(16)-C(15)-H(15)	119.5	C(17)-C(16)-C(15)	119.3(8)
C(17)-C(16)-H(16)	120.4	C(15)-C(16)-H(16)	120.4
C(16)-C(17)-C(18)	119.9(8)	C(16)-C(17)-H(17)	120.1
C(18)-C(17)-H(17)	120.1	C(19)-C(18)-C(17)	119.6(7)
C(19)-C(18)-H(18)	120.2	C(17)-C(18)-H(18)	120.2
C(18)-C(19)-C(14)	120.2(8)	C(18)-C(19)-H(19)	119.9
C(14)-C(19)-H(19)	119.9	C(21)-C(20)-C(25)	120.1(7)
C(21)-C(20)-P(2)	123.1(6)	C(25)-C(20)-P(2)	116.7(5)
C(20)-C(21)-C(22)	120.0(7)	C(20)-C(21)-H(21)	120.0
C(22)-C(21)-H(21)	120.0	C(23)-C(22)-C(21)	119.4(8)
C(23)-C(22)-H(22)	120.3	C(21)-C(22)-H(22)	120.3
C(24)-C(23)-C(22)	120.2(8)	C(24)-C(23)-H(23)	119.9
C(22)-C(23)-H(23	119.9	C(23)-C(24)-C(25)	120.7(8)
C(23)-C(24)-H(24)	119.6	C(25)-C(24)-H(24)	119.6
C(24)-C(25)-C(20)	119.5(7)	C(24)-C(25)-H(25)	120.3
C(20)-C(25)-H(25)	120.2	C(27)-C(26)-C(31)	118.4(7)
C(27)-C(26)-P(3)	118.9(6)	C(31)-C(26)-P(3)	122.7(6)
C(26)-C(27)-C(28)	121.1(8)	C(26)-C(27)-H(27)	119.5
C(28)-C(27)-H(27)	119.5	C(29)-C(28)-C(27)	119.7(8)
C(29)-C(28)-H(28)	120.2	C(27)-C(28)-H(28)	120.2
C(30)-C(29)-C(28)	119.6(8)	C(30)-C(29)-H(29)	120.2
C(28)-C(29)-H(29)	120.2	C(31)-C(30)-C(29)	121.2(7)
C(31)-C(30)-H(30)	119.4	C(29)-C(30)-H(30)	119.4
C(30)-C(31)-C(26)	120.0(7)	C(30)-C(31)-H(31)	120.0
C(26)-C(31)-H(31)	120.0	C(33)-C(32)-C(37)	119.4(7)
C(33)-C(32)-P(3)	121.6(6)	C(37)-C(32)-P(3)	118.9(5)
C(32)-C(33)-C(34)	119.5(8)	C(32)-C(33)-H(33)	120.2
C(34)-C(33)-H(33)	120.2	C(35)-C(34)-C(33)	120.8(7)
C(35)-C(34)-H(34)	119.6	C(33)-C(34)-H(34)	119.6
C(36)-C(35)-C(34)	118.8(7)	C(36)-C(35)-H(35)	120.6
C(34)-C(35)-H(35)	120.6	C(35)-C(36)-C(37)	121.1(8)
C(35)-C(36)-H(36)	119.5	C(37)-C(36)-H(36)	119.5
C(32)-C(37)-C(36)	120.4(7)	C(32)-C(37)-H(37)	119.8
C(36)-C(37)-H(37)	119.8	C(43)-C(38)-C(39)	118.4(7)
C(43)-C(38)-P(3)	124.2(6)	C(39)-C(38)-P(3)	117.4(6)
C(40)-C(39)-C(38)	120.6(8)	C(40)-C(39)-H(39)	119.7

C(38)-C(39)-H(39)	119.7	C(41)-C(40)-C(39)	119.2(8)
C(41)-C(40)-H(40)	120.4	C(39)-C(40)-H(40)	120.4
C(42)-C(41)-C(40)	120.7(7)	C(42)-C(41)-H(41)	119.7
C(40)-C(41)-H(41)	119.7	C(41)-C(42)-C(43)	119(1)
C(41)-C(42)-H(42)	120.4	C(43)-C(42)-H(42)	120.4
C(38)-C(43)-C(42)	121.8(8)	C(38)-C(43)-H(43)	119.1
C(42)-C(43)-H(43)	119.1	C(46)-Ir(2)-C(44)	85.1(3)
C(46)-Ir(2)-P(6)	97.7(2)	C(44)-Ir(2)-P(6)	177.1(2)
C(46)-Ir(2)-S(4)	163.6(2)	C(44)-Ir(2)-S(4)	78.6(2)
P(6)-Ir(2)-S(4)	98.67(6)	C(46)-Ir(2)-S(3)	87.9(2)
C(44)-Ir(2)-S(3)	75.2(2)	P(6)-Ir(2)-S(3)	103.91(6)
S(4)-Ir(2)-S(3)	87.48(6)	C(46)-Ir(2)-P(4)	64.3(2)
C(44)-Ir(2)-P(4)	40.5(2)	P(6)-Ir(2)-P(4)	140.18(6)
S(4)-Ir(2)-P(4)	101.96(6)	S(3)-Ir(2)-P(4)	44.21(5)
C(46)-Ir(2)-H(2IR)	49(3)	C(44)-Ir(2)-H(2IR)	98(3)
P(6)-Ir(2)-H(2IR)	85(3)	S(4)-Ir(2)-H(2IR)	134(3)
S(3)-Ir(2)-H(2IR)	136(3)	P(4)-Ir(2)-H(2IR)	104(3)
P(4)-S(3)-Ir(2)	70.55(7)	P(5)-S(4)-Ir(2)	81.07(8)
C(44)-P(4)-C(45)	100.0(3)	C(44)-P(4)-C(51)	118.8(3)
C(45)-P(4)-C(51)	109.0(3)	C(44)-P(4)-S(3)	103.3(2)
C(45)-P(4)-S(3)	107.9(2)	C(51)-P(4)-S(3)	116.2(3)
C(44)-P(4)-Ir(2)	54.8(2)	C(45)-P(4)-Ir(2)	76.3(2)
C(51)-P(4)-Ir(2)	172.9(3)	S(3)-P(4)-Ir(2)	65.23(7)
C(44)-P(5)-C(57)	112.9(3)	C(44)-P(5)-C(63)	108.7(3)
C(57)-P(5)-C(63)	106.9(3)	C(44)-P(5)-S(4)	105.2(2)
C(57)-P(5)-S(4)	112.5(3)	C(63)-P(5)-S(4)	110.6(3)
C(75)-P(6)-C(81)	100.4(3)	C(75)-P(6)-C(69)	102.6(3)
C(81)-P(6)-C(69)	102.4(3)	C(75)-P(6)-Ir(2)	118.1(2)
C(81)-P(6)-Ir(2)	114.7(2)	C(69)-P(6)-Ir(2)	116.2(2)
P(4)-C(44)-P(5)	123.5(4)	P(4)-C(44)-Ir(2)	84.7(3)
P(5)-C(44)-Ir(2)	95.1(3)	P(4)-C(44)-H(44)	115.3
P(5)-C(44)-H(44)	115.3	Ir(2)-C(44)-H(44)	115.3
C(46)-C(45)-C(50)	124.0(7)	C(46)-C(45)-P(4)	108.5(5)
C(50)-C(45)-P(4)	127.4(6)	C(45)-C(46)-C(47)	116.1(6)
C(45)-C(46)-Ir(2)	110.8(5)	C(47)-C(46)-Ir(2)	133.1(5)
C(48)-C(47)-C(46)	121.4(7)	C(48)-C(47)-H(47)	119.3
C(46)-C(47)-H(47)	119.3	C(47)-C(48)-C(49)	121.5(7)
C(47)-C(48)-H(48)	119.3	C(49)-C(48)-H(48)	119.3
C(50)-C(49)-C(48)	119.1(7)	C(50)-C(49)-H(49)	120.5
C(48)-C(49)-H(49)	120.5	C(49)-C(50)-C(45)	117.9(7)
C(49)-C(50)-H(50)	121.1	C(45)-C(50)-H(50)	121.1
C(52)-C(51)-C(56)	120.4(8)	C(52)-C(51)-P(4)	122.4(7)
C(56)-C(51)-P(4)	117.2(6)	C(51)-C(52)-C(53)	121(1)
C(51)-C(52)-H(52)	119.6	C(53)-C(52)-H(52)	119.6
C(54)-C(53)-C(52)	120(1)	C(54)-C(53)-H(53)	120.1
C(52)-C(53)-H(53)	120.1	C(53)-C(54)-C(55)	120(1)
C(53)-C(54)-H(54)	120.2	C(55)-C(54)-H(54)	120.2
C(56)-C(55)-C(54)	121(1)	C(56)-C(55)-H(55)	119.7
C(54)-C(55)-H(55)	119.7	C(55)-C(56)-C(51)	119(1)
C(55)-C(56)-H(56)	120.6	C(51)-C(56)-H(56)	120.6
C(62)-C(57)-C(58)	119.5(7)	C(62)-C(57)-P(5)	120.6(6)
C(58)-C(57)-P(5)	119.9(6)	C(59)-C(58)-C(57)	120.1(8)
C(59)-C(58)-H(58)	119.9	C(57)-C(58)-H(58)	119.9
C(60)-C(59)-C(58)	120(1)	C(60)-C(59)-H(59)	119.8
C(58)-C(59)-H(59)	119.8	C(59)-C(60)-C(61)	119.5(8)
C(59)-C(60)-H(60)	120.3	C(61)-C(60)-H(60)	120.3
C(60)-C(61)-C(62)	121(1)	C(60)-C(61)-H(61)	119.5
C(62)-C(61)-H(61)	119.5	C(57)-C(62)-C(61)	119.5(8)
C(57)-C(62)-H(62)	120.3	C(61)-C(62)-H(62)	120.3
C(68)-C(63)-C(64)	118.0(7)	C(68)-C(63)-P(5)	118.3(6)
C(64)-C(63)-P(5)	123.6(6)	C(63)-C(64)-C(65)	121.3(8)
C(63)-C(64)-H(64)	119.3	C(65)-C(64)-H(64)	119.3
C(66)-C(65)-C(64)	118.1(8)	C(66)-C(65)-H(65)	121.0

C(64)-C(65)-H(65)	121.0	C(67)-C(66)-C(65)	121.1(8)
C(67)-C(66)-H(66)	119.4	C(65)-C(66)-H(66)	119.4
C(66)-C(67)-C(68)	120.6(8)	C(66)-C(67)-H(67)	119.7
C(68)-C(67)-H(67)	119.7	C(63)-C(68)-C(67)	120.9(8)
C(63)-C(68)-H(68)	119.6	C(67)-C(68)-H(68)	119.6
C(74)-C(69)-C(70)	118.9(7)	C(74)-C(69)-P(6)	123.2(5)
C(70)-C(69)-P(6)	117.9(5)	C(71)-C(70)-C(69)	119.8(7)
C(71)-C(70)-H(70)	120.1	C(69)-C(70)-H(70)	120.1
C(70)-C(71)-C(72)	120.9(8)	C(70)-C(71)-H(71)	119.6
C(72)-C(71)-H(71)	119.6	C(73)-C(72)-C(71)	119.7(7)
C(73)-C(72)-H(72)	120.2	C(71)-C(72)-H(72)	120.2
C(72)-C(73)-C(74)	119.7(8)	C(72)-C(73)-H(73)	120.1
C(74)-C(73)-H(73)	120.1	C(69)-C(74)-C(73)	120.9(7)
C(69)-C(74)-H(74)	119.5	C(73)-C(74)-H(74)	119.5
C(80)-C(75)-C(76)	119.1(7)	C(80)-C(75)-P(6)	118.3(5)
C(76)-C(75)-P(6)	122.5(6)	C(77)-C(76)-C(75)	119.3(7)
C(77)-C(76)-H(76)	120.3	C(75)-C(76)-H(76)	120.3
C(778)-C(77)-C(76)	121.5(7)	C(778)-C(77)-H(77)	119.2
C(76)-C(77)-H(77)	119.2	C(778)-C(79)-C(80)	119.4(7)
C(778)-C(79)-H(79)	120.3	C(80)-C(79)-H(79)	120.3
C(75)-C(80)-C(79)	121.3(7)	C(75)-C(80)-H(80)	119.3
C(79)-C(80)-H(80)	119.3	C(86)-C(81)-C(82)	118.5(7)
C(86)-C(81)-P(6)	123.1(6)	C(82)-C(81)-P(6)	118.4(5)
C(83)-C(82)-C(81)	120.7(7)	C(83)-C(82)-H(82)	119.6
C(81)-C(82)-H(82)	119.6	C(82)-C(83)-C(84)	121.1(7)
C(82)-C(83)-H(83)	119.4	C(84)-C(83)-H(83)	119.4
C(83)-C(84)-C(85)	118.9(7)	C(83)-C(84)-H(84)	120.6
C(85)-C(84)-H(84)	120.6	C(84)-C(85)-C(86)	120.1(7)
C(84)-C(85)-H(85)	119.9	C(86)-C(85)-H(85)	119.9
C(81)-C(86)-C(85)	120.7(7)	C(81)-C(86)-H(86)	119.6
C(85)-C(86)-H(86)	119.6	C(77)-C(778)-C(79)	119.3(7)
C(77)-C(778)-H(778)	120.3	C(79)-C(778)-H(778)	120.3

Table S2-4: Anisotropic displacement parameters for 3

atom	U11	U22	U33	U23	U13	U12
Ir(1)	22(1)	16(1)	24(1)	0(1)	16(1)	0(1)
S(1)	25(1)	23(1)	28(1)	4(1)	19(1)	4(1)
S(2)	34(1)	20(1)	34(1)	-1(1)	27(1)	0(1)
P(1)	24(1)	19(1)	25(1)	0(1)	18(1)	1(1)
P(2)	22(1)	18(1)	24(1)	1(1)	17(1)	0(1)
P(3)	23(1)	19(1)	25(1)	1(1)	18(1)	1(1)
C(1)	18(3)	19(3)	24(3)	0(3)	15(3)	1(2)
C(2)	24(3)	22(3)	28(4)	5(3)	19(3)	3(3)
C(3)	22(3)	20(3)	33(4)	4(3)	22(3)	5(2)
C(4)	32(4)	26(4)	33(4)	1(3)	24(3)	-2(3)
C(5)	31(4)	26(4)	43(5)	4(3)	29(4)	-1(3)
C(6)	36(4)	27(4)	44(5)	8(3)	34(4)	7(3)
C(7)	37(4)	23(3)	34(4)	2(3)	28(4)	4(3)
C(8)	35(4)	24(3)	30(4)	0(3)	25(3)	-2(3)
C(9)	41(4)	40(5)	36(5)	-4(4)	28(4)	2(4)
C(10)	61(6)	38(5)	49(6)	-16(4)	41(5)	-5(4)
C(11)	85(8)	50(6)	46(6)	-25(5)	48(6)	-35(6)
C(12)	59(6)	55(6)	28(5)	-9(4)	23(5)	-21(5)
C(13)	53(5)	32(4)	30(4)	-2(3)	24(4)	-5(4)
C(14)	23(3)	20(3)	26(4)	3(3)	17(3)	-1(2)
C(15)	30(4)	22(3)	31(4)	3(3)	21(3)	2(3)
C(16)	35(4)	35(4)	27(4)	-3(3)	19(4)	-7(3)
C(17)	24(4)	41(5)	32(4)	9(4)	11(3)	1(3)
C(18)	28(4)	32(4)	49(5)	9(4)	23(4)	5(3)
C(19)	27(3)	23(3)	42(5)	4(3)	23(4)	1(3)

C(20)	22(3)	21(3)	24(3)	1(3)	17(3)	4(2)
C(21)	28(4)	32(4)	35(5)	3(3)	17(4)	-2(3)
C(22)	41(4)	26(4)	44(5)	11(4)	26(4)	1(3)
C(23)	39(5)	49(5)	30(5)	12(4)	19(4)	8(4)
C(24)	33(4)	44(5)	26(4)	4(4)	11(4)	-6(4)
C(25)	31(4)	34(4)	30(4)	-2(3)	14(4)	-9(3)
C(26)	24(3)	19(3)	26(4)	-3(3)	16(3)	-5(2)
C(27)	45(4)	28(4)	30(4)	-1(3)	24(4)	5(3)
C(28)	58(5)	30(4)	33(5)	6(3)	30(4)	7(4)
C(29)	46(5)	25(4)	38(5)	10(3)	25(4)	5(3)
C(30)	36(4)	27(4)	50(5)	9(3)	33(4)	9(3)
C(31)	35(4)	14(3)	45(5)	3(3)	32(4)	1(3)
C(32)	30(3)	19(3)	29(4)	-4(3)	21(3)	-4(3)
C(33)	32(4)	27(4)	38(5)	6(3)	16(4)	-7(3)
C(34)	33(4)	22(4)	57(6)	4(4)	22(4)	-6(3)
C(35)	32(4)	28(4)	35(5)	-4(3)	17(4)	-10(3)
C(36)	29(4)	33(4)	24(4)	-1(3)	13(3)	-2(3)
C(37)	33(4)	21(3)	33(4)	3(3)	20(4)	-2(3)
C(38)	34(4)	18(3)	29(4)	3(3)	24(3)	2(3)
C(39)	33(4)	24(4)	40(4)	5(3)	28(4)	4(3)
C(40)	46(5)	27(4)	69(6)	9(4)	49(5)	10(3)
C(41)	61(6)	38(5)	62(6)	7(4)	55(6)	11(4)
C(42)	63(6)	51(6)	41(5)	-1(4)	41(5)	2(5)
C(43)	42(4)	31(4)	41(5)	0(3)	32(4)	0(3)
Ir(2)	19(1)	17(1)	19(1)	1(1)	12(1)	2(1)
S(3)	25(1)	25(1)	25(1)	-4(1)	17(1)	-1(1)
S(4)	23(1)	21(1)	25(1)	2(1)	11(1)	1(1)
P(4)	21(1)	21(1)	22(1)	-1(1)	14(1)	1(1)
P(5)	23(1)	19(1)	21(1)	2(1)	13(1)	3(1)
P(6)	20(1)	20(1)	20(1)	0(1)	13(1)	1(1)
C(44)	21(3)	15(3)	27(4)	0(2)	15(3)	1(2)
C(45)	20(3)	22(3)	22(3)	-4(3)	11(3)	0(2)
C(46)	22(3)	23(3)	25(3)	0(3)	17(3)	8(3)
C(47)	31(4)	22(3)	24(4)	1(3)	17(3)	0(3)
C(48)	36(4)	36(4)	22(4)	5(3)	16(3)	15(3)
C(49)	29(4)	32(4)	20(4)	-9(3)	8(3)	4(3)
C(50)	23(3)	29(4)	28(4)	-3(3)	15(3)	4(3)
C(51)	20(3)	35(4)	31(4)	2(3)	14(3)	1(3)
C(52)	37(4)	43(5)	49(5)	10(4)	33(4)	3(4)
C(53)	41(5)	61(7)	86(8)	23(6)	47(6)	5(5)
C(54)	48(6)	69(8)	80(10)	15(7)	28(6)	-22(6)
C(55)	62(7)	51(6)	80(10)	-17(6)	43(7)	-34(5)
C(56)	46(5)	31(4)	50(6)	-10(4)	30(5)	-15(4)
C(57)	32(4)	23(3)	25(4)	6(3)	20(3)	8(3)
C(58)	38(4)	27(4)	37(4)	6(3)	28(4)	6(3)
C(59)	63(6)	27(4)	63(6)	3(4)	52(6)	3(4)
C(60)	88(8)	33(5)	62(7)	5(4)	64(7)	7(5)
C(61)	93(8)	34(5)	42(5)	2(4)	50(6)	11(5)
C(62)	49(5)	25(4)	28(4)	-1(3)	26(4)	3(3)
C(63)	26(3)	21(3)	20(3)	1(3)	12(3)	8(3)
C(64)	47(5)	31(4)	37(5)	6(3)	33(4)	7(3)
C(65)	61(6)	33(4)	50(6)	5(4)	43(5)	12(4)
C(66)	49(5)	46(5)	54(6)	2(4)	40(5)	18(4)
C(67)	62(6)	42(5)	83(8)	1(5)	62(7)	6(4)
C(68)	53(5)	28(4)	58(6)	5(4)	46(5)	6(4)
C(69)	22(3)	22(3)	27(4)	-2(3)	16(3)	-1(3)
C(70)	26(4)	30(4)	39(5)	-12(3)	17(4)	-1(3)
C(71)	28(4)	42(5)	55(6)	-9(4)	24(4)	6(3)
C(72)	38(4)	34(4)	59(6)	-7(4)	37(5)	1(3)
C(73)	41(4)	22(4)	41(5)	-6(3)	27(4)	0(3)
C(74)	27(3)	30(4)	26(4)	0(3)	15(3)	1(3)
C(75)	26(3)	21(3)	22(3)	3(3)	15(3)	0(3)
C(76)	44(4)	21(3)	33(4)	1(3)	28(4)	2(3)

C(77)	47(5)	23(4)	38(5)	5(3)	31(4)	2(3)
C(79)	29(3)	31(4)	35(4)	2(3)	25(3)	3(3)
C(80)	29(3)	23(3)	31(4)	5(3)	21(3)	2(3)
C(81)	18(3)	22(3)	29(4)	-1(3)	16(3)	1(2)
C(82)	32(4)	20(3)	21(4)	1(3)	15(3)	2(3)
C(83)	28(3)	23(3)	23(4)	0(3)	13(3)	6(3)
C(84)	25(3)	38(4)	28(4)	-3(3)	12(3)	2(3)
C(85)	25(4)	48(5)	35(5)	-6(4)	19(4)	-7(3)
C(86)	28(3)	31(4)	30(4)	0(3)	21(3)	0(3)
C(778)	35(4)	32(4)	28(4)	2(3)	23(3)	-1(3)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table S2-5: Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3

atom	x	y	z	U(eq)
H(1IR)	2510(10)	4120(60)	950(20)	29
H(1)	2228	2534	339	24
H(4)	2725	5769	504	34
H(5)	2892	5686	6.0000	36
H(6)	2577	4591	-732.9999	36
H(7)	2089	3552	-968	35
H(9)	1964	1518	-624	45
H(10)	1670	344	-1320	56
H(11)	1071	660	-2136	69
H(12)	749	2132	-2274	63
H(13)	1029	3314	-1566	50
H(15)	1453	1100	-415.0000	34
H(16)	850	546	-1171	40
H(17)	326	1242	-1358	47
H(18)	412	2482	-771	46
H(19)	1017	3059	-38	37
H(21)	1602	529	527	42
H(22)	1962	-715.0001	1207	47
H(23)	2601	-392	1958	51
H(24)	2863	1165	2051	50
H(25)	2506	2416	1385	45
H(27)	1908	6439	-369	43
H(28)	1542	7592	-1085	49
H(29)	1214	8895	-1074	47
H(30)	1297	9121	-320	41
H(31)	1669	8006	400	32
H(33)	2441	8228	805	47
H(34)	3055	8927	1375	53
H(35)	3577	7905	2002	44
H(36)	3492	6172	2032	40
H(37)	2891	5462	1458	37
H(39)	1477	5915	466	36
H(40)	1296	6152	948	47
H(41)	1725	6864	1808	51
H(42)	2338	7226	2206	56
H(43)	2511	6998	1717	41
H(2IR)	620(20)	7030(60)	690(20)	29
H(44)	547	4918	950	26
H(47)	258	8040	86	32
H(48)	-349.0000	7845	-729	42
H(49)	-785	6815	-817	42
H(50)	-583	5853	-70	35

H(52)	-207	5651	1441	48
H(53)	-631	4488	1301	71
H(54)	-818	3060	758	91
H(55)	-584	2816	342	84
H(56)	-159.0000	3983	482	54
H(58)	494	3552	1729	39
H(59)	373	2920	2240	52
H(60)	739	3441	3125	60
H(61)	1203	4681	3484	62
H(62)	1316	5371	2970	41
H(64)	1066	2778	1975	42
H(65)	1386	1553	1903	52
H(66)	1773	2123	1760	54
H(67)	1829	3827	1676	62
H(68)	1520	5041	1761	47
H(70)	135	9005	798	44
H(71)	-200	10240	818	54
H(72)	111	11435	1509	48
H(73)	763	11443	2162	42
H(74)	1106	10271	2115	36
H(76)	690	10603	837	36
H(77)	719	11305	236	41
H(79)	1085	8627	151	35
H(80)	1036	7901	731	32
H(82)	1370	8342	2500	33
H(83)	1996	8597	3267	34
H(84)	2416	9288	3215	42
H(85)	2196	9724	2373	45
H(86)	1560	9486	1597	35
H(778)	900	10326	-124	37

I.10. Crystallographic data for II-29

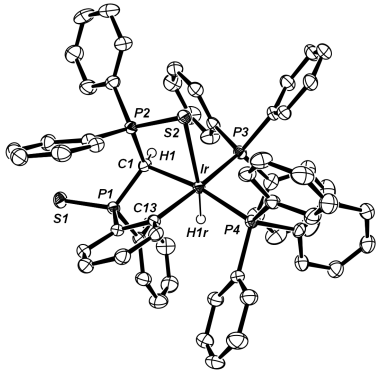


Table S3-1: Crystal data for 4

Compound	xj343
Molecular formula	$C_{61}H_{51}IrP_4S_2,C_4H_8O$
Molecular weight	1236.32
Crystal habit	Colorless Block

Crystal dimensions(mm)	0.20x0.18x0.14
Crystal system	triclinic
Space group	P-1
a(Å)	11.848(1)
b(Å)	13.236(1)
c(Å)	18.046(1)
α(°)	85.575(1)
β(°)	85.233(1)
γ(°)	78.766(1)
V(Å^3)	2760.8(3)
Z	2
d(g-cm^{-3})	1.487
F(000)	1252
μ(cm^{-1})	2.653
Absorption corrections	multi-scan ; 0.6190 min, 0.7077 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-16 16 ; -18 12 ; -25 25
Reflections measured	36125
Unique data	16046
Rint	0.0420
Reflections used	13380
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	661
Reflections / parameter	20
wR2	0.0976
R1	0.0346
Weights a, b	0.0488 ; 0.0000
GoF	1.076
difference peak / hole (e Å^{-3})	1.668(0.148) / -2.279(0.148)

Table S3-2: . Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 4

atom	x	y	z	U(eq)
Ir(1)	2619(1)	1673(1)	7136(1)	17(1)
S(1)	2832(1)	-1703(1)	8705(1)	28(1)
S(2)	4569(1)	1060(1)	6379(1)	22(1)
P(1)	2378(1)	-353(1)	8165(1)	20(1)
P(2)	4532(1)	-148(1)	7114(1)	20(1)
P(3)	3501(1)	2848(1)	7691(1)	20(1)
P(4)	1457(1)	2887(1)	6400(1)	19(1)
C(1)	3481(3)	366(2)	7828(2)	19(1)

C(2)	1395(3)	463(3)	8798(2)	23(1)
C(3)	1803(3)	851(3)	9388(2)	30(1)
C(4)	1055(3)	1389(3)	9904(2)	37(1)
C(5)	-118(3)	1539(3)	9853(2)	38(1)
C(6)	-537(3)	1147(3)	9271(2)	38(1)
C(7)	208(3)	618(3)	8740(2)	29(1)
C(8)	1722(3)	-339(3)	7305(2)	20(1)
C(9)	1259(3)	-1179(3)	7126(2)	25(1)
C(10)	878(3)	-1186(3)	6414(2)	27(1)
C(11)	992(3)	-379(3)	5895(2)	26(1)
C(12)	1468(3)	437(3)	6076(2)	23(1)
C(13)	1840(3)	499(2)	6783(2)	19(1)
C(14)	5924(3)	-629(3)	7489(2)	24(1)
C(15)	5979(3)	-1181(3)	8174(2)	33(1)
C(16)	7055(3)	-1572(3)	8458(2)	40(1)
C(17)	8051(3)	-1397(4)	8049(2)	41(1)
C(18)	7982(3)	-831(3)	7367(2)	39(1)
C(19)	6926(3)	-458(3)	7087(2)	29(1)
C(20)	4271(3)	-1256(3)	6666(2)	22(1)
C(21)	4033(3)	-1145(3)	5912(2)	27(1)
C(22)	3890(3)	-1997(3)	5554(2)	32(1)
C(23)	3962(3)	-2956(3)	5946(2)	34(1)
C(24)	4208(3)	-3070(3)	6686(2)	34(1)
C(25)	4378(3)	-2221(3)	7043(2)	28(1)
C(26)	4461(3)	3529(3)	7079(2)	22(1)
C(27)	4353(3)	3601(3)	6317(2)	23(1)
C(28)	5061(3)	4103(3)	5828(2)	29(1)
C(29)	5917(3)	4519(3)	6096(2)	35(1)
C(30)	6051(3)	4445(3)	6851(2)	34(1)
C(31)	5330(3)	3966(3)	7341(2)	29(1)
C(32)	4492(3)	2266(3)	8409(2)	23(1)
C(33)	5559(3)	1689(3)	8182(2)	27(1)
C(34)	6326(3)	1201(3)	8701(2)	31(1)
C(35)	6044(3)	1292(3)	9455(2)	39(1)
C(36)	4995(4)	1867(4)	9686(2)	46(1)
C(37)	4205(3)	2356(3)	9167(2)	36(1)
C(38)	2555(3)	3863(3)	8211(2)	26(1)
C(39)	2759(4)	4862(3)	8213(2)	37(1)
C(40)	2060(5)	5559(4)	8654(3)	53(1)
C(41)	1161(5)	5288(4)	9104(3)	58(1)
C(42)	944(4)	4314(4)	9102(2)	46(1)
C(43)	1622(3)	3599(3)	8660(2)	33(1)
C(44)	1038(3)	4215(3)	6705(2)	23(1)
C(45)	1652(3)	4979(3)	6444(2)	30(1)
C(46)	1306(3)	5977(3)	6671(2)	37(1)
C(47)	366(3)	6208(3)	7164(2)	38(1)
C(48)	-238(3)	5460(3)	7442(2)	33(1)
C(49)	99(3)	4472(3)	7214(2)	27(1)
C(50)	13(3)	2567(3)	6338(2)	21(1)
C(51)	-555(3)	2186(3)	6971(2)	27(1)
C(52)	-1643(3)	1953(3)	6949(2)	34(1)
C(53)	-2181(3)	2082(3)	6296(2)	37(1)
C(54)	-1623(3)	2449(3)	5668(2)	38(1)
C(55)	-537(3)	2700(3)	5678(2)	29(1)
C(56)	1900(3)	3126(3)	5410(2)	22(1)
C(57)	1383(3)	3999(3)	4993(2)	30(1)
C(58)	1648(3)	4118(3)	4231(2)	36(1)
C(59)	2437(3)	3361(3)	3882(2)	36(1)
C(60)	2976(3)	2500(3)	4284(2)	32(1)
C(61)	2708(3)	2381(3)	5051(2)	26(1)
O(1)	2665(5)	5172(5)	1680(3)	97(2)
C(62)	2417(6)	6045(6)	1240(5)	95(2)
C(63)	3280(10)	5860(10)	570(5)	158(5)

C(64)	3560(10)	4760(10)	570(7)	183(6)
C(65)	3330(10)	4417(8)	1278(7)	186(6)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table S3-3: Bond lengths (Å) and angles (°) for 4

Ir(1)-C(13)	2.117(3)	Ir(1)-C(1)	2.189(3)
Ir(1)-P(4)	2.313(1)	Ir(1)-P(3)	2.3592(8)
Ir(1)-S(2)	2.6034(8	Ir(1)-H(1R)	1.37(3)
S(1)-P(1)	1.969(1)	S(2)-P(2)	2.003(1)
P(1)-C(8)	1.788(3)	P(1)-C(1)	1.802(3)
P(1)-C(2)	1.818(3)	P(2)-C(1)	1.792(3)
P(2)-C(14)	1.815(3)	P(2)-C(20)	1.817(3)
P(3)-C(26)	1.834(3)	P(3)-C(38)	1.838(4)
P(3)-C(32)	1.843(3)	P(4)-C(56)	1.842(3)
P(4)-C(44)	1.845(3)	P(4)-C(50)	1.855(3)
C(1)-H(1)	1.0000	C(2)-C(3)	1.378(5)
C(2)-C(7)	1.393(5)	C(3)-C(4)	1.371(5)
C(3)-H(3)	0.9500	C(4)-C(5)	1.375(5)
C(4)-H(4)	0.9500	C(5)-C(6)	1.375(6)
C(5)-H(5)	0.9500	C(6)-C(7)	1.382(5)
C(6)-H(6)	0.9500	C(7)-H(7)	0.9500
C(8)-C(9)	1.402(4)	C(8)-C(13)	1.420(4)
C(9)-C(10)	1.398(5)	C(9)-H(9)	0.9500
C(10)-C(11)	1.385(5)	C(10)-H(10)	0.9500
C(11)-C(12)	1.383(5)	C(11)-H(11)	0.9500
C(12)-C(13)	1.396(4)	C(12)-H(12)	0.9500
C(14)-C(15)	1.386(5)	C(14)-C(19)	1.388(5)
C(15)-C(16)	1.402(5)	C(15)-H(15)	0.9500
C(16)-C(17)	1.388(6)	C(16)-H(16)	0.9500
C(17)-C(18)	1.390(6)	C(17)-H(17)	0.9500
C(18)-C(19)	1.374(5)	C(18)-H(18)	0.9500
C(19)-H(19)	0.9500	C(20)-C(25)	1.388(5)
C(20)-C(21)	1.402(5)	C(21)-C(22)	1.387(5)
C(21)-H(21)	0.9500	C(22)-C(23)	1.396(6)
C(22)-H(22)	0.9500	C(23)-C(24)	1.381(6)
C(23)-H(23)	0.9500	C(24)-C(25)	1.394(5)
C(24)-H(24)	0.9500	C(25)-H(25)	0.9500
C(26)-C(27)	1.386(5)	C(26)-C(31)	1.404(4)
C(27)-C(28)	1.388(5)	C(27)-H(27)	0.9500
C(28)-C(29)	1.380(5)	C(28)-H(28)	0.9500
C(29)-C(30)	1.379(6)	C(29)-H(29)	0.9500
C(30)-C(31)	1.383(5)	C(30)-H(30)	0.9500
C(31)-H(31)	0.9500	C(32)-C(37)	1.390(5)
C(32)-C(33)	1.391(5)	C(33)-C(34)	1.391(5)
C(33)-H(33)	0.9500	C(34)-C(35)	1.382(5)
C(34)-H(34)	0.9500	C(35)-C(36)	1.375(6)
C(35)-H(35)	0.9500	C(36)-C(37)	1.411(6)
C(36)-H(36)	0.9500	C(37)-H(37)	0.9500
C(38)-C(39)	1.389(5)	C(38)-C(43)	1.399(5)
C(39)-C(40)	1.370(6)	C(39)-H(39)	0.9500
C(40)-C(41)	1.373(7)	C(40)-H(40)	0.9500
C(41)-C(42)	1.363(7)	C(41)-H(41)	0.9500
C(42)-C(43)	1.375(5)	C(42)-H(42)	0.9500
C(43)-H(43)	0.9500	C(44)-C(49)	1.389(5)
C(44)-C(45)	1.389(5)	C(45)-C(46)	1.387(5)
C(45)-H(45)	0.9500	C(46)-C(47)	1.367(6)
C(46)-H(46)	0.9500	C(47)-C(48)	1.373(5)
C(47)-H(47)	0.9500	C(48)-C(49)	1.375(5)
C(48)-H(48)	0.9500	C(49)-H(49)	0.9500
C(50)-C(55)	1.387(5)	C(50)-C(51)	1.388(5)

C(51)-C(52)	1.387(5)	C(51)-H(51)	0.9500
C(52)-C(53)	1.370(5)	C(52)-H(52)	0.9500
C(53)-C(54)	1.368(6)	C(53)-H(53)	0.9500
C(54)-C(55)	1.392(5)	C(54)-H(54)	0.9500
C(55)-H(55)	0.9500	C(56)-C(61)	1.391(5)
C(56)-C(57)	1.394(5)	C(57)-C(58)	1.388(5)
C(57)-H(57)	0.9500	C(58)-C(59)	1.381(6)
C(58)-H(58)	0.9500	C(59)-C(60)	1.379(6)
C(59)-H(59)	0.9500	C(60)-C(61)	1.398(5)
C(60)-H(60)	0.9500	C(61)-H(61)	0.9500
O(1)-C(62)	1.348(8)	O(1)-C(65)	1.36(1)
C(62)-C(63)	1.52(1)	C(62)-H(62A)	0.9900
C(62)-H(62B)	0.9900	C(63)-C(64)	1.43(1)
C(63)-H(63A)	0.9900	C(63)-H(63B)	0.9900
C(64)-C(65)	1.35(1)	C(64)-H(64A)	0.9900
C(64)-H(64B)	0.9900	C(65)-H(65A)	0.9900
C(65)-H(65B)	0.9900		

C(13)-Ir(1)-C(1)	80.8(1)	C(13)-Ir(1)-P(4)	90.0(1)
C(1)-Ir(1)-P(4)	169.99(8)	C(13)-Ir(1)-P(3)	172.0(1)
C(1)-Ir(1)-P(3)	92.25(8)	P(4)-Ir(1)-P(3)	96.58(3)
C(13)-Ir(1)-S(2)	93.81(8)	C(1)-Ir(1)-S(2)	76.33(8)
P(4)-Ir(1)-S(2)	108.55(3)	P(3)-Ir(1)-S(2)	88.44(3)
C(13)-Ir(1)-H(1R)	88(1)	C(1)-Ir(1)-H(1R)	91(2)
P(4)-Ir(1)-H(1R)	84(2)	P(3)-Ir(1)-H(1R)	88(1)
S(2)-Ir(1)-H(1R)	167(2)	P(2)-S(2)-Ir(1)	79.14(4)
C(8)-P(1)-C(1)	97.9(2)	C(8)-P(1)-C(2)	109.1(2)
C(1)-P(1)-C(2)	106.2(2)	C(8)-P(1)-S(1)	117.1(1)
C(1)-P(1)-S(1)	118.8(1)	C(2)-P(1)-S(1)	107.0(1)
C(1)-P(2)-C(14)	110.9(2)	C(1)-P(2)-C(20)	117.0(2)
C(14)-P(2)-C(20)	102.6(2)	C(1)-P(2)-S(2)	103.3(1)
C(14)-P(2)-S(2)	112.1(1)	C(20)-P(2)-S(2)	111.2(1)
C(26)-P(3)-C(38)	104.8(2)	C(26)-P(3)-C(32)	100.0(2)
C(38)-P(3)-C(32)	100.4(2)	C(26)-P(3)-Ir(1)	116.8(1)
C(38)-P(3)-Ir(1)	117.4(1)	C(32)-P(3)-Ir(1)	114.9(1)
C(56)-P(4)-C(44)	101.4(2)	C(56)-P(4)-C(50)	101.4(2)
C(44)-P(4)-C(50)	100.2(2)	C(56)-P(4)-Ir(1)	120.0(1)
C(44)-P(4)-Ir(1)	118.4(1)	C(50)-P(4)-Ir(1)	112.4(1)
P(2)-C(1)-P(1)	118.8(2)	P(2)-C(1)-Ir(1)	96.0(1)
P(1)-C(1)-Ir(1)	105.6(1)	P(2)-C(1)-H(1)	111.7
P(1)-C(1)-H(1)	111.7	Ir(1)-C(1)-H(1)	111.7
C(3)-C(2)-C(7)	118.8(3)	C(3)-C(2)-P(1)	120.4(3)
C(7)-C(2)-P(1)	120.4(3)	C(4)-C(3)-C(2)	120.6(3)
C(4)-C(3)-H(3)	119.7	C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	121.0(4)	C(3)-C(4)-H(4)	119.5
C(5)-C(4)-H(4)	119.5	C(4)-C(5)-C(6)	119.0(4)
C(4)-C(5)-H(5)	120.5	C(6)-C(5)-H(5)	120.5
C(5)-C(6)-C(7)	120.6(4)	C(5)-C(6)-H(6)	119.7
C(7)-C(6)-H(6)	119.7	C(6)-C(7)-C(2)	120.0(3)
C(6)-C(7)-H(7)	120.0	C(2)-C(7)-H(7)	120.0
C(9)-C(8)-C(13)	122.2(3)	C(9)-C(8)-P(1)	121.2(3)
C(13)-C(8)-P(1)	116.1(2)	C(10)-C(9)-C(8)	119.1(3)
C(10)-C(9)-H(9)	120.4	C(8)-C(9)-H(9)	120.4
C(11)-C(10)-C(9)	119.5(3)	C(11)-C(10)-H(10)	120.2
C(9)-C(10)-H(10)	120.2	C(12)-C(11)-C(10)	120.6(3)
C(12)-C(11)-H(11)	119.7	C(10)-C(11)-H(11)	119.7
C(11)-C(12)-C(13)	122.5(3)	C(11)-C(12)-H(12)	118.8
C(13)-C(12)-H(12)	118.8	C(12)-C(13)-C(8)	116.0(3)
C(12)-C(13)-Ir(1)	126.8(3)	C(8)-C(13)-Ir(1)	117.1(2)
C(15)-C(14)-C(19)	120.3(3)	C(15)-C(14)-P(2)	119.5(3)
C(19)-C(14)-P(2)	120.1(3)	C(14)-C(15)-C(16)	119.6(4)
C(14)-C(15)-H(15)	120.2	C(16)-C(15)-H(15)	120.2

C(17)-C(16)-C(15)	119.4(4)	C(17)-C(16)-H(16)	120.3
C(15)-C(16)-H(16)	120.3	C(16)-C(17)-C(18)	120.4(4)
C(16)-C(17)-H(17)	119.8	C(18)-C(17)-H(17)	119.8
C(19)-C(18)-C(17)	120.1(4)	C(19)-C(18)-H(18)	119.9
C(17)-C(18)-H(18)	119.9	C(18)-C(19)-C(14)	120.2(4)
C(18)-C(19)-H(19)	119.9	C(14)-C(19)-H(19)	119.9
C(25)-C(20)-C(21)	119.7(3)	C(25)-C(20)-P(2)	121.0(3)
C(21)-C(20)-P(2)	119.1(3)	C(22)-C(21)-C(20)	119.7(4)
C(22)-C(21)-H(21)	120.2	C(20)-C(21)-H(21)	120.2
C(21)-C(22)-C(23)	120.1(4)	C(21)-C(22)-H(22)	120.0
C(23)-C(22)-H(22)	120.0	C(24)-C(23)-C(22)	120.4(3)
C(24)-C(23)-H(23)	119.8	C(22)-C(23)-H(23)	119.8
C(23)-C(24)-C(25)	119.7(4)	C(23)-C(24)-H(24)	120.1
C(25)-C(24)-H(24)	120.1	C(20)-C(25)-C(24)	120.4(3)
C(20)-C(25)-H(25)	119.8	C(24)-C(25)-H(25)	119.8
C(27)-C(26)-C(31)	117.7(3)	C(27)-C(26)-P(3)	119.1(2)
C(31)-C(26)-P(3)	123.2(3)	C(26)-C(27)-C(28)	121.4(3)
C(26)-C(27)-H(27)	119.3	C(28)-C(27)-H(27)	119.3
C(29)-C(28)-C(27)	120.1(3)	C(29)-C(28)-H(28)	120.0
C(27)-C(28)-H(28)	120.0	C(30)-C(29)-C(28)	119.5(3)
C(30)-C(29)-H(29)	120.2	C(28)-C(29)-H(29)	120.2
C(29)-C(30)-C(31)	120.6(3)	C(29)-C(30)-H(30)	119.7
C(31)-C(30)-H(30)	119.7	C(30)-C(31)-C(26)	120.7(3)
C(30)-C(31)-H(31)	119.6	C(26)-C(31)-H(31)	119.6
C(37)-C(32)-C(33)	118.7(3)	C(37)-C(32)-P(3)	122.8(3)
C(33)-C(32)-P(3)	118.5(2)	C(34)-C(33)-C(32)	121.0(3)
C(34)-C(33)-H(33)	119.5	C(32)-C(33)-H(33)	119.5
C(35)-C(34)-C(33)	120.4(4)	C(35)-C(34)-H(34)	119.8
C(33)-C(34)-H(34)	119.8	C(36)-C(35)-C(34)	119.2(4)
C(36)-C(35)-H(35)	120.4	C(34)-C(35)-H(35)	120.4
C(35)-C(36)-C(37)	121.0(4)	C(35)-C(36)-H(36)	119.5
C(37)-C(36)-H(36)	119.5	C(32)-C(37)-C(36)	119.7(4)
C(32)-C(37)-H(37)	120.2	C(36)-C(37)-H(37)	120.2
C(39)-C(38)-C(43)	118.6(3)	C(39)-C(38)-P(3)	123.2(3)
C(43)-C(38)-P(3)	118.2(3)	C(40)-C(39)-C(38)	119.9(4)
C(40)-C(39)-H(39)	120.0	C(38)-C(39)-H(39)	120.0
C(39)-C(40)-C(41)	121.2(5)	C(39)-C(40)-H(40)	119.4
C(41)-C(40)-H(40)	119.4	C(42)-C(41)-C(40)	119.5(4)
C(42)-C(41)-H(41)	120.3	C(40)-C(41)-H(41)	120.3
C(41)-C(42)-C(43)	120.7(4)	C(41)-C(42)-H(42)	119.6
C(43)-C(42)-H(42)	119.6	C(42)-C(43)-C(38)	120.1(4)
C(42)-C(43)-H(43)	120.0	C(38)-C(43)-H(43)	120.0
C(49)-C(44)-C(45)	118.2(3)	C(49)-C(44)-P(4)	120.3(3)
C(45)-C(44)-P(4)	121.6(3)	C(46)-C(45)-C(44)	120.4(4)
C(46)-C(45)-H(45)	119.8	C(44)-C(45)-H(45)	119.8
C(47)-C(46)-C(45)	119.9(4)	C(47)-C(46)-H(46)	120.0
C(45)-C(46)-H(46)	120.0	C(46)-C(47)-C(48)	120.7(4)
C(46)-C(47)-H(47)	119.7	C(48)-C(47)-H(47)	119.7
C(47)-C(48)-C(49)	119.5(4)	C(47)-C(48)-H(48)	120.2
C(49)-C(48)-H(48)	120.2	C(48)-C(49)-C(44)	121.3(3)
C(48)-C(49)-H(49)	119.4	C(44)-C(49)-H(49)	119.4
C(55)-C(50)-C(51)	118.0(3)	C(55)-C(50)-P(4)	122.5(3)
C(51)-C(50)-P(4)	119.5(2)	C(52)-C(51)-C(50)	121.3(3)
C(52)-C(51)-H(51)	119.4	C(50)-C(51)-H(51)	119.4
C(53)-C(52)-C(51)	120.6(4)	C(53)-C(52)-H(52)	119.7
C(51)-C(52)-H(52)	119.7	C(54)-C(53)-C(52)	118.5(3)
C(54)-C(53)-H(53)	120.7	C(52)-C(53)-H(53)	120.7
C(53)-C(54)-C(55)	122.0(4)	C(53)-C(54)-H(54)	119.0
C(55)-C(54)-H(54)	119.0	C(50)-C(55)-C(54)	119.7(4)
C(50)-C(55)-H(55)	120.1	C(54)-C(55)-H(55)	120.1
C(61)-C(56)-C(57)	118.8(3)	C(61)-C(56)-P(4)	119.3(3)
C(57)-C(56)-P(4)	121.7(3)	C(58)-C(57)-C(56)	120.9(4)
C(58)-C(57)-H(57)	119.5	C(56)-C(57)-H(57)	119.5

C(59)-C(58)-C(57)	119.5(4)	C(59)-C(58)-H(58)	120.3
C(57)-C(58)-H(58)	120.3	C(60)-C(59)-C(58)	120.7(4)
C(60)-C(59)-H(59)	119.6	C(58)-C(59)-H(59)	119.6
C(59)-C(60)-C(61)	119.7(4)	C(59)-C(60)-H(60)	120.1
C(61)-C(60)-H(60)	120.1	C(56)-C(61)-C(60)	120.3(3)
C(56)-C(61)-H(61)	119.8	C(60)-C(61)-H(61)	119.8
C(62)-O(1)-C(65)	109.5(7)	O(1)-C(62)-C(63)	103.9(7)
O(1)-C(62)-H(62A)	111.0	C(63)-C(62)-H(62A)	111.0
O(1)-C(62)-H(62B)	111.0	C(63)-C(62)-H(62B)	111.0
H(62A)-C(62)-H(62B)	109.0	C(64)-C(63)-C(62)	103.0(8)
C(64)-C(63)-H(63A)	111.2	C(62)-C(63)-H(63A)	111.2
C(64)-C(63)-H(63B)	111.2	C(62)-C(63)-H(63B)	111.2
H(63A)-C(63)-H(63B)	109.1	C(65)-C(64)-C(63)	105(1)
C(65)-C(64)-H(64A)	110.7	C(63)-C(64)-H(64A)	110.7
C(65)-C(64)-H(64B)	110.7	C(63)-C(64)-H(64B)	110.7
H(64A)-C(64)-H(64B)	108.8	C(64)-C(65)-O(1)	112(1)
C(64)-C(65)-H(65A)	109.3	O(1)-C(65)-H(65A)	109.3
C(64)-C(65)-H(65B)	109.3	O(1)-C(65)-H(65B)	109.3
H(65A)-C(65)-H(65B)	107.9		

Table S3-4: Anisotropic displacement parameters for 4

atom	U11	U22	U33	U23	U13	U12
Ir(1)	17(1)	18(1)	17(1)	2(1)	-1(1)	-4(1)
S(1)	31(1)	23(1)	26(1)	8(1)	0(1)	-5(1)
S(2)	21(1)	23(1)	22(1)	3(1)	1(1)	-5(1)
P(1)	19(1)	20(1)	20(1)	4(1)	-1(1)	-5(1)
P(2)	17(1)	20(1)	21(1)	2(1)	-1(1)	-3(1)
P(3)	22(1)	21(1)	17(1)	2(1)	-1(1)	-6(1)
P(4)	18(1)	19(1)	20(1)	2(1)	-1(1)	-4(1)
C(1)	19(1)	20(2)	15(1)	2(1)	-1(1)	-1(1)
C(2)	23(2)	22(2)	22(2)	5(1)	3(1)	-6(1)
C(3)	25(2)	39(2)	25(2)	1(2)	-1(1)	-4(2)
C(4)	40(2)	48(3)	24(2)	-4(2)	-3(2)	-8(2)
C(5)	36(2)	39(2)	33(2)	-3(2)	12(2)	-3(2)
C(6)	26(2)	45(3)	42(2)	-3(2)	6(2)	-6(2)
C(7)	23(2)	32(2)	31(2)	-1(2)	0(1)	-8(2)
C(8)	15(1)	19(2)	25(2)	-1(1)	-1(1)	-4(1)
C(9)	22(2)	21(2)	33(2)	2(1)	-2(1)	-7(1)
C(10)	23(2)	24(2)	35(2)	-5(2)	-5(1)	-6(1)
C(11)	24(2)	26(2)	28(2)	-3(2)	-7(1)	-3(1)
C(12)	21(2)	22(2)	25(2)	1(1)	-5(1)	-1(1)
C(13)	15(1)	17(2)	24(2)	-4(1)	2(1)	-5(1)
C(14)	21(2)	25(2)	26(2)	-2(1)	-4(1)	-2(1)
C(15)	25(2)	38(2)	34(2)	7(2)	-5(2)	-6(2)
C(16)	35(2)	42(3)	41(2)	10(2)	-13(2)	-3(2)
C(17)	21(2)	52(3)	47(3)	-6(2)	-12(2)	7(2)
C(18)	21(2)	50(3)	45(2)	-7(2)	3(2)	-4(2)
C(19)	21(2)	36(2)	28(2)	-1(2)	0(1)	-2(2)
C(20)	18(2)	22(2)	25(2)	-2(1)	2(1)	-1(1)
C(21)	20(2)	26(2)	33(2)	-2(2)	-2(1)	-3(1)
C(22)	28(2)	39(2)	33(2)	-8(2)	-3(2)	-9(2)
C(23)	31(2)	29(2)	42(2)	-13(2)	9(2)	-8(2)
C(24)	32(2)	23(2)	42(2)	-1(2)	11(2)	-2(2)
C(25)	28(2)	25(2)	29(2)	1(2)	4(1)	-2(2)
C(26)	23(2)	18(2)	25(2)	4(1)	0(1)	-7(1)
C(27)	22(2)	23(2)	23(2)	1(1)	0(1)	-6(1)
C(28)	32(2)	25(2)	28(2)	6(2)	5(1)	-5(2)
C(29)	30(2)	28(2)	46(2)	8(2)	9(2)	-9(2)
C(30)	31(2)	30(2)	43(2)	9(2)	-6(2)	-15(2)

C(31)	29(2)	29(2)	30(2)	1(2)	-4(1)	-12(2)
C(32)	26(2)	25(2)	19(2)	3(1)	-4(1)	-11(1)
C(33)	27(2)	30(2)	24(2)	0(2)	-5(1)	-9(2)
C(34)	26(2)	32(2)	37(2)	0(2)	-7(2)	-6(2)
C(35)	38(2)	49(3)	31(2)	11(2)	-15(2)	-9(2)
C(36)	43(2)	72(3)	19(2)	9(2)	-5(2)	-7(2)
C(37)	29(2)	52(3)	24(2)	3(2)	-1(2)	-5(2)
C(38)	32(2)	28(2)	17(2)	-2(1)	-3(1)	-1(2)
C(39)	48(2)	32(2)	30(2)	-4(2)	5(2)	-4(2)
C(40)	76(3)	40(3)	40(3)	-8(2)	9(2)	-6(2)
C(41)	85(4)	44(3)	33(2)	-10(2)	9(2)	14(3)
C(42)	43(2)	60(3)	28(2)	-5(2)	8(2)	2(2)
C(43)	32(2)	39(2)	26(2)	-2(2)	0(2)	-2(2)
C(44)	23(2)	19(2)	24(2)	4(1)	-7(1)	0(1)
C(45)	23(2)	24(2)	41(2)	3(2)	-2(2)	-3(1)
C(46)	31(2)	22(2)	58(3)	-3(2)	-3(2)	-8(2)
C(47)	39(2)	23(2)	52(3)	-6(2)	-5(2)	-3(2)
C(48)	33(2)	28(2)	36(2)	-4(2)	1(2)	-3(2)
C(49)	32(2)	23(2)	25(2)	2(1)	-1(1)	-6(2)
C(50)	16(1)	21(2)	25(2)	1(1)	-2(1)	-3(1)
C(51)	22(2)	30(2)	30(2)	2(2)	-1(1)	-7(1)
C(52)	25(2)	35(2)	42(2)	4(2)	2(2)	-9(2)
C(53)	22(2)	42(2)	50(3)	3(2)	-9(2)	-13(2)
C(54)	31(2)	48(3)	40(2)	-1(2)	-12(2)	-12(2)
C(55)	24(2)	33(2)	31(2)	2(2)	-4(1)	-6(2)
C(56)	20(2)	27(2)	21(2)	4(1)	-3(1)	-6(1)
C(57)	25(2)	31(2)	29(2)	5(2)	-4(1)	-1(2)
C(58)	38(2)	39(2)	29(2)	13(2)	-6(2)	-7(2)
C(59)	31(2)	54(3)	24(2)	6(2)	-2(2)	-13(2)
C(60)	24(2)	45(2)	26(2)	-3(2)	1(1)	-3(2)
C(61)	21(2)	32(2)	25(2)	2(2)	-3(1)	-4(1)
O(1)	111(4)	106(4)	82(3)	6(3)	2(3)	-46(3)
C(62)	82(5)	108(7)	104(6)	-7(5)	-37(4)	-24(4)
C(63)	270(10)	190(10)	60(5)	3(6)	12(7)	-160(10)
C(64)	270(20)	110(10)	150(10)	-50(10)	60(10)	-10(10)
C(65)	300(20)	79(7)	170(10)	-30(8)	80(10)	-60(10)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table S3-5: Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 4

atom	x	y	z	U(eq)
H(1R)	1720(30)	1870(30)	7660(20)	21
H(1)	3850	599	8247	22
H(3)	2611	745	9438	36
H(4)	1351	1663	10302	45
H(5)	-631	1907	10216	45
H(6)	-1346	1242	9233	46
H(7)	-90.0000	359	8335	34
H(9)	1204	-1737	7483	30
H(10)	543	-1740	6287	32
H(11)	741	-385	5409	31
H(12)	1544	974	5707	28
H(15)	5291	-1294	8450	39
H(16)	7102	-1953	8926	48
H(17)	8783	-1665	8235	49
H(18)	8666	-702.0001	7094	47

H(19)	6883	-81	6617	35
H(21)	3971	-489	5649	32
H(22)	3743	-1928	5041	39
H(23)	3841	-3533	5703	40
H(24)	4262	-3725	6950	41
H(25)	4568	-2302	7548	34
H(27)	3782	3299	6125	27
H(28)	4957	4160	5310	35
H(29)	6409	4854	5762	42
H(30)	6643	4727	7037	41
H(31)	5423	3931	7860	34
H(33)	5768	1627	7666	32
H(34)	7046	803	8535	38
H(35)	6569	961	9808	47
H(36)	4800	1935	10203	55
H(37)	3481	2746	9334	43
H(39)	3382	5061	7907	45
H(40)	2201	6242	8648	63
H(41)	694	5775	9415	70
H(42)	317	4127	9409	55
H(43)	1456	2926	8658	40
H(45)	2314	4818	6109	36
H(46)	1720	6499	6484	44
H(47)	129	6894	7315	45
H(48)	-885	5624	7789	39
H(49)	-318.0000	3953	7409	32
H(51)	-191.0000	2083	7427	33
H(52)	-2018	1701	7391	41
H(53)	-2925	1921	6279	44
H(54)	-1988	2535	5212	46
H(55)	-174	2961	5235	35
H(57)	842	4520	5233	35
H(58)	1289	4715	3952	43
H(59)	2609	3435	3359	44
H(60)	3528	1989	4041	39
H(61)	3080	1787	5329	31
H(62A)	2514	6653	1498	114
H(62B)	1615	6153	1087	114
H(63A)	2937	6168	104	189
H(63B)	3976	6156	631	189
H(64A)	3095	4505	223	219
H(64B)	4391	4530	416	219
H(65A)	4055	4158	1518	223
H(65B)	2913	3835	1275	223

I.11. Crystallographic data for II-31

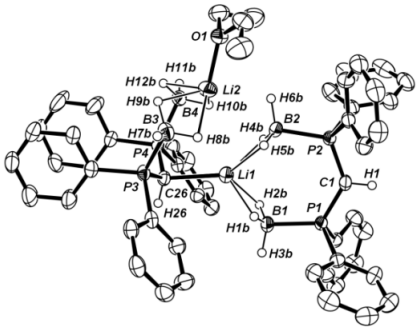


Table 1. Crystal data for xj288

Compound	xj288
Molecular formula	$C_{54}H_{64}B_4Li_2OP_4$
Molecular weight	910.05
Crystal habit	colorless block
Crystal dimensions(mm)	0.40x0.40x0.20
Crystal system	triclinic
Space group	P -1
a(Å)	9.875(1)
b(Å)	11.398(1)
c(Å)	25.171(1)
α(°)	99.319(1)
β(°)	95.282(1)
γ(°)	107.191(1)
V(Å^3)	2641.3(4)
Z	2
d(g-cm^{-3})	1.144
F(000)	964
μ(cm^{-1})	0.179
Absorption corrections	multi-scan ; 0.9318 min, 0.9651 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03

HKL ranges	-12 13 ; -16 16 ; -35 35
Reflections measured	31105
Unique data	15121
Rint	0.0311
Reflections used	11550
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	588
Reflections / parameter	19
wR2	0.1688
R1	0.0577
Weights a, b	0.0810 ; 1.6426
GoF	1.014
difference peak / hole (e Å^{-3})	0.500(0.106) / -0.705(0.106)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for xj288

atom	x	y	z	U(eq)
P(1)	513(1)	3059(1)	1349(1)	28(1)
P(2)	821(1)	419(1)	1361(1)	26(1)
P(3)	-2106(1)	1653(1)	3592(1)	27(1)
P(4)	1128(1)	2471(1)	3983(1)	26(1)
O(1)	58(2)	-2163(1)	2945(1)	39(1)
C(1)	807(2)	1685(2)	1080(1)	34(1)
C(2)	-910(2)	3252(2)	887(1)	30(1)
C(3)	-2294(2)	3027(2)	1017(1)	40(1)
C(4)	-3405(3)	3064(2)	647(1)	49(1)
C(5)	-3148(3)	3335(2)	141(1)	46(1)
C(6)	-1775(3)	3560(2)	7(1)	44(1)
C(7)	-670(2)	3521(2)	375(1)	37(1)
C(8)	2066(2)	4388(2)	1311(1)	30(1)
C(9)	1977(2)	5606(2)	1399(1)	36(1)
C(10)	3179(3)	6626(2)	1399(1)	42(1)
C(11)	4460(3)	6437(2)	1304(1)	48(1)
C(12)	4558(3)	5233(2)	1216(1)	50(1)
C(13)	3364(2)	4213(2)	1220(1)	40(1)
C(14)	-484(2)	-998(2)	945(1)	29(1)
C(15)	-1555(2)	-916(2)	564(1)	37(1)
C(16)	-2592(2)	-1999(2)	269(1)	45(1)
C(17)	-2578(2)	-3162(2)	355(1)	46(1)
C(18)	-1521(3)	-3261(2)	734(1)	41(1)
C(19)	-480(2)	-2184(2)	1022(1)	36(1)
C(20)	2525(2)	111(2)	1293(1)	31(1)
C(21)	3539(2)	335(2)	1750(1)	44(1)
C(22)	4894(3)	226(3)	1702(1)	57(1)
C(23)	5246(3)	-95(2)	1193(1)	56(1)
C(24)	4239(3)	-348(2)	733(1)	52(1)
C(25)	2880(3)	-252(2)	781(1)	41(1)
C(26)	-350(2)	2655(2)	3602(1)	27(1)
C(27)	-3251(2)	2362(2)	3240(1)	29(1)
C(28)	-2725(2)	3285(2)	2941(1)	36(1)
C(29)	-3654(3)	3749(2)	2654(1)	45(1)
C(30)	-5107(2)	3339(2)	2675(1)	42(1)
C(31)	-5634(2)	2443(2)	2979(1)	39(1)
C(32)	-4733(2)	1947(2)	3255(1)	34(1)

C(33)	-2662(2)	1710(2)	4267(1)	30(1)
C(34)	-2890(3)	2757(2)	4540(1)	55(1)
C(35)	-3231(3)	2832(3)	5066(1)	55(1)
C(36)	-3355(3)	1851(3)	5319(1)	53(1)
C(37)	-3131(7)	813(4)	5054(2)	127(2)
C(38)	-2789(6)	734(3)	4526(2)	104(2)
C(39)	1071(2)	2712(2)	4715(1)	29(1)
C(40)	934(3)	3800(2)	4995(1)	45(1)
C(41)	860(3)	3971(3)	5549(1)	54(1)
C(42)	937(3)	3061(3)	5831(1)	46(1)
C(43)	1100(5)	1984(3)	5561(1)	78(1)
C(44)	1162(4)	1800(2)	5005(1)	70(1)
C(45)	2640(2)	3806(2)	3931(1)	27(1)
C(46)	2545(2)	4599(2)	3570(1)	30(1)
C(47)	3751(2)	5582(2)	3532(1)	37(1)
C(48)	5035(2)	5788(2)	3853(1)	43(1)
C(49)	5135(2)	5012(2)	4217(1)	46(1)
C(50)	3952(2)	4023(2)	4254(1)	37(1)
C(51)	-2051(4)	-3012(3)	2308(1)	68(1)
C(52)	-654(3)	-3150(2)	2502(1)	58(1)
C(53)	1438(3)	-2215(3)	3194(1)	52(1)
C(54)	2610(3)	-1788(3)	2882(2)	69(1)
B(1)	70(3)	3375(2)	2078(1)	40(1)
B(2)	441(3)	439(2)	2098(1)	32(1)
B(3)	-2477(3)	-59(2)	3222(1)	36(1)
B(4)	1500(3)	912(2)	3748(1)	32(1)
Li(1)	-85(4)	2077(3)	2710(2)	38(1)
Li(2)	-288(4)	-591(3)	3019(2)	41(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for xj288

P(1)-C(1)	1.719(2)	P(1)-C(2)	1.828(2)
P(1)-C(8)	1.833(2)	P(1)-B(1)	1.928(2)
P(2)-C(1)	1.710(2)	P(2)-C(14)	1.827(2)
P(2)-C(20)	1.835(2)	P(2)-B(2)	1.923(2)
P(3)-C(26)	1.768(2)	P(3)-C(27)	1.818(2)
P(3)-C(33)	1.829(2)	P(3)-B(3)	1.934(2)
P(4)-C(26)	1.757(2)	P(4)-C(45)	1.822(2)
P(4)-C(39)	1.826(2)	P(4)-B(4)	1.932(2)
O(1)-C(52)	1.409(3)	O(1)-C(53)	1.468(3)
O(1)-Li(2)	1.905(4)	C(1)-H(1)	0.9500
C(2)-C(3)	1.394(3)	C(2)-C(7)	1.397(3)
C(3)-C(4)	1.387(3)	C(3)-H(3)	0.9500
C(4)-C(5)	1.386(4)	C(4)-H(4)	0.9500
C(5)-C(6)	1.387(4)	C(5)-H(5)	0.9500
C(6)-C(7)	1.382(3)	C(6)-H(6)	0.9500
C(7)-H(7)	0.9500	C(8)-C(13)	1.388(3)
C(8)-C(9)	1.400(3)	C(9)-C(10)	1.394(3)
C(9)-H(9)	0.9500	C(10)-C(11)	1.380(4)
C(10)-H(10)	0.9500	C(11)-C(12)	1.387(3)
C(11)-H(11)	0.9500	C(12)-C(13)	1.392(3)
C(12)-H(12)	0.9500	C(13)-H(13)	0.9500
C(14)-C(15)	1.394(3)	C(14)-C(19)	1.398(3)
C(15)-C(16)	1.393(3)	C(15)-H(15)	0.9500
C(16)-C(17)	1.382(4)	C(16)-H(16)	0.9500
C(17)-C(18)	1.391(4)	C(17)-H(17)	0.9500
C(18)-C(19)	1.385(3)	C(18)-H(18)	0.9500
C(19)-H(19)	0.9500	C(20)-C(21)	1.389(3)
C(20)-C(25)	1.397(3)	C(21)-C(22)	1.394(3)
C(21)-H(21)	0.9500	C(22)-C(23)	1.377(4)
C(22)-H(22)	0.9500	C(23)-C(24)	1.387(4)

C(23)-H(23)	0.9500	C(24)-C(25)	1.393(3)
C(24)-H(24)	0.9500	C(25)-H(25)	0.9500
C(26)-Li(1)	2.295(4)	C(26)-H(26)	1.0000
C(27)-C(28)	1.395(3)	C(27)-C(32)	1.405(3)
C(28)-C(29)	1.390(3)	C(28)-H(28)	0.9500
C(29)-C(30)	1.380(3)	C(29)-H(29)	0.9500
C(30)-C(31)	1.383(3)	C(30)-H(30)	0.9500
C(31)-C(32)	1.380(3)	C(31)-H(31)	0.9500
C(32)-H(32)	0.9500	C(33)-C(38)	1.359(3)
C(33)-C(34)	1.368(3)	C(34)-C(35)	1.389(3)
C(34)-H(34)	0.9500	C(35)-C(36)	1.355(4)
C(35)-H(35)	0.9500	C(36)-C(37)	1.349(4)
C(36)-H(36)	0.9500	C(37)-C(38)	1.397(4)
C(37)-H(37)	0.9500	C(38)-H(38)	0.9500
C(39)-C(40)	1.373(3)	C(39)-C(44)	1.383(3)
C(40)-C(41)	1.389(3)	C(40)-H(40)	0.9500
C(41)-C(42)	1.363(4)	C(41)-H(41)	0.9500
C(42)-C(43)	1.364(4)	C(42)-H(42)	0.9500
C(43)-C(44)	1.391(4)	C(43)-H(43)	0.9500
C(44)-H(44)	0.9500	C(45)-C(50)	1.397(3)
C(45)-C(46)	1.399(3)	C(46)-C(47)	1.397(3)
C(46)-H(46)	0.9500	C(47)-C(48)	1.376(3)
C(47)-H(47)	0.9500	C(48)-C(49)	1.387(3)
C(48)-H(48)	0.9500	C(49)-C(50)	1.386(3)
C(49)-H(49)	0.9500	C(50)-H(50)	0.9500
C(51)-C(52)	1.482(4)	C(51)-H(51A)	0.9800
C(51)-H(51B)	0.9800	C(51)-H(51C)	0.9800
C(52)-H(52A)	0.9900	C(52)-H(52B)	0.9900
C(53)-C(54)	1.467(4)	C(53)-H(53A)	0.9900
C(53)-H(53B)	0.9900	C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800	C(54)-H(54C)	0.9800
B(1)-Li(1)	2.326(4)	B(1)-H(1B)	1.1208
B(1)-H(2B)	1.1953	B(1)-H(3B)	1.0831
B(2)-Li(1)	2.434(4)	B(2)-Li(2)	2.822(4)
B(2)-H(4B)	1.1103	B(2)-H(5B)	1.0958
B(2)-H(6B)	1.1174	B(3)-Li(2)	2.485(5)
B(3)-H(7B)	1.1205	B(3)-H(8B)	1.0983
B(3)-H(9B)	1.1816	B(4)-Li(2)	2.452(5)
B(4)-H(10B)	1.1550	B(4)-H(11B)	1.0773
B(4)-H(12B)	1.1405	Li(1)-Li(2)	3.213(5)
Li(1)-H(1B)	1.9198	Li(1)-H(2B)	2.0102
Li(1)-H(4B)	1.9329	Li(1)-H(5B)	2.1089
Li(2)-H(6B)	2.2691	Li(2)-H(8B)	2.1579
Li(2)-H(9B)	1.9978	Li(2)-H(10B)	1.9621
Li(2)-H(12B)	2.1108		

C(1)-P(1)-C(2)	107.8(1)	C(1)-P(1)-C(8)	109.3(1)
C(2)-P(1)-C(8)	102.76(8)	C(1)-P(1)-B(1)	121.6(1)
C(2)-P(1)-B(1)	107.7(1)	C(8)-P(1)-B(1)	106.0(1)
C(1)-P(2)-C(14)	109.7(1)	C(1)-P(2)-C(20)	108.9(1)
C(14)-P(2)-C(20)	102.3(1)	C(1)-P(2)-B(2)	118.4(1)
C(14)-P(2)-B(2)	106.4(1)	C(20)-P(2)-B(2)	109.8(1)
C(26)-P(3)-C(27)	104.15(8)	C(26)-P(3)-C(33)	113.2(1)
C(27)-P(3)-C(33)	103.26(8)	C(26)-P(3)-B(3)	114.8(1)
C(27)-P(3)-B(3)	109.7(1)	C(33)-P(3)-B(3)	110.9(1)
C(26)-P(4)-C(45)	104.77(8)	C(26)-P(4)-C(39)	113.6(1)
C(45)-P(4)-C(39)	102.25(8)	C(26)-P(4)-B(4)	114.9(1)
C(45)-P(4)-B(4)	111.1(1)	C(39)-P(4)-B(4)	109.4(1)
C(52)-O(1)-C(53)	114.8(2)	C(52)-O(1)-Li(2)	121.2(2)
C(53)-O(1)-Li(2)	119.3(2)	P(2)-C(1)-P(1)	130.7(1)
P(2)-C(1)-H(1)	114.6	P(1)-C(1)-H(1)	114.6

C(3)-C(2)-C(7)	118.3(2)	C(3)-C(2)-P(1)	120.7(2)
C(7)-C(2)-P(1)	120.8(2)	C(4)-C(3)-C(2)	120.8(2)
C(4)-C(3)-H(3)	119.6	C(2)-C(3)-H(3)	119.6
C(5)-C(4)-C(3)	120.2(2)	C(5)-C(4)-H(4)	119.9
C(3)-C(4)-H(4)	119.9	C(4)-C(5)-C(6)	119.4(2)
C(4)-C(5)-H(5)	120.3	C(6)-C(5)-H(5)	120.3
C(7)-C(6)-C(5)	120.4(2)	C(7)-C(6)-H(6)	119.8
C(5)-C(6)-H(6)	119.8	C(6)-C(7)-C(2)	120.9(2)
C(6)-C(7)-H(7)	119.6	C(2)-C(7)-H(7)	119.6
C(13)-C(8)-C(9)	118.9(2)	C(13)-C(8)-P(1)	120.7(2)
C(9)-C(8)-P(1)	120.3(2)	C(10)-C(9)-C(8)	120.4(2)
C(10)-C(9)-H(9)	119.8	C(8)-C(9)-H(9)	119.8
C(11)-C(10)-C(9)	120.1(2)	C(11)-C(10)-H(10)	120.0
C(9)-C(10)-H(10)	120.0	C(10)-C(11)-C(12)	120.0(2)
C(10)-C(11)-H(11)	120.0	C(12)-C(11)-H(11)	120.0
C(11)-C(12)-C(13)	120.2(2)	C(11)-C(12)-H(12)	119.9
C(13)-C(12)-H(12)	119.9	C(8)-C(13)-C(12)	120.5(2)
C(8)-C(13)-H(13)	119.8	C(12)-C(13)-H(13)	119.8
C(15)-C(14)-C(19)	118.6(2)	C(15)-C(14)-P(2)	120.6(2)
C(19)-C(14)-P(2)	120.7(2)	C(16)-C(15)-C(14)	120.3(2)
C(16)-C(15)-H(15)	119.8	C(14)-C(15)-H(15)	119.8
C(17)-C(16)-C(15)	120.2(2)	C(17)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9	C(16)-C(17)-C(18)	120.2(2)
C(16)-C(17)-H(17)	119.9	C(18)-C(17)-H(17)	119.9
C(19)-C(18)-C(17)	119.4(2)	C(19)-C(18)-H(18)	120.3
C(17)-C(18)-H(18)	120.3	C(18)-C(19)-C(14)	121.2(2)
C(18)-C(19)-H(19)	119.4	C(14)-C(19)-H(19)	119.4
C(21)-C(20)-C(25)	118.6(2)	C(21)-C(20)-P(2)	120.3(2)
C(25)-C(20)-P(2)	120.9(2)	C(20)-C(21)-C(22)	121.1(2)
C(20)-C(21)-H(21)	119.4	C(22)-C(21)-H(21)	119.4
C(23)-C(22)-C(21)	119.7(3)	C(23)-C(22)-H(22)	120.1
C(21)-C(22)-H(22)	120.1	C(22)-C(23)-C(24)	120.0(2)
C(22)-C(23)-H(23)	120.0	C(24)-C(23)-H(23)	120.0
C(23)-C(24)-C(25)	120.3(2)	C(23)-C(24)-H(24)	119.8
C(25)-C(24)-H(24)	119.8	C(24)-C(25)-C(20)	120.2(2)
C(24)-C(25)-H(25)	119.9	C(20)-C(25)-H(25)	119.9
P(4)-C(26)-P(3)	120.9(1)	P(4)-C(26)-Li(1)	104.8(1)
P(3)-C(26)-Li(1)	99.6(1)	P(4)-C(26)-H(26)	110.2
P(3)-C(26)-H(26)	110.2	Li(1)-C(26)-H(26)	110.2
C(28)-C(27)-C(32)	118.2(2)	C(28)-C(27)-P(3)	122.7(1)
C(32)-C(27)-P(3)	119.1(2)	C(29)-C(28)-C(27)	120.5(2)
C(29)-C(28)-H(28)	119.8	C(27)-C(28)-H(28)	119.8
C(30)-C(29)-C(28)	120.7(2)	C(30)-C(29)-H(29)	119.6
C(28)-C(29)-H(29)	119.6	C(29)-C(30)-C(31)	119.2(2)
C(29)-C(30)-H(30)	120.4	C(31)-C(30)-H(30)	120.4
C(32)-C(31)-C(30)	120.9(2)	C(32)-C(31)-H(31)	119.5
C(30)-C(31)-H(31)	119.5	C(31)-C(32)-C(27)	120.4(2)
C(31)-C(32)-H(32)	119.8	C(27)-C(32)-H(32)	119.8
C(38)-C(33)-C(34)	117.6(2)	C(38)-C(33)-P(3)	121.0(2)
C(34)-C(33)-P(3)	121.4(2)	C(33)-C(34)-C(35)	121.6(2)
C(33)-C(34)-H(34)	119.2	C(35)-C(34)-H(34)	119.2
C(36)-C(35)-C(34)	120.1(2)	C(36)-C(35)-H(35)	119.9
C(34)-C(35)-H(35)	119.9	C(37)-C(36)-C(35)	118.9(2)
C(37)-C(36)-H(36)	120.6	C(35)-C(36)-H(36)	120.6
C(36)-C(37)-C(38)	121.1(3)	C(36)-C(37)-H(37)	119.4
C(38)-C(37)-H(37)	119.4	C(33)-C(38)-C(37)	120.7(3)
C(33)-C(38)-H(38)	119.7	C(37)-C(38)-H(38)	119.7
C(40)-C(39)-C(44)	117.8(2)	C(40)-C(39)-P(4)	121.3(2)
C(44)-C(39)-P(4)	120.9(2)	C(39)-C(40)-C(41)	121.2(2)
C(39)-C(40)-H(40)	119.4	C(41)-C(40)-H(40)	119.4
C(42)-C(41)-C(40)	120.5(2)	C(42)-C(41)-H(41)	119.7
C(40)-C(41)-H(41)	119.7	C(41)-C(42)-C(43)	119.1(2)
C(41)-C(42)-H(42)	120.5	C(43)-C(42)-H(42)	120.5

C(42)-C(43)-C(44)	120.8(2)	C(42)-C(43)-H(43)	119.6
C(44)-C(43)-H(43)	119.6	C(39)-C(44)-C(43)	120.6(3)
C(39)-C(44)-H(44)	119.7	C(43)-C(44)-H(44)	119.7
C(50)-C(45)-C(46)	118.9(2)	C(50)-C(45)-P(4)	118.7(1)
C(46)-C(45)-P(4)	122.4(1)	C(47)-C(46)-C(45)	120.1(2)
C(47)-C(46)-H(46)	120.0	C(45)-C(46)-H(46)	120.0
C(48)-C(47)-C(46)	120.4(2)	C(48)-C(47)-H(47)	119.8
C(46)-C(47)-H(47)	119.8	C(47)-C(48)-C(49)	119.8(2)
C(47)-C(48)-H(48)	120.1	C(49)-C(48)-H(48)	120.1
C(50)-C(49)-C(48)	120.4(2)	C(50)-C(49)-H(49)	119.8
C(48)-C(49)-H(49)	119.8	C(49)-C(50)-C(45)	120.4(2)
C(49)-C(50)-H(50)	119.8	C(45)-C(50)-H(50)	119.8
C(52)-C(51)-H(51A)	109.5	C(52)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51B)	109.5	C(52)-C(51)-H(51C)	109.5
H(51A)-C(51)-H(51C)	109.5	H(51B)-C(51)-H(51C)	109.5
O(1)-C(52)-C(51)	109.0(2)	O(1)-C(52)-H(52A)	109.9
C(51)-C(52)-H(52A)	109.9	O(1)-C(52)-H(52B)	109.9
C(51)-C(52)-H(52B)	109.9	H(52A)-C(52)-H(52B)	108.3
C(54)-C(53)-O(1)	113.4(2)	C(54)-C(53)-H(53A)	108.9
O(1)-C(53)-H(53A)	108.9	C(54)-C(53)-H(53B)	108.9
O(1)-C(53)-H(53B)	108.9	H(53A)-C(53)-H(53B)	107.7
C(53)-C(54)-H(54A)	109.5	C(53)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5	C(53)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5	H(54B)-C(54)-H(54C)	109.5
P(1)-B(1)-Li(1)	127.3(1)	P(1)-B(1)-H(1B)	111.2
Li(1)-B(1)-H(1B)	55.1	P(1)-B(1)-H(2B)	105.6
Li(1)-B(1)-H(2B)	59.8	H(1B)-B(1)-H(2B)	114.9
P(1)-B(1)-H(3B)	102.5	Li(1)-B(1)-H(3B)	130.2
H(1B)-B(1)-H(3B)	112.7	H(2B)-B(1)-H(3B)	109.0
P(2)-B(2)-Li(1)	128.0(1)	P(2)-B(2)-Li(2)	156.2(1)
Li(1)-B(2)-Li(2)	75.0(1)	P(2)-B(2)-H(4B)	111.3
Li(1)-B(2)-H(4B)	50.8	Li(2)-B(2)-H(4B)	87.7
P(2)-B(2)-H(5B)	106.0	Li(1)-B(2)-H(5B)	59.9
Li(2)-B(2)-H(5B)	79.0	H(4B)-B(2)-H(5B)	110.5
P(2)-B(2)-H(6B)	107.8	Li(1)-B(2)-H(6B)	124.1
Li(2)-B(2)-H(6B)	49.9	H(4B)-B(2)-H(6B)	111.2
H(5B)-B(2)-H(6B)	109.9	P(3)-B(3)-Li(2)	114.1(1)
P(3)-B(3)-H(7B)	108.1	Li(2)-B(3)-H(7B)	137.5
P(3)-B(3)-H(8B)	104.5	Li(2)-B(3)-H(8B)	60.1
H(7B)-B(3)-H(8B)	105.5	P(3)-B(3)-H(9B)	111.3
Li(2)-B(3)-H(9B)	52.4	H(7B)-B(3)-H(9B)	115.1
H(8B)-B(3)-H(9B)	111.5	P(4)-B(4)-Li(2)	115.2(1)
P(4)-B(4)-H(10B)	104.1	Li(2)-B(4)-H(10B)	51.9
P(4)-B(4)-H(11B)	109.3	Li(2)-B(4)-H(11B)	134.8
H(10B)-B(4)-H(11B)	110.5	P(4)-B(4)-H(12B)	109.3
Li(2)-B(4)-H(12B)	59.3	H(10B)-B(4)-H(12B)	110.8
H(11B)-B(4)-H(12B)	112.4	C(26)-Li(1)-B(1)	124.0(2)
C(26)-Li(1)-B(2)	141.5(2)	B(1)-Li(1)-B(2)	93.9(1)
C(26)-Li(1)-Li(2)	84.7(1)	B(1)-Li(1)-Li(2)	151.2(2)
B(2)-Li(1)-Li(2)	58.0(1)	C(26)-Li(1)-H(1B)	122.4
B(1)-Li(1)-H(1B)	28.6	B(2)-Li(1)-H(1B)	93.7
Li(2)-Li(1)-H(1B)	136.2	C(26)-Li(1)-H(2B)	116.4
B(1)-Li(1)-H(2B)	30.9	B(2)-Li(1)-H(2B)	92.3
Li(2)-Li(1)-H(2B)	142.7	H(1B)-Li(1)-H(2B)	59.5
C(26)-Li(1)-H(4B)	132.0	B(1)-Li(1)-H(4B)	92.4
B(2)-Li(1)-H(4B)	26.4	Li(2)-Li(1)-H(4B)	65.7
H(1B)-Li(1)-H(4B)	104.7	H(2B)-Li(1)-H(4B)	77.9
C(26)-Li(1)-H(5B)	139.3	B(1)-Li(1)-H(5B)	92.2
B(2)-Li(1)-H(5B)	26.7	Li(2)-Li(1)-H(5B)	59.9
H(1B)-Li(1)-H(5B)	79.8	H(2B)-Li(1)-H(5B)	104.3
H(4B)-Li(1)-H(5B)	53.1	O(1)-Li(2)-B(4)	108.6(2)
O(1)-Li(2)-B(3)	129.5(2)	B(4)-Li(2)-B(3)	100.4(2)
O(1)-Li(2)-B(2)	108.6(2)	B(4)-Li(2)-B(2)	101.7(2)

B(3)-Li(2)-B(2)	104.7(2)	O(1)-Li(2)-Li(1)	154.9(2)
B(4)-Li(2)-Li(1)	76.4(1)	B(3)-Li(2)-Li(1)	71.2(1)
B(2)-Li(2)-Li(1)	47.0(1)	O(1)-Li(2)-H(6B)	86.5
B(4)-Li(2)-H(6B)	108.9	B(3)-Li(2)-H(6B)	121.9
B(2)-Li(2)-H(6B)	22.1	Li(1)-Li(2)-H(6B)	68.9
O(1)-Li(2)-H(8B)	135.6	B(4)-Li(2)-H(8B)	112.4
B(3)-Li(2)-H(8B)	26.2	B(2)-Li(2)-H(8B)	79.3
Li(1)-Li(2)-H(8B)	55.6	H(6B)-Li(2)-H(8B)	95.8
O(1)-Li(2)-H(9B)	110.0	B(4)-Li(2)-H(9B)	91.1
B(3)-Li(2)-H(9B)	28.0	B(2)-Li(2)-H(9B)	132.6
Li(1)-Li(2)-H(9B)	94.2	H(6B)-Li(2)-H(9B)	148.9
H(8B)-Li(2)-H(9B)	53.8	O(1)-Li(2)-H(10B)	112.3
B(4)-Li(2)-H(10B)	27.6	B(3)-Li(2)-H(10B)	112.5
B(2)-Li(2)-H(10B)	74.6	Li(1)-Li(2)-H(10B)	60.8
H(6B)-Li(2)-H(10B)	81.7	H(8B)-Li(2)-H(10B)	111.9
H(9B)-Li(2)-H(10B)	113.5	O(1)-Li(2)-H(12B)	97.7
B(4)-Li(2)-H(12B)	27.7	B(3)-Li(2)-H(12B)	89.3
B(2)-Li(2)-H(12B)	129.2	Li(1)-Li(2)-H(12B)	96.5
H(6B)-Li(2)-H(12B)	135.0	H(8B)-Li(2)-H(12B)	110.7
H(9B)-Li(2)-H(12B)	70.6	H(10B)-Li(2)-H(12B)	55.1

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for xj288

atom	U11	U22	U33	U23	U13	U12
P(1)	39(1)	24(1)	24(1)	7(1)	10(1)	10(1)
P(2)	33(1)	23(1)	23(1)	5(1)	8(1)	8(1)
P(3)	26(1)	28(1)	26(1)	5(1)	10(1)	6(1)
P(4)	28(1)	25(1)	22(1)	5(1)	6(1)	6(1)
O(1)	48(1)	31(1)	44(1)	10(1)	14(1)	16(1)
C(1)	53(1)	29(1)	24(1)	7(1)	15(1)	14(1)
C(2)	37(1)	23(1)	31(1)	7(1)	9(1)	8(1)
C(3)	39(1)	39(1)	44(1)	12(1)	13(1)	11(1)
C(4)	35(1)	46(1)	62(2)	7(1)	8(1)	9(1)
C(5)	44(1)	35(1)	52(1)	4(1)	-10(1)	9(1)
C(6)	46(1)	47(1)	36(1)	12(1)	-2(1)	9(1)
C(7)	39(1)	40(1)	31(1)	12(1)	6(1)	9(1)
C(8)	38(1)	27(1)	23(1)	5(1)	3(1)	8(1)
C(9)	42(1)	29(1)	35(1)	8(1)	4(1)	9(1)
C(10)	50(1)	28(1)	43(1)	7(1)	2(1)	5(1)
C(11)	44(1)	38(1)	52(2)	9(1)	1(1)	-1(1)
C(12)	38(1)	45(1)	62(2)	7(1)	7(1)	8(1)
C(13)	41(1)	34(1)	44(1)	4(1)	7(1)	11(1)
C(14)	34(1)	28(1)	25(1)	4(1)	9(1)	8(1)
C(15)	36(1)	38(1)	34(1)	7(1)	5(1)	10(1)
C(16)	36(1)	51(1)	39(1)	4(1)	0(1)	7(1)
C(17)	38(1)	40(1)	45(1)	-3(1)	10(1)	-3(1)
C(18)	46(1)	28(1)	43(1)	2(1)	11(1)	3(1)
C(19)	42(1)	27(1)	36(1)	6(1)	6(1)	8(1)
C(20)	34(1)	21(1)	37(1)	3(1)	10(1)	6(1)
C(21)	37(1)	43(1)	45(1)	-6(1)	3(1)	12(1)
C(22)	37(1)	52(1)	72(2)	-9(1)	-2(1)	13(1)
C(23)	39(1)	36(1)	91(2)	3(1)	23(1)	9(1)
C(24)	61(2)	38(1)	62(2)	10(1)	37(1)	16(1)
C(25)	50(1)	36(1)	40(1)	9(1)	19(1)	15(1)
C(26)	27(1)	28(1)	25(1)	6(1)	8(1)	7(1)
C(27)	27(1)	32(1)	25(1)	2(1)	8(1)	5(1)
C(28)	29(1)	40(1)	43(1)	14(1)	11(1)	11(1)
C(29)	41(1)	46(1)	55(2)	22(1)	11(1)	18(1)
C(30)	38(1)	51(1)	41(1)	7(1)	3(1)	22(1)
C(31)	27(1)	52(1)	33(1)	-2(1)	4(1)	10(1)
C(32)	25(1)	41(1)	29(1)	3(1)	6(1)	5(1)

C(33)	29(1)	35(1)	28(1)	8(1)	9(1)	9(1)
C(34)	97(2)	37(1)	36(1)	9(1)	29(1)	23(1)
C(35)	79(2)	49(1)	37(1)	2(1)	24(1)	20(1)
C(36)	62(2)	78(2)	36(1)	22(1)	25(1)	35(1)
C(37)	273(7)	113(3)	84(3)	75(3)	122(4)	134(4)
C(38)	217(5)	83(2)	77(2)	56(2)	104(3)	102(3)
C(39)	30(1)	31(1)	23(1)	7(1)	4(1)	4(1)
C(40)	70(2)	51(1)	26(1)	7(1)	8(1)	35(1)
C(41)	75(2)	71(2)	27(1)	2(1)	10(1)	44(2)
C(42)	44(1)	65(2)	24(1)	11(1)	9(1)	7(1)
C(43)	147(3)	50(2)	32(1)	21(1)	16(2)	17(2)
C(44)	145(3)	38(1)	30(1)	12(1)	17(2)	28(2)
C(45)	25(1)	29(1)	24(1)	2(1)	6(1)	6(1)
C(46)	30(1)	28(1)	31(1)	7(1)	5(1)	7(1)
C(47)	35(1)	34(1)	42(1)	12(1)	12(1)	6(1)
C(48)	30(1)	41(1)	48(1)	7(1)	10(1)	-1(1)
C(49)	28(1)	58(1)	43(1)	11(1)	1(1)	3(1)
C(50)	31(1)	48(1)	32(1)	12(1)	4(1)	10(1)
C(51)	73(2)	42(1)	71(2)	5(1)	-9(2)	2(1)
C(52)	83(2)	36(1)	53(2)	0(1)	11(1)	20(1)
C(53)	54(1)	48(1)	64(2)	22(1)	14(1)	24(1)
C(54)	57(2)	68(2)	93(3)	35(2)	19(2)	22(2)
B(1)	66(2)	32(1)	27(1)	9(1)	19(1)	21(1)
B(2)	43(1)	31(1)	23(1)	8(1)	8(1)	13(1)
B(3)	34(1)	32(1)	38(1)	2(1)	11(1)	6(1)
B(4)	37(1)	28(1)	29(1)	3(1)	5(1)	9(1)
Li(1)	53(2)	36(2)	30(2)	9(1)	13(2)	18(2)
Li(2)	46(2)	30(2)	47(2)	5(2)	7(2)	13(2)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for xj288

atom	x	y	z	U(eq)
H(1)	993	1619	714	41
H(3)	-2480	2845	1364	48
H(4)	-4344	2902	740	59
H(5)	-3906	3367	-112.0000	56
H(6)	-1594	3743	-339	53
H(7)	266	3678	279	44
H(9)	1093	5738	1459	43
H(10)	3116	7451	1465	51
H(11)	5274	7131	1298	58
H(12)	5442	5105	1153	60
H(13)	3439	3392	1160	48
H(15)	-1577	-119	506	44
H(16)	-3312	-1937	7.0000	53
H(17)	-3292.9998	-3897	154	55
H(18)	-1512	-4060	795	49
H(19)	250	-2252	1277	43
H(21)	3305	567	2101	52
H(22)	5571	372	2018	68
H(23)	6178	-144	1158	68
H(24)	4478	-587	384	62
H(25)	2193	-433	464	49
H(26)	-325	3550	3680	32
H(28)	-1723	3599	2934	44
H(29)	-3286	4354	2442	54
H(30)	-5736	3669	2484	50

H(31)	-6632	2164	2998	47
H(32)	-5116.9995	1321	3456	40
H(34)	-2814	3450	4367	66
H(35)	-3378	3573	5248	66
H(36)	-3595	1894	5677	64
H(37)	-3208	122	5230	153
H(38)	-2644	-9	4346	124
H(40)	888	4447	4806	54
H(41)	756	4728	5734	65
H(42)	878	3176	6208	55
H(43)	1171	1351	5756	94
H(44)	1269	1041	4824	84
H(46)	1658	4469	3349	36
H(47)	3685	6111	3282	45
H(48)	5852	6460	3827	51
H(49)	6020	5159	4441	55
H(50)	4035	3490	4500	45
H(51A)	-2638	-3052	2602	102
H(51B)	-2548	-3690	1997	102
H(51C)	-1890	-2203	2197	102
H(52A)	-809	-3965	2617	70
H(52B)	-63	-3127	2205	70
H(53A)	1692	-1688	3565	62
H(53B)	1333	-3088	3231	62
H(54A)	2406	-2350	2526	103
H(54B)	3509	-1796	3080	103
H(54C)	2699	-935.0001	2833	103
H(1B)	-937	2652	2129	47
H(2B)	1119	3429	2372	47
H(3B)	-35	4303	2117	47
H(4B)	1191	1276	2381	38
H(5B)	-665	452	2093	38
H(6B)	532	-446	2211	38
H(7B)	-3667	-518	3128	43
H(8B)	-2112	21	2825	43
H(9B)	-1851	-584	3468	43
H(10B)	1471	827	3283	38
H(11B)	2547	974	3939	38
H(12B)	615	108	3845	38

I.12. Crystallographic data for II-32

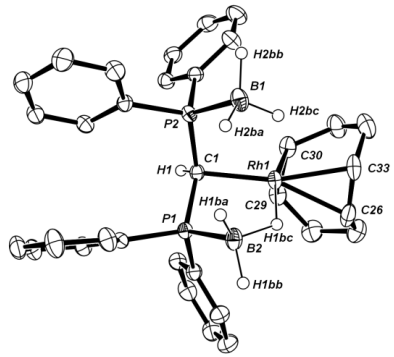


Table 1. Crystal data for xj297

Compound	xj297
Molecular formula	$C_{33}H_{39}B_2P_2Rh, 2C_7H_8$
Molecular weight	806.38
Crystal habit	yellow block
Crystal dimensions(mm)	0.20x0.20x0.20
Crystal system	monoclinic
Space group	P 2_1/c
a(Å)	8.882(1)
b(Å)	14.231(1)
c(Å)	32.194(1)
α(°)	90.00
β(°)	104.564(1)
γ(°)	90.00
V(Å^3)	3938.6(5)
Z	4
d(g-cm^{-3})	1.360
F(000)	1688
μ(cm^{-1})	0.548
Absorption corrections	multi-scan ; 0.8983 min, 0.8983 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-11 12 ; -19 17 ; -37 45
Reflections measured	25762
Unique data	11398
Rint	0.0247
Reflections used	9222
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	364
Reflections / parameter	25
wR2	0.1429
R1	0.0414
Weights a, b	0.0895 ; 0.0000
GoF	1.121
difference peak / hole (e Å^{-3})	0.632(0.174) / -1.153(0.174)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for xj297

atom	x	y	z	U(eq)
Rh(1)	5673(1)	5996(1)	1538(1)	20(1)
P(1)	3569(1)	7256(1)	1798(1)	18(1)
P(2)	3023(1)	6682(1)	823(1)	19(1)
C(1)	3254(2)	6398(2)	1379(1)	19(1)
C(2)	3534(2)	6581(2)	2275(1)	21(1)
C(3)	2444(3)	5867(2)	2272(1)	25(1)
C(4)	2521(3)	5336(2)	2640(1)	31(1)
C(5)	3652(3)	5522(2)	3016(1)	35(1)
C(6)	4711(3)	6244(2)	3022(1)	36(1)
C(7)	4656(3)	6765(2)	2656(1)	28(1)
C(8)	2032(2)	8133(2)	1745(1)	20(1)
C(9)	569(3)	7917(2)	1812(1)	24(1)
C(10)	-606(3)	8585(2)	1732(1)	28(1)
C(11)	-337(3)	9470(2)	1590(1)	32(1)
C(12)	1110(3)	9699(2)	1537(1)	36(1)
C(13)	2294(3)	9031(2)	1612(1)	28(1)
C(14)	1393(2)	7473(2)	616(1)	21(1)
C(15)	51(3)	7466(2)	768(1)	24(1)
C(16)	-1184(3)	8063(2)	594(1)	28(1)
C(17)	-1092(3)	8677(2)	268(1)	32(1)
C(18)	237(3)	8695(2)	113(1)	34(1)
C(19)	1491(3)	8101(2)	289(1)	28(1)
C(20)	2376(3)	5560(2)	564(1)	22(1)
C(21)	1049(3)	5126(2)	627(1)	24(1)
C(22)	600(3)	4244(2)	452(1)	28(1)
C(23)	1494(3)	3795(2)	215(1)	32(1)
C(24)	2794(4)	4221(2)	144(1)	37(1)
C(25)	3249(3)	5113(2)	317(1)	30(1)
C(26)	8016(3)	5612(2)	1940(1)	34(1)
C(27)	7970(3)	4743(2)	2204(1)	40(1)
C(28)	6332(3)	4488(2)	2220(1)	38(1)
C(29)	5129(3)	4748(2)	1816(1)	28(1)
C(30)	5225(3)	4568(2)	1393(1)	27(1)
C(31)	6590(4)	4066(2)	1281(1)	40(1)
C(32)	7884(3)	4715(2)	1240(1)	43(1)
C(33)	8021(3)	5593(2)	1514(1)	33(1)
B(1)	5554(3)	7810(2)	1819(1)	25(1)
B(2)	4926(3)	7109(2)	706(1)	28(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for xj297

Rh(1)-C(29)	2.100(2)	Rh(1)-C(30)	2.100(2)
Rh(1)-C(1)	2.157(2)	Rh(1)-C(33)	2.183(2)
Rh(1)-C(26)	2.225(2)	Rh(1)-P(1)	2.8626(6)
Rh(1)-H(1BC)	1.83(3)	P(1)-C(1)	1.786(2)
P(1)-C(2)	1.819(2)	P(1)-C(8)	1.826(2)
P(1)-B(1)	1.917(3)	P(2)-C(1)	1.796(2)
P(2)-C(14)	1.824(2)	P(2)-C(20)	1.825(2)
P(2)-B(2)	1.923(3)	C(1)-H(1)	1.07(3)
C(2)-C(7)	1.397(3)	C(2)-C(3)	1.402(3)
C(3)-C(4)	1.392(3)	C(3)-H(3)	0.9500
C(4)-C(5)	1.391(4)	C(4)-H(4)	0.9500
C(5)-C(6)	1.391(4)	C(5)-H(5)	0.9500
C(6)-C(7)	1.382(4)	C(6)-H(6)	0.9500
C(7)-H(7)	0.9500	C(8)-C(13)	1.385(3)
C(8)-C(9)	1.404(3)	C(9)-C(10)	1.387(3)
C(9)-H(9)	0.9500	C(10)-C(11)	1.381(4)
C(10)-H(10)	0.9500	C(11)-C(12)	1.377(4)
C(11)-H(11)	0.9500	C(12)-C(13)	1.394(3)
C(12)-H(12)	0.9500	C(13)-H(13)	0.9500
C(14)-C(15)	1.397(3)	C(14)-C(19)	1.400(3)

C(15)-C(16)	1.389(3)	C(15)-H(15)	0.9500
C(16)-C(17)	1.386(4)	C(16)-H(16)	0.9500
C(17)-C(18)	1.391(4)	C(17)-H(17)	0.9500
C(18)-C(19)	1.400(3)	C(18)-H(18)	0.9500
C(19)-H(19)	0.9500	C(20)-C(21)	1.390(3)
C(20)-C(25)	1.396(3)	C(21)-C(22)	1.393(3)
C(21)-H(21)	0.9500	C(22)-C(23)	1.389(4)
C(22)-H(22)	0.9500	C(23)-C(24)	1.372(4)
C(23)-H(23)	0.9500	C(24)-C(25)	1.406(4)
C(24)-H(24)	0.9500	C(25)-H(25)	0.9500
C(26)-C(33)	1.374(4)	C(26)-C(27)	1.507(4)
C(26)-H(26)	0.9500	C(27)-C(28)	1.513(4)
C(27)-H(27A)	0.9900	C(27)-H(27B)	0.9900
C(28)-C(29)	1.508(4)	C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900	C(29)-C(30)	1.411(4)
C(29)-H(29)	0.9500	C(30)-C(31)	1.526(4)
C(30)-H(30)	0.9500	C(31)-C(32)	1.506(4)
C(31)-H(31A)	0.9900	C(31)-H(31B)	0.9900
C(32)-C(33)	1.517(4)	C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900	C(33)-H(33)	0.9500
B(1)-H(1BA)	1.12(3)	B(1)-H(1BB)	1.17(3)
B(1)-H(1BC)	1.32(3)	B(2)-H(2BA)	1.23(3)
B(2)-H(2BB)	1.22(3)	B(2)-H(2BC)	1.13(3)

C(29)-Rh(1)-C(30)	39.3(1)	C(29)-Rh(1)-C(1)	90.2(1)
C(30)-Rh(1)-C(1)	94.7(1)	C(29)-Rh(1)-C(33)	96.8(1)
C(30)-Rh(1)-C(33)	82.4(1)	C(1)-Rh(1)-C(33)	164.8(1)
C(29)-Rh(1)-C(26)	79.9(1)	C(30)-Rh(1)-C(26)	89.4(1)
C(1)-Rh(1)-C(26)	158.9(1)	C(33)-Rh(1)-C(26)	36.3(1)
C(29)-Rh(1)-P(1)	99.64(7)	C(30)-Rh(1)-P(1)	124.74(7)
C(1)-Rh(1)-P(1)	38.57(6)	C(33)-Rh(1)-P(1)	150.98(8)
C(26)-Rh(1)-P(1)	124.55(8)	C(29)-Rh(1)-H(1BC)	129(1)
C(30)-Rh(1)-H(1BC)	163(1)	C(1)-Rh(1)-H(1BC)	98(1)
C(33)-Rh(1)-H(1BC)	89(1)	C(26)-Rh(1)-H(1BC)	75(1)
P(1)-Rh(1)-H(1BC)	62(1)	C(1)-P(1)-C(2)	104.1(1)
C(1)-P(1)-C(8)	115.1(1)	C(2)-P(1)-C(8)	105.6(1)
C(1)-P(1)-B(1)	106.1(1)	C(2)-P(1)-B(1)	113.4(1)
C(8)-P(1)-B(1)	112.4(1)	C(1)-P(1)-Rh(1)	48.83(6)
C(2)-P(1)-Rh(1)	93.87(7)	C(8)-P(1)-Rh(1)	158.22(7)
B(1)-P(1)-Rh(1)	66.82(8)	C(1)-P(2)-C(14)	112.7(1)
C(1)-P(2)-C(20)	101.7(1)	C(14)-P(2)-C(20)	104.1(1)
C(1)-P(2)-B(2)	112.4(1)	C(14)-P(2)-B(2)	112.9(1)
C(20)-P(2)-B(2)	112.2(1)	P(1)-C(1)-P(2)	123.7(1)
P(1)-C(1)-Rh(1)	92.6(1)	P(2)-C(1)-Rh(1)	98.8(1)
P(1)-C(1)-H(1)	111(2)	P(2)-C(1)-H(1)	108(2)
Rh(1)-C(1)-H(1)	122(1)	C(7)-C(2)-C(3)	118.8(2)
C(7)-C(2)-P(1)	118.8(2)	C(3)-C(2)-P(1)	122.4(2)
C(4)-C(3)-C(2)	120.1(2)	C(4)-C(3)-H(3)	120.0
C(2)-C(3)-H(3)	120.0	C(5)-C(4)-C(3)	120.6(2)
C(5)-C(4)-H(4)	119.7	C(3)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	119.3(2)	C(4)-C(5)-H(5)	120.3
C(6)-C(5)-H(5)	120.3	C(7)-C(6)-C(5)	120.4(3)
C(7)-C(6)-H(6)	119.8	C(5)-C(6)-H(6)	119.8
C(6)-C(7)-C(2)	120.8(2)	C(6)-C(7)-H(7)	119.6
C(2)-C(7)-H(7)	119.6	C(13)-C(8)-C(9)	118.9(2)
C(13)-C(8)-P(1)	118.7(2)	C(9)-C(8)-P(1)	122.4(2)
C(10)-C(9)-C(8)	120.3(2)	C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9	C(11)-C(10)-C(9)	120.1(2)
C(11)-C(10)-H(10)	120.0	C(9)-C(10)-H(10)	120.0
C(12)-C(11)-C(10)	120.1(2)	C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9	C(11)-C(12)-C(13)	120.2(2)
C(11)-C(12)-H(12)	119.9	C(13)-C(12)-H(12)	119.9

C(8)-C(13)-C(12)	120.4(2)	C(8)-C(13)-H(13)	119.8
C(12)-C(13)-H(13)	119.8	C(15)-C(14)-C(19)	119.2(2)
C(15)-C(14)-P(2)	122.3(2)	C(19)-C(14)-P(2)	118.4(2)
C(16)-C(15)-C(14)	120.7(2)	C(16)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6	C(17)-C(16)-C(15)	120.0(2)
C(17)-C(16)-H(16)	120.0	C(15)-C(16)-H(16)	120.0
C(16)-C(17)-C(18)	120.0(2)	C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0	C(17)-C(18)-C(19)	120.4(2)
C(17)-C(18)-H(18)	119.8	C(19)-C(18)-H(18)	119.8
C(14)-C(19)-C(18)	119.6(2)	C(14)-C(19)-H(19)	120.2
C(18)-C(19)-H(19)	120.2	C(21)-C(20)-C(25)	119.5(2)
C(21)-C(20)-P(2)	120.2(2)	C(25)-C(20)-P(2)	120.2(2)
C(20)-C(21)-C(22)	120.6(2)	C(20)-C(21)-H(21)	119.7
C(22)-C(21)-H(21)	119.7	C(23)-C(22)-C(21)	119.5(2)
C(23)-C(22)-H(22)	120.2	C(21)-C(22)-H(22)	120.2
C(24)-C(23)-C(22)	120.6(2)	C(24)-C(23)-H(23)	119.7
C(22)-C(23)-H(23)	119.7	C(23)-C(24)-C(25)	120.2(2)
C(23)-C(24)-H(24)	119.9	C(25)-C(24)-H(24)	119.9
C(20)-C(25)-C(24)	119.5(2)	C(20)-C(25)-H(25)	120.3
C(24)-C(25)-H(25)	120.3	C(33)-C(26)-C(27)	123.7(3)
C(33)-C(26)-Rh(1)	70.2(1)	C(27)-C(26)-Rh(1)	112.1(2)
C(33)-C(26)-H(26)	118.1	C(27)-C(26)-H(26)	118.1
Rh(1)-C(26)-H(26)	87.8	C(26)-C(27)-C(28)	112.3(2)
C(26)-C(27)-H(27A)	109.2	C(28)-C(27)-H(27A)	109.2
C(26)-C(27)-H(27B)	109.2	C(28)-C(27)-H(27B)	109.2
H(27A)-C(27)-H(27B)	107.9	C(29)-C(28)-C(27)	113.0(2)
C(29)-C(28)-H(28A)	109.0	C(27)-C(28)-H(28A)	109.0
C(29)-C(28)-H(28B)	109.0	C(27)-C(28)-H(28B)	109.0
H(28A)-C(28)-H(28B)	107.8	C(30)-C(29)-C(28)	126.0(2)
C(30)-C(29)-Rh(1)	70.4(1)	C(28)-C(29)-Rh(1)	112.8(2)
C(30)-C(29)-H(29)	117.0	C(28)-C(29)-H(29)	117.0
Rh(1)-C(29)-H(29)	86.8	C(29)-C(30)-C(31)	123.9(2)
C(29)-C(30)-Rh(1)	70.4(1)	C(31)-C(30)-Rh(1)	112.8(2)
C(29)-C(30)-H(30)	118.1	C(31)-C(30)-H(30)	118.1
Rh(1)-C(30)-H(30)	86.8	C(32)-C(31)-C(30)	113.7(2)
C(32)-C(31)-H(31A)	108.8	C(30)-C(31)-H(31A)	108.8
C(32)-C(31)-H(31B)	108.8	C(30)-C(31)-H(31B)	108.8
H(31A)-C(31)-H(31B)	107.7	C(31)-C(32)-C(33)	113.9(2)
C(31)-C(32)-H(32A)	108.8	C(33)-C(32)-H(32A)	108.8
C(31)-C(32)-H(32B)	108.8	C(33)-C(32)-H(32B)	108.8
H(32A)-C(32)-H(32B)	107.7	C(26)-C(33)-C(32)	125.2(3)
C(26)-C(33)-Rh(1)	73.5(1)	C(32)-C(33)-Rh(1)	107.4(2)
C(26)-C(33)-H(33)	117.4	C(32)-C(33)-H(33)	117.4
Rh(1)-C(33)-H(33)	89.1	P(1)-B(1)-H(1BA)	106(2)
P(1)-B(1)-H(1BB)	111(1)	H(1BA)-B(1)-H(1BB)	120(2)
P(1)-B(1)-H(1BC)	104(1)	H(1BA)-B(1)-H(1BC)	115(2)
H(1BB)-B(1)-H(1BC)	100(2)	P(2)-B(2)-H(2BA)	103(1)
P(2)-B(2)-H(2BB)	101(1)	H(2BA)-B(2)-H(2BB)	125(2)
P(2)-B(2)-H(2BC)	112(2)	H(2BA)-B(2)-H(2BC)	107(2)
H(2BB)-B(2)-H(2BC)	108(2)		

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for xj297

atom	U11	U22	U33	U23	U13	U12
Rh(1)	16(1)	18(1)	28(1)	1(1)	7(1)	1(1)
P(1)	17(1)	17(1)	21(1)	0(1)	6(1)	-1(1)
P(2)	19(1)	18(1)	21(1)	0(1)	8(1)	1(1)
C(1)	16(1)	18(1)	22(1)	0(1)	5(1)	-1(1)
C(2)	21(1)	19(1)	23(1)	1(1)	6(1)	1(1)
C(3)	25(1)	25(1)	25(1)	2(1)	9(1)	-2(1)
C(4)	35(1)	26(1)	36(1)	7(1)	18(1)	2(1)

C(5)	36(1)	41(2)	30(1)	14(1)	13(1)	10(1)
C(6)	35(1)	47(2)	24(1)	3(1)	3(1)	4(1)
C(7)	29(1)	30(1)	25(1)	1(1)	5(1)	-2(1)
C(8)	20(1)	22(1)	19(1)	-2(1)	6(1)	1(1)
C(9)	21(1)	24(1)	30(1)	-1(1)	9(1)	-3(1)
C(10)	23(1)	30(1)	34(1)	-1(1)	12(1)	3(1)
C(11)	30(1)	33(1)	37(1)	5(1)	14(1)	12(1)
C(12)	36(1)	23(1)	53(2)	12(1)	21(1)	7(1)
C(13)	26(1)	24(1)	39(1)	4(1)	16(1)	0(1)
C(14)	21(1)	20(1)	22(1)	0(1)	4(1)	2(1)
C(15)	26(1)	22(1)	25(1)	-2(1)	9(1)	2(1)
C(16)	24(1)	31(1)	30(1)	-5(1)	7(1)	4(1)
C(17)	34(1)	26(1)	33(1)	-1(1)	4(1)	9(1)
C(18)	42(1)	25(1)	34(1)	8(1)	8(1)	6(1)
C(19)	31(1)	25(1)	29(1)	4(1)	11(1)	2(1)
C(20)	25(1)	21(1)	18(1)	0(1)	5(1)	3(1)
C(21)	27(1)	22(1)	24(1)	-1(1)	7(1)	2(1)
C(22)	31(1)	26(1)	26(1)	-2(1)	3(1)	0(1)
C(23)	44(2)	23(1)	26(1)	-5(1)	2(1)	3(1)
C(24)	45(2)	32(1)	35(1)	-9(1)	14(1)	8(1)
C(25)	32(1)	30(1)	32(1)	-5(1)	15(1)	1(1)
C(26)	18(1)	37(1)	43(2)	0(1)	0(1)	4(1)
C(27)	34(1)	41(2)	41(2)	7(1)	2(1)	9(1)
C(28)	43(2)	32(1)	37(2)	13(1)	9(1)	5(1)
C(29)	29(1)	19(1)	39(1)	8(1)	12(1)	3(1)
C(30)	26(1)	14(1)	41(1)	0(1)	6(1)	1(1)
C(31)	40(2)	29(1)	52(2)	-5(1)	15(1)	10(1)
C(32)	36(1)	44(2)	53(2)	0(1)	19(1)	13(1)
C(33)	18(1)	33(1)	49(2)	7(1)	12(1)	5(1)
B(1)	19(1)	21(1)	36(1)	1(1)	7(1)	-2(1)
B(2)	23(1)	27(1)	38(2)	4(1)	15(1)	0(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for xj297

atom	x	y	z	U(eq)
H(1)	2360(30)	5920(20)	1400(10)	22
H(3)	1652	5745	2019	30
H(4)	1794	4844	2634	37
H(5)	3702	5158	3267	42
H(6)	5475	6382	3279	43
H(7)	5392	7253	2663	34
H(9)	383	7311	1913	29
H(10)	-1597.0001	8434	1775	34
H(11)	-1151	9920	1527	39
H(12)	1302	10316	1450	43
H(13)	3287	9192	1573	34
H(15)	-17	7048	992	29
H(16)	-2092	8049	699	34
H(17)	-1936	9087	149	38
H(18)	293	9114	-112.0000	41
H(19)	2405	8123	186	33
H(21)	443	5432	791	29
H(22)	-311	3951	494	34
H(23)	1204	3186	100	39
H(24)	3388	3911	-22	44
H(25)	4144	5411	267	36
H(26)	8042	6206	2076	41

H(27A)	8610	4848	2500	48
H(27B)	8430	4211	2081	48
H(28A)	6280	3802	2268	45
H(28B)	6085	4812	2467	45
H(29)	4223	5062	1850	34
H(30)	4391	4772	1163	33
H(31A)	7013	3594	1506	47
H(31B)	6204	3726	1005	47
H(32A)	7711	4904	935	51
H(32B)	8880	4368	1321	51
H(33)	8119	6177	1380	39
H(1BA)	5360(30)	8310(20)	1540(10)	30
H(1BB)	6130(30)	8080(20)	2170(10)	30
H(1BC)	6470(30)	7090(20)	1800(10)	30
H(2BA)	5050(30)	7920(20)	840(10)	34
H(2BB)	4720(30)	6890(20)	330(10)	34
H(2BC)	5980(30)	6710(20)	900(10)	34

II. X-RAY CRYSTAL STRUCTURES OF PART IV

II.1. Crystallographic data for IV-9

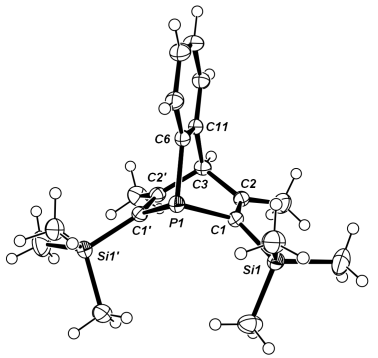


Table 1. Crystal data for mb428

Compound	mb428
Molecular formula	$C_{19}H_{29}PSi_2$
Molecular weight	344.57
Crystal habit	colorless block
Crystal dimensions(mm)	0.40x0.20x0.08
Crystal system	orthorhombic
Space group	P n m a
a(Å)	15.043(1)
b(Å)	16.246(1)

c(Å)	8.401(1)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
V(Å^3)	2053.1(3)
Z	4
d(g-cm^{-3})	1.115
F(000)	744
μ(cm^{-1})	0.247
Absorption corrections	multi-scan ; 0.9077 min, 0.9805 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.00
HKL ranges	-13 21 ; -21 22 ; -11 7
Reflections measured	12956
Unique data	3085
Rint	0.0412
Reflections used	2154
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	116
Reflections / parameter	18
wR2	0.1174
R1	0.0415
Weights a, b	0.0548 ; 0.5825
GoF	1.019
difference peak / hole (e Å^{-3})	0.429(0.059) / -0.303(0.059)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb428

atom	x	y	z	U(eq)
P(1)	3215(1)	2500	8269(1)	21(1)
Si(1)	3399(1)	808(1)	10008(1)	26(1)
C(1)	2632(1)	1638(1)	9292(2)	21(1)
C(2)	1747(1)	1726(1)	9365(2)	22(1)
C(3)	1334(1)	2500	8609(3)	22(1)
C(6)	2487(1)	2500	6516(3)	21(1)
C(7)	2775(2)	2500	4951(3)	26(1)
C(8)	2164(2)	2500	3714(3)	33(1)
C(9)	1257(2)	2500	4053(3)	31(1)
C(10)	957(2)	2500	5628(3)	26(1)
C(11)	1575(1)	2500	6852(3)	21(1)
C(12)	1089(1)	1139(1)	10099(2)	34(1)
C(14)	4250(1)	640(1)	8422(2)	37(1)
C(15)	2860(2)	-200(1)	10456(3)	47(1)
C(16)	3962(1)	1192(1)	11839(2)	40(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb428

P(1)-C(6)	1.835(2)	P(1)-C(1)#8	1.863(2)
P(1)-C(1)	1.863(2)	Si(1)-C(16)	1.864(2)
Si(1)-C(15)	1.866(2)	Si(1)-C(14)	1.868(2)
Si(1)-C(1)	1.874(2)	C(1)-C(2)	1.342(2)
C(2)-C(12)	1.506(2)	C(2)-C(3)	1.540(2)
C(3)-C(11)	1.520(3)	C(3)-C(2)#8	1.540(2)
C(3)-H(3)	1.0000	C(6)-C(7)	1.384(3)
C(6)-C(11)	1.400(3)	C(7)-C(8)	1.388(3)
C(7)-H(7)	0.9500	C(8)-C(9)	1.394(4)
C(8)-H(8)	0.9500	C(9)-C(10)	1.398(3)
C(9)-H(9)	0.9500	C(10)-C(11)	1.386(3)
C(10)-H(10)	0.9500	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800		

C(6)-P(1)-C(1)#8	95.12(7)	C(6)-P(1)-C(1)	95.12(7)
C(1)#8-P(1)-C(1)	97.5(1)	C(16)-Si(1)-C(15)	109.0(1)
C(16)-Si(1)-C(14)	109.0(1)	C(15)-Si(1)-C(14)	108.3(1)
C(16)-Si(1)-C(1)	107.65(8)	C(15)-Si(1)-C(1)	115.4(1)
C(14)-Si(1)-C(1)	107.33(8)	C(2)-C(1)-P(1)	114.1(1)
C(2)-C(1)-Si(1)	132.3(1)	P(1)-C(1)-Si(1)	113.56(8)
C(1)-C(2)-C(12)	127.1(2)	C(1)-C(2)-C(3)	118.0(1)
C(12)-C(2)-C(3)	114.9(2)	C(11)-C(3)-C(2)#8	107.7(1)
C(11)-C(3)-C(2)	107.7(1)	C(2)#8-C(3)-C(2)	109.5(2)
C(11)-C(3)-H(3)	110.6	C(2)#8-C(3)-H(3)	110.6
C(2)-C(3)-H(3)	110.6	C(7)-C(6)-C(11)	119.9(2)
C(7)-C(6)-P(1)	125.1(2)	C(11)-C(6)-P(1)	115.0(2)
C(6)-C(7)-C(8)	120.3(2)	C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9	C(7)-C(8)-C(9)	119.7(2)
C(7)-C(8)-H(8)	120.1	C(9)-C(8)-H(8)	120.1
C(8)-C(9)-C(10)	120.6(2)	C(8)-C(9)-H(9)	119.7
C(10)-C(9)-H(9)	119.7	C(11)-C(10)-C(9)	119.1(2)
C(11)-C(10)-H(10)	120.5	C(9)-C(10)-H(10)	120.5
C(10)-C(11)-C(6)	120.5(2)	C(10)-C(11)-C(3)	124.1(2)
C(6)-C(11)-C(3)	115.4(2)	C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5		

Estimated standard deviations are given in the parenthesis.
Symmetry operators ::
1: x, y, z 2: -x+1/2, -y, z+1/2 3: x+1/2, -y+1/2, -z+1/
4: -x, y+1/2, -z 5: -x, -y, -z 6: x-1/2, y, -z-1/2

7: -x-1/2, y-1/2, z-1/2 8: x, -y-1/2, z

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb428

atom	U11	U22	U33	U23	U13	U12
P(1)	20(1)	20(1)	23(1)	0	1(1)	0
Si(1)	31(1)	21(1)	26(1)	0(1)	-3(1)	4(1)
C(1)	25(1)	20(1)	19(1)	1(1)	-1(1)	-1(1)
C(2)	26(1)	23(1)	18(1)	1(1)	0(1)	-3(1)
C(3)	17(1)	26(1)	22(1)	0	0(1)	0
C(6)	23(1)	19(1)	21(1)	0	0(1)	0
C(7)	28(1)	26(1)	24(1)	0	2(1)	0
C(8)	44(2)	34(1)	21(1)	0	0(1)	0
C(9)	37(1)	35(1)	23(1)	0	-7(1)	0
C(10)	26(1)	27(1)	26(1)	0	-3(1)	0
C(11)	25(1)	17(1)	21(1)	0	-2(1)	0
C(12)	30(1)	35(1)	37(1)	9(1)	2(1)	-7(1)
C(14)	38(1)	34(1)	37(1)	-5(1)	-1(1)	10(1)
C(15)	60(1)	25(1)	57(1)	9(1)	0(1)	2(1)
C(16)	41(1)	42(1)	36(1)	-8(1)	-11(1)	15(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb428

atom	x	y	z	U(eq)
H(3)	674	2500	8749	26
H(7)	3394	2500	4723	31
H(8)	2362	2500	2640	40
H(9)	838	2500	3206	38
H(10)	339	2500	5856	31
H(12A)	1408	680	10595	51
H(12B)	691	927	9271	51
H(12C)	739	1428	10908	51
H(14A)	3959	628	7379	55
H(14B)	4554	115	8607	55
H(14C)	4685	1089	8448	55
H(15A)	2493	-147	11415	71
H(15B)	3318	-619	10631	71
H(15C)	2484	-364	9557	71
H(16A)	4243	1724	11615	59
H(16B)	4416	796	12174	59
H(16C)	3523	1260	12690	59

II.2. Crystallographic data for IV-12

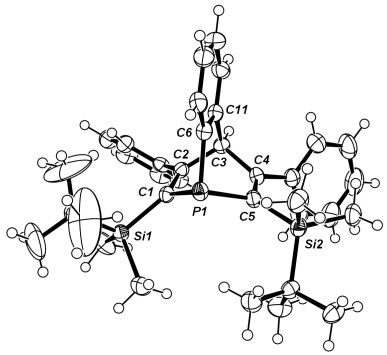


Table 1. Crystal data for mbcg4

Compound	mbcg4
Molecular formula	$C_{35}H_{45}PSi_2$
Molecular weight	552.86
Crystal habit	Colorless Plate
Crystal dimensions(mm)	0.24x0.18x0.04
Crystal system	triclinic
Space group	P-1
a(Å)	10.268(1)
b(Å)	12.077(1)
c(Å)	14.822(1)
α(°)	69.796(1)
β(°)	86.817(1)
γ(°)	72.065(1)
V(Å^3)	1638.4(2)
Z	2
d(g-cm^{-3})	1.121
F(000)	596
μ(cm^{-1})	0.178
Absorption corrections	multi-scan ; 0.9585 min, 0.9929 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	26.37
HKL ranges	-12 12 ; -15 15 ; -18 17
Reflections measured	18293

Unique data	6693
Rint	0.0576
Reflections used	4099
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	353
Reflections / parameter	11
wR2	0.1764
R1	0.0637
Weights a, b	0.0878 ; 0.1487
GoF	1.038
difference peak / hole (e Å^{-3})	0.783(0.062) / -0.626(0.062)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mbcg4

atom	x	y	z	U(eq)
P(1)	3307(1)	1898(1)	8387(1)	29(1)
Si(1)	3187(1)	1374(1)	6420(1)	28(1)
Si(2)	3887(1)	4189(1)	8686(1)	31(1)
C(1)	2263(3)	2012(3)	7355(2)	26(1)
C(2)	920(3)	2626(3)	7350(2)	27(1)
C(3)	448(3)	3187(3)	8143(2)	28(1)
C(4)	1284(3)	4049(3)	8127(2)	28(1)
C(5)	2649(3)	3560(3)	8281(2)	28(1)
C(6)	2143(3)	1415(3)	9315(2)	29(1)
C(7)	2540(3)	450(3)	10195(3)	36(1)
C(8)	1579(4)	195(3)	10854(3)	43(1)
C(9)	214(4)	904(3)	10643(3)	42(1)
C(10)	-195(3)	1877(3)	9772(3)	36(1)
C(11)	752(3)	2130(3)	9112(2)	30(1)
C(12)	-178(3)	2798(3)	6652(2)	28(1)
C(13)	-570(3)	1802(3)	6658(2)	33(1)
C(14)	-1602(3)	1955(3)	6022(3)	42(1)
C(15)	-2244(3)	3109(4)	5370(3)	45(1)
C(16)	-1869(3)	4114(4)	5358(3)	46(1)
C(17)	-847(3)	3971(3)	6003(2)	36(1)
C(18)	479(3)	5368(3)	7952(2)	32(1)
C(19)	-482(3)	5695(3)	8595(3)	46(1)
C(20)	-1188(4)	6935(4)	8428(4)	60(1)
C(21)	-988(4)	7842(4)	7619(4)	60(1)
C(22)	-80(4)	7533(3)	6961(3)	54(1)
C(23)	659(3)	6293(3)	7131(3)	40(1)
C(24)	2151(4)	1937(4)	5270(3)	54(1)
C(25)	4688(4)	1971(4)	6114(3)	52(1)
C(26)	3810(4)	-383(3)	6926(3)	47(1)
C(27)	2870(10)	-900(5)	7510(10)	273(8)
C(28)	4445(8)	-943(4)	6223(4)	119(3)
C(29)	5080(10)	-794(6)	7648(6)	204(5)
C(30)	2984(3)	5617(3)	8971(3)	43(1)
C(31)	4709(4)	2955(3)	9844(3)	45(1)
C(32)	5258(3)	4476(3)	7805(2)	31(1)
C(33)	4614(4)	5234(3)	6782(3)	46(1)
C(34)	6281(3)	3245(3)	7801(3)	42(1)
C(35)	6058(3)	5202(3)	8094(3)	43(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mbcg4

P(1)-C(6)	1.831(3)	P(1)-C(1)	1.858(3)
P(1)-C(5)	1.863(3)	Si(1)-C(24)	1.859(4)
Si(1)-C(25)	1.866(4)	Si(1)-C(1)	1.885(3)
Si(1)-C(26)	1.895(3)	Si(2)-C(30)	1.867(3)
Si(2)-C(31)	1.871(4)	Si(2)-C(5)	1.883(3)
Si(2)-C(32)	1.895(3)	C(1)-C(2)	1.349(4)
C(2)-C(12)	1.489(4)	C(2)-C(3)	1.537(4)
C(3)-C(11)	1.526(4)	C(3)-C(4)	1.533(4)
C(3)-H(3)	1.0000	C(4)-C(5)	1.341(4)
C(4)-C(18)	1.489(4)	C(6)-C(7)	1.393(4)
C(6)-C(11)	1.409(4)	C(7)-C(8)	1.377(5)
C(7)-H(7)	0.9500	C(8)-C(9)	1.386(5)
C(8)-H(8)	0.9500	C(9)-C(10)	1.391(5)
C(9)-H(9)	0.9500	C(10)-C(11)	1.366(5)
C(10)-H(10)	0.9500	C(12)-C(13)	1.379(4)
C(12)-C(17)	1.392(4)	C(13)-C(14)	1.384(4)
C(13)-H(13)	0.9500	C(14)-C(15)	1.373(5)
C(14)-H(14)	0.9500	C(15)-C(16)	1.376(5)
C(15)-H(15)	0.9500	C(16)-C(17)	1.389(5)
C(16)-H(16)	0.9500	C(17)-H(17)	0.9500
C(18)-C(23)	1.387(5)	C(18)-C(19)	1.397(5)
C(19)-C(20)	1.387(5)	C(19)-H(19)	0.9500
C(20)-C(21)	1.373(6)	C(20)-H(20)	0.9500
C(21)-C(22)	1.377(6)	C(21)-H(21)	0.9500
C(22)-C(23)	1.394(5)	C(22)-H(22)	0.9500
C(23)-H(23)	0.9500	C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800	C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800	C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800	C(26)-C(27)	1.403(7)
C(26)-C(28)	1.452(6)	C(26)-C(29)	1.576(8)
C(27)-H(27A)	0.9941	C(27)-H(27B)	0.9941
C(27)-H(27C)	0.9951	C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800	C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9801	C(29)-H(29B)	0.9801
C(29)-H(29C)	0.9801	C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800	C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800	C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800	C(32)-C(34)	1.534(4)
C(32)-C(33)	1.534(5)	C(32)-C(35)	1.539(4)
C(33)-H(33A)	0.9800	C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800	C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800	C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800	C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800		

C(6)-P(1)-C(1)	96.3(1)	C(6)-P(1)-C(5)	94.3(1)
C(1)-P(1)-C(5)	97.5(1)	C(24)-Si(1)-C(25)	105.7(2)
C(24)-Si(1)-C(1)	113.5(2)	C(25)-Si(1)-C(1)	106.7(2)
C(24)-Si(1)-C(26)	110.8(2)	C(25)-Si(1)-C(26)	109.5(2)
C(1)-Si(1)-C(26)	110.2(2)	C(30)-Si(2)-C(31)	106.9(2)
C(30)-Si(2)-C(5)	111.9(1)	C(31)-Si(2)-C(5)	104.4(2)
C(30)-Si(2)-C(32)	110.5(2)	C(31)-Si(2)-C(32)	109.3(2)
C(5)-Si(2)-C(32)	113.4(1)	C(2)-C(1)-P(1)	113.9(2)
C(2)-C(1)-Si(1)	128.2(2)	P(1)-C(1)-Si(1)	117.8(2)
C(1)-C(2)-C(12)	126.2(3)	C(1)-C(2)-C(3)	118.0(3)
C(12)-C(2)-C(3)	115.9(2)	C(11)-C(3)-C(4)	108.4(2)
C(11)-C(3)-C(2)	108.1(2)	C(4)-C(3)-C(2)	108.8(2)
C(11)-C(3)-H(3)	110.5	C(4)-C(3)-H(3)	110.5
C(2)-C(3)-H(3)	110.5	C(5)-C(4)-C(18)	126.0(3)

C(5)-C(4)-C(3)	118.2(2)	C(18)-C(4)-C(3)	115.8(2)
C(4)-C(5)-P(1)	113.8(2)	C(4)-C(5)-Si(2)	128.4(2)
P(1)-C(5)-Si(2)	116.1(2)	C(7)-C(6)-C(11)	119.3(3)
C(7)-C(6)-P(1)	125.2(2)	C(11)-C(6)-P(1)	115.5(2)
C(8)-C(7)-C(6)	120.2(3)	C(8)-C(7)-H(7)	119.9
C(6)-C(7)-H(7)	119.9	C(7)-C(8)-C(9)	119.8(3)
C(7)-C(8)-H(8)	120.1	C(9)-C(8)-H(8)	120.1
C(8)-C(9)-C(10)	120.6(3)	C(8)-C(9)-H(9)	119.7
C(10)-C(9)-H(9)	119.7	C(11)-C(10)-C(9)	119.9(3)
C(11)-C(10)-H(10)	120.1	C(9)-C(10)-H(10)	120.1
C(10)-C(11)-C(6)	120.2(3)	C(10)-C(11)-C(3)	125.2(3)
C(6)-C(11)-C(3)	114.6(3)	C(13)-C(12)-C(17)	119.0(3)
C(13)-C(12)-C(2)	120.4(3)	C(17)-C(12)-C(2)	120.5(3)
C(12)-C(13)-C(14)	120.9(3)	C(12)-C(13)-H(13)	119.6
C(14)-C(13)-H(13)	119.6	C(15)-C(14)-C(13)	120.0(3)
C(15)-C(14)-H(14)	120.0	C(13)-C(14)-H(14)	120.0
C(14)-C(15)-C(16)	119.9(3)	C(14)-C(15)-H(15)	120.1
C(16)-C(15)-H(15)	120.1	C(15)-C(16)-C(17)	120.5(3)
C(15)-C(16)-H(16)	119.8	C(17)-C(16)-H(16)	119.7
C(16)-C(17)-C(12)	119.7(3)	C(16)-C(17)-H(17)	120.1
C(12)-C(17)-H(17)	120.1	C(23)-C(18)-C(19)	119.0(3)
C(23)-C(18)-C(4)	120.0(3)	C(19)-C(18)-C(4)	121.1(3)
C(20)-C(19)-C(18)	119.8(4)	C(20)-C(19)-H(19)	120.1
C(18)-C(19)-H(19)	120.1	C(21)-C(20)-C(19)	120.6(4)
C(21)-C(20)-H(20)	119.7	C(19)-C(20)-H(20)	119.7
C(20)-C(21)-C(22)	120.4(4)	C(20)-C(21)-H(21)	119.8
C(22)-C(21)-H(21)	119.8	C(21)-C(22)-C(23)	119.5(4)
C(21)-C(22)-H(22)	120.3	C(23)-C(22)-H(22)	120.2
C(18)-C(23)-C(22)	120.7(4)	C(18)-C(23)-H(23)	119.7
C(22)-C(23)-H(23)	119.7	Si(1)-C(24)-H(24A)	109.5
Si(1)-C(24)-H(24B)	109.5	H(24A)-C(24)-H(24B)	109.5
Si(1)-C(24)-H(24C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5	Si(1)-C(25)-H(25A)	109.5
Si(1)-C(25)-H(25B)	109.5	H(25A)-C(25)-H(25B)	109.5
Si(1)-C(25)-H(25C)	109.5	H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5	C(27)-C(26)-C(28)	116.9(6)
C(27)-C(26)-C(29)	103.0(8)	C(28)-C(26)-C(29)	100.3(5)
C(27)-C(26)-Si(1)	113.5(3)	C(28)-C(26)-Si(1)	113.3(3)
C(29)-C(26)-Si(1)	107.9(3)	C(26)-C(27)-H(27A)	110.8
C(26)-C(27)-H(27B)	110.8	H(27A)-C(27)-H(27B)	107.9
C(26)-C(27)-H(27C)	111.5	H(27A)-C(27)-H(27C)	108.0
H(27B)-C(27)-H(27C)	107.7	C(26)-C(28)-H(28A)	109.4
C(26)-C(28)-H(28B)	109.5	H(28A)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5	H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5	C(26)-C(29)-H(29A)	109.6
C(26)-C(29)-H(29B)	109.3	H(29A)-C(29)-H(29B)	109.5
C(26)-C(29)-H(29C)	109.5	H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5	Si(2)-C(30)-H(30A)	109.5
Si(2)-C(30)-H(30B)	109.5	H(30A)-C(30)-H(30B)	109.5
Si(2)-C(30)-H(30C)	109.5	H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5	Si(2)-C(31)-H(31A)	109.5
Si(2)-C(31)-H(31B)	109.5	H(31A)-C(31)-H(31B)	109.5
Si(2)-C(31)-H(31C)	109.5	H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5	C(34)-C(32)-C(33)	108.8(3)
C(34)-C(32)-C(35)	108.1(3)	C(33)-C(32)-C(35)	108.4(3)
C(34)-C(32)-Si(2)	110.8(2)	C(33)-C(32)-Si(2)	110.7(2)
C(35)-C(32)-Si(2)	110.0(2)	C(32)-C(33)-H(33A)	109.5
C(32)-C(33)-H(33B)	109.5	H(33A)-C(33)-H(33B)	109.5
C(32)-C(33)-H(33C)	109.5	H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5	C(32)-C(34)-H(34A)	109.5
C(32)-C(34)-H(34B)	109.5	H(34A)-C(34)-H(34B)	109.5
C(32)-C(34)-H(34C)	109.5	H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5	C(32)-C(35)-H(35A)	109.5

C(32)-C(35)-H(35B)	109.5	H(35A)-C(35)-H(35B)	109.5
C(32)-C(35)-H(35C)	109.5	H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5		

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mbcg4

atom	U11	U22	U33	U23	U13	U12
P(1)	26(1)	30(1)	33(1)	-14(1)	-2(1)	-7(1)
Si(1)	27(1)	29(1)	30(1)	-13(1)	2(1)	-8(1)
Si(2)	31(1)	33(1)	33(1)	-15(1)	-2(1)	-13(1)
C(1)	27(2)	26(2)	26(2)	-10(1)	0(1)	-9(1)
C(2)	25(2)	26(2)	31(2)	-10(1)	2(1)	-10(1)
C(3)	22(1)	32(2)	33(2)	-14(2)	1(1)	-9(1)
C(4)	31(2)	30(2)	26(2)	-14(1)	1(1)	-8(1)
C(5)	29(2)	30(2)	30(2)	-15(1)	2(1)	-9(1)
C(6)	30(2)	28(2)	31(2)	-12(1)	-1(1)	-9(1)
C(7)	41(2)	34(2)	33(2)	-14(2)	-1(2)	-9(2)
C(8)	60(2)	38(2)	31(2)	-8(2)	0(2)	-18(2)
C(9)	50(2)	44(2)	36(2)	-13(2)	11(2)	-23(2)
C(10)	33(2)	45(2)	38(2)	-20(2)	7(2)	-15(2)
C(11)	33(2)	32(2)	32(2)	-16(2)	4(2)	-14(1)
C(12)	22(2)	34(2)	28(2)	-13(1)	4(1)	-7(1)
C(13)	28(2)	38(2)	35(2)	-14(2)	0(1)	-11(1)
C(14)	37(2)	54(2)	44(2)	-22(2)	2(2)	-21(2)
C(15)	33(2)	69(3)	36(2)	-18(2)	-5(2)	-20(2)
C(16)	36(2)	54(2)	36(2)	-7(2)	-3(2)	-8(2)
C(17)	34(2)	39(2)	34(2)	-11(2)	1(2)	-11(2)
C(18)	29(2)	34(2)	35(2)	-15(2)	-1(2)	-8(1)
C(19)	44(2)	46(2)	53(3)	-25(2)	12(2)	-13(2)
C(20)	46(2)	61(3)	87(4)	-51(3)	13(2)	-7(2)
C(21)	57(2)	35(2)	84(4)	-26(2)	-13(2)	1(2)
C(22)	63(2)	36(2)	58(3)	-13(2)	-13(2)	-9(2)
C(23)	45(2)	35(2)	38(2)	-12(2)	-2(2)	-10(2)
C(24)	41(2)	76(3)	39(3)	-29(2)	-2(2)	-1(2)
C(25)	46(2)	70(3)	64(3)	-43(2)	25(2)	-31(2)
C(26)	58(2)	27(2)	48(3)	-13(2)	20(2)	-8(2)
C(27)	203(8)	26(3)	510(20)	-29(6)	240(10)	-35(4)
C(28)	220(7)	38(2)	78(4)	-28(3)	48(4)	-6(3)
C(29)	300(10)	66(4)	172(8)	-33(5)	-140(10)	66(6)
C(30)	45(2)	49(2)	49(3)	-30(2)	2(2)	-20(2)
C(31)	52(2)	49(2)	40(2)	-15(2)	-6(2)	-22(2)
C(32)	29(2)	35(2)	31(2)	-10(2)	-2(1)	-12(1)
C(33)	41(2)	59(2)	36(2)	-11(2)	0(2)	-17(2)
C(34)	32(2)	48(2)	51(3)	-24(2)	5(2)	-11(2)
C(35)	40(2)	47(2)	48(3)	-15(2)	0(2)	-23(2)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mbcg4

atom	x	y	z	U(eq)
H(3)	-554	3653	8043	34
H(7)	3476	-33	10340	43
H(8)	1851	-466	11452	52
H(9)	-448.0000	724	11098	51
H(10)	-1131	2365	9635	44
H(13)	-126	1000	7105	39

H(14)	-1866	1261	6036	50
H(15)	-2945	3213	4929	54
H(16)	-2313	4911	4906	55
H(17)	-606	4671	6000	43
H(19)	-651	5071	9144	56
H(20)	-1815	7158	8878	73
H(21)	-1481	8687	7511	72
H(22)	43	8161	6395	65
H(23)	1292	6078	6681	48
H(24A)	2746	1741	4770	80
H(24B)	1722	2837	5073	80
H(24C)	1437	1531	5360	80
H(25A)	5150	1725	5585	79
H(25B)	5330	1623	6680	79
H(25C)	4373	2877	5917	79
H(27A)	3357	-1558	8095	409
H(27B)	2426	-1250	7156	409
H(27C)	2177	-255	7684	409
H(28A)	3743	-820	5745	179
H(28B)	4888	-1833	6549	179
H(28C)	5133	-554	5899	179
H(29A)	5914	-816	7291	306
H(29B)	5171	-1621	8118	306
H(29C)	4945	-201	7986	306
H(30A)	2235	5473	9389	64
H(30B)	2610	6309	8372	64
H(30C)	3633	5819	9301	64
H(31A)	5073	2157	9746	67
H(31B)	4026	2900	10333	67
H(31C)	5459	3163	10061	67
H(33A)	4162	4756	6567	70
H(33B)	5332	5420	6346	70
H(33C)	3938	6011	6781	70
H(34A)	6976	3414	7338	63
H(34B)	5793	2767	7618	63
H(34C)	6727	2769	8446	63
H(35A)	6786	5320	7649	65
H(35B)	6463	4736	8751	65
H(35C)	5432	6012	8067	65

II.3. Crystallographic data for IV-21

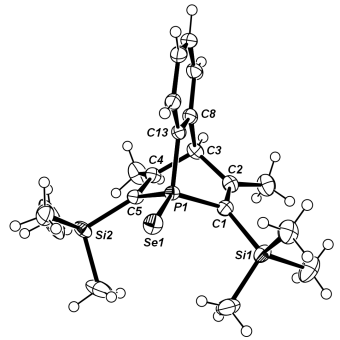


Table 1. Crystal data for mb628

Compound	mb628
Molecular formula	$C_{19}H_{29}PSeSi_2$
Molecular weight	423.53
Crystal habit	Colorless Block
Crystal dimensions(mm)	0.80x0.40x0.40
Crystal system	orthorhombic
Space group	$Pna2_1$
a(Å)	12.480(1)
b(Å)	11.431(1)
c(Å)	15.153(1)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
V(Å^3)	2161.7(3)
Z	4
d(g-cm^{-3})	1.301
F(000)	880
μ(cm^{-1})	1.920
Absorption corrections	multi-scan ; 0.3088 min, 0.5139 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	293(2)
Scan mode	phi and omega scans

Maximum θ	30.03
HKL ranges	-15 17 ; -15 16 ; -21 19
Reflections measured	18793
Unique data	6024
Rint	0.0480
Reflections used	5365
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	216
Reflections / parameter	24
wR2	0.0744
R1	0.0304
Flack's parameter	0.025(6)
Weights a, b	0.0437 ; 0.0000
GoF	0.998
difference peak / hole (e Å^{-3})	0.468(0.057) / -0.394(0.057)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb628

atom	x	y	z	U(eq)
Se(1)	18547(1)	15757(1)	7857(1)	29(1)
P(1)	17718(1)	14517(1)	7090(1)	18(1)
Si(1)	15585(1)	16155(1)	7108(1)	27(1)
Si(2)	18155(1)	12638(1)	8629(1)	27(1)
C(1)	17607(2)	13011(2)	7497(1)	22(1)
C(2)	17122(2)	12337(2)	6888(1)	25(1)
C(3)	16769(2)	12913(2)	6012(2)	25(1)
C(4)	15987(2)	13918(2)	6229(1)	24(1)
C(5)	16341(2)	14807(2)	6740(1)	21(1)
C(6)	16870(2)	11058(2)	6936(2)	39(1)
C(7)	14887(2)	13736(2)	5855(2)	39(1)
C(8)	17738(2)	13416(2)	5546(1)	24(1)
C(9)	18065(2)	13132(2)	4694(2)	30(1)
C(10)	18977(2)	13660(2)	4351(2)	35(1)
C(11)	19567(2)	14449(2)	4838(2)	33(1)
C(12)	19231(2)	14757(2)	5688(2)	26(1)
C(13)	18316(2)	14237(2)	6028(2)	22(1)
C(14)	14300(3)	16359(4)	6509(4)	97(2)
C(15)	16385(2)	17505(2)	6909(2)	45(1)
C(16)	15306(3)	15951(3)	8309(2)	58(1)
C(17)	17551(2)	13654(3)	9459(2)	43(1)
C(18)	19641(2)	12760(2)	8580(2)	37(1)
C(19)	17818(2)	11127(3)	9014(2)	49(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb628

Se(1)-P(1)	2.1041(5	P(1)-C(13)	1.804(2)
P(1)-C(5)	1.828(2)	P(1)-C(1)	1.834(2)
Si(1)-C(14)	1.858(3)	Si(1)-C(15)	1.862(3)
Si(1)-C(16)	1.867(3)	Si(1)-C(5)	1.890(2)
Si(2)-C(18)	1.861(2)	Si(2)-C(19)	1.871(3)
Si(2)-C(17)	1.871(3)	Si(2)-C(1)	1.895(2)

C(1)-C(2)	1.346(3)	C(2)-C(6)	1.498(3)
C(2)-C(3)	1.546(3)	C(3)-C(8)	1.514(3)
C(3)-C(4)	1.542(3)	C(3)-H(3)	0.9800
C(4)-C(5)	1.352(3)	C(4)-C(7)	1.499(3)
C(6)-H(6A)	0.9600	C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600	C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600	C(7)-H(7C)	0.9600
C(8)-C(13)	1.392(3)	C(8)-C(9)	1.393(3)
C(9)-C(10)	1.389(4)	C(9)-H(9)	0.9300
C(10)-C(11)	1.378(4)	C(10)-H(10)	0.9300
C(11)-C(12)	1.400(3)	C(11)-H(11)	0.9300
C(12)-C(13)	1.386(3)	C(12)-H(12)	0.9300
C(14)-H(14A)	0.9600	C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600	C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600	C(15)-H(15C)	0.9600
C(16)-H(16A)	0.9600	C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600	C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600	C(17)-H(17C)	0.9600
C(18)-H(18A)	0.9600	C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600	C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600	C(19)-H(19C)	0.9600

C(13)-P(1)-C(5)	99.3(1)	C(13)-P(1)-C(1)	99.4(1)
C(5)-P(1)-C(1)	101.3(1)	C(13)-P(1)-Se(1)	114.11(7)
C(5)-P(1)-Se(1)	120.06(7)	C(1)-P(1)-Se(1)	118.93(7)
C(14)-Si(1)-C(15)	106.3(2)	C(14)-Si(1)-C(16)	109.3(2)
C(15)-Si(1)-C(16)	111.2(2)	C(14)-Si(1)-C(5)	112.9(1)
C(15)-Si(1)-C(5)	111.1(1)	C(16)-Si(1)-C(5)	106.1(1)
C(18)-Si(2)-C(19)	107.8(1)	C(18)-Si(2)-C(17)	112.4(1)
C(19)-Si(2)-C(17)	105.8(1)	C(18)-Si(2)-C(1)	107.8(1)
C(19)-Si(2)-C(1)	114.2(1)	C(17)-Si(2)-C(1)	108.9(1)
C(2)-C(1)-P(1)	109.9(2)	C(2)-C(1)-Si(2)	130.9(2)
P(1)-C(1)-Si(2)	119.2(1)	C(1)-C(2)-C(6)	128.3(2)
C(1)-C(2)-C(3)	118.3(2)	C(6)-C(2)-C(3)	113.4(2)
C(8)-C(3)-C(4)	108.8(2)	C(8)-C(3)-C(2)	109.5(2)
C(4)-C(3)-C(2)	108.3(2)	C(8)-C(3)-H(3)	110.1
C(4)-C(3)-H(3)	110.1	C(2)-C(3)-H(3)	110.1
C(5)-C(4)-C(7)	128.3(2)	C(5)-C(4)-C(3)	118.4(2)
C(7)-C(4)-C(3)	113.3(2)	C(4)-C(5)-P(1)	109.7(2)
C(4)-C(5)-Si(1)	128.2(2)	P(1)-C(5)-Si(1)	122.1(1)
C(2)-C(6)-H(6A)	109.5	C(2)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5	C(2)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5	H(6B)-C(6)-H(6C)	109.5
C(4)-C(7)-H(7A)	109.5	C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5	C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5	H(7B)-C(7)-H(7C)	109.5
C(13)-C(8)-C(9)	119.5(2)	C(13)-C(8)-C(3)	115.2(2)
C(9)-C(8)-C(3)	125.3(2)	C(10)-C(9)-C(8)	119.1(2)
C(10)-C(9)-H(9)	120.5	C(8)-C(9)-H(9)	120.5
C(11)-C(10)-C(9)	121.4(2)	C(11)-C(10)-H(10)	119.3
C(9)-C(10)-H(10)	119.3	C(10)-C(11)-C(12)	119.9(2)
C(10)-C(11)-H(11)	120.1	C(12)-C(11)-H(11)	120.1
C(13)-C(12)-C(11)	118.7(2)	C(13)-C(12)-H(12)	120.7
C(11)-C(12)-H(12)	120.7	C(12)-C(13)-C(8)	121.5(2)
C(12)-C(13)-P(1)	126.6(2)	C(8)-C(13)-P(1)	111.9(2)
Si(1)-C(14)-H(14A)	109.5	Si(1)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	Si(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
Si(1)-C(15)-H(15A)	109.5	Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5	Si(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
Si(1)-C(16)-H(16A)	109.5	Si(1)-C(16)-H(16B)	109.5

H(16A)-C(16)-H(16B)	109.5	Si(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(16B)-C(16)-H(16C)	109.5
Si(2)-C(17)-H(17A)	109.5	Si(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5	Si(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(17B)-C(17)-H(17C)	109.5
Si(2)-C(18)-H(18A)	109.5	Si(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5	Si(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5	H(18B)-C(18)-H(18C)	109.5
Si(2)-C(19)-H(19A)	109.5	Si(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5	Si(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5	H(19B)-C(19)-H(19C)	109.5

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb628

atom	U11	U22	U33	U23	U13	U12
Se(1)	30(1)	30(1)	29(1)	-3(1)	-10(1)	-5(1)
P(1)	15(1)	23(1)	17(1)	-1(1)	-2(1)	-1(1)
Si(1)	19(1)	32(1)	29(1)	-10(1)	-1(1)	4(1)
Si(2)	20(1)	36(1)	26(1)	10(1)	0(1)	0(1)
C(1)	15(1)	27(1)	25(1)	3(1)	2(1)	-1(1)
C(2)	18(1)	25(1)	31(1)	-2(1)	2(1)	-1(1)
C(3)	22(1)	25(1)	27(1)	-9(1)	-3(1)	-1(1)
C(4)	19(1)	29(1)	24(1)	-2(1)	-1(1)	1(1)
C(5)	14(1)	30(1)	19(1)	-3(1)	-2(1)	1(1)
C(6)	37(1)	27(1)	52(2)	-1(1)	0(1)	-6(1)
C(7)	25(1)	40(1)	51(2)	-12(1)	-14(1)	1(1)
C(8)	23(1)	28(1)	22(1)	-1(1)	-3(1)	6(1)
C(9)	34(1)	33(1)	23(1)	-5(1)	-3(1)	9(1)
C(10)	43(1)	39(1)	23(1)	5(1)	9(1)	18(1)
C(11)	31(1)	35(1)	33(1)	11(1)	12(1)	9(1)
C(12)	21(1)	27(1)	29(1)	7(1)	4(1)	3(1)
C(13)	20(1)	25(1)	21(1)	2(1)	1(1)	6(1)
C(14)	62(2)	77(2)	153(4)	-70(3)	-69(3)	44(2)
C(15)	52(2)	34(1)	49(2)	12(1)	16(1)	7(1)
C(16)	81(2)	37(1)	54(2)	-17(1)	44(2)	-18(2)
C(17)	41(2)	64(2)	24(1)	5(1)	5(1)	4(1)
C(18)	21(1)	44(1)	46(1)	3(1)	-7(1)	1(1)
C(19)	44(2)	49(2)	54(2)	26(1)	-5(1)	-9(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb628

atom	x	y	z	U(eq)
H(3)	16415	12334	5633	30
H(6A)	17238	10717	7429	58
H(6B)	17098	10682	6402	58
H(6C)	16111	10954	7008	58
H(7A)	14400	14286	6117	58
H(7B)	14651	12954	5983	58
H(7C)	14905	13850	5228	58
H(9)	17679	12596	4359	36
H(10)	19195	13477	3781	42
H(11)	20186	14775	4603	39
H(12)	19614	15301	6019	31
H(14A)	13992	17099	6668	146
H(14B)	13814	15741	6664	146

H(14C)	14428	16341	5884	146
H(15A)	16696	17473	6330	67
H(15B)	16944	17560	7342	67
H(15C)	15927	18177	6951	67
H(16A)	14829	16554	8508	86
H(16B)	15966	15994	8633	86
H(16C)	14981	15200	8402	86
H(17A)	16792	13529	9486	64
H(17B)	17692	14448	9289	64
H(17C)	17861	13507	10028	64
H(18A)	19936	12618	9155	56
H(18B)	19835	13532	8387	56
H(18C)	19918	12194	8171	56
H(19A)	18089	11015	9601	74
H(19B)	18139	10563	8625	74
H(19C)	17055	11026	9013	74

II.4. Crystallographic data for IV-24

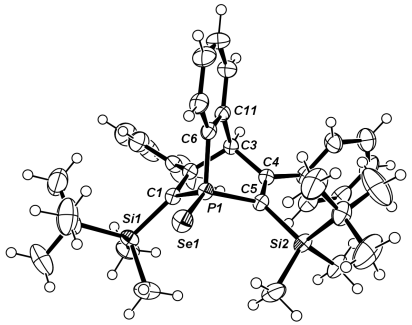


Table 1. Crystal data for mbcg4se

Compound	mbcg4se
Molecular formula	$C_{35}H_{45}PSeSi_2$
Molecular weight	631.82
Crystal habit	Colorless Block
Crystal dimensions(mm)	0.50x0.40x0.30
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	12.854(1)
b(Å)	12.098(1)
c(Å)	22.255(1)
α(°)	90.00
β(°)	93.548(1)
γ(°)	90.00

V(Å^3)	3454.2(4)
Z	4
d(g-cm^{-3})	1.215
F(000)	1328
μ(cm^{-1})	1.224
Absorption corrections	multi-scan ; 0.5797 min, 0.7103 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-17 18 ; -17 15 ; -31 21
Reflections measured	27004
Unique data	9999
Rint	0.0356
Reflections used	7193
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	362
Reflections / parameter	19
wR2	0.1113
R1	0.0385
Weights a, b	0.0542 ; 0.3814
GoF	1.063
difference peak / hole (e Å^{-3})	0.476(0.058) / -0.545(0.058)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mbcg4se

atom	x	y	z	U(eq)
Se(1)	3263(1)	-27(1)	8390(1)	36(1)
P(1)	2761(1)	1429(1)	8788(1)	23(1)
Si(1)	336(1)	1060(1)	8257(1)	31(1)
Si(2)	4237(1)	3005(1)	7974(1)	28(1)
C(1)	1360(1)	1747(1)	8788(1)	24(1)
C(2)	1219(1)	2634(1)	9144(1)	24(1)
C(3)	2178(1)	3227(1)	9439(1)	23(1)
C(4)	2907(1)	3570(1)	8949(1)	23(1)
C(5)	3277(1)	2794(1)	8583(1)	23(1)
C(6)	3092(1)	1463(1)	9593(1)	26(1)
C(7)	3643(2)	651(2)	9923(1)	34(1)
C(8)	3843(2)	827(2)	10536(1)	47(1)
C(9)	3507(2)	1767(2)	10807(1)	46(1)
C(10)	2959(2)	2582(2)	10479(1)	36(1)
C(11)	2757(1)	2422(1)	9863(1)	25(1)
C(12)	216(1)	3124(2)	9308(1)	29(1)
C(13)	-418(2)	2579(2)	9685(1)	44(1)
C(14)	-1337(2)	3058(2)	9860(1)	60(1)
C(15)	-1614(2)	4095(2)	9651(1)	61(1)
C(16)	-986(2)	4650(2)	9292(1)	63(1)

C(17)	-61(2)	4181(2)	9125(1)	52(1)
C(18)	3140(2)	4783(1)	8953(1)	27(1)
C(19)	2564(2)	5506(2)	8577(1)	37(1)
C(20)	2754(2)	6638(2)	8616(1)	46(1)
C(21)	3510(2)	7050(2)	9020(1)	50(1)
C(22)	4065(2)	6342(2)	9395(1)	53(1)
C(23)	3875(2)	5211(2)	9370(1)	40(1)
C(24)	906(2)	874(2)	7511(1)	48(1)
C(25)	-784(2)	2040(2)	8115(1)	46(1)
C(26)	-186(2)	-308(2)	8537(1)	44(1)
C(27)	637(2)	-1196(2)	8602(2)	76(1)
C(28)	-702(3)	-169(2)	9135(1)	68(1)
C(29)	-1036(2)	-712(3)	8063(2)	81(1)
C(30)	3987(2)	1990(2)	7352(1)	45(1)
C(31)	4075(2)	4391(2)	7612(1)	40(1)
C(32)	5621(2)	2864(2)	8313(1)	40(1)
C(33)	5968(2)	3906(3)	8632(2)	95(1)
C(34)	6328(2)	2707(3)	7786(1)	82(1)
C(35)	5745(2)	1857(3)	8713(1)	73(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mbcg4se

Se(1)-P(1)	2.0918(5	P(1)-C(6)	1.816(2)
P(1)-C(1)	1.841(2)	P(1)-C(5)	1.848(2)
Si(1)-C(24)	1.869(2)	Si(1)-C(25)	1.876(2)
Si(1)-C(1)	1.905(2)	Si(1)-C(26)	1.905(2)
Si(2)-C(30)	1.863(2)	Si(2)-C(31)	1.867(2)
Si(2)-C(32)	1.896(2)	Si(2)-C(5)	1.907(2)
C(1)-C(2)	1.352(2)	C(2)-C(12)	1.486(2)
C(2)-C(3)	1.538(2)	C(3)-C(11)	1.519(2)
C(3)-C(4)	1.538(2)	C(3)-H(3)	1.0000
C(4)-C(5)	1.348(2)	C(4)-C(18)	1.497(2)
C(6)-C(11)	1.387(3)	C(6)-C(7)	1.393(2)
C(7)-C(8)	1.389(3)	C(7)-H(7)	0.9500
C(8)-C(9)	1.370(3)	C(8)-H(8)	0.9500
C(9)-C(10)	1.392(3)	C(9)-H(9)	0.9500
C(10)-C(11)	1.392(2)	C(10)-H(10)	0.9500
C(12)-C(13)	1.375(3)	C(12)-C(17)	1.382(3)
C(13)-C(14)	1.393(3)	C(13)-H(13)	0.9500
C(14)-C(15)	1.377(4)	C(14)-H(14)	0.9500
C(15)-C(16)	1.349(4)	C(15)-H(15)	0.9500
C(16)-C(17)	1.389(3)	C(16)-H(16)	0.9500
C(17)-H(17)	0.9500	C(18)-C(23)	1.382(3)
C(18)-C(19)	1.392(3)	C(19)-C(20)	1.393(3)
C(19)-H(19)	0.9500	C(20)-C(21)	1.376(4)
C(20)-H(20)	0.9500	C(21)-C(22)	1.365(3)
C(21)-H(21)	0.9500	C(22)-C(23)	1.391(3)
C(22)-H(22)	0.9500	C(23)-H(23)	0.9500
C(24)-H(24A)	0.9800	C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800	C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800	C(25)-H(25C)	0.9800
C(26)-C(27)	1.508(3)	C(26)-C(28)	1.533(4)
C(26)-C(29)	1.551(3)	C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800	C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800	C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800	C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800	C(29)-H(29C)	0.9800
C(30)-H(30A)	0.9800	C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800	C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800	C(31)-H(31C)	0.9800
C(32)-C(33)	1.501(4)	C(32)-C(35)	1.511(3)

C(32)-C(34)	1.538(3)	C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800	C(33)-H(33C)	0.9800
C(34)-H(34A)	0.9800	C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800	C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800	C(35)-H(35C)	0.9800

C(6)-P(1)-C(1)	99.51(8)	C(6)-P(1)-C(5)	99.08(8)
C(1)-P(1)-C(5)	100.34(8)	C(6)-P(1)-Se(1)	112.18(6)
C(1)-P(1)-Se(1)	120.21(6)	C(5)-P(1)-Se(1)	121.53(6)
C(24)-Si(1)-C(25)	105.4(1)	C(24)-Si(1)-C(1)	108.1(1)
C(25)-Si(1)-C(1)	108.8(1)	C(24)-Si(1)-C(26)	110.6(1)
C(25)-Si(1)-C(26)	108.8(1)	C(1)-Si(1)-C(26)	114.8(1)
C(30)-Si(2)-C(31)	105.2(1)	C(30)-Si(2)-C(32)	110.5(1)
C(31)-Si(2)-C(32)	109.3(1)	C(30)-Si(2)-C(5)	110.5(1)
C(31)-Si(2)-C(5)	111.52(8)	C(32)-Si(2)-C(5)	109.74(8)
C(2)-C(1)-P(1)	109.4(1)	C(2)-C(1)-Si(1)	126.7(1)
P(1)-C(1)-Si(1)	123.2(1)	C(1)-C(2)-C(12)	127.6(2)
C(1)-C(2)-C(3)	119.2(2)	C(12)-C(2)-C(3)	113.2(1)
C(11)-C(3)-C(2)	108.3(1)	C(11)-C(3)-C(4)	108.5(1)
C(2)-C(3)-C(4)	109.3(1)	C(11)-C(3)-H(3)	110.2
C(2)-C(3)-H(3)	110.2	C(4)-C(3)-H(3)	110.2
C(5)-C(4)-C(18)	127.5(2)	C(5)-C(4)-C(3)	119.5(2)
C(18)-C(4)-C(3)	113.0(1)	C(4)-C(5)-P(1)	109.1(1)
C(4)-C(5)-Si(2)	127.2(1)	P(1)-C(5)-Si(2)	123.6(1)
C(11)-C(6)-C(7)	121.6(2)	C(11)-C(6)-P(1)	112.7(1)
C(7)-C(6)-P(1)	125.8(1)	C(8)-C(7)-C(6)	117.8(2)
C(8)-C(7)-H(7)	121.1	C(6)-C(7)-H(7)	121.1
C(9)-C(8)-C(7)	121.0(2)	C(9)-C(8)-H(8)	119.5
C(7)-C(8)-H(8)	119.5	C(8)-C(9)-C(10)	121.3(2)
C(8)-C(9)-H(9)	119.4	C(10)-C(9)-H(9)	119.4
C(11)-C(10)-C(9)	118.4(2)	C(11)-C(10)-H(10)	120.8
C(9)-C(10)-H(10)	120.8	C(6)-C(11)-C(10)	119.9(2)
C(6)-C(11)-C(3)	114.9(1)	C(10)-C(11)-C(3)	125.2(2)
C(13)-C(12)-C(17)	118.2(2)	C(13)-C(12)-C(2)	121.0(2)
C(17)-C(12)-C(2)	120.6(2)	C(12)-C(13)-C(14)	121.0(2)
C(12)-C(13)-H(13)	119.5	C(14)-C(13)-H(13)	119.5
C(15)-C(14)-C(13)	119.4(2)	C(15)-C(14)-H(14)	120.3
C(13)-C(14)-H(14)	120.3	C(16)-C(15)-C(14)	120.1(2)
C(16)-C(15)-H(15)	120.0	C(14)-C(15)-H(15)	120.0
C(15)-C(16)-C(17)	120.6(3)	C(15)-C(16)-H(16)	119.7
C(17)-C(16)-H(16)	119.7	C(12)-C(17)-C(16)	120.5(2)
C(12)-C(17)-H(17)	119.7	C(16)-C(17)-H(17)	119.7
C(23)-C(18)-C(19)	118.9(2)	C(23)-C(18)-C(4)	120.0(2)
C(19)-C(18)-C(4)	120.9(2)	C(18)-C(19)-C(20)	119.7(2)
C(18)-C(19)-H(19)	120.1	C(20)-C(19)-H(19)	120.1
C(21)-C(20)-C(19)	120.7(2)	C(21)-C(20)-H(20)	119.6
C(19)-C(20)-H(20)	119.6	C(22)-C(21)-C(20)	119.6(2)
C(22)-C(21)-H(21)	120.2	C(20)-C(21)-H(21)	120.2
C(21)-C(22)-C(23)	120.5(2)	C(21)-C(22)-H(22)	119.7
C(23)-C(22)-H(22)	119.7	C(18)-C(23)-C(22)	120.5(2)
C(18)-C(23)-H(23)	119.8	C(22)-C(23)-H(23)	119.8
Si(1)-C(24)-H(24A)	109.5	Si(1)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5	Si(1)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5	H(24B)-C(24)-H(24C)	109.5
Si(1)-C(25)-H(25A)	109.5	Si(1)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5	Si(1)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5	H(25B)-C(25)-H(25C)	109.5
C(27)-C(26)-C(28)	109.5(2)	C(27)-C(26)-C(29)	107.5(2)
C(28)-C(26)-C(29)	107.5(2)	C(27)-C(26)-Si(1)	113.1(2)
C(28)-C(26)-Si(1)	111.7(2)	C(29)-C(26)-Si(1)	107.4(2)
C(26)-C(27)-H(27A)	109.5	C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5	C(26)-C(27)-H(27C)	109.5

H(27A)-C(27)-H(27C)	109.5	H(27B)-C(27)-H(27C)	109.5
C(26)-C(28)-H(28A)	109.5	C(26)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5	C(26)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5	H(28B)-C(28)-H(28C)	109.5
C(26)-C(29)-H(29A)	109.5	C(26)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5	C(26)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5	H(29B)-C(29)-H(29C)	109.5
Si(2)-C(30)-H(30A)	109.5	Si(2)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5	Si(2)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5	H(30B)-C(30)-H(30C)	109.5
Si(2)-C(31)-H(31A)	109.5	Si(2)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5	Si(2)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5	H(31B)-C(31)-H(31C)	109.5
C(33)-C(32)-C(35)	112.4(2)	C(33)-C(32)-C(34)	107.0(3)
C(35)-C(32)-C(34)	107.7(2)	C(33)-C(32)-Si(2)	110.9(2)
C(35)-C(32)-Si(2)	111.7(2)	C(34)-C(32)-Si(2)	107.0(2)
C(32)-C(33)-H(33A)	109.5	C(32)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5	C(32)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5	H(33B)-C(33)-H(33C)	109.5
C(32)-C(34)-H(34A)	109.5	C(32)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5	C(32)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5	H(34B)-C(34)-H(34C)	109.5
C(32)-C(35)-H(35A)	109.5	C(32)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5	C(32)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5	H(35B)-C(35)-H(35C)	109.5

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mbcg4se

atom	U11	U22	U33	U23	U13	U12
Se(1)	41(1)	24(1)	45(1)	-4(1)	11(1)	7(1)
P(1)	23(1)	19(1)	27(1)	1(1)	4(1)	4(1)
Si(1)	27(1)	35(1)	30(1)	-5(1)	-4(1)	2(1)
Si(2)	28(1)	26(1)	31(1)	6(1)	9(1)	6(1)
C(1)	23(1)	23(1)	27(1)	1(1)	2(1)	3(1)
C(2)	24(1)	23(1)	27(1)	2(1)	4(1)	2(1)
C(3)	24(1)	20(1)	26(1)	-3(1)	4(1)	1(1)
C(4)	20(1)	22(1)	27(1)	3(1)	0(1)	4(1)
C(5)	23(1)	20(1)	27(1)	4(1)	3(1)	4(1)
C(6)	23(1)	26(1)	29(1)	6(1)	2(1)	0(1)
C(7)	32(1)	29(1)	40(1)	10(1)	1(1)	4(1)
C(8)	48(1)	48(1)	43(1)	19(1)	-9(1)	4(1)
C(9)	54(1)	56(1)	27(1)	8(1)	-7(1)	-1(1)
C(10)	38(1)	40(1)	29(1)	-1(1)	1(1)	-2(1)
C(11)	23(1)	27(1)	25(1)	3(1)	3(1)	-1(1)
C(12)	23(1)	32(1)	32(1)	-9(1)	3(1)	3(1)
C(13)	34(1)	54(1)	44(1)	-3(1)	12(1)	3(1)
C(14)	36(1)	87(2)	58(2)	-20(1)	24(1)	-3(1)
C(15)	25(1)	78(2)	78(2)	-47(2)	4(1)	10(1)
C(16)	41(1)	49(1)	100(2)	-14(2)	8(2)	21(1)
C(17)	37(1)	40(1)	79(2)	2(1)	14(1)	13(1)
C(18)	28(1)	21(1)	32(1)	3(1)	9(1)	3(1)
C(19)	39(1)	31(1)	41(1)	7(1)	8(1)	10(1)
C(20)	59(2)	26(1)	56(1)	16(1)	23(1)	16(1)
C(21)	70(2)	21(1)	60(1)	3(1)	25(1)	-3(1)
C(22)	67(2)	31(1)	60(1)	-3(1)	2(1)	-16(1)
C(23)	46(1)	27(1)	45(1)	4(1)	-5(1)	-5(1)
C(24)	48(1)	65(2)	32(1)	-7(1)	-3(1)	10(1)
C(25)	35(1)	57(1)	44(1)	-4(1)	-10(1)	11(1)
C(26)	37(1)	39(1)	55(1)	-7(1)	-3(1)	-10(1)
C(27)	56(2)	42(1)	129(3)	18(2)	7(2)	-3(1)
C(28)	77(2)	57(2)	73(2)	4(1)	22(2)	-20(1)

C(29)	67(2)	68(2)	103(2)	-22(2)	-20(2)	-24(2)
C(30)	61(2)	44(1)	31(1)	2(1)	15(1)	3(1)
C(31)	38(1)	35(1)	49(1)	16(1)	17(1)	7(1)
C(32)	27(1)	40(1)	52(1)	7(1)	8(1)	5(1)
C(33)	58(2)	79(2)	143(3)	-15(2)	-48(2)	3(2)
C(34)	38(1)	113(3)	97(2)	42(2)	30(1)	23(2)
C(35)	40(1)	93(2)	85(2)	52(2)	-7(1)	5(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mbcg4se

atom	x	y	z	U(eq)
H(3)	1957	3890	9666	28
H(7)	3874	-1	9735	41
H(8)	4219	287	10771	56
H(9)	3650	1865	11228	55
H(10)	2728	3231	10670	43
H(13)	-226	1863	9829	52
H(14)	-1768	2673	10121	72
H(15)	-2249	4420	9760	73
H(16)	-1179	5367	9152	76
H(17)	385	4590	8882	62
H(19)	2043	5228	8295	44
H(20)	2357	7131	8361	55
H(21)	3644	7821	9038	59
H(22)	4585	6625	9676	64
H(23)	4253	4729	9640	48
H(24A)	1410	265	7536	72
H(24B)	1259	1557	7401	72
H(24C)	348	704	7205	72
H(25A)	-1220	1789	7764	69
H(25B)	-516	2781	8036	69
H(25C)	-1202	2060	8468	69
H(27A)	1168	-982	8915	113
H(27B)	961	-1289.9999	8219	113
H(27C)	314	-1894	8715	113
H(28A)	-969	-885	9263	102
H(28B)	-1280	357	9083	102
H(28C)	-189	108	9442	102
H(29A)	-1331	-1410	8198	121
H(29B)	-725	-827	7677	121
H(29C)	-1588.9999	-155	8015	121
H(30A)	3255	2037	7202	67
H(30B)	4136	1242	7503	67
H(30C)	4438	2158	7024	67
H(31A)	4551	4457	7286	60
H(31B)	4233	4969	7912	60
H(31C)	3353	4476	7447	60
H(33A)	5572	4003	8991	143
H(33B)	5844	4539	8362	143
H(33C)	6713	3856	8751	143
H(34A)	7058	2795	7932	122
H(34B)	6152	3260	7475	122
H(34C)	6223	1965	7616	122
H(35A)	6488	1716	8808	110
H(35B)	5430	1215	8504	110
H(35C)	5398	1987	9086	110

II.5. Crystallographic data for IV-27

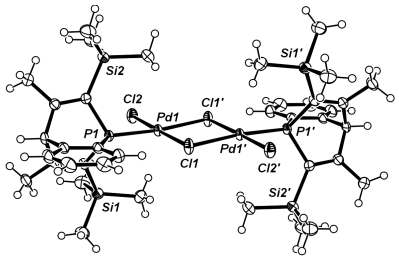


Table 1. Crystal data for mb433

Compound	mb433
Molecular formula	$C_{38}H_{58}Cl_4P_2Pd_2Si_4,2(C_4H_8O)$
Molecular weight	1187.95
Crystal habit	Orange Block
Crystal dimensions(mm)	0.20x0.10x0.10
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	11.470(1)
b(Å)	15.186(1)
c(Å)	17.526(1)
α(°)	90.00
β(°)	115.987(1)
γ(°)	90.00
V(Å^3)	2744.1(3)
Z	2
d(g-cm^{-3})	1.438
F(000)	1224
μ(cm^{-1})	1.030
Absorption corrections	multi-scan ; 0.8205 min, 0.9040 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.01
HKL ranges	-14 16 ; -19 21 ; -24 23
Reflections measured	17921
Unique data	7963
Rint	0.0447
Reflections used	6073

Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	279
Reflections / parameter	21
wR2	0.0951
R1	0.0370
Weights a, b	0.0404 ; 0.1848
GoF	1.064
difference peak / hole (e Å^{-3})	1.361(0.098) / -1.356(0.098)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb433

atom	x	y	z	U(eq)
Pd(1)	128(1)	-901(1)	-597(1)	20(1)
Cl(1)	-617(1)	543(1)	-863(1)	29(1)
Cl(2)	846(1)	-2319(1)	-251(1)	30(1)
P(1)	-102(1)	-1308(1)	-1871(1)	19(1)
Si(1)	-2425(1)	-2728(1)	-2027(1)	26(1)
Si(2)	3110(1)	-1402(1)	-1021(1)	27(1)
C(1)	-1208(2)	-2225(2)	-2370(1)	22(1)
C(2)	-1113(2)	-2484(2)	-3077(1)	22(1)
C(3)	-197(2)	-1973(2)	-3348(1)	23(1)
C(4)	1190(2)	-1999(2)	-2636(1)	22(1)
C(5)	1429(2)	-1655(2)	-1875(1)	21(1)
C(6)	-643(2)	-570(2)	-2794(1)	21(1)
C(7)	-629(2)	-1023(2)	-3490(1)	23(1)
C(8)	-993(2)	-587(2)	-4253(2)	30(1)
C(9)	-1354(2)	295(2)	-4326(2)	35(1)
C(10)	-1350(3)	744(2)	-3640(2)	33(1)
C(11)	-997(2)	307(2)	-2869(2)	28(1)
C(12)	-1849(2)	-3214(2)	-3666(2)	31(1)
C(13)	2187(2)	-2377(2)	-2891(2)	31(1)
C(14)	-2587(3)	-2102(2)	-1163(2)	36(1)
C(15)	-4064(2)	-2729(2)	-2973(2)	36(1)
C(16)	-1936(3)	-3877(2)	-1664(2)	36(1)
C(17)	3133(3)	-620(2)	-193(2)	42(1)
C(18)	3994(3)	-2421(2)	-489(2)	43(1)
C(19)	4002(3)	-818(2)	-1555(2)	45(1)
O(1)	4875(2)	-3922(2)	-1658(2)	57(1)
C(20)	5320(4)	-4454(3)	-915(2)	69(1)
C(21)	5233(7)	-5370(3)	-1184(3)	135(3)
C(22)	4205(3)	-5388(2)	-2069(2)	59(1)
C(23)	4215(3)	-4463(2)	-2373(2)	58(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb433

Pd(1)-P(1)	2.2190(6	Pd(1)-Cl(2)	2.2894(7)
Pd(1)-Cl(1)	2.3256(6	Pd(1)-Cl(1)#3	2.4286(6)
Cl(1)-Pd(1)#3	2.4286(6	P(1)-C(1)	1.827(2)
P(1)-C(5)	1.836(2)	P(1)-C(6)	1.838(2)
Si(1)-C(16)	1.859(3)	Si(1)-C(14)	1.864(3)
Si(1)-C(15)	1.884(3)	Si(1)-C(1)	1.905(2)
Si(2)-C(18)	1.861(3)	Si(2)-C(17)	1.866(3)
Si(2)-C(19)	1.884(3)	Si(2)-C(5)	1.891(2)

C(1)-C(2)	1.348(3)	C(2)-C(12)	1.499(3)
C(2)-C(3)	1.540(3)	C(3)-C(7)	1.511(4)
C(3)-C(4)	1.533(3)	C(3)-H(3)	1.0000
C(4)-C(5)	1.345(3)	C(4)-C(13)	1.511(3)
C(6)-C(11)	1.381(4)	C(6)-C(7)	1.407(3)
C(7)-C(8)	1.382(3)	C(8)-C(9)	1.391(4)
C(8)-H(8)	0.9500	C(9)-C(10)	1.381(4)
C(9)-H(9)	0.9500	C(10)-C(11)	1.397(3)
C(10)-H(10)	0.9500	C(11)-H(11)	0.9500
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800	C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800
O(1)-C(23)	1.409(4)	O(1)-C(20)	1.424(4)
C(20)-C(21)	1.457(6)	C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900	C(21)-C(22)	1.481(6)
C(21)-H(21A)	0.9900	C(21)-H(21B)	0.9900
C(22)-C(23)	1.505(5)	C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900	C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900		

P(1)-Pd(1)-Cl(2)	82.82(2)	P(1)-Pd(1)-Cl(1)	100.92(2)
Cl(2)-Pd(1)-Cl(1)	176.10(2)	P(1)-Pd(1)-Cl(1)#3	173.46(2)
Cl(2)-Pd(1)-Cl(1)#3	92.40(2)	Cl(1)-Pd(1)-Cl(1)#3	83.96(2)
Pd(1)-Cl(1)-Pd(1)#3	96.04(2)	C(1)-P(1)-C(5)	104.1(1)
C(1)-P(1)-C(6)	98.5(1)	C(5)-P(1)-C(6)	97.3(1)
C(1)-P(1)-Pd(1)	116.46(7)	C(5)-P(1)-Pd(1)	113.01(7)
C(6)-P(1)-Pd(1)	124.13(8)	C(16)-Si(1)-C(14)	108.8(1)
C(16)-Si(1)-C(15)	109.6(1)	C(14)-Si(1)-C(15)	107.4(1)
C(16)-Si(1)-C(1)	109.3(1)	C(14)-Si(1)-C(1)	113.6(1)
C(15)-Si(1)-C(1)	108.0(1)	C(18)-Si(2)-C(17)	108.7(2)
C(18)-Si(2)-C(19)	110.2(1)	C(17)-Si(2)-C(19)	105.1(1)
C(18)-Si(2)-C(5)	111.7(1)	C(17)-Si(2)-C(5)	114.0(1)
C(19)-Si(2)-C(5)	106.9(1)	C(2)-C(1)-P(1)	110.1(2)
C(2)-C(1)-Si(1)	122.6(2)	P(1)-C(1)-Si(1)	127.2(1)
C(1)-C(2)-C(12)	127.0(2)	C(1)-C(2)-C(3)	118.5(2)
C(12)-C(2)-C(3)	114.5(2)	C(7)-C(3)-C(4)	107.9(2)
C(7)-C(3)-C(2)	108.2(2)	C(4)-C(3)-C(2)	109.9(2)
C(7)-C(3)-H(3)	110.2	C(4)-C(3)-H(3)	110.2
C(2)-C(3)-H(3)	110.2	C(5)-C(4)-C(13)	126.1(2)
C(5)-C(4)-C(3)	119.0(2)	C(13)-C(4)-C(3)	114.8(2)
C(4)-C(5)-P(1)	109.6(2)	C(4)-C(5)-Si(2)	123.9(2)
P(1)-C(5)-Si(2)	125.8(1)	C(11)-C(6)-C(7)	120.2(2)
C(11)-C(6)-P(1)	130.1(2)	C(7)-C(6)-P(1)	109.7(2)
C(8)-C(7)-C(6)	119.5(2)	C(8)-C(7)-C(3)	123.7(2)
C(6)-C(7)-C(3)	116.9(2)	C(7)-C(8)-C(9)	120.1(2)
C(7)-C(8)-H(8)	119.9	C(9)-C(8)-H(8)	119.9
C(10)-C(9)-C(8)	120.5(2)	C(10)-C(9)-H(9)	119.7
C(8)-C(9)-H(9)	119.7	C(9)-C(10)-C(11)	119.7(3)
C(9)-C(10)-H(10)	120.1	C(11)-C(10)-H(10)	120.1
C(6)-C(11)-C(10)	120.0(2)	C(6)-C(11)-H(11)	120.0
C(10)-C(11)-H(11)	120.0	C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5

H(12B)-C(12)-H(12C)	109.5	C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	Si(2)-C(19)-H(19A)	109.5
Si(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(23)-O(1)-C(20)	108.7(3)
O(1)-C(20)-C(21)	107.4(3)	O(1)-C(20)-H(20A)	110.2
C(21)-C(20)-H(20A)	110.2	O(1)-C(20)-H(20B)	110.2
C(21)-C(20)-H(20B)	110.2	H(20A)-C(20)-H(20B)	108.5
C(20)-C(21)-C(22)	105.5(4)	C(20)-C(21)-H(21A)	110.6
C(22)-C(21)-H(21A)	110.6	C(20)-C(21)-H(21B)	110.6
C(22)-C(21)-H(21B)	110.6	H(21A)-C(21)-H(21B)	108.8
C(21)-C(22)-C(23)	103.2(3)	C(21)-C(22)-H(22A)	111.1
C(23)-C(22)-H(22A)	111.1	C(21)-C(22)-H(22B)	111.1
C(23)-C(22)-H(22B)	111.1	H(22A)-C(22)-H(22B)	109.1
O(1)-C(23)-C(22)	108.3(3)	O(1)-C(23)-H(23A)	110.0
C(22)-C(23)-H(23A)	110.0	O(1)-C(23)-H(23B)	110.0
C(22)-C(23)-H(23B)	110.0	H(23A)-C(23)-H(23B)	108.4

Estimated standard deviations are given in the parenthesis.
Symmetry operators ::
1: x, y, z 2: -x, y+1/2, -z+1/2 3: -x, -y, -z
4: x, -y-1/2, z-1/2

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb433

atom	U11	U22	U33	U23	U13	U12
Pd(1)	25(1)	19(1)	16(1)	-2(1)	10(1)	0(1)
Cl(1)	46(1)	22(1)	19(1)	0(1)	16(1)	6(1)
Cl(2)	42(1)	23(1)	24(1)	1(1)	14(1)	5(1)
P(1)	22(1)	21(1)	15(1)	-2(1)	8(1)	0(1)
Si(1)	25(1)	29(1)	25(1)	-1(1)	12(1)	-4(1)
Si(2)	22(1)	32(1)	23(1)	-6(1)	6(1)	-1(1)
C(1)	23(1)	23(1)	19(1)	-2(1)	8(1)	-3(1)
C(2)	22(1)	25(1)	18(1)	-3(1)	7(1)	-2(1)
C(3)	26(1)	29(1)	15(1)	-7(1)	10(1)	-2(1)
C(4)	23(1)	22(1)	21(1)	-1(1)	10(1)	-2(1)
C(5)	21(1)	20(1)	22(1)	-2(1)	10(1)	-1(1)
C(6)	21(1)	26(1)	17(1)	0(1)	7(1)	-2(1)
C(7)	22(1)	27(1)	18(1)	-2(1)	9(1)	-5(1)
C(8)	31(1)	41(2)	16(1)	-2(1)	10(1)	-6(1)

C(9)	38(1)	41(2)	20(1)	9(1)	8(1)	-2(1)
C(10)	36(1)	30(2)	29(1)	9(1)	10(1)	2(1)
C(11)	31(1)	27(2)	24(1)	-1(1)	11(1)	1(1)
C(12)	31(1)	36(2)	25(1)	-11(1)	12(1)	-11(1)
C(13)	27(1)	39(2)	30(1)	-9(1)	13(1)	0(1)
C(14)	33(1)	48(2)	33(1)	-7(1)	21(1)	-4(1)
C(15)	30(1)	41(2)	34(1)	-1(1)	10(1)	-4(1)
C(16)	35(1)	36(2)	39(2)	6(1)	17(1)	-4(1)
C(17)	30(1)	49(2)	43(2)	-23(2)	12(1)	-11(1)
C(18)	34(1)	48(2)	35(1)	1(1)	5(1)	10(1)
C(19)	34(2)	57(2)	47(2)	-11(2)	20(1)	-16(1)
O(1)	72(2)	46(2)	51(1)	-1(1)	24(1)	2(1)
C(20)	84(3)	60(3)	47(2)	3(2)	14(2)	24(2)
C(21)	230(7)	54(3)	60(3)	4(2)	7(4)	-8(4)
C(22)	56(2)	53(2)	74(2)	-1(2)	32(2)	-7(2)
C(23)	51(2)	51(2)	59(2)	0(2)	10(2)	-5(2)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb433

atom	x	y	z	U(eq)
H(3)	-223	-2230	-3881	28
H(8)	-996.9999	-891.0001	-4728	35
H(9)	-1605	590	-4852	42
H(10)	-1586	1349	-3692	39
H(11)	-1000	612	-2397	33
H(12A)	-2356	-3534	-3429	46
H(12B)	-1238	-3619	-3737	46
H(12C)	-2435	-2967	-4219	46
H(13A)	2306	-1976.0001	-3289	47
H(13B)	1888	-2951	-3164	47
H(13C)	3013	-2451	-2385	47
H(14A)	-3330	-2328	-1088	54
H(14B)	-2721	-1477	-1315	54
H(14C)	-1795	-2173	-633	54
H(15A)	-4166	-3270	-3300.0002	54
H(15B)	-4134	-2218	-3332	54
H(15C)	-4744	-2699	-2778	54
H(16A)	-1099	-3874	-1159	54
H(16B)	-1856	-4213	-2117	54
H(16C)	-2593	-4151	-1526	54
H(17A)	2767	-908.9999	154	63
H(17B)	2615	-99	-467	63
H(17C)	4028	-443	170	63
H(18A)	4882	-2270	-84	64
H(18B)	4018	-2828	-916	64
H(18C)	3549	-2702.0002	-188	64
H(19A)	4908	-727	-1144	68
H(19B)	3592	-247.0000	-1769	68
H(19C)	3971	-1176	-2028	68
H(20A)	4777	-4356	-614	82
H(20B)	6229	-4304	-527	82
H(21A)	4999	-5754	-816	162
H(21B)	6070	-5572	-1159	162
H(22A)	3352	-5536	-2087	71
H(22B)	4410	-5820	-2415	71
H(23A)	4657	-4447	-2746.9998	70
H(23B)	3315	-4250	-2700	70

II.6. Crystallographic data for IV-28

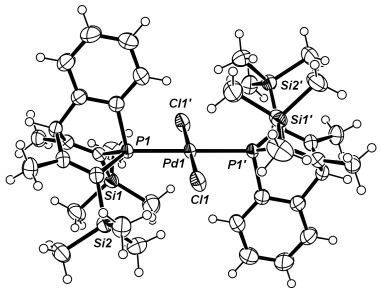


Table 1. Crystal data for mb433bis

Compound	mb433bis
Molecular formula	$C_{38}H_{58}Cl_2P_2PdSi_4$,2($C_4O$)
Molecular weight	994.52
Crystal habit	Pale Yellow Block
Crystal dimensions(mm)	0.18x0.16x0.12
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	11.252(1)
b(Å)	18.038(1)
c(Å)	13.611(1)
α(°)	90.00
β(°)	109.550(1)
γ(°)	90.00
V(Å^3)	2603.3(3)
Z	2
d(g-cm^{-3})	1.269
F(000)	1032
μ(cm^{-1})	0.646
Absorption corrections	multi-scan ; 0.8926 min, 0.9265 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	27.50
HKL ranges	-10 14 ; -23 19 ; -17 17
Reflections measured	15017
Unique data	5809

Rint	0.0451
Reflections used	4481
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	267
Reflections / parameter	16
wR2	0.1400
R1	0.0485
Weights a, b	0.0743 ; 1.6711
GoF	1.061
difference peak / hole (e Å^{-3})	0.977(0.089) / -0.657(0.089)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb433bis

atom	x	y	z	U(eq)
Pd(1)	5000	0	0	33(1)
Cl(1)	4393(1)	768(1)	-1429(1)	47(1)
P(1)	4457(1)	986(1)	888(1)	31(1)
Si(1)	3683(1)	190(1)	2767(1)	39(1)
Si(2)	1625(1)	1418(1)	-774(1)	42(1)
C(1)	4334(3)	983(2)	2199(3)	34(1)
C(2)	4438(3)	1681(2)	2587(3)	35(1)
C(3)	4470(3)	2334(2)	1879(3)	34(1)
C(4)	3343(3)	2274(2)	860(3)	34(1)
C(5)	3164(3)	1648(2)	291(3)	33(1)
C(6)	5786(3)	1624(2)	1104(3)	37(1)
C(7)	5666(3)	2272(2)	1618(3)	38(1)
C(8)	6618(4)	2801(2)	1873(4)	54(1)
C(9)	7676(4)	2683(2)	1595(5)	72(2)
C(10)	7790(4)	2045(2)	1066(4)	68(1)
C(11)	6854(3)	1508(2)	825(4)	52(1)
C(12)	4571(4)	1897(2)	3689(3)	47(1)
C(13)	2551(3)	2962(2)	593(3)	41(1)
C(14)	4939(4)	-365(2)	3730(3)	49(1)
C(15)	2651(3)	-374(2)	1667(3)	48(1)
C(16)	2550(4)	556(2)	3403(4)	57(1)
C(17)	1469(4)	413(2)	-1122(4)	60(1)
C(18)	1424(4)	1978(3)	-1968(3)	64(1)
C(19)	336(4)	1618(3)	-225(4)	60(1)
O(1)	9120(10)	760(10)	3610(10)	430(10)
C(20)	7932(8)	600(10)	3620(10)	214(7)
C(21)	7850(10)	1024(8)	4420(10)	203(6)
C(22)	9160(10)	1298(7)	5070(10)	173(5)
C(23)	9835(7)	1102(7)	4500(10)	194(6)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb433bis

Pd(1)-Cl(1)#3	2.297(1)	Pd(1)-Cl(1)	2.297(1)
Pd(1)-P(1)#3	2.3435(7	Pd(1)-P(1)	2.3435(7)
P(1)-C(6)	1.831(3)	P(1)-C(1)	1.835(4)
P(1)-C(5)	1.847(3)	Si(1)-C(15)	1.860(4)
Si(1)-C(14)	1.865(4)	Si(1)-C(16)	1.884(4)
Si(1)-C(1)	1.888(3)	Si(2)-C(18)	1.861(5)
Si(2)-C(17)	1.867(4)	Si(2)-C(19)	1.876(4)

Si(2)-C(5)	1.895(3)	C(1)-C(2)	1.355(4)
C(2)-C(12)	1.509(5)	C(2)-C(3)	1.530(5)
C(3)-C(7)	1.506(4)	C(3)-C(4)	1.539(4)
C(3)-H(3)	1.0000	C(4)-C(5)	1.346(4)
C(4)-C(13)	1.500(4)	C(6)-C(11)	1.391(5)
C(6)-C(7)	1.393(5)	C(7)-C(8)	1.389(5)
C(8)-C(9)	1.381(6)	C(8)-H(8)	0.9500
C(9)-C(10)	1.386(6)	C(9)-H(9)	0.9500
C(10)-C(11)	1.387(5)	C(10)-H(10)	0.9500
C(11)-H(11)	0.9500	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800	C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800	C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800	C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800	C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800	C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800	C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800	O(1)-C(23)	1.36(1)
O(1)-C(20)	1.37(2)	C(20)-C(21)	1.36(1)
C(21)-C(22)	1.53(1)	C(22)-C(23)	1.31(1)

Cl(1)#3-Pd(1)-Cl(1)	180.00(5)	Cl(1)#3-Pd(1)-P(1)#3	85.65(3)
Cl(1)-Pd(1)-P(1)#3	94.35(3)	Cl(1)#3-Pd(1)-P(1)	94.35(3)
Cl(1)-Pd(1)-P(1)	85.65(3)	P(1)#3-Pd(1)-P(1)	180.00(4)
C(6)-P(1)-C(1)	99.7(2)	C(6)-P(1)-C(5)	98.4(1)
C(1)-P(1)-C(5)	97.2(1)	C(6)-P(1)-Pd(1)	102.7(1)
C(1)-P(1)-Pd(1)	128.1(1)	C(5)-P(1)-Pd(1)	124.5(1)
C(15)-Si(1)-C(14)	113.3(2)	C(15)-Si(1)-C(16)	103.0(2)
C(14)-Si(1)-C(16)	109.6(2)	C(15)-Si(1)-C(1)	107.9(2)
C(14)-Si(1)-C(1)	112.8(2)	C(16)-Si(1)-C(1)	109.7(2)
C(18)-Si(2)-C(17)	109.4(2)	C(18)-Si(2)-C(19)	111.0(2)
C(17)-Si(2)-C(19)	105.5(2)	C(18)-Si(2)-C(5)	111.2(2)
C(17)-Si(2)-C(5)	113.0(2)	C(19)-Si(2)-C(5)	106.5(2)
C(2)-C(1)-P(1)	110.6(3)	C(2)-C(1)-Si(1)	122.6(3)
P(1)-C(1)-Si(1)	124.5(2)	C(1)-C(2)-C(12)	126.4(3)
C(1)-C(2)-C(3)	119.2(3)	C(12)-C(2)-C(3)	114.4(3)
C(7)-C(3)-C(2)	107.6(3)	C(7)-C(3)-C(4)	108.3(3)
C(2)-C(3)-C(4)	109.1(2)	C(7)-C(3)-H(3)	110.6
C(2)-C(3)-H(3)	110.6	C(4)-C(3)-H(3)	110.6
C(5)-C(4)-C(13)	126.4(3)	C(5)-C(4)-C(3)	119.9(3)
C(13)-C(4)-C(3)	113.8(3)	C(4)-C(5)-P(1)	110.2(2)
C(4)-C(5)-Si(2)	123.1(2)	P(1)-C(5)-Si(2)	125.4(2)
C(11)-C(6)-C(7)	120.1(3)	C(11)-C(6)-P(1)	126.5(3)
C(7)-C(6)-P(1)	113.4(2)	C(8)-C(7)-C(6)	120.4(3)
C(8)-C(7)-C(3)	124.4(3)	C(6)-C(7)-C(3)	115.2(3)
C(9)-C(8)-C(7)	119.3(4)	C(9)-C(8)-H(8)	120.4
C(7)-C(8)-H(8)	120.4	C(8)-C(9)-C(10)	120.5(4)
C(8)-C(9)-H(9)	119.7	C(10)-C(9)-H(9)	119.7
C(9)-C(10)-C(11)	120.5(4)	C(9)-C(10)-H(10)	119.7
C(11)-C(10)-H(10)	119.7	C(10)-C(11)-C(6)	119.1(4)
C(10)-C(11)-H(11)	120.4	C(6)-C(11)-H(11)	120.4
C(2)-C(12)-H(12A)	109.5	C(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5	C(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5	H(12B)-C(12)-H(12C)	109.5
C(4)-C(13)-H(13A)	109.5	C(4)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5	C(4)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5	H(13B)-C(13)-H(13C)	109.5
Si(1)-C(14)-H(14A)	109.5	Si(1)-C(14)-H(14B)	109.5

H(14A)-C(14)-H(14B)	109.5	Si(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
Si(1)-C(15)-H(15A)	109.5	Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5	Si(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
Si(1)-C(16)-H(16A)	109.5	Si(1)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5	Si(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(16B)-C(16)-H(16C)	109.5
Si(2)-C(17)-H(17A)	109.5	Si(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5	Si(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(17B)-C(17)-H(17C)	109.5
Si(2)-C(18)-H(18A)	109.5	Si(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5	Si(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5	H(18B)-C(18)-H(18C)	109.5
Si(2)-C(19)-H(19A)	109.5	Si(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5	Si(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5	H(19B)-C(19)-H(19C)	109.5
C(23)-O(1)-C(20)	112(1)	C(21)-C(20)-O(1)	103(1)
C(20)-C(21)-C(22)	109(1)	C(23)-C(22)-C(21)	102.1(8)
C(22)-C(23)-O(1)	111(1)		

Estimated standard deviations are given in the parenthesis.

Symmetry operators ::

1: x, y, z 2: -x, y+1/2, -z+1/2 3: -x, -y, -z

4: x, -y-1/2, z-1/2

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb433bis

atom	U11	U22	U33	U23	U13	U12
Pd(1)	35(1)	30(1)	37(1)	-9(1)	19(1)	-1(1)
Cl(1)	53(1)	50(1)	43(1)	-1(1)	24(1)	12(1)
P(1)	31(1)	30(1)	36(1)	-10(1)	16(1)	-2(1)
Si(1)	44(1)	36(1)	42(1)	1(1)	19(1)	2(1)
Si(2)	31(1)	57(1)	40(1)	-11(1)	14(1)	-4(1)
C(1)	35(2)	33(2)	35(2)	-3(1)	12(1)	2(1)
C(2)	37(2)	34(2)	34(2)	-5(1)	13(1)	3(1)
C(3)	36(2)	29(2)	39(2)	-7(1)	14(1)	0(1)
C(4)	32(2)	34(2)	38(2)	-2(1)	14(1)	0(1)
C(5)	33(2)	35(2)	34(2)	-3(1)	16(1)	-2(1)
C(6)	34(2)	37(2)	41(2)	-4(1)	13(1)	-1(1)
C(7)	36(2)	35(2)	45(2)	-2(1)	14(1)	-1(1)
C(8)	47(2)	40(2)	76(3)	-13(2)	21(2)	-8(2)
C(9)	45(2)	56(3)	122(5)	-23(3)	36(3)	-18(2)
C(10)	44(2)	63(3)	109(4)	-16(3)	41(2)	-11(2)
C(11)	45(2)	49(2)	69(3)	-13(2)	30(2)	-2(2)
C(12)	58(2)	46(2)	36(2)	-8(2)	16(2)	5(2)
C(13)	50(2)	35(2)	44(2)	1(2)	22(2)	5(1)
C(14)	64(2)	44(2)	41(2)	5(2)	19(2)	6(2)
C(15)	48(2)	41(2)	53(3)	5(2)	15(2)	-4(2)
C(16)	64(2)	61(2)	63(3)	0(2)	41(2)	5(2)
C(17)	46(2)	69(3)	63(3)	-26(2)	15(2)	-10(2)
C(18)	43(2)	101(3)	42(3)	1(2)	5(2)	-3(2)
C(19)	40(2)	79(3)	71(3)	-21(2)	29(2)	-10(2)
O(1)	170(10)	740(30)	330(20)	-260(20)	20(10)	-30(10)
C(20)	65(5)	420(20)	150(10)	-100(10)	19(5)	-16(8)
C(21)	105(7)	320(20)	170(10)	-120(10)	28(7)	7(8)
C(22)	108(6)	250(10)	170(10)	-110(10)	49(6)	0(7)
C(23)	72(5)	230(10)	260(10)	-150(10)	23(7)	-42(6)

The anisotropic displacement factor exponent takes the form

2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb433bis

atom	x	y	z	U(eq)
H(3)	4446	2816	2236	41
H(8)	6542	3239	2235	65
H(9)	8331	3042	1767	87
H(10)	8516	1974	868	82
H(11)	6941	1067	473	62
H(12A)	3810	2159	3693	70
H(12B)	5305	2222	3971	70
H(12C)	4686	1450	4121	70
H(13A)	1905	2904	-94	62
H(13B)	3088	3388	582	62
H(13C)	2145	3044	1118	62
H(14A)	4550	-734	4055	74
H(14B)	5478	-35	4268	74
H(14C)	5450	-617	3374	74
H(15A)	3167	-623	1313	72
H(15B)	2037	-50	1173	72
H(15C)	2203	-746.0001	1936	72
H(16A)	1978	158	3450	86
H(16B)	2058	964	2985	86
H(16C)	3023	736	4104	86
H(17A)	592	304	-1541	90
H(17B)	1711	115	-483.0000	90
H(17C)	2020	292	-1524	90
H(18A)	1309	2500	-1824	96
H(18B)	683	1802	-2534	96
H(18C)	2176	1926	-2173	96
H(19A)	351	2145	-48.0000	91
H(19B)	465	1319	403	91
H(19C)	-481.0000	1494	-744	91

II.7. Crystallographic data for IV-29

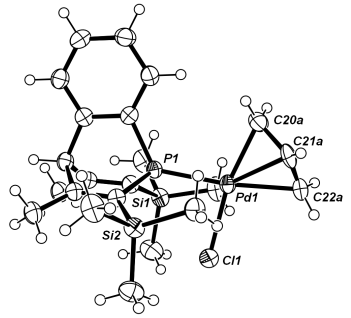


Table 1. Crystal data for mb453

Compound	mb453
Molecular formula	$C_{22}H_{34}ClPPdSi_2$
Molecular weight	527.49
Crystal habit	pale yellow block
Crystal dimensions(mm)	0.24x0.18x0.04
Crystal system	triclinic
Space group	P-1
a(Å)	10.056(1)
b(Å)	15.490(1)
c(Å)	16.211(1)
α(°)	86.602(1)
β(°)	83.472(1)
γ(°)	89.719(1)
V(Å^3)	2504.4(3)
Z	4
d(g-cm^{-3})	1.399
F(000)	1088
μ(cm^{-1})	1.013
Absorption corrections	multi-scan ; 0.7931 min, 0.9606 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	27.48
HKL ranges	-13 13 ; -19 20 ; -21 19
Reflections measured	22441

Unique data	11297
Rint	0.0598
Reflections used	8707
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	523
Reflections / parameter	16
wR2	0.1479
R1	0.0536
Weights a, b	0.0703 ; 3.1896
GoF	1.054
difference peak / hole (e Å^{-3})	2.098(0.120) / -1.420(0.120)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb453

atom	x	y	z	U(eq)
Pd(1)	-615(1)	1851(1)	6049(1)	29(1)
Cl(1)	-1748(1)	3195(1)	5957(1)	39(1)
P(1)	723(1)	2331(1)	4874(1)	25(1)
Si(1)	-1902(1)	2218(1)	3816(1)	33(1)
Si(2)	1880(1)	3879(1)	5919(1)	32(1)
C(1)	-141(4)	2561(3)	3941(3)	30(1)
C(2)	689(4)	2949(3)	3313(2)	29(1)
C(3)	2160(4)	3071(3)	3442(3)	30(1)
C(4)	2219(4)	3636(3)	4180(3)	29(1)
C(5)	1626(4)	3357(3)	4928(2)	28(1)
C(6)	2138(4)	1736(3)	4367(2)	27(1)
C(7)	2625(5)	936(3)	4617(3)	35(1)
C(8)	3708(5)	578(3)	4146(3)	41(1)
C(9)	4298(5)	1022(3)	3424(3)	39(1)
C(10)	3832(5)	1828(3)	3181(3)	35(1)
C(11)	2754(4)	2192(3)	3652(2)	29(1)
C(12)	327(5)	3304(3)	2487(3)	37(1)
C(13)	2947(5)	4475(3)	3970(3)	38(1)
C(14)	-2671(5)	1473(3)	4684(3)	45(1)
C(15)	-1783(6)	1548(3)	2879(3)	47(1)
C(16)	-3030(5)	3159(3)	3704(4)	50(1)
C(17)	1536(5)	3095(3)	6844(3)	37(1)
C(18)	832(5)	4862(3)	6059(3)	44(1)
C(19)	3706(5)	4175(3)	5872(3)	47(1)
C(20A)	101(5)	592(3)	6350(3)	42(1)
C(21A)	-600(10)	942(6)	7094(5)	41(3)
C(22A)	-1807(7)	1222(4)	7149(4)	62(2)
C(20B)	101(5)	592(3)	6350(3)	42(1)
C(21B)	-1230(20)	659(8)	6730(10)	46(5)
C(22B)	-1807(7)	1222(4)	7149(4)	62(2)
Pd(2)	6975(1)	8043(1)	-525(1)	32(1)
Cl(2)	6045(1)	6920(1)	-1210(1)	42(1)
P(2)	5820(1)	7507(1)	699(1)	27(1)
Si(3)	3020(1)	8017(1)	-98(1)	36(1)
Si(4)	7635(1)	5726(1)	563(1)	32(1)
C(23)	3980(4)	7461(3)	719(3)	31(1)
C(24)	3416(4)	7026(3)	1407(3)	32(1)
C(25)	4293(4)	6713(3)	2077(3)	31(1)
C(26)	5302(4)	6078(3)	1665(3)	31(1)
C(27)	6173(4)	6377(3)	1025(3)	30(1)

C(28)	5842(4)	7959(3)	1718(3)	31(1)
C(29)	6510(5)	8693(3)	1895(3)	36(1)
C(30)	6385(5)	8950(3)	2709(3)	43(1)
C(31)	5586(5)	8480(3)	3331(3)	42(1)
C(32)	4896(5)	7745(3)	3150(3)	37(1)
C(33)	5030(4)	7486(3)	2338(3)	32(1)
C(34)	1959(5)	6767(3)	1614(3)	40(1)
C(35)	5151(5)	5151(3)	1997(3)	38(1)
C(36)	2448(6)	7238(3)	-817(3)	47(1)
C(37)	4017(5)	8897(3)	-721(3)	46(1)
C(38)	1522(5)	8573(3)	440(4)	50(1)
C(39)	8444(6)	5126(3)	1424(3)	47(1)
C(40)	7109(6)	4957(3)	-180(3)	47(1)
C(41)	8980(5)	6453(3)	37(3)	47(1)
C(42A)	7984(5)	9136(3)	-186(3)	45(1)
C(43A)	8690(10)	8838(5)	-956(5)	43(3)
C(44A)	8090(7)	8753(4)	-1605(4)	66(2)
C(42B)	7984(5)	9136(3)	-186(3)	45(1)
C(43B)	7790(20)	9260(10)	-1060(10)	51(5)
C(44B)	8090(7)	8753(4)	-1605(4)	66(2)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb453

Pd(1)-C(20A)	2.123(5)	Pd(1)-C(21A)	2.139(7)
Pd(1)-C(21B)	2.15(1)	Pd(1)-C(22A)	2.210(5)
Pd(1)-P(1)	2.291(1)	Pd(1)-Cl(1)	2.374(1)
P(1)-C(6)	1.833(4)	P(1)-C(1)	1.845(4)
P(1)-C(5)	1.846(4)	Si(1)-C(16)	1.856(5)
Si(1)-C(14)	1.865(5)	Si(1)-C(15)	1.881(5)
Si(1)-C(1)	1.887(5)	Si(2)-C(18)	1.858(5)
Si(2)-C(17)	1.874(5)	Si(2)-C(5)	1.885(4)
Si(2)-C(19)	1.886(5)	C(1)-C(2)	1.353(6)
C(2)-C(12)	1.500(6)	C(2)-C(3)	1.532(6)
C(3)-C(11)	1.521(6)	C(3)-C(4)	1.530(6)
C(3)-H(3)	1.0000	C(4)-C(5)	1.338(6)
C(4)-C(13)	1.496(6)	C(6)-C(7)	1.385(6)
C(6)-C(11)	1.403(6)	C(7)-C(8)	1.389(6)
C(7)-H(7)	0.9500	C(8)-C(9)	1.395(7)
C(8)-H(8)	0.9500	C(9)-C(10)	1.383(6)
C(9)-H(9)	0.9500	C(10)-C(11)	1.390(6)
C(10)-H(10)	0.9500	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800	C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800	C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800	C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800	C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800	C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800	C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800	C(20A)-C(21A)	1.46(1)
C(20A)-H(20A)	0.9900	C(20A)-H(20B)	0.9900
C(21A)-C(22A)	1.28(1)	C(21A)-H(21A)	0.9500
C(22A)-H(22A)	0.9900	C(22A)-H(22B)	0.9900
C(21B)-H(21B)	0.9500	Pd(2)-C(42A)	2.110(5)
Pd(2)-C(43A)	2.154(7)	Pd(2)-C(43B)	2.16(1)
Pd(2)-C(44A)	2.208(5)	Pd(2)-P(2)	2.293(1)
Pd(2)-Cl(2)	2.370(1)	P(2)-C(28)	1.835(4)
P(2)-C(27)	1.843(4)	P(2)-C(23)	1.848(4)

Si(3)-C(36)	1.864(5)	Si(3)-C(37)	1.872(5)
Si(3)-C(38)	1.884(5)	Si(3)-C(23)	1.890(5)
Si(4)-C(41)	1.860(5)	Si(4)-C(40)	1.862(5)
Si(4)-C(27)	1.888(4)	Si(4)-C(39)	1.889(5)
C(23)-C(24)	1.338(6)	C(24)-C(34)	1.516(6)
C(24)-C(25)	1.532(6)	C(25)-C(33)	1.518(6)
C(25)-C(26)	1.535(6)	C(25)-H(25)	1.0000
C(26)-C(27)	1.341(6)	C(26)-C(35)	1.506(6)
C(28)-C(29)	1.385(6)	C(28)-C(33)	1.395(6)
C(29)-C(30)	1.392(6)	C(29)-H(29)	0.9500
C(30)-C(31)	1.388(7)	C(30)-H(30)	0.9500
C(31)-C(32)	1.399(7)	C(31)-H(31)	0.9500
C(32)-C(33)	1.390(6)	C(32)-H(32)	0.9500
C(34)-H(34A)	0.9800	C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800	C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800	C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800	C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800	C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800	C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800	C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800	C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800	C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800	C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800	C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800	C(41)-H(41C)	0.9800
C(42A)-C(43A)	1.46(1)	C(42A)-H(42A)	0.9900
C(42A)-H(42B)	0.9900	C(43A)-C(44A)	1.29(1)
C(43A)-H(43A)	0.9500	C(44A)-H(44A)	0.9900
C(44A)-H(44B)	0.9900	C(43B)-H(43B)	0.9500

C(20A)-Pd(1)-C(21A)	40.0(3)	C(20A)-Pd(1)-C(21B)	38.5(4)
C(21A)-Pd(1)-C(21B)	27.7(4)	C(20A)-Pd(1)-C(22A)	68.0(2)
C(21A)-Pd(1)-C(22A)	34.1(3)	C(21B)-Pd(1)-C(22A)	33.1(4)
C(20A)-Pd(1)-P(1)	105.0(1)	C(21A)-Pd(1)-P(1)	140.5(2)
C(21B)-Pd(1)-P(1)	139.7(4)	C(22A)-Pd(1)-P(1)	172.7(2)
C(20A)-Pd(1)-Cl(1)	168.1(1)	C(21A)-Pd(1)-Cl(1)	128.9(2)
C(21B)-Pd(1)-Cl(1)	130.1(4)	C(22A)-Pd(1)-Cl(1)	100.1(2)
P(1)-Pd(1)-Cl(1)	86.89(4)	C(6)-P(1)-C(1)	97.0(2)
C(6)-P(1)-C(5)	96.6(2)	C(1)-P(1)-C(5)	101.3(2)
C(6)-P(1)-Pd(1)	125.3(1)	C(1)-P(1)-Pd(1)	115.6(1)
C(5)-P(1)-Pd(1)	116.6(1)	C(16)-Si(1)-C(14)	108.4(3)
C(16)-Si(1)-C(15)	111.7(3)	C(14)-Si(1)-C(15)	104.2(2)
C(16)-Si(1)-C(1)	112.0(2)	C(14)-Si(1)-C(1)	113.7(2)
C(15)-Si(1)-C(1)	106.6(2)	C(18)-Si(2)-C(17)	110.4(2)
C(18)-Si(2)-C(5)	111.7(2)	C(17)-Si(2)-C(5)	111.1(2)
C(18)-Si(2)-C(19)	109.8(2)	C(17)-Si(2)-C(19)	105.7(2)
C(5)-Si(2)-C(19)	108.0(2)	C(2)-C(1)-P(1)	111.3(3)
C(2)-C(1)-Si(1)	122.9(3)	P(1)-C(1)-Si(1)	125.5(2)
C(1)-C(2)-C(12)	127.1(4)	C(1)-C(2)-C(3)	118.4(4)
C(12)-C(2)-C(3)	114.5(4)	C(11)-C(3)-C(4)	108.6(3)
C(11)-C(3)-C(2)	108.7(4)	C(4)-C(3)-C(2)	108.3(3)
C(11)-C(3)-H(3)	110.4	C(4)-C(3)-H(3)	110.4
C(2)-C(3)-H(3)	110.4	C(5)-C(4)-C(13)	126.5(4)
C(5)-C(4)-C(3)	119.0(4)	C(13)-C(4)-C(3)	114.5(4)
C(4)-C(5)-P(1)	111.4(3)	C(4)-C(5)-Si(2)	123.3(3)
P(1)-C(5)-Si(2)	124.8(2)	C(7)-C(6)-C(11)	120.1(4)
C(7)-C(6)-P(1)	127.7(3)	C(11)-C(6)-P(1)	112.1(3)
C(6)-C(7)-C(8)	119.7(4)	C(6)-C(7)-H(7)	120.1
C(8)-C(7)-H(7)	120.1	C(7)-C(8)-C(9)	120.1(4)
C(7)-C(8)-H(8)	120.0	C(9)-C(8)-H(8)	120.0
C(10)-C(9)-C(8)	120.4(4)	C(10)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8	C(9)-C(10)-C(11)	119.7(4)

C(9)-C(10)-H(10)	120.1	C(11)-C(10)-H(10)	120.1
C(10)-C(11)-C(6)	119.9(4)	C(10)-C(11)-C(3)	124.1(4)
C(6)-C(11)-C(3)	116.0(4)	C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	Si(2)-C(19)-H(19A)	109.5
Si(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(21A)-C(20A)-Pd(1)	70.5(3)
C(21A)-C(20A)-H(20A)	116.6	Pd(1)-C(20A)-H(20A)	116.6
C(21A)-C(20A)-H(20B)	116.6	Pd(1)-C(20A)-H(20B)	116.6
H(20A)-C(20A)-H(20B)	113.6	C(22A)-C(21A)-C(20A)	125(1)
C(22A)-C(21A)-Pd(1)	76.0(4)	C(20A)-C(21A)-Pd(1)	69.4(3)
C(22A)-C(21A)-H(21A)	117.8	C(20A)-C(21A)-H(21A)	117.8
Pd(1)-C(21A)-H(21A)	129.6	C(21A)-C(22A)-Pd(1)	69.9(4)
C(21A)-C(22A)-H(22A)	116.7	Pd(1)-C(22A)-H(22A)	116.7
C(21A)-C(22A)-H(22B)	116.7	Pd(1)-C(22A)-H(22B)	116.7
H(22A)-C(22A)-H(22B)	113.7	Pd(1)-C(21B)-H(21B)	135.9
C(42A)-Pd(2)-C(43A)	40.1(3)	C(42A)-Pd(2)-C(43B)	39.8(5)
C(43A)-Pd(2)-C(43B)	30.6(5)	C(42A)-Pd(2)-C(44A)	67.5(2)
C(43A)-Pd(2)-C(44A)	34.3(3)	C(43B)-Pd(2)-C(44A)	32.8(4)
C(42A)-Pd(2)-P(2)	104.1(1)	C(43A)-Pd(2)-P(2)	139.7(2)
C(43B)-Pd(2)-P(2)	138.2(4)	C(44A)-Pd(2)-P(2)	171.0(2)
C(42A)-Pd(2)-Cl(2)	167.2(1)	C(43A)-Pd(2)-Cl(2)	128.2(2)
C(43B)-Pd(2)-Cl(2)	128.1(4)	C(44A)-Pd(2)-Cl(2)	99.6(2)
P(2)-Pd(2)-Cl(2)	88.68(4)	C(28)-P(2)-C(27)	97.2(2)
C(28)-P(2)-C(23)	96.7(2)	C(27)-P(2)-C(23)	100.4(2)
C(28)-P(2)-Pd(2)	125.7(2)	C(27)-P(2)-Pd(2)	116.3(1)
C(23)-P(2)-Pd(2)	115.9(1)	C(36)-Si(3)-C(37)	109.1(2)
C(36)-Si(3)-C(38)	109.3(3)	C(37)-Si(3)-C(38)	105.3(2)
C(36)-Si(3)-C(23)	111.9(2)	C(37)-Si(3)-C(23)	112.3(2)
C(38)-Si(3)-C(23)	108.7(2)	C(41)-Si(4)-C(40)	110.2(3)
C(41)-Si(4)-C(27)	110.6(2)	C(40)-Si(4)-C(27)	111.5(2)
C(41)-Si(4)-C(39)	104.2(3)	C(40)-Si(4)-C(39)	110.5(2)
C(27)-Si(4)-C(39)	109.6(2)	C(24)-C(23)-P(2)	111.3(3)
C(24)-C(23)-Si(3)	124.6(3)	P(2)-C(23)-Si(3)	124.0(2)
C(23)-C(24)-C(34)	127.5(4)	C(23)-C(24)-C(25)	119.3(4)
C(34)-C(24)-C(25)	113.2(4)	C(33)-C(25)-C(24)	108.4(4)
C(33)-C(25)-C(26)	109.7(3)	C(24)-C(25)-C(26)	106.1(3)
C(33)-C(25)-H(25)	110.8	C(24)-C(25)-H(25)	110.8
C(26)-C(25)-H(25)	110.8	C(27)-C(26)-C(35)	126.0(4)
C(27)-C(26)-C(25)	118.5(4)	C(35)-C(26)-C(25)	115.4(4)
C(26)-C(27)-P(2)	111.9(3)	C(26)-C(27)-Si(4)	123.3(3)
P(2)-C(27)-Si(4)	124.7(2)	C(29)-C(28)-C(33)	120.9(4)
C(29)-C(28)-P(2)	127.3(3)	C(33)-C(28)-P(2)	111.7(3)

C(28)-C(29)-C(30)	119.2(4)	C(28)-C(29)-H(29)	120.4
C(30)-C(29)-H(29)	120.4	C(31)-C(30)-C(29)	120.2(4)
C(31)-C(30)-H(30)	119.9	C(29)-C(30)-H(30)	119.9
C(30)-C(31)-C(32)	120.6(4)	C(30)-C(31)-H(31)	119.7
C(32)-C(31)-H(31)	119.7	C(33)-C(32)-C(31)	119.0(4)
C(33)-C(32)-H(32)	120.5	C(31)-C(32)-H(32)	120.5
C(32)-C(33)-C(28)	120.0(4)	C(32)-C(33)-C(25)	122.9(4)
C(28)-C(33)-C(25)	117.1(4)	C(24)-C(34)-H(34A)	109.5
C(24)-C(34)-H(34B)	109.5	H(34A)-C(34)-H(34B)	109.5
C(24)-C(34)-H(34C)	109.5	H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5	C(26)-C(35)-H(35A)	109.5
C(26)-C(35)-H(35B)	109.5	H(35A)-C(35)-H(35B)	109.5
C(26)-C(35)-H(35C)	109.5	H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5	Si(3)-C(36)-H(36A)	109.5
Si(3)-C(36)-H(36B)	109.5	H(36A)-C(36)-H(36B)	109.5
Si(3)-C(36)-H(36C)	109.5	H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5	Si(3)-C(37)-H(37A)	109.5
Si(3)-C(37)-H(37B)	109.5	H(37A)-C(37)-H(37B)	109.5
Si(3)-C(37)-H(37C)	109.5	H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5	Si(3)-C(38)-H(38A)	109.5
Si(3)-C(38)-H(38B)	109.5	H(38A)-C(38)-H(38B)	109.5
Si(3)-C(38)-H(38C)	109.5	H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5	Si(4)-C(39)-H(39A)	109.5
Si(4)-C(39)-H(39B)	109.5	H(39A)-C(39)-H(39B)	109.5
Si(4)-C(39)-H(39C)	109.5	H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5	Si(4)-C(40)-H(40A)	109.5
Si(4)-C(40)-H(40B)	109.5	H(40A)-C(40)-H(40B)	109.5
Si(4)-C(40)-H(40C)	109.5	H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5	Si(4)-C(41)-H(41A)	109.5
Si(4)-C(41)-H(41B)	109.5	H(41A)-C(41)-H(41B)	109.5
Si(4)-C(41)-H(41C)	109.5	H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5	C(43A)-C(42A)-Pd(2)	71.6(4)
C(43A)-C(42A)-H(42A)	116.4	Pd(2)-C(42A)-H(42A)	116.4
C(43A)-C(42A)-H(42B)	116.4	Pd(2)-C(42A)-H(42B)	116.4
H(42A)-C(42A)-H(42B)	113.4	C(44A)-C(43A)-C(42A)	121.5(8)
C(44A)-C(43A)-Pd(2)	75.1(4)	C(42A)-C(43A)-Pd(2)	68.3(3)
C(44A)-C(43A)-H(43A)	119.3	C(42A)-C(43A)-H(43A)	119.3
Pd(2)-C(43A)-H(43A)	129.8	C(43A)-C(44A)-Pd(2)	70.5(4)
C(43A)-C(44A)-H(44A)	116.6	Pd(2)-C(44A)-H(44A)	116.6
C(43A)-C(44A)-H(44B)	116.6	Pd(2)-C(44A)-H(44B)	116.6
H(44A)-C(44A)-H(44B)	113.6	Pd(2)-C(43B)-H(43B)	133.2

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb453

atom	U11	U22	U33	U23	U13	U12
Pd(1)	31(1)	32(1)	23(1)	0(1)	-4(1)	-2(1)
Cl(1)	38(1)	36(1)	42(1)	0(1)	1(1)	2(1)
P(1)	27(1)	28(1)	22(1)	0(1)	-5(1)	-1(1)
Si(1)	32(1)	36(1)	32(1)	1(1)	-12(1)	-3(1)
Si(2)	36(1)	32(1)	29(1)	-5(1)	-11(1)	-2(1)
C(1)	34(2)	32(2)	25(2)	-3(2)	-7(2)	-1(2)
C(2)	33(2)	31(2)	25(2)	-3(2)	-8(2)	2(2)
C(3)	30(2)	35(2)	25(2)	1(2)	-4(2)	-1(2)
C(4)	29(2)	31(2)	28(2)	-1(2)	-6(2)	0(2)
C(5)	28(2)	30(2)	27(2)	-3(2)	-6(2)	-1(2)
C(6)	24(2)	32(2)	27(2)	-6(2)	-7(2)	-3(2)
C(7)	39(2)	33(2)	33(2)	-1(2)	-3(2)	-4(2)
C(8)	37(3)	34(2)	51(3)	-1(2)	-5(2)	4(2)
C(9)	32(2)	46(3)	38(2)	-7(2)	-1(2)	6(2)
C(10)	34(2)	39(2)	30(2)	-2(2)	-4(2)	-3(2)
C(11)	33(2)	32(2)	25(2)	-5(2)	-9(2)	-2(2)

C(12)	45(3)	42(3)	25(2)	4(2)	-9(2)	0(2)
C(13)	36(2)	37(2)	42(3)	4(2)	-4(2)	-9(2)
C(14)	47(3)	51(3)	38(3)	2(2)	-15(2)	-18(2)
C(15)	60(3)	52(3)	34(2)	-2(2)	-23(2)	-9(2)
C(16)	35(3)	46(3)	71(4)	1(3)	-20(3)	1(2)
C(17)	41(3)	44(3)	27(2)	-2(2)	-9(2)	-3(2)
C(18)	54(3)	37(3)	44(3)	-11(2)	-14(2)	2(2)
C(19)	47(3)	53(3)	44(3)	2(2)	-20(2)	-12(2)
C(20A)	53(3)	34(2)	37(2)	4(2)	-4(2)	5(2)
C(21A)	56(6)	40(5)	26(4)	16(3)	-9(4)	-7(4)
C(22A)	80(4)	43(3)	52(3)	20(3)	29(3)	8(3)
C(20B)	53(3)	34(2)	37(2)	4(2)	-4(2)	5(2)
C(21B)	60(10)	31(7)	43(8)	14(6)	1(7)	-3(6)
C(22B)	80(4)	43(3)	52(3)	20(3)	29(3)	8(3)
Pd(2)	32(1)	33(1)	30(1)	-1(1)	-4(1)	-3(1)
Cl(2)	56(1)	40(1)	29(1)	-2(1)	-7(1)	-10(1)
P(2)	27(1)	30(1)	26(1)	-4(1)	-5(1)	-1(1)
Si(3)	32(1)	35(1)	41(1)	1(1)	-12(1)	0(1)
Si(4)	35(1)	35(1)	27(1)	-7(1)	-9(1)	5(1)
C(23)	27(2)	34(2)	32(2)	-5(2)	-6(2)	-1(2)
C(24)	29(2)	36(2)	32(2)	-11(2)	-5(2)	-1(2)
C(25)	31(2)	38(2)	24(2)	-4(2)	-3(2)	-5(2)
C(26)	32(2)	37(2)	25(2)	-6(2)	-8(2)	-4(2)
C(27)	33(2)	30(2)	26(2)	-6(2)	-7(2)	1(2)
C(28)	26(2)	34(2)	33(2)	-6(2)	-7(2)	3(2)
C(29)	31(2)	36(2)	41(2)	-8(2)	-9(2)	1(2)
C(30)	45(3)	40(3)	48(3)	-16(2)	-17(2)	3(2)
C(31)	38(3)	50(3)	40(3)	-20(2)	-11(2)	7(2)
C(32)	34(2)	47(3)	31(2)	-10(2)	-7(2)	5(2)
C(33)	29(2)	39(2)	29(2)	-8(2)	-7(2)	4(2)
C(34)	37(3)	46(3)	37(2)	-7(2)	-5(2)	-4(2)
C(35)	46(3)	39(3)	30(2)	-2(2)	-11(2)	-5(2)
C(36)	51(3)	51(3)	42(3)	6(2)	-24(2)	-5(2)
C(37)	44(3)	39(3)	55(3)	9(2)	-12(2)	0(2)
C(38)	32(3)	43(3)	72(4)	4(3)	-8(2)	4(2)
C(39)	55(3)	49(3)	40(3)	-8(2)	-19(2)	16(2)
C(40)	62(3)	43(3)	41(3)	-14(2)	-23(2)	13(2)
C(41)	30(2)	58(3)	52(3)	4(2)	-3(2)	2(2)
C(42A)	45(3)	42(3)	49(3)	-6(2)	-2(2)	-16(2)
C(43A)	34(5)	42(5)	51(5)	2(4)	-1(4)	-16(4)
C(44A)	89(5)	61(4)	45(3)	4(3)	9(3)	-36(3)
C(42B)	45(3)	42(3)	49(3)	-6(2)	-2(2)	-16(2)
C(43B)	50(10)	38(8)	60(10)	8(7)	-1(7)	-15(7)
C(44B)	89(5)	61(4)	45(3)	4(3)	9(3)	-36(3)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb453

atom	x	y	z	U(eq)
H(3)	2667	3350	2929	36
H(7)	2221	634	5108	42
H(8)	4047	30	4316	49
H(9)	5026	769	3097	47
H(10)	4247	2132	2694	42
H(12A)	-628	3206	2456	55
H(12B)	856	3012	2041	55
H(12C)	515	3926	2425	55
H(13A)	3911	4366	3875	57

H(13B)	2761	4855	4432	57
H(13C)	2644	4754	3466	57
H(14A)	-3467.0002	1200	4516	67
H(14B)	-2929	1802	5175	67
H(14C)	-2022	1027	4818	67
H(15A)	-1244	1857	2413	71
H(15B)	-2682	1446	2728	71
H(15C)	-1359	993	3009	71
H(16A)	-3930	2954	3635	74
H(16B)	-2688	3528	3213	74
H(16C)	-3068	3492	4201	74
H(17A)	1949	3306	7313	55
H(17B)	1911	2530	6707	55
H(17C)	567	3041	6995	55
H(18A)	1018	5264	5569	66
H(18B)	1042	5141	6555	66
H(18C)	-116	4699	6125	66
H(19A)	4245	3773	5529	70
H(19B)	3975	4139	6434	70
H(19C)	3845	4766	5626	70
H(20A)	-335	105	6118	50
H(20B)	1083	527	6338	50
H(21A)	-138	963	7571	49
H(22A)	-2087	1592	7615	75
H(22B)	-2505	809	7040	75
H(20C)	252	201	5887	50
H(20D)	807	555	6729	50
H(21B)	-1781	184	6644	55
H(22C)	-1491	1305	7695	75
H(22D)	-2791.9998	1251	7159	75
H(25)	3738	6422	2565	37
H(29)	7048	9017	1467	43
H(30)	6847	9449	2839	51
H(31)	5507	8660	3884	50
H(32)	4345	7427	3576	44
H(34A)	1477	6906	1130	60
H(34B)	1559	7084	2086	60
H(34C)	1898	6145	1759	60
H(35A)	5679	4778	1617	57
H(35B)	4206	4983	2043	57
H(35C)	5470	5089	2546	57
H(36A)	3224	7020	-1165	70
H(36B)	1837	7530	-1172	70
H(36C)	1983	6753	-492.0000	70
H(37A)	4407	9271	-345	69
H(37B)	3431	9240	-1057	69
H(37C)	4735	8641	-1089	69
H(38A)	854	8139	671	74
H(38B)	1132	8968	38	74
H(38C)	1800	8902	889	74
H(39A)	9281	4863	1191	70
H(39B)	7835	4673	1690	70
H(39C)	8634	5532	1837	70
H(40A)	6768	5281	-649.0001	71
H(40B)	6404	4577	104	71
H(40C)	7878	4608	-385	71
H(41A)	9823	6132	-38	70
H(41B)	9088	6943	379	70
H(41C)	8737	6667	-507	70
H(42A)	7511	9696	-230	54
H(42B)	8452	9058	319	54
H(43A)	9620	8706	-976	51
H(44A)	8549	8398	-2040	80

H(44B)	7656	9276	-1831	80
H(42C)	7462	9516	200	54
H(42D)	8916	9044	-60	54
H(43B)	7397	9794	-1227	61
H(44C)	9052	8611	-1722	80
H(44D)	7629	8832	-2112	80

II.8. Crystallographic data for IV-30

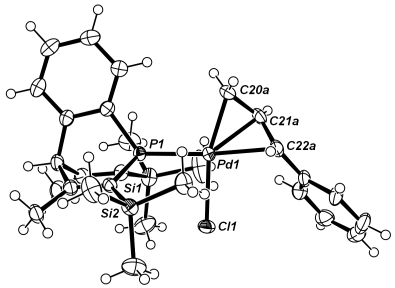


Table 1. Crystal data for mb682

Compound	mb682
Molecular formula	$C_{28}H_{38}ClPPdSi_2$
Molecular weight	603.58
Crystal habit	Yellow Block
Crystal dimensions(mm)	0.50x0.30x0.30
Crystal system	monoclinic
Space group	P 2_1/n
a(Å)	11.436(1)
b(Å)	13.864(1)
c(Å)	19.143(1)
α(°)	90.00
β(°)	95.287(1)
γ(°)	90.00
V(Å^3)	3022.2(4)
Z	4
d(g-cm^{-3})	1.327
F(000)	1248
μ(cm^{-1})	0.849
Absorption corrections	multi-scan ; 0.6762 min, 0.7848 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans

Maximum θ	30.02
HKL ranges	-16 14 ; -19 19 ; -25 26
Reflections measured	25392
Unique data	8688
Rint	0.0259
Reflections used	7262
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	329
Reflections / parameter	22
wR2	0.0683
R1	0.0267
Weights a, b	0.0271 ; 1.2432
GoF	1.049
difference peak / hole (e Å^{-3})	0.593(0.063) / -0.611(0.063)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb682

atom	x	y	z	U(eq)
Pd(1)	8299(1)	3150(1)	392(1)	21(1)
Cl(1A)	8318(8)	1877(4)	1238(2)	29(1)
Cl(1B)	8000(30)	1931(7)	1180(6)	35(2)
P(1)	8016(1)	4223(1)	1272(1)	20(1)
Si(1)	5248(1)	3458(1)	1253(1)	32(1)
Si(2)	10561(1)	3600(1)	2118(1)	27(1)
C(1)	6603(1)	4094(1)	1660(1)	26(1)
C(2)	6553(2)	4666(1)	2224(1)	27(1)
C(3)	7591(2)	5340(1)	2433(1)	27(1)
C(4)	8695(2)	4727(1)	2581(1)	26(1)
C(5)	9064(1)	4180(1)	2065(1)	23(1)
C(6)	7972(1)	5539(1)	1187(1)	24(1)
C(7)	8120(2)	6072(1)	591(1)	30(1)
C(8)	8024(2)	7076(1)	616(1)	37(1)
C(9)	7784(2)	7525(1)	1232(1)	39(1)
C(10)	7640(2)	6995(1)	1834(1)	34(1)
C(11)	7738(2)	5997(1)	1811(1)	27(1)
C(12)	5563(2)	4751(1)	2685(1)	37(1)
C(13)	9272(2)	4815(1)	3319(1)	34(1)
C(14)	5446(2)	2818(2)	419(1)	70(1)
C(15)	4686(2)	2557(2)	1869(1)	50(1)
C(16)	4132(2)	4424(2)	1027(1)	47(1)
C(17)	10629(2)	2527(2)	2707(1)	48(1)
C(18)	11682(2)	4521(2)	2441(1)	45(1)
C(19)	10967(2)	3240(1)	1232(1)	35(1)
C(20A)	8464(2)	3970(1)	-528(1)	32(1)
C(21A)	8041(2)	3014(2)	-721(1)	32(1)
C(22A)	8739(2)	2224(2)	-520(1)	29(1)
C(23A)	8366(2)	1205(2)	-584(1)	27(1)
C(24A)	9197(3)	512(2)	-717(2)	37(1)
C(25A)	8888(3)	-456(2)	-792(2)	43(1)
C(26A)	7754(3)	-744(2)	-714(2)	42(1)
C(27A)	6911(3)	-60(2)	-561(2)	40(1)
C(28A)	7228(3)	909(2)	-503(2)	34(1)
C(20B)	8464(2)	3970(1)	-528(1)	32(1)
C(21B)	8771(7)	3018(4)	-664(4)	32(1)

C(22B)	7935(6)	2295(4)	-631(4)	29(1)
C(23B)	7950(7)	1285(4)	-621(5)	27(1)
C(24B)	8998(6)	866(5)	-779(5)	37(1)
C(25B)	9106(8)	-133(5)	-793(5)	43(1)
C(26B)	8170(10)	-712(4)	-649(6)	42(1)
C(27B)	7118(8)	-293(6)	-491(7)	40(1)
C(28B)	7010(6)	705(6)	-477(6)	34(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb682

Pd(1)-C(20A)	2.119(2)	Pd(1)-C(21A)	2.133(2)
Pd(1)-C(21B)	2.148(7)	Pd(1)-C(22A)	2.260(2)
Pd(1)-P(1)	2.2929(4	Pd(1)-C(22B)	2.293(6)
Pd(1)-Cl(1B)	2.310(8)	Pd(1)-Cl(1A)	2.394(5)
P(1)-C(6)	1.832(2)	P(1)-C(5)	1.845(2)
P(1)-C(1)	1.848(2)	Si(1)-C(14)	1.858(2)
Si(1)-C(15)	1.872(2)	Si(1)-C(16)	1.872(2)
Si(1)-C(1)	1.887(2)	Si(2)-C(17)	1.865(2)
Si(2)-C(19)	1.867(2)	Si(2)-C(18)	1.874(2)
Si(2)-C(5)	1.886(2)	C(1)-C(2)	1.345(2)
C(2)-C(12)	1.503(2)	C(2)-C(3)	1.534(2)
C(3)-C(11)	1.520(2)	C(3)-C(4)	1.527(2)
C(3)-H(3)	1.0000	C(4)-C(5)	1.344(2)
C(4)-C(13)	1.507(2)	C(6)-C(7)	1.382(2)
C(6)-C(11)	1.401(2)	C(7)-C(8)	1.398(3)
C(7)-H(7)	0.9500	C(8)-C(9)	1.384(3)
C(8)-H(8)	0.9500	C(9)-C(10)	1.389(3)
C(9)-H(9)	0.9500	C(10)-C(11)	1.389(2)
C(10)-H(10)	0.9500	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800	C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800	C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800	C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800	C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800	C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800	C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800	C(20A)-C(21A)	1.447(3)
C(20A)-H(20A)	0.9900	C(20A)-H(20B)	0.9900
C(21A)-C(22A)	1.388(3)	C(21A)-H(21A)	0.9500
C(22A)-C(23A)	1.478(3)	C(22A)-H(22A)	0.9500
C(23A)-C(28A)	1.386(4)	C(23A)-C(24A)	1.391(3)
C(24A)-C(25A)	1.392(4)	C(24A)-H(24A)	0.9500
C(25A)-C(26A)	1.378(4)	C(25A)-H(25A)	0.9500
C(26A)-C(27A)	1.402(4)	C(26A)-H(26A)	0.9500
C(27A)-C(28A)	1.392(4)	C(27A)-H(27A)	0.9500
C(28A)-H(28A)	0.9500	C(21B)-C(22B)	1.391(7)
C(21B)-H(21B)	0.9500	C(22B)-C(23B)	1.401(6)
C(22B)-H(22B)	0.9500	C(23B)-C(24B)	1.3900
C(23B)-C(28B)	1.3900	C(24B)-C(25B)	1.3900
C(24B)-H(24B)	0.9500	C(25B)-C(26B)	1.3900
C(25B)-H(25B)	0.9500	C(26B)-C(27B)	1.3900
C(26B)-H(26B)	0.9500	C(27B)-C(28B)	1.3900
C(27B)-H(27B)	0.9500	C(28B)-H(28B)	0.9500

C(20A)-Pd(1)-C(21A)	39.80(8)	C(20A)-Pd(1)-C(21B)	38.2(2)
C(21A)-Pd(1)-C(21B)	22.4(2)	C(20A)-Pd(1)-C(22A)	67.63(8)

C(21A)-Pd(1)-C(22A)	36.7(1)	C(21B)-Pd(1)-C(22A)	29.7(2)
C(20A)-Pd(1)-P(1)	106.97(5)	C(21A)-Pd(1)-P(1)	140.87(7)
C(21B)-Pd(1)-P(1)	144.2(2)	C(22A)-Pd(1)-P(1)	172.91(6)
C(20A)-Pd(1)-C(22B)	65.8(2)	C(21A)-Pd(1)-C(22B)	26.3(2)
C(21B)-Pd(1)-C(22B)	36.3(2)	C(22A)-Pd(1)-C(22B)	23.5(2)
P(1)-Pd(1)-C(22B)	159.4(2)	C(20A)-Pd(1)-Cl(1B)	164.7(3)
C(21A)-Pd(1)-Cl(1B)	124.9(4)	C(21B)-Pd(1)-Cl(1B)	128.1(3)
C(22A)-Pd(1)-Cl(1B)	98.4(2)	P(1)-Pd(1)-Cl(1B)	87.5(2)
C(22B)-Pd(1)-Cl(1B)	98.8(3)	C(20A)-Pd(1)-Cl(1A)	164.1(1)
C(21A)-Pd(1)-Cl(1A)	127.1(1)	C(21B)-Pd(1)-Cl(1A)	125.9(2)
C(22A)-Pd(1)-Cl(1A)	96.6(1)	P(1)-Pd(1)-Cl(1A)	88.5(1)
C(22B)-Pd(1)-Cl(1A)	100.7(2)	Cl(1B)-Pd(1)-Cl(1A)	8.9(6)
C(6)-P(1)-C(5)	96.64(7)	C(6)-P(1)-C(1)	96.56(7)
C(5)-P(1)-C(1)	101.08(7)	C(6)-P(1)-Pd(1)	125.83(5)
C(5)-P(1)-Pd(1)	117.31(5)	C(1)-P(1)-Pd(1)	114.81(5)
C(14)-Si(1)-C(15)	107.3(1)	C(14)-Si(1)-C(16)	106.1(1)
C(15)-Si(1)-C(16)	110.8(1)	C(14)-Si(1)-C(1)	114.7(1)
C(15)-Si(1)-C(1)	111.6(1)	C(16)-Si(1)-C(1)	106.2(1)
C(17)-Si(2)-C(19)	109.7(1)	C(17)-Si(2)-C(18)	110.8(1)
C(19)-Si(2)-C(18)	105.2(1)	C(17)-Si(2)-C(5)	111.1(1)
C(19)-Si(2)-C(5)	111.47(8)	C(18)-Si(2)-C(5)	108.5(1)
C(2)-C(1)-P(1)	111.6(1)	C(2)-C(1)-Si(1)	120.8(1)
P(1)-C(1)-Si(1)	126.5(1)	C(1)-C(2)-C(12)	127.4(2)
C(1)-C(2)-C(3)	118.7(2)	C(12)-C(2)-C(3)	113.8(2)
C(11)-C(3)-C(4)	109.2(1)	C(11)-C(3)-C(2)	107.4(1)
C(4)-C(3)-C(2)	108.4(1)	C(11)-C(3)-H(3)	110.6
C(4)-C(3)-H(3)	110.6	C(2)-C(3)-H(3)	110.6
C(5)-C(4)-C(13)	126.5(2)	C(5)-C(4)-C(3)	119.2(1)
C(13)-C(4)-C(3)	114.3(1)	C(4)-C(5)-P(1)	111.3(1)
C(4)-C(5)-Si(2)	123.1(1)	P(1)-C(5)-Si(2)	125.1(1)
C(7)-C(6)-C(11)	120.6(2)	C(7)-C(6)-P(1)	127.0(1)
C(11)-C(6)-P(1)	112.4(1)	C(6)-C(7)-C(8)	119.3(2)
C(6)-C(7)-H(7)	120.4	C(8)-C(7)-H(7)	120.4
C(9)-C(8)-C(7)	119.9(2)	C(9)-C(8)-H(8)	120.0
C(7)-C(8)-H(8)	120.0	C(8)-C(9)-C(10)	121.1(2)
C(8)-C(9)-H(9)	119.4	C(10)-C(9)-H(9)	119.4
C(9)-C(10)-C(11)	119.1(2)	C(9)-C(10)-H(10)	120.5
C(11)-C(10)-H(10)	120.5	C(10)-C(11)-C(6)	120.0(2)
C(10)-C(11)-C(3)	123.9(2)	C(6)-C(11)-C(3)	116.1(1)
C(2)-C(12)-H(12A)	109.5	C(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5	C(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5	H(12B)-C(12)-H(12C)	109.5
C(4)-C(13)-H(13A)	109.5	C(4)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5	C(4)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5	H(13B)-C(13)-H(13C)	109.5
Si(1)-C(14)-H(14A)	109.5	Si(1)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	Si(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
Si(1)-C(15)-H(15A)	109.5	Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5	Si(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
Si(1)-C(16)-H(16A)	109.5	Si(1)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5	Si(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(16B)-C(16)-H(16C)	109.5
Si(2)-C(17)-H(17A)	109.5	Si(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5	Si(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(17B)-C(17)-H(17C)	109.5
Si(2)-C(18)-H(18A)	109.5	Si(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5	Si(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5	H(18B)-C(18)-H(18C)	109.5
Si(2)-C(19)-H(19A)	109.5	Si(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5	Si(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5	H(19B)-C(19)-H(19C)	109.5

C(21A)-C(20A)-Pd(1)	70.6(1)	C(21A)-C(20A)-H(20A)	116.6
Pd(1)-C(20A)-H(20A)	116.6	C(21A)-C(20A)-H(20B)	116.6
Pd(1)-C(20A)-H(20B)	116.6	H(20A)-C(20A)-H(20B)	113.6
C(22A)-C(21A)-C(20A)	118.7(2)	C(22A)-C(21A)-Pd(1)	76.6(1)
C(20A)-C(21A)-Pd(1)	69.6(1)	C(22A)-C(21A)-H(21A)	120.6
C(20A)-C(21A)-H(21A)	120.6	Pd(1)-C(21A)-H(21A)	124.7
C(21A)-C(22A)-C(23A)	125.2(2)	C(21A)-C(22A)-Pd(1)	66.7(1)
C(23A)-C(22A)-Pd(1)	121.6(2)	C(21A)-C(22A)-H(22A)	117.4
C(23A)-C(22A)-H(22A)	117.4	Pd(1)-C(22A)-H(22A)	82.0
C(28A)-C(23A)-C(24A)	118.6(2)	C(28A)-C(23A)-C(22A)	122.8(2)
C(24A)-C(23A)-C(22A)	118.6(2)	C(23A)-C(24A)-C(25A)	120.9(3)
C(23A)-C(24A)-H(24A)	119.5	C(25A)-C(24A)-H(24A)	119.5
C(26A)-C(25A)-C(24A)	120.0(3)	C(26A)-C(25A)-H(25A)	120.0
C(24A)-C(25A)-H(25A)	120.0	C(25A)-C(26A)-C(27A)	120.0(2)
C(25A)-C(26A)-H(26A)	120.0	C(27A)-C(26A)-H(26A)	120.0
C(28A)-C(27A)-C(26A)	119.3(3)	C(28A)-C(27A)-H(27A)	120.4
C(26A)-C(27A)-H(27A)	120.4	C(23A)-C(28A)-C(27A)	121.2(3)
C(23A)-C(28A)-H(28A)	119.4	C(27A)-C(28A)-H(28A)	119.4
C(22B)-C(21B)-Pd(1)	77.5(4)	C(22B)-C(21B)-H(21B)	120.4
Pd(1)-C(21B)-H(21B)	123.7	C(21B)-C(22B)-C(23B)	135.5(6)
C(21B)-C(22B)-Pd(1)	66.2(4)	C(23B)-C(22B)-Pd(1)	120.3(5)
C(21B)-C(22B)-H(22B)	112.2	C(23B)-C(22B)-H(22B)	112.2
Pd(1)-C(22B)-H(22B)	82.4	C(24B)-C(23B)-C(28B)	120.0
C(24B)-C(23B)-C(22B)	115.2(5)	C(28B)-C(23B)-C(22B)	124.8(5)
C(23B)-C(24B)-C(25B)	120.0	C(23B)-C(24B)-H(24B)	120.0
C(25B)-C(24B)-H(24B)	120.0	C(26B)-C(25B)-C(24B)	120.0
C(26B)-C(25B)-H(25B)	120.0	C(24B)-C(25B)-H(25B)	120.0
C(25B)-C(26B)-C(27B)	120.0	C(25B)-C(26B)-H(26B)	120.0
C(27B)-C(26B)-H(26B)	120.0	C(28B)-C(27B)-C(26B)	120.0
C(28B)-C(27B)-H(27B)	120.0	C(26B)-C(27B)-H(27B)	120.0
C(27B)-C(28B)-C(23B)	120.0	C(27B)-C(28B)-H(28B)	120.0
C(23B)-C(28B)-H(28B)	120.0		

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb682

atom	U11	U22	U33	U23	U13	U12
Pd(1)	24(1)	22(1)	18(1)	-1(1)	3(1)	0(1)
Cl(1A)	36(1)	27(1)	26(1)	7(1)	4(1)	-3(1)
Cl(1B)	50(6)	29(1)	27(2)	8(1)	7(2)	-1(2)
P(1)	20(1)	22(1)	20(1)	-2(1)	3(1)	1(1)
Si(1)	19(1)	37(1)	39(1)	-6(1)	3(1)	0(1)
Si(2)	22(1)	32(1)	25(1)	0(1)	0(1)	2(1)
C(1)	20(1)	28(1)	29(1)	-3(1)	6(1)	1(1)
C(2)	26(1)	27(1)	30(1)	0(1)	8(1)	3(1)
C(3)	30(1)	27(1)	25(1)	-6(1)	7(1)	1(1)
C(4)	28(1)	26(1)	23(1)	-2(1)	4(1)	-3(1)
C(5)	24(1)	24(1)	20(1)	0(1)	1(1)	-1(1)
C(6)	22(1)	24(1)	27(1)	-1(1)	2(1)	2(1)
C(7)	27(1)	31(1)	30(1)	2(1)	2(1)	0(1)
C(8)	40(1)	30(1)	41(1)	9(1)	2(1)	-1(1)
C(9)	41(1)	22(1)	52(1)	1(1)	2(1)	1(1)
C(10)	33(1)	26(1)	42(1)	-8(1)	5(1)	2(1)
C(11)	26(1)	25(1)	30(1)	-3(1)	5(1)	1(1)
C(12)	36(1)	37(1)	41(1)	-5(1)	18(1)	3(1)
C(13)	43(1)	38(1)	22(1)	-6(1)	2(1)	-5(1)
C(14)	30(1)	111(2)	68(2)	-51(2)	4(1)	-15(1)
C(15)	40(1)	37(1)	71(2)	6(1)	-3(1)	-8(1)
C(16)	29(1)	56(1)	55(1)	10(1)	-1(1)	5(1)
C(17)	48(1)	48(1)	45(1)	15(1)	-5(1)	10(1)
C(18)	31(1)	65(1)	40(1)	-12(1)	3(1)	-12(1)
C(19)	24(1)	43(1)	37(1)	-7(1)	5(1)	4(1)

C(20A)	43(1)	32(1)	20(1)	5(1)	5(1)	5(1)
C(21A)	41(1)	38(1)	14(1)	-1(1)	0(1)	4(1)
C(22A)	33(1)	34(1)	20(1)	-4(1)	5(1)	3(1)
C(23A)	32(2)	29(1)	21(1)	-6(1)	5(1)	8(1)
C(24A)	45(2)	29(2)	38(1)	-10(1)	8(1)	8(1)
C(25A)	54(2)	26(2)	48(1)	-15(1)	-2(1)	7(2)
C(26A)	59(2)	28(1)	35(1)	-1(1)	-18(2)	0(1)
C(27A)	46(2)	38(2)	34(1)	3(1)	-9(1)	-3(1)
C(28A)	37(1)	32(2)	34(1)	-6(1)	2(1)	-2(1)
C(20B)	43(1)	32(1)	20(1)	5(1)	5(1)	5(1)
C(21B)	41(1)	38(1)	14(1)	-1(1)	0(1)	4(1)
C(22B)	33(1)	34(1)	20(1)	-4(1)	5(1)	3(1)
C(23B)	32(2)	29(1)	21(1)	-6(1)	5(1)	8(1)
C(24B)	45(2)	29(2)	38(1)	-10(1)	8(1)	8(1)
C(25B)	54(2)	26(2)	48(1)	-15(1)	-2(1)	7(2)
C(26B)	59(2)	28(1)	35(1)	-1(1)	-18(2)	0(1)
C(27B)	46(2)	38(2)	34(1)	3(1)	-9(1)	-3(1)
C(28B)	37(1)	32(2)	34(1)	-6(1)	2(1)	-2(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb682

atom	x	y	z	U(eq)
H(3)	7439	5728	2856	32
H(7)	8286	5759	170	35
H(8)	8123	7450	209	45
H(9)	7716	8208	1244	46
H(10)	7477	7310	2255	40
H(12A)	4961	4269	2544	56
H(12B)	5220	5398	2637	56
H(12C)	5863	4642	3175	56
H(13A)	9901	4335	3393	52
H(13B)	8687	4703	3653	52
H(13C)	9603	5463	3389	52
H(14A)	4686	2575	215	104
H(14B)	5989	2277	514	104
H(14C)	5768	3265	89	104
H(15A)	4066	2168	1618	75
H(15B)	4366	2896	2258	75
H(15C)	5330	2136	2052	75
H(16A)	4438	4879	697	71
H(16B)	3967	4766	1455	71
H(16C)	3407	4130	811	71
H(17A)	10056	2045	2521	72
H(17B)	10448	2723	3177	72
H(17C)	11420	2248	2734	72
H(18A)	11561	4702	2924	68
H(18B)	11602	5094	2140	68
H(18C)	12471	4249	2428	68
H(19A)	11790	3035	1267	52
H(19B)	10858	3790	911	52
H(19C)	10463	2706	1052	52
H(20A)	7902	4507	-621	38
H(20B)	9273	4128	-634	38
H(21A)	7300	2928	-981	38
H(22A)	9519	2349	-325	35
H(24A)	9986	703	-758	44
H(25A)	9459	-919	-898	52

H(26A)	7544	-1405	-763	50
H(27A)	6132	-255	-497	48
H(28A)	6655	1374	-407	41
H(20C)	7725	4209	-778	38
H(20D)	9109	4449	-503.0000	38
H(21B)	9541	2867	-779	38
H(22B)	7167	2548	-609	35
H(24B)	9641	1262	-878.0001	44
H(25B)	9822	-419	-901	52
H(26B)	8240	-1394	-658.0001	50
H(27B)	6476	-688.9999	-392	48
H(28B)	6294	992	-369	41

II.9. Crystallographic data for IV-32

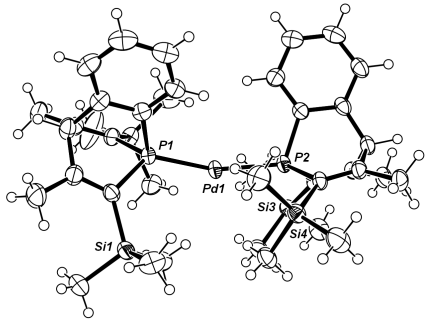


Table 1. Crystal data for mb462

Compound	mb462
Molecular formula	$C_{38}H_{58}P_2PdSi_4$
Molecular weight	795.54
Crystal habit	Pale Yellow Plate
Crystal dimensions(mm)	0.50x0.26x0.04
Crystal system	orthorhombic
Space group	Pbca
a(Å)	10.310(1)
b(Å)	18.846(1)
c(Å)	43.610(1)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
V(Å^3)	8473.5(10)
Z	8
d(g-cm^{-3})	1.247
F(000)	3344
μ(cm^{-1})	0.651
Absorption corrections	multi-scan ; 0.7367 min, 0.9744 max

Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	28.70
HKL ranges	-13 12 ; -25 25 ; -58 58
Reflections measured	44281
Unique data	10810
Rint	0.0872
Reflections used	7801
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	422
Reflections / parameter	18
wR2	0.2271
R1	0.0647
Weights a, b	0.1630 ; 0.0000
GoF	1.005
difference peak / hole (e Å^{-3})	1.710(0.165) / -1.876(0.165)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb462

atom	x	y	z	U(eq)
Pd(1)	9789(1)	-462(1)	-1211(1)	29(1)
P(1)	10746(1)	61(1)	-1623(1)	28(1)
P(2)	8321(1)	-705(1)	-838(1)	28(1)
Si(1)	11435(1)	-1422(1)	-1959(1)	38(1)
Si(2)	13004(1)	720(1)	-1217(1)	37(1)
Si(3)	10375(1)	-1325(1)	-360(1)	33(1)
Si(4)	6797(1)	-1709(1)	-1306(1)	34(1)
C(1)	11294(4)	-428(2)	-1971(1)	34(1)
C(2)	11606(4)	5(2)	-2206(1)	41(1)
C(3)	11598(4)	810(2)	-2144(1)	41(1)
C(4)	12482(4)	960(2)	-1870(1)	37(1)
C(5)	12192(4)	654(2)	-1595(1)	34(1)
C(6)	9673(4)	690(2)	-1818(1)	32(1)
C(7)	8414(4)	845(2)	-1734(1)	39(1)
C(8)	7706(5)	1345(2)	-1904(1)	48(1)
C(9)	8264(5)	1701(2)	-2139(1)	53(1)
C(10)	9521(5)	1543(2)	-2232(1)	47(1)
C(11)	10225(4)	1029(2)	-2067(1)	38(1)
C(12)	11976(7)	-204(3)	-2531(1)	64(2)
C(13)	13616(5)	1430(2)	-1941(1)	48(1)
C(14)	12858(6)	-1738(3)	-2190(1)	64(2)
C(15)	11806(4)	-1701(2)	-1562(1)	47(1)
C(16)	9895(5)	-1810(3)	-2101(1)	51(1)
C(17)	11917(6)	1221(3)	-951(1)	68(2)
C(18)	14629(7)	1153(5)	-1229(2)	102(3)
C(19)	13292(5)	-190(2)	-1065(1)	47(1)
C(20)	8651(4)	-1082(2)	-449(1)	30(1)
C(21)	7591(4)	-1094(2)	-270(1)	33(1)

C(22)	6306(4)	-816(2)	-403(1)	35(1)
C(23)	5993(4)	-1245(2)	-698(1)	34(1)
C(24)	6845(3)	-1240(2)	-925(1)	30(1)
C(25)	7498(4)	92(2)	-697(1)	30(1)
C(26)	7817(4)	786(2)	-771(1)	37(1)
C(27)	7143(5)	1346(2)	-638(1)	42(1)
C(28)	6153(5)	1208(2)	-433(1)	47(1)
C(29)	5815(5)	514(2)	-358(1)	41(1)
C(30)	6511(4)	-45(2)	-488(1)	34(1)
C(31)	7495(5)	-1326(2)	60(1)	42(1)
C(32)	4730(4)	-1652(2)	-675(1)	43(1)
C(33)	11329(5)	-482(2)	-335(1)	54(1)
C(34)	10996(4)	-1910(2)	-673(1)	42(1)
C(35)	10606(5)	-1819(3)	10(1)	52(1)
C(36)	8325(4)	-2231(2)	-1337(1)	43(1)
C(37)	5430(5)	-2356(3)	-1356(2)	57(1)
C(38)	6689(5)	-1036(3)	-1618(1)	53(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb462

Pd(1)-P(2)	2.268(1)	Pd(1)-P(1)	2.274(1)
P(1)-C(6)	1.833(4)	P(1)-C(1)	1.861(4)
P(1)-C(5)	1.867(4)	P(2)-C(25)	1.831(4)
P(2)-C(24)	1.865(4)	P(2)-C(20)	1.873(4)
Si(1)-C(15)	1.849(5)	Si(1)-C(16)	1.854(5)
Si(1)-C(14)	1.878(5)	Si(1)-C(1)	1.879(4)
Si(2)-C(5)	1.855(4)	Si(2)-C(19)	1.863(4)
Si(2)-C(18)	1.865(6)	Si(2)-C(17)	1.868(5)
Si(3)-C(34)	1.868(4)	Si(3)-C(33)	1.872(4)
Si(3)-C(20)	1.875(4)	Si(3)-C(35)	1.877(5)
Si(4)-C(36)	1.861(4)	Si(4)-C(38)	1.862(5)
Si(4)-C(37)	1.877(5)	Si(4)-C(24)	1.883(4)
C(1)-C(2)	1.352(6)	C(2)-C(12)	1.519(6)
C(2)-C(3)	1.541(6)	C(3)-C(11)	1.512(6)
C(3)-C(4)	1.531(6)	C(3)-H(3)	1.0000
C(4)-C(5)	1.362(6)	C(4)-C(13)	1.499(6)
C(6)-C(7)	1.380(6)	C(6)-C(11)	1.382(6)
C(7)-C(8)	1.404(6)	C(7)-H(7)	0.9500
C(8)-C(9)	1.353(7)	C(8)-H(8)	0.9500
C(9)-C(10)	1.391(7)	C(9)-H(9)	0.9500
C(10)-C(11)	1.408(6)	C(10)-H(10)	0.9500
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800	C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800
C(20)-C(21)	1.342(5)	C(21)-C(31)	1.508(5)
C(21)-C(22)	1.537(5)	C(22)-C(30)	1.514(6)
C(22)-C(23)	1.555(6)	C(22)-H(22)	1.0000
C(23)-C(24)	1.324(5)	C(23)-C(32)	1.514(5)
C(25)-C(26)	1.386(5)	C(25)-C(30)	1.391(6)
C(26)-C(27)	1.389(6)	C(26)-H(26)	0.9500
C(27)-C(28)	1.381(7)	C(27)-H(27)	0.9500
C(28)-C(29)	1.392(6)	C(28)-H(28)	0.9500

C(29)-C(30)	1.396(5)	C(29)-H(29)	0.9500
C(31)-H(31A)	0.9800	C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800	C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800	C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800	C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800	C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800	C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800	C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800	C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800	C(36)-H(36C)	0.9800
C(37)-H(37A)	0.9800	C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800	C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800	C(38)-H(38C)	0.9800

P(2)-Pd(1)-P(1)	160.65(4)	C(6)-P(1)-C(1)	97.2(2)
C(6)-P(1)-C(5)	97.2(2)	C(1)-P(1)-C(5)	96.2(2)
C(6)-P(1)-Pd(1)	112.7(1)	C(1)-P(1)-Pd(1)	124.1(1)
C(5)-P(1)-Pd(1)	123.7(1)	C(25)-P(2)-C(24)	97.7(2)
C(25)-P(2)-C(20)	95.2(2)	C(24)-P(2)-C(20)	97.3(2)
C(25)-P(2)-Pd(1)	112.6(1)	C(24)-P(2)-Pd(1)	120.5(1)
C(20)-P(2)-Pd(1)	127.3(1)	C(15)-Si(1)-C(16)	112.2(2)
C(15)-Si(1)-C(14)	104.5(2)	C(16)-Si(1)-C(14)	111.4(3)
C(15)-Si(1)-C(1)	108.9(2)	C(16)-Si(1)-C(1)	108.6(2)
C(14)-Si(1)-C(1)	111.3(2)	C(5)-Si(2)-C(19)	109.1(2)
C(5)-Si(2)-C(18)	114.2(2)	C(19)-Si(2)-C(18)	105.6(3)
C(5)-Si(2)-C(17)	108.4(2)	C(19)-Si(2)-C(17)	109.9(2)
C(18)-Si(2)-C(17)	109.6(4)	C(34)-Si(3)-C(33)	111.3(2)
C(34)-Si(3)-C(20)	108.6(2)	C(33)-Si(3)-C(20)	107.6(2)
C(34)-Si(3)-C(35)	106.9(2)	C(33)-Si(3)-C(35)	107.8(3)
C(20)-Si(3)-C(35)	114.7(2)	C(36)-Si(4)-C(38)	111.0(2)
C(36)-Si(4)-C(37)	106.5(2)	C(38)-Si(4)-C(37)	108.2(3)
C(36)-Si(4)-C(24)	106.8(2)	C(38)-Si(4)-C(24)	109.1(2)
C(37)-Si(4)-C(24)	115.3(2)	C(2)-C(1)-P(1)	113.2(3)
C(2)-C(1)-Si(1)	127.1(3)	P(1)-C(1)-Si(1)	119.7(2)
C(1)-C(2)-C(12)	127.8(4)	C(1)-C(2)-C(3)	117.3(4)
C(12)-C(2)-C(3)	114.9(4)	C(11)-C(3)-C(4)	109.4(3)
C(11)-C(3)-C(2)	108.2(3)	C(4)-C(3)-C(2)	108.4(3)
C(11)-C(3)-H(3)	110.2	C(4)-C(3)-H(3)	110.2
C(2)-C(3)-H(3)	110.2	C(5)-C(4)-C(13)	127.1(4)
C(5)-C(4)-C(3)	118.6(4)	C(13)-C(4)-C(3)	114.4(4)
C(4)-C(5)-Si(2)	130.9(3)	C(4)-C(5)-P(1)	111.8(3)
Si(2)-C(5)-P(1)	117.3(2)	C(7)-C(6)-C(11)	120.0(4)
C(7)-C(6)-P(1)	125.5(3)	C(11)-C(6)-P(1)	114.5(3)
C(6)-C(7)-C(8)	119.3(4)	C(6)-C(7)-H(7)	120.3
C(8)-C(7)-H(7)	120.3	C(9)-C(8)-C(7)	120.7(5)
C(9)-C(8)-H(8)	119.6	C(7)-C(8)-H(8)	119.6
C(8)-C(9)-C(10)	120.8(4)	C(8)-C(9)-H(9)	119.6
C(10)-C(9)-H(9)	119.6	C(9)-C(10)-C(11)	118.6(4)
C(9)-C(10)-H(10)	120.7	C(11)-C(10)-H(10)	120.7
C(6)-C(11)-C(10)	120.4(4)	C(6)-C(11)-C(3)	115.7(4)
C(10)-C(11)-C(3)	123.8(4)	C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5

H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	Si(2)-C(19)-H(19A)	109.5
Si(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(21)-C(20)-P(2)	112.6(3)
C(21)-C(20)-Si(3)	130.4(3)	P(2)-C(20)-Si(3)	116.9(2)
C(20)-C(21)-C(31)	127.7(4)	C(20)-C(21)-C(22)	118.6(3)
C(31)-C(21)-C(22)	113.6(3)	C(30)-C(22)-C(21)	107.3(3)
C(30)-C(22)-C(23)	109.0(3)	C(21)-C(22)-C(23)	108.2(3)
C(30)-C(22)-H(22)	110.7	C(21)-C(22)-H(22)	110.7
C(23)-C(22)-H(22)	110.7	C(24)-C(23)-C(32)	128.6(4)
C(24)-C(23)-C(22)	118.6(4)	C(32)-C(23)-C(22)	112.7(3)
C(23)-C(24)-P(2)	113.1(3)	C(23)-C(24)-Si(4)	129.8(3)
P(2)-C(24)-Si(4)	117.0(2)	C(26)-C(25)-C(30)	120.0(4)
C(26)-C(25)-P(2)	125.9(3)	C(30)-C(25)-P(2)	114.0(3)
C(25)-C(26)-C(27)	120.1(4)	C(25)-C(26)-H(26)	119.9
C(27)-C(26)-H(26)	119.9	C(28)-C(27)-C(26)	119.7(4)
C(28)-C(27)-H(27)	120.1	C(26)-C(27)-H(27)	120.1
C(27)-C(28)-C(29)	120.9(4)	C(27)-C(28)-H(28)	119.5
C(29)-C(28)-H(28)	119.5	C(28)-C(29)-C(30)	119.0(4)
C(28)-C(29)-H(29)	120.5	C(30)-C(29)-H(29)	120.5
C(25)-C(30)-C(29)	120.1(4)	C(25)-C(30)-C(22)	116.2(3)
C(29)-C(30)-C(22)	123.6(4)	C(21)-C(31)-H(31A)	109.5
C(21)-C(31)-H(31B)	109.5	H(31A)-C(31)-H(31B)	109.5
C(21)-C(31)-H(31C)	109.5	H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5	C(23)-C(32)-H(32A)	109.5
C(23)-C(32)-H(32B)	109.5	H(32A)-C(32)-H(32B)	109.5
C(23)-C(32)-H(32C)	109.5	H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5	Si(3)-C(33)-H(33A)	109.5
Si(3)-C(33)-H(33B)	109.5	H(33A)-C(33)-H(33B)	109.5
Si(3)-C(33)-H(33C)	109.5	H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5	Si(3)-C(34)-H(34A)	109.5
Si(3)-C(34)-H(34B)	109.5	H(34A)-C(34)-H(34B)	109.5
Si(3)-C(34)-H(34C)	109.5	H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5	Si(3)-C(35)-H(35A)	109.5
Si(3)-C(35)-H(35B)	109.5	H(35A)-C(35)-H(35B)	109.5
Si(3)-C(35)-H(35C)	109.5	H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5	Si(4)-C(36)-H(36A)	109.5
Si(4)-C(36)-H(36B)	109.5	H(36A)-C(36)-H(36B)	109.5
Si(4)-C(36)-H(36C)	109.5	H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5	Si(4)-C(37)-H(37A)	109.5
Si(4)-C(37)-H(37B)	109.5	H(37A)-C(37)-H(37B)	109.5
Si(4)-C(37)-H(37C)	109.5	H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5	Si(4)-C(38)-H(38A)	109.5
Si(4)-C(38)-H(38B)	109.5	H(38A)-C(38)-H(38B)	109.5
Si(4)-C(38)-H(38C)	109.5	H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5		

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb462

atom	U11	U22	U33	U23	U13	U12
Pd(1)	23(1)	37(1)	28(1)	2(1)	5(1)	-1(1)
P(1)	26(1)	33(1)	26(1)	0(1)	3(1)	-2(1)

P(2)	22(1)	35(1)	27(1)	3(1)	3(1)	1(1)
Si(1)	34(1)	37(1)	42(1)	-5(1)	9(1)	0(1)
Si(2)	33(1)	41(1)	37(1)	5(1)	-8(1)	-7(1)
Si(3)	27(1)	38(1)	35(1)	0(1)	-3(1)	2(1)
Si(4)	25(1)	39(1)	37(1)	-3(1)	-1(1)	1(1)
C(1)	33(2)	36(2)	34(2)	-8(2)	6(2)	-3(1)
C(2)	46(2)	40(2)	37(2)	0(2)	6(2)	-7(2)
C(3)	48(3)	44(2)	30(2)	2(2)	5(2)	-10(2)
C(4)	39(2)	34(2)	37(2)	0(2)	4(2)	-4(2)
C(5)	29(2)	34(2)	40(2)	1(2)	3(2)	-4(2)
C(6)	39(2)	33(2)	25(2)	-4(2)	-6(2)	-1(2)
C(7)	32(2)	42(2)	42(2)	-3(2)	-4(2)	2(2)
C(8)	43(2)	47(2)	53(3)	-12(2)	-16(2)	6(2)
C(9)	60(3)	43(2)	56(3)	-6(2)	-24(3)	8(2)
C(10)	65(3)	41(2)	34(2)	7(2)	-17(2)	-7(2)
C(11)	41(2)	37(2)	35(2)	2(2)	-6(2)	-5(2)
C(12)	95(5)	56(3)	40(3)	-8(2)	23(3)	-10(3)
C(13)	52(3)	50(2)	43(3)	6(2)	7(2)	-13(2)
C(14)	69(4)	54(3)	70(4)	-9(3)	34(3)	3(3)
C(15)	41(2)	45(2)	53(3)	-1(2)	-10(2)	5(2)
C(16)	52(3)	46(2)	53(3)	1(2)	-20(2)	-2(2)
C(17)	112(5)	63(3)	30(2)	-7(2)	-11(3)	27(3)
C(18)	75(5)	150(7)	80(5)	56(5)	-40(4)	-71(5)
C(19)	45(3)	52(2)	45(3)	12(2)	-9(2)	5(2)
C(20)	30(2)	34(2)	26(2)	5(2)	0(2)	2(1)
C(21)	32(2)	37(2)	31(2)	1(2)	1(2)	2(2)
C(22)	27(2)	44(2)	33(2)	4(2)	8(2)	3(2)
C(23)	25(2)	38(2)	37(2)	9(2)	5(2)	3(1)
C(24)	21(2)	37(2)	31(2)	3(2)	2(2)	1(1)
C(25)	31(2)	35(2)	24(2)	1(1)	-1(2)	4(1)
C(26)	33(2)	39(2)	40(2)	4(2)	-4(2)	1(2)
C(27)	48(3)	40(2)	37(2)	-4(2)	-8(2)	8(2)
C(28)	53(3)	46(2)	42(3)	-10(2)	-2(2)	17(2)
C(29)	40(2)	55(2)	30(2)	4(2)	7(2)	13(2)
C(30)	30(2)	44(2)	27(2)	4(2)	2(2)	9(2)
C(31)	41(2)	56(2)	30(2)	10(2)	5(2)	5(2)
C(32)	30(2)	48(2)	52(3)	6(2)	8(2)	-3(2)
C(33)	35(2)	48(2)	77(4)	-8(2)	0(3)	-7(2)
C(34)	31(2)	47(2)	49(3)	-2(2)	2(2)	6(2)
C(35)	47(3)	69(3)	40(3)	10(2)	-6(2)	12(2)
C(36)	31(2)	49(2)	48(3)	-6(2)	4(2)	1(2)
C(37)	34(2)	64(3)	73(4)	-20(3)	-1(2)	-5(2)
C(38)	66(3)	61(3)	30(2)	10(2)	-6(2)	5(2)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb462

atom	x	y	z	U(eq)
H(3)	11911	1073	-2329	49
H(7)	8031	616	-1562.0001	46
H(8)	6824	1434	-1852.9999	57
H(9)	7791	2063	-2241	63
H(10)	9898	1778	-2403	56
H(12A)	12880	-69	-2570	96
H(12B)	11408	40	-2676.9998	96
H(12C)	11880	-718	-2556	96
H(13A)	14053	1562	-1750	72
H(13B)	13312	1859	-2045	72

H(13C)	14225	1175	-2074	72
H(14A)	13591	-1415	-2160	96
H(14B)	12623	-1747.9999	-2408	96
H(14C)	13103	-2216	-2124	96
H(15A)	11107	-1547	-1425	70
H(15B)	12625	-1483.9999	-1497	70
H(15C)	11884	-2218	-1553.9999	70
H(16A)	9818	-2300	-2028	76
H(16B)	9892	-1805	-2326	76
H(16C)	9163	-1530	-2024	76
H(17A)	11780	1702	-1031	102
H(17B)	12320	1248	-748	102
H(17C)	11081	976	-935.0001	102
H(18A)	15190	898	-1373	153
H(18B)	15017	1141	-1024	153
H(18C)	14534	1646	-1295	153
H(19A)	12465	-444	-1050	71
H(19B)	13688	-159.0000	-861	71
H(19C)	13875	-447	-1203	71
H(22)	5590	-864	-249	42
H(26)	8497	879	-912	44
H(27)	7363	1821	-688	50
H(28)	5695	1592	-343	56
H(29)	5122	423	-220	50
H(31A)	8340	-1502	129	63
H(31B)	6849	-1705	78	63
H(31C)	7233	-922.0001	187	63
H(32A)	4437	-1785	-881	65
H(32B)	4072	-1351.9999	-577	65
H(32C)	4863	-2081	-552	65
H(33A)	11087	-225.0000	-148	80
H(33B)	11142	-186	-515	80
H(33C)	12257	-593	-330	80
H(34A)	11892	-2049	-627.0001	64
H(34B)	10968	-1654	-868	64
H(34C)	10453	-2336	-687	64
H(35A)	9979	-2209	21	78
H(35B)	10470	-1495	182	78
H(35C)	11488	-2011.0001	18	78
H(36A)	8388	-2440	-1542	64
H(36B)	8322	-2609	-1182	64
H(36C)	9069	-1918	-1301	64
H(37A)	4601	-2105	-1341	86
H(37B)	5478	-2720.0002	-1196	86
H(37C)	5498	-2583	-1558	86
H(38A)	5928	-734	-1584	79
H(38B)	6607	-1277	-1816	79
H(38C)	7474	-743	-1618	79

II.10. Crystallographic data for IV-33

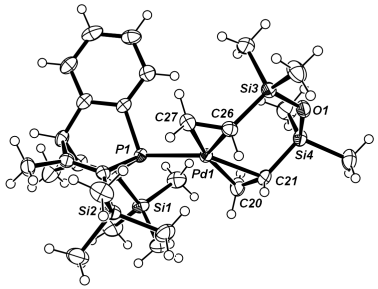


Table 1. Crystal data for mb788

Compound	mb788
Molecular formula	$C_{27}H_{47}OPPdSi_4$
Molecular weight	637.38
Crystal habit	White Needle
Crystal dimensions(mm)	0.22x0.08x0.06
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	9.218(1)
b(Å)	22.874(1)
c(Å)	16.629(1)
α(°)	90.00
β(°)	108.854(4)
γ(°)	90.00
V(Å^3)	3318.1(4)
Z	4
d(g-cm^{-3})	1.276
F(000)	1336
μ(cm^{-1})	0.769
Absorption corrections	multi-scan ; 0.8490 min, 0.9553 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-12 10 ; -32 28 ; -23 23
Reflections measured	38552
Unique data	9676
Rint	0.0393
Reflections used	7443

Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	319
Reflections / parameter	23
wR2	0.0777
R1	0.0308
Weights a, b	0.0358 ; 0.2713
GoF	1.031
difference peak / hole (e Å^{-3})	0.471(0.068) / -0.577(0.068)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb788

atom	x	y	z	U(eq)
Pd(1)	2169(1)	-861(1)	3172(1)	23(1)
P(1)	2774(1)	-1772(1)	3857(1)	21(1)
Si(1)	6277(1)	-2012(1)	3970(1)	29(1)
Si(2)	2765(1)	-1197(1)	5681(1)	28(1)
Si(3)	-1057(1)	-212(1)	1901(1)	29(1)
Si(4)	1848(1)	12(1)	1495(1)	29(1)
O(1)	53(1)	115(1)	1438(1)	32(1)
C(1)	4450(2)	-2288(1)	4105(1)	26(1)
C(2)	4172(2)	-2790(1)	4435(1)	31(1)
C(3)	2622(2)	-2880(1)	4575(1)	28(1)
C(4)	2406(2)	-2384(1)	5149(1)	25(1)
C(5)	2526(2)	-1828(1)	4918(1)	23(1)
C(6)	1339(2)	-2316(1)	3292(1)	23(1)
C(7)	277(2)	-2239(1)	2490(1)	30(1)
C(8)	-751(2)	-2687(1)	2126(1)	37(1)
C(9)	-692(2)	-3210(1)	2551(1)	39(1)
C(10)	376(2)	-3292(1)	3347(1)	33(1)
C(11)	1389(2)	-2843(1)	3718(1)	26(1)
C(12)	5213(3)	-3311(1)	4706(2)	53(1)
C(13)	2102(2)	-2590(1)	5936(1)	35(1)
C(14)	6738(2)	-1313(1)	4584(1)	37(1)
C(15)	8001(2)	-2489(1)	4411(1)	44(1)
C(16)	5980(2)	-1924(1)	2814(1)	43(1)
C(17)	4353(3)	-1384(1)	6681(1)	48(1)
C(18)	960(2)	-1051(1)	5935(1)	44(1)
C(19)	3351(3)	-505(1)	5280(1)	42(1)
C(20)	4133(2)	-588(1)	2812(2)	42(1)
C(21)	3056(2)	-137(1)	2599(1)	31(1)
C(22)	2497(2)	704(1)	1132(1)	40(1)
C(23)	1980(3)	-598(1)	788(2)	48(1)
C(24)	-2680(2)	298(1)	1811(1)	46(1)
C(25)	-1855(3)	-894(1)	1315(1)	47(1)
C(26)	29(2)	-371(1)	3025(1)	27(1)
C(27)	-16(2)	-900(1)	3430(1)	28(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb788

Pd(1)-C(20)	2.174(2)	Pd(1)-C(27)	2.193(2)
Pd(1)-C(21)	2.196(2)	Pd(1)-C(26)	2.213(2)
Pd(1)-P(1)	2.3527(5	P(1)-C(6)	1.838(2)
P(1)-C(5)	1.856(2)	P(1)-C(1)	1.882(2)

Si(1)-C(16)	1.863(2)	Si(1)-C(14)	1.869(2)
Si(1)-C(15)	1.872(2)	Si(1)-C(1)	1.879(2)
Si(2)-C(19)	1.864(2)	Si(2)-C(18)	1.874(2)
Si(2)-C(17)	1.875(2)	Si(2)-C(5)	1.886(2)
Si(3)-O(1)	1.645(1)	Si(3)-C(26)	1.849(2)
Si(3)-C(25)	1.859(2)	Si(3)-C(24)	1.865(2)
Si(4)-O(1)	1.644(1)	Si(4)-C(21)	1.845(2)
Si(4)-C(23)	1.855(2)	Si(4)-C(22)	1.860(2)
C(1)-C(2)	1.333(3)	C(2)-C(12)	1.505(3)
C(2)-C(3)	1.534(2)	C(3)-C(11)	1.510(3)
C(3)-C(4)	1.537(3)	C(3)-H(3)	1.0000
C(4)-C(5)	1.342(3)	C(4)-C(13)	1.501(3)
C(6)-C(7)	1.387(2)	C(6)-C(11)	1.392(3)
C(7)-C(8)	1.394(3)	C(7)-H(7)	0.9500
C(8)-C(9)	1.382(3)	C(8)-H(8)	0.9500
C(9)-C(10)	1.384(3)	C(9)-H(9)	0.9500
C(10)-C(11)	1.391(3)	C(10)-H(10)	0.9500
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800	C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800
C(20)-C(21)	1.396(3)	C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900	C(21)-H(21)	0.9500
C(22)-H(22A)	0.9800	C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800	C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800	C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800	C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800	C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800	C(25)-H(25C)	0.9800
C(26)-C(27)	1.391(3)	C(26)-H(26)	0.9499
C(27)-H(27A)	0.9899	C(27)-H(27B)	0.9900

C(20)-Pd(1)-C(27)	164.77(8)	C(20)-Pd(1)-C(21)	37.27(8)
C(27)-Pd(1)-C(21)	127.55(7)	C(20)-Pd(1)-C(26)	128.05(8)
C(27)-Pd(1)-C(26)	36.80(7)	C(21)-Pd(1)-C(26)	90.79(7)
C(20)-Pd(1)-P(1)	107.43(6)	C(27)-Pd(1)-P(1)	87.61(5)
C(21)-Pd(1)-P(1)	144.55(5)	C(26)-Pd(1)-P(1)	124.39(5)
C(6)-P(1)-C(5)	98.60(8)	C(6)-P(1)-C(1)	95.22(8)
C(5)-P(1)-C(1)	95.32(8)	C(6)-P(1)-Pd(1)	109.47(6)
C(5)-P(1)-Pd(1)	116.07(6)	C(1)-P(1)-Pd(1)	135.32(6)
C(16)-Si(1)-C(14)	113.8(1)	C(16)-Si(1)-C(15)	106.9(1)
C(14)-Si(1)-C(15)	105.7(1)	C(16)-Si(1)-C(1)	108.7(1)
C(14)-Si(1)-C(1)	106.1(1)	C(15)-Si(1)-C(1)	115.9(1)
C(19)-Si(2)-C(18)	108.0(1)	C(19)-Si(2)-C(17)	106.1(1)
C(18)-Si(2)-C(17)	109.7(1)	C(19)-Si(2)-C(5)	113.1(1)
C(18)-Si(2)-C(5)	111.6(1)	C(17)-Si(2)-C(5)	108.1(1)
O(1)-Si(3)-C(26)	110.29(8)	O(1)-Si(3)-C(25)	109.7(1)
C(26)-Si(3)-C(25)	111.0(1)	O(1)-Si(3)-C(24)	106.4(1)
C(26)-Si(3)-C(24)	111.2(1)	C(25)-Si(3)-C(24)	108.2(1)
O(1)-Si(4)-C(21)	110.87(8)	O(1)-Si(4)-C(23)	110.0(1)
C(21)-Si(4)-C(23)	110.5(1)	O(1)-Si(4)-C(22)	106.44(8)
C(21)-Si(4)-C(22)	109.0(1)	C(23)-Si(4)-C(22)	109.9(1)
Si(4)-O(1)-Si(3)	132.4(1)	C(2)-C(1)-Si(1)	129.6(1)
C(2)-C(1)-P(1)	112.2(1)	Si(1)-C(1)-P(1)	117.8(1)

C(1)-C(2)-C(12)	128.1(2)	C(1)-C(2)-C(3)	119.3(2)
C(12)-C(2)-C(3)	112.6(2)	C(11)-C(3)-C(2)	107.7(2)
C(11)-C(3)-C(4)	109.6(1)	C(2)-C(3)-C(4)	108.0(2)
C(11)-C(3)-H(3)	110.5	C(2)-C(3)-H(3)	110.5
C(4)-C(3)-H(3)	110.5	C(5)-C(4)-C(13)	127.1(2)
C(5)-C(4)-C(3)	118.8(2)	C(13)-C(4)-C(3)	114.1(2)
C(4)-C(5)-P(1)	112.6(1)	C(4)-C(5)-Si(2)	122.3(1)
P(1)-C(5)-Si(2)	124.3(1)	C(7)-C(6)-C(11)	119.7(2)
C(7)-C(6)-P(1)	125.0(2)	C(11)-C(6)-P(1)	115.3(1)
C(6)-C(7)-C(8)	119.7(2)	C(6)-C(7)-H(7)	120.2
C(8)-C(7)-H(7)	120.2	C(9)-C(8)-C(7)	120.3(2)
C(9)-C(8)-H(8)	119.9	C(7)-C(8)-H(8)	119.9
C(8)-C(9)-C(10)	120.4(2)	C(8)-C(9)-H(9)	119.8
C(10)-C(9)-H(9)	119.8	C(9)-C(10)-C(11)	119.5(2)
C(9)-C(10)-H(10)	120.3	C(11)-C(10)-H(10)	120.3
C(10)-C(11)-C(6)	120.5(2)	C(10)-C(11)-C(3)	124.7(2)
C(6)-C(11)-C(3)	114.8(2)	C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	Si(2)-C(19)-H(19A)	109.5
Si(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(21)-C(20)-Pd(1)	72.2(1)
C(21)-C(20)-H(20A)	116.4	Pd(1)-C(20)-H(20A)	116.4
C(21)-C(20)-H(20B)	116.1	Pd(1)-C(20)-H(20B)	116.4
H(20A)-C(20)-H(20B)	113.4	C(20)-C(21)-Si(4)	122.6(2)
C(20)-C(21)-Pd(1)	70.5(1)	Si(4)-C(21)-Pd(1)	112.4(1)
C(20)-C(21)-H(21)	118.6	Si(4)-C(21)-H(21)	118.7
Pd(1)-C(21)-H(21)	86.9	Si(4)-C(22)-H(22A)	109.5
Si(4)-C(22)-H(22B)	109.5	H(22A)-C(22)-H(22B)	109.5
Si(4)-C(22)-H(22C)	109.5	H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5	Si(4)-C(23)-H(23A)	109.5
Si(4)-C(23)-H(23B)	109.5	H(23A)-C(23)-H(23B)	109.5
Si(4)-C(23)-H(23C)	109.5	H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5	Si(3)-C(24)-H(24A)	109.5
Si(3)-C(24)-H(24B)	109.5	H(24A)-C(24)-H(24B)	109.5
Si(3)-C(24)-H(24C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5	Si(3)-C(25)-H(25A)	109.5
Si(3)-C(25)-H(25B)	109.5	H(25A)-C(25)-H(25B)	109.5
Si(3)-C(25)-H(25C)	109.5	H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5	C(27)-C(26)-Si(3)	124.7(2)
C(27)-C(26)-Pd(1)	70.8(1)	Si(3)-C(26)-Pd(1)	112.54(8)
C(27)-C(26)-H(26)	117.6	Si(3)-C(26)-H(26)	117.7
Pd(1)-C(26)-H(26)	86.2	C(26)-C(27)-Pd(1)	72.4(1)
C(26)-C(27)-H(27A)	116.1	Pd(1)-C(27)-H(27A)	116.3

C(26)-C(27)-H(27B)	116.5	Pd(1)-C(27)-H(27B)	116.5
H(27A)-C(27)-H(27B)	113.4		

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb788

atom	U11	U22	U33	U23	U13	U12
Pd(1)	22(1)	21(1)	26(1)	2(1)	7(1)	-1(1)
P(1)	19(1)	20(1)	27(1)	1(1)	11(1)	1(1)
Si(1)	18(1)	34(1)	37(1)	-4(1)	11(1)	0(1)
Si(2)	26(1)	30(1)	27(1)	-4(1)	6(1)	2(1)
Si(3)	26(1)	31(1)	28(1)	5(1)	7(1)	-1(1)
Si(4)	31(1)	26(1)	32(1)	5(1)	12(1)	1(1)
O(1)	30(1)	33(1)	32(1)	10(1)	9(1)	2(1)
C(1)	18(1)	25(1)	37(1)	-3(1)	12(1)	3(1)
C(2)	23(1)	25(1)	46(1)	0(1)	14(1)	5(1)
C(3)	26(1)	18(1)	41(1)	5(1)	13(1)	3(1)
C(4)	19(1)	27(1)	28(1)	3(1)	6(1)	2(1)
C(5)	18(1)	25(1)	24(1)	2(1)	7(1)	3(1)
C(6)	22(1)	22(1)	30(1)	-4(1)	14(1)	-1(1)
C(7)	31(1)	34(1)	28(1)	-3(1)	15(1)	-2(1)
C(8)	34(1)	48(1)	30(1)	-13(1)	12(1)	-9(1)
C(9)	36(1)	41(1)	46(1)	-20(1)	20(1)	-15(1)
C(10)	34(1)	25(1)	47(1)	-7(1)	22(1)	-4(1)
C(11)	24(1)	22(1)	37(1)	-4(1)	17(1)	0(1)
C(12)	36(1)	31(1)	99(2)	13(1)	29(1)	13(1)
C(13)	36(1)	35(1)	33(1)	10(1)	11(1)	1(1)
C(14)	27(1)	40(1)	40(1)	-5(1)	7(1)	-3(1)
C(15)	23(1)	49(2)	59(1)	-3(1)	14(1)	6(1)
C(16)	38(1)	52(2)	42(1)	-8(1)	18(1)	-6(1)
C(17)	44(1)	49(2)	39(1)	-6(1)	-4(1)	1(1)
C(18)	41(1)	56(2)	38(1)	-8(1)	16(1)	9(1)
C(19)	52(1)	29(1)	44(1)	-10(1)	14(1)	-9(1)
C(20)	23(1)	48(1)	54(1)	22(1)	12(1)	-4(1)
C(21)	29(1)	29(1)	35(1)	7(1)	10(1)	-9(1)
C(22)	40(1)	37(1)	49(1)	16(1)	22(1)	4(1)
C(23)	53(1)	44(2)	48(1)	-8(1)	17(1)	3(1)
C(24)	34(1)	57(2)	44(1)	15(1)	11(1)	12(1)
C(25)	54(1)	47(2)	30(1)	2(1)	1(1)	-17(1)
C(26)	24(1)	28(1)	28(1)	0(1)	7(1)	2(1)
C(27)	24(1)	35(1)	29(1)	4(1)	13(1)	4(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb788

atom	x	y	z	U(eq)
H(3)	2590	-3268	4844	33
H(7)	251	-1884	2191	36
H(8)	-1497	-2632.0002	1583	45
H(9)	-1388	-3515	2296	47
H(10)	418	-3652.0002	3638	40
H(12A)	6128	-3254	4538	80
H(12B)	4671	-3664	4433	80
H(12C)	5516	-3355	5325	80
H(13A)	1908	-2252	6250	52
H(13B)	2995	-2805	6296	52
H(13C)	1203	-2847	5778	52

H(14A)	5798	-1085	4488	55
H(14B)	7474	-1088	4396	55
H(14C)	7185	-1402	5191	55
H(15A)	8150	-2572	5011	65
H(15B)	8908	-2289	4361	65
H(15C)	7848	-2857	4092	65
H(16A)	6044	-2308	2563	64
H(16B)	6773	-1666	2736	64
H(16C)	4967	-1753	2533	64
H(17A)	5259	-1506	6539	72
H(17B)	4023	-1703.0001	6975	72
H(17C)	4605	-1039	7051	72
H(18A)	1161	-758	6387	66
H(18B)	605	-1414	6123	66
H(18C)	168	-905	5426	66
H(19A)	3490	-198	5709	63
H(19B)	2555	-387	4755	63
H(19C)	4318	-568	5165	63
H(20A)	5092	-509	3283	50
H(20B)	4301	-800	2330	50
H(21)	2938	102	3042	37
H(22A)	1766	818	582	61
H(22B)	3511	644	1073	61
H(22C)	2556	1013	1550	61
H(23A)	1713	-966.0001	1008	72
H(23B)	3028	-623	767	72
H(23C)	1268	-528	214	72
H(24A)	-2281	664	2106	68
H(24B)	-3388.0002	119	2069	68
H(24C)	-3224	379	1210	68
H(25A)	-2578.0002	-793	756	70
H(25B)	-2389	-1117	1637	70
H(25C)	-1018.9999	-1130	1243	70
H(26)	670	-72	3348	33
H(27A)	-770	-1190	3098	34
H(27B)	41	-877	4034	34

II.11. Crystallographic data for IV-37

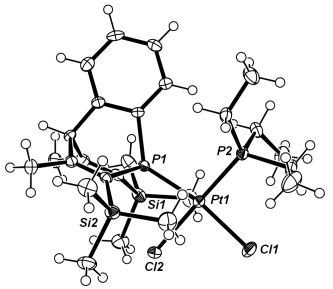


Table 1. Crystal data for mb471

Compound	mb471

Molecular formula	$C_{25}H_{44}Cl_2P_2PtSi_2$
Molecular weight	728.71
Crystal habit	Pale Yellow Block
Crystal dimensions(mm)	0.24x0.10x0.06
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	11.255(1)
b(Å)	16.209(1)
c(Å)	16.760(1)
α(°)	90.00
β(°)	99.903(1)
γ(°)	90.00
V(Å^3)	3012.0(4)
Z	4
d(g-cm^{-3})	1.607
F(000)	1456
μ(cm^{-1})	5.035
Absorption corrections	multi-scan ; 0.3779 min, 0.7521 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	29.99
HKL ranges	-15 13 ; -22 20 ; -23 23
Reflections measured	24225
Unique data	8740
Rint	0.0643
Reflections used	5943
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	300
Reflections / parameter	19
wR2	0.0773
R1	0.0374
Weights a, b	0.0225 ; 0.0000
GoF	0.959
difference peak / hole (e Å^{-3})	1.685(0.180) / -1.417(0.180)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb471

atom	x	y	z	U(eq)
Pt(1)	5806(1)	1484(1)	2127(1)	18(1)
Cl(1)	3900(1)	866(1)	2098(1)	36(1)
Cl(2)	6683(1)	156(1)	2379(1)	25(1)
P(1)	7763(1)	1828(1)	2210(1)	16(1)
P(2)	4947(1)	2725(1)	1869(1)	20(1)
Si(1)	8298(1)	1150(1)	4111(1)	24(1)
Si(2)	7581(1)	771(1)	475(1)	22(1)
C(1)	8800(4)	1450(3)	3123(2)	19(1)
C(2)	9936(4)	1530(3)	3032(2)	20(1)
C(3)	10228(4)	1942(3)	2259(2)	19(1)
C(4)	9624(4)	1447(3)	1525(2)	19(1)
C(5)	8426(4)	1358(2)	1387(2)	16(1)
C(6)	8468(4)	2858(3)	2253(2)	15(1)
C(7)	7975(4)	3629(3)	2367(2)	19(1)
C(8)	8694(4)	4327(3)	2431(2)	24(1)
C(9)	9916(4)	4264(3)	2392(2)	27(1)
C(10)	10425(4)	3496(3)	2309(2)	24(1)
C(11)	9714(4)	2795(3)	2248(2)	18(1)
C(12)	11040(4)	1309(3)	3643(2)	28(1)
C(13)	10484(4)	1094(3)	1017(2)	26(1)
C(14)	8475(4)	20(3)	4304(2)	33(1)
C(15)	9241(4)	1744(3)	4959(2)	36(1)
C(16)	6721(4)	1446(3)	4155(2)	33(1)
C(17)	7867(4)	-365(3)	603(2)	32(1)
C(18)	8097(4)	1111(3)	-481(2)	33(1)
C(19)	5928(4)	953(3)	251(2)	34(1)
C(20)	5010(4)	3313(3)	2810(2)	24(1)
C(21)	4122(4)	2970(3)	3334(2)	35(1)
C(22)	3331(4)	2739(3)	1446(2)	29(1)
C(23)	3004(4)	2467(4)	559(2)	45(2)
C(24)	5551(4)	3337(3)	1108(2)	21(1)
C(25)	5188(4)	4250(3)	1045(3)	34(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb471

Pt(1)-P(2)	2.241(1)	Pt(1)-P(1)	2.253(1)
Pt(1)-Cl(1)	2.361(1)	Pt(1)-Cl(2)	2.376(1)
P(1)-C(5)	1.842(4)	P(1)-C(6)	1.845(4)
P(1)-C(1)	1.861(4)	P(2)-C(20)	1.834(4)
P(2)-C(22)	1.835(4)	P(2)-C(24)	1.836(4)
Si(1)-C(16)	1.853(5)	Si(1)-C(14)	1.865(5)
Si(1)-C(15)	1.886(4)	Si(1)-C(1)	1.902(4)
Si(2)-C(19)	1.857(5)	Si(2)-C(17)	1.875(5)
Si(2)-C(18)	1.877(4)	Si(2)-C(5)	1.911(4)
C(1)-C(2)	1.319(6)	C(2)-C(12)	1.510(5)
C(2)-C(3)	1.543(5)	C(3)-C(11)	1.499(6)
C(3)-C(4)	1.526(5)	C(3)-H(3)	1.0000
C(4)-C(5)	1.336(5)	C(4)-C(13)	1.509(5)
C(6)-C(7)	1.394(6)	C(6)-C(11)	1.407(5)
C(7)-C(8)	1.383(6)	C(7)-H(7)	0.9500
C(8)-C(9)	1.392(6)	C(8)-H(8)	0.9500
C(9)-C(10)	1.387(6)	C(9)-H(9)	0.9500
C(10)-C(11)	1.383(6)	C(10)-H(10)	0.9500
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800	C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800
C(20)-C(21)	1.543(6)	C(20)-H(20A)	0.9900

C(20)-H(20B)	0.9900	C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800	C(21)-H(21C)	0.9800
C(22)-C(23)	1.533(6)	C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900	C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800	C(23)-H(23C)	0.9800
C(24)-C(25)	1.534(6)	C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900	C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800	C(25)-H(25C)	0.9800

P(2)-Pt(1)-P(1)	100.07(4)	P(2)-Pt(1)-Cl(1)	90.91(4)
P(1)-Pt(1)-Cl(1)	169.01(4)	P(2)-Pt(1)-Cl(2)	178.73(4)
P(1)-Pt(1)-Cl(2)	80.86(4)	Cl(1)-Pt(1)-Cl(2)	88.16(4)
C(5)-P(1)-C(6)	100.1(2)	C(5)-P(1)-C(1)	101.6(2)
C(6)-P(1)-C(1)	93.5(2)	C(5)-P(1)-Pt(1)	111.7(1)
C(6)-P(1)-Pt(1)	129.5(1)	C(1)-P(1)-Pt(1)	116.0(1)
C(20)-P(2)-C(22)	102.4(2)	C(20)-P(2)-C(24)	110.6(2)
C(22)-P(2)-C(24)	100.7(2)	C(20)-P(2)-Pt(1)	110.4(1)
C(22)-P(2)-Pt(1)	116.9(2)	C(24)-P(2)-Pt(1)	114.8(1)
C(16)-Si(1)-C(14)	108.8(2)	C(16)-Si(1)-C(15)	104.9(2)
C(14)-Si(1)-C(15)	109.9(2)	C(16)-Si(1)-C(1)	113.5(2)
C(14)-Si(1)-C(1)	111.3(2)	C(15)-Si(1)-C(1)	108.2(2)
C(19)-Si(2)-C(17)	109.0(2)	C(19)-Si(2)-C(18)	103.1(2)
C(17)-Si(2)-C(18)	108.3(2)	C(19)-Si(2)-C(5)	115.2(2)
C(17)-Si(2)-C(5)	110.2(2)	C(18)-Si(2)-C(5)	110.6(2)
C(2)-C(1)-P(1)	110.9(3)	C(2)-C(1)-Si(1)	124.3(3)
P(1)-C(1)-Si(1)	124.1(2)	C(1)-C(2)-C(12)	126.8(4)
C(1)-C(2)-C(3)	119.3(3)	C(12)-C(2)-C(3)	113.7(4)
C(11)-C(3)-C(4)	111.0(3)	C(11)-C(3)-C(2)	105.8(3)
C(4)-C(3)-C(2)	108.7(3)	C(11)-C(3)-H(3)	110.4
C(4)-C(3)-H(3)	110.4	C(2)-C(3)-H(3)	110.4
C(5)-C(4)-C(13)	126.0(4)	C(5)-C(4)-C(3)	119.5(4)
C(13)-C(4)-C(3)	114.5(4)	C(4)-C(5)-P(1)	110.6(3)
C(4)-C(5)-Si(2)	122.7(3)	P(1)-C(5)-Si(2)	126.6(2)
C(7)-C(6)-C(11)	119.1(4)	C(7)-C(6)-P(1)	129.6(3)
C(11)-C(6)-P(1)	110.9(3)	C(8)-C(7)-C(6)	120.2(4)
C(8)-C(7)-H(7)	119.9	C(6)-C(7)-H(7)	119.9
C(7)-C(8)-C(9)	120.4(4)	C(7)-C(8)-H(8)	119.8
C(9)-C(8)-H(8)	119.8	C(10)-C(9)-C(8)	119.9(4)
C(10)-C(9)-H(9)	120.1	C(8)-C(9)-H(9)	120.1
C(11)-C(10)-C(9)	120.1(4)	C(11)-C(10)-H(10)	120.0
C(9)-C(10)-H(10)	120.0	C(10)-C(11)-C(6)	120.3(4)
C(10)-C(11)-C(3)	122.8(4)	C(6)-C(11)-C(3)	116.7(4)
C(2)-C(12)-H(12A)	109.5	C(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5	C(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5	H(12B)-C(12)-H(12C)	109.5
C(4)-C(13)-H(13A)	109.5	C(4)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5	C(4)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5	H(13B)-C(13)-H(13C)	109.5
Si(1)-C(14)-H(14A)	109.5	Si(1)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	Si(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
Si(1)-C(15)-H(15A)	109.5	Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5	Si(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
Si(1)-C(16)-H(16A)	109.5	Si(1)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5	Si(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(16B)-C(16)-H(16C)	109.5
Si(2)-C(17)-H(17A)	109.5	Si(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5	Si(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(17B)-C(17)-H(17C)	109.5
Si(2)-C(18)-H(18A)	109.5	Si(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5	Si(2)-C(18)-H(18C)	109.5

H(18A)-C(18)-H(18C)	109.5	H(18B)-C(18)-H(18C)	109.5
Si(2)-C(19)-H(19A)	109.5	Si(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5	Si(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5	H(19B)-C(19)-H(19C)	109.5
C(21)-C(20)-P(2)	111.6(3)	C(21)-C(20)-H(20A)	109.3
P(2)-C(20)-H(20A)	109.3	C(21)-C(20)-H(20B)	109.3
P(2)-C(20)-H(20B)	109.3	H(20A)-C(20)-H(20B)	108.0
C(20)-C(21)-H(21A)	109.5	C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5	C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5	H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-P(2)	115.3(3)	C(23)-C(22)-H(22A)	108.4
P(2)-C(22)-H(22A)	108.4	C(23)-C(22)-H(22B)	108.4
P(2)-C(22)-H(22B)	108.4	H(22A)-C(22)-H(22B)	107.5
C(22)-C(23)-H(23A)	109.5	C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5	C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5	H(23B)-C(23)-H(23C)	109.5
C(25)-C(24)-P(2)	116.3(3)	C(25)-C(24)-H(24A)	108.2
P(2)-C(24)-H(24A)	108.2	C(25)-C(24)-H(24B)	108.2
P(2)-C(24)-H(24B)	108.2	H(24A)-C(24)-H(24B)	107.4
C(24)-C(25)-H(25A)	109.5	C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5	C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5	H(25B)-C(25)-H(25C)	109.5

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb471

atom	U11	U22	U33	U23	U13	U12
Pt(1)	16(1)	17(1)	21(1)	1(1)	5(1)	-1(1)
Cl(1)	19(1)	32(1)	57(1)	10(1)	7(1)	-6(1)
Cl(2)	25(1)	16(1)	34(1)	2(1)	7(1)	-1(1)
P(1)	17(1)	14(1)	17(1)	0(1)	4(1)	0(1)
P(2)	17(1)	22(1)	21(1)	3(1)	5(1)	2(1)
Si(1)	32(1)	23(1)	18(1)	4(1)	4(1)	6(1)
Si(2)	26(1)	21(1)	21(1)	-4(1)	5(1)	-2(1)
C(1)	23(3)	15(2)	17(2)	1(2)	1(2)	4(2)
C(2)	24(3)	16(2)	19(2)	-3(2)	-1(2)	2(2)
C(3)	13(2)	17(2)	25(2)	-2(2)	1(2)	-4(2)
C(4)	21(2)	16(2)	21(2)	4(2)	8(2)	1(2)
C(5)	21(2)	13(2)	15(2)	2(2)	6(2)	2(2)
C(6)	19(2)	13(2)	14(2)	0(2)	2(2)	-3(2)
C(7)	21(3)	18(3)	17(2)	0(2)	4(2)	-3(2)
C(8)	31(3)	15(2)	27(2)	-2(2)	6(2)	2(2)
C(9)	33(3)	18(2)	29(2)	0(2)	5(2)	-12(2)
C(10)	20(2)	28(3)	23(2)	2(2)	2(2)	-3(2)
C(11)	21(3)	18(2)	15(2)	3(2)	3(2)	-2(2)
C(12)	22(3)	28(3)	32(2)	2(2)	-2(2)	4(2)
C(13)	22(3)	26(3)	31(2)	-1(2)	9(2)	2(2)
C(14)	39(3)	29(3)	29(2)	13(2)	1(2)	0(3)
C(15)	45(3)	36(3)	23(2)	-7(2)	-2(2)	13(3)
C(16)	36(3)	41(3)	24(2)	5(2)	9(2)	6(3)
C(17)	45(3)	20(3)	34(2)	-7(2)	13(2)	-6(3)
C(18)	40(3)	34(3)	24(2)	-1(2)	5(2)	0(3)
C(19)	33(3)	39(3)	28(2)	-7(2)	-1(2)	-2(3)
C(20)	25(3)	25(3)	25(2)	2(2)	8(2)	8(2)
C(21)	32(3)	50(4)	25(2)	2(2)	13(2)	4(3)
C(22)	14(2)	35(3)	38(2)	9(2)	6(2)	2(2)
C(23)	29(3)	60(4)	41(3)	10(3)	-8(2)	-11(3)
C(24)	17(2)	25(3)	23(2)	3(2)	6(2)	3(2)
C(25)	38(3)	30(3)	36(2)	12(2)	13(2)	12(3)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb471

atom	x	y	z	U(eq)
H(3)	11120	1965	2277	22
H(7)	7144	3675	2400	22
H(8)	8350	4851	2502	29
H(9)	10400	4747	2422	32
H(10)	11262	3452	2294	29
H(12A)	11402	1813	3901	42
H(12B)	11625	1027	3368	42
H(12C)	10807	944	4056	42
H(13A)	10118	610	721	39
H(13B)	11236	930	1368	39
H(13C)	10659	1511	630	39
H(14A)	8264	-110	4833	49
H(14B)	9313	-140	4299	49
H(14C)	7940	-283	3881	49
H(15A)	9361	2308	4779	53
H(15B)	10026	1473	5112	53
H(15C)	8827	1759	5427	53
H(16A)	6168	1108	3773	50
H(16B)	6600	2030	4011	50
H(16C)	6560	1357	4705	50
H(17A)	7462	-575	1035	49
H(17B)	8736	-464	746	49
H(17C)	7551	-650	95	49
H(18A)	7699	775	-936	49
H(18B)	8973	1042	-421	49
H(18C)	7889	1693	-584	49
H(19A)	5603	743	-291	51
H(19B)	5768	1546	273	51
H(19C)	5542	666	653	51
H(20A)	5840	3292	3123	29
H(20B)	4813	3898	2676	29
H(21A)	3292	3078	3065	52
H(21B)	4266	3240	3865	52
H(21C)	4244	2374	3404	52
H(22A)	2907	2375	1779	35
H(22B)	3025	3307	1494	35
H(23A)	3308	2873	211	67
H(23B)	2125	2425	409	67
H(23C)	3369	1928	491	67
H(24A)	6442	3305	1229	26
H(24B)	5288	3077	572	26
H(25A)	4306	4294	951	51
H(25B)	5501	4505	593	51
H(25C)	5523	4532	1550	51

II.12. Crystallographic data for IV-38

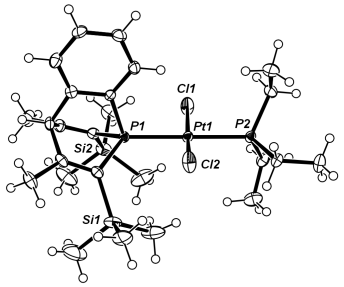


Table 1. Crystal data for mb471bis

Compound	mb471bis
Molecular formula	$C_{25}H_{44}Cl_2P_2PtSi_2$
Molecular weight	728.71
Crystal habit	Pale Yellow Block
Crystal dimensions(mm)	0.22x0.20x0.18
Crystal system	monoclinic
Space group	$P2_1$
a(Å)	10.828(1)
b(Å)	12.364(1)
c(Å)	11.796(1)
α(°)	90.00
β(°)	95.672(1)
γ(°)	90.00
V(Å^3)	1571.5(2)
Z	2
d(g-cm^{-3})	1.540
F(000)	728
μ(cm^{-1})	4.825
Absorption corrections	multi-scan ; 0.4166 min, 0.4771 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.02
HKL ranges	-11 15 ; -15 17 ; -16 15
Reflections measured	11148
Unique data	7378
Rint	0.0268
Reflections used	6991

Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	300
Reflections / parameter	23
wR2	0.0442
R1	0.0219
Flack's parameter	-0.006(3)
Weights a, b	0.0000 ; 0.0000
GoF	0.983
difference peak / hole (e Å^{-3})	0.805(0.094) / -1.094(0.094)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb471bis

atom	x	y	z	U(eq)
Pt(1)	1959(1)	1936(1)	7098(1)	16(1)
Cl(1)	222(1)	3030(1)	6829(1)	38(1)
Cl(2)	3597(1)	748(1)	7132(1)	34(1)
P(1)	3233(1)	3224(1)	6375(1)	15(1)
P(2)	708(1)	654(1)	7802(1)	17(1)
Si(1)	5710(1)	2803(1)	8179(1)	29(1)
Si(2)	2179(1)	5507(1)	7396(1)	26(1)
C(1)	4932(3)	3240(2)	6755(3)	18(1)
C(2)	5487(3)	3839(2)	6003(3)	20(1)
C(3)	4683(3)	4454(3)	5060(3)	20(1)
C(4)	3746(3)	5151(2)	5627(3)	20(1)
C(5)	2998(3)	4701(2)	6342(3)	19(1)
C(6)	6856(3)	3992(3)	5957(4)	30(1)
C(7)	3770(4)	6337(2)	5298(3)	32(1)
C(8)	3196(3)	2963(2)	4851(3)	15(1)
C(9)	2498(3)	2172(2)	4250(3)	22(1)
C(10)	2581(3)	2063(4)	3077(3)	27(1)
C(11)	3352(4)	2740(3)	2524(3)	26(1)
C(12)	4048(3)	3532(3)	3134(3)	25(1)
C(13)	3973(3)	3641(2)	4291(3)	19(1)
C(14)	6716(4)	1589(3)	8097(4)	37(1)
C(15)	4587(4)	2587(4)	9248(3)	48(1)
C(16)	6729(5)	3941(4)	8758(4)	64(2)
C(17)	3226(4)	6666(3)	7919(4)	51(1)
C(18)	654(4)	6052(3)	6757(4)	37(1)
C(19)	1963(5)	4689(4)	8688(4)	52(1)
C(20)	1464(3)	-603(2)	8283(3)	22(1)
C(21)	618(4)	-1382(3)	8869(3)	32(1)
C(22)	48(3)	1182(3)	9057(3)	24(1)
C(23)	1045(4)	1394(3)	10036(3)	34(1)
C(24)	-595(3)	231(3)	6799(3)	26(1)
C(25)	-169(4)	-482(3)	5846(3)	34(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb471bis

Pt(1)-P(2)	2.2933(8	Pt(1)-Cl(2)	2.301(1)
Pt(1)-Cl(1)	2.312(1)	Pt(1)-P(1)	2.3236(8)
P(1)-C(8)	1.822(3)	P(1)-C(5)	1.844(3)
P(1)-C(1)	1.850(3)	P(2)-C(20)	1.820(3)
P(2)-C(24)	1.826(3)	P(2)-C(22)	1.827(3)

Si(1)-C(15)	1.856(4)	Si(1)-C(14)	1.862(3)
Si(1)-C(16)	1.874(4)	Si(1)-C(1)	1.882(3)
Si(2)-C(19)	1.863(5)	Si(2)-C(18)	1.872(4)
Si(2)-C(5)	1.883(3)	Si(2)-C(17)	1.892(4)
C(1)-C(2)	1.343(5)	C(2)-C(6)	1.501(5)
C(2)-C(3)	1.543(5)	C(3)-C(13)	1.512(5)
C(3)-C(4)	1.534(5)	C(3)-H(3)	1.0000
C(4)-C(5)	1.346(5)	C(4)-C(7)	1.519(4)
C(6)-H(6A)	0.9800	C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800	C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800	C(7)-H(7C)	0.9800
C(8)-C(9)	1.387(4)	C(8)-C(13)	1.399(4)
C(9)-C(10)	1.403(4)	C(9)-H(9)	0.9500
C(10)-C(11)	1.390(5)	C(10)-H(10)	0.9500
C(11)-C(12)	1.392(5)	C(11)-H(11)	0.9500
C(12)-C(13)	1.382(5)	C(12)-H(12)	0.9500
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800
C(20)-C(21)	1.540(5)	C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900	C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800	C(21)-H(21C)	0.9800
C(22)-C(23)	1.524(5)	C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900	C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800	C(23)-H(23C)	0.9800
C(24)-C(25)	1.535(5)	C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900	C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800	C(25)-H(25C)	0.9800

P(2)-Pt(1)-Cl(2)	91.94(3)	P(2)-Pt(1)-Cl(1)	87.29(3)
Cl(2)-Pt(1)-Cl(1)	172.30(4)	P(2)-Pt(1)-P(1)	179.48(3)
Cl(2)-Pt(1)-P(1)	87.66(3)	Cl(1)-Pt(1)-P(1)	93.06(3)
C(8)-P(1)-C(5)	99.5(1)	C(8)-P(1)-C(1)	99.5(1)
C(5)-P(1)-C(1)	97.2(1)	C(8)-P(1)-Pt(1)	106.6(1)
C(5)-P(1)-Pt(1)	126.9(1)	C(1)-P(1)-Pt(1)	122.1(1)
C(20)-P(2)-C(24)	104.6(2)	C(20)-P(2)-C(22)	104.6(2)
C(24)-P(2)-C(22)	106.8(2)	C(20)-P(2)-Pt(1)	116.1(1)
C(24)-P(2)-Pt(1)	114.2(1)	C(22)-P(2)-Pt(1)	109.8(1)
C(15)-Si(1)-C(14)	110.2(2)	C(15)-Si(1)-C(16)	105.2(2)
C(14)-Si(1)-C(16)	107.3(2)	C(15)-Si(1)-C(1)	112.4(2)
C(14)-Si(1)-C(1)	113.4(2)	C(16)-Si(1)-C(1)	107.8(2)
C(19)-Si(2)-C(18)	110.3(2)	C(19)-Si(2)-C(5)	111.0(2)
C(18)-Si(2)-C(5)	112.3(2)	C(19)-Si(2)-C(17)	105.3(2)
C(18)-Si(2)-C(17)	109.6(2)	C(5)-Si(2)-C(17)	108.1(2)
C(2)-C(1)-P(1)	110.2(2)	C(2)-C(1)-Si(1)	123.9(3)
P(1)-C(1)-Si(1)	124.1(2)	C(1)-C(2)-C(6)	127.0(3)
C(1)-C(2)-C(3)	119.4(3)	C(6)-C(2)-C(3)	113.6(3)
C(13)-C(3)-C(4)	108.4(3)	C(13)-C(3)-C(2)	108.8(3)
C(4)-C(3)-C(2)	108.2(3)	C(13)-C(3)-H(3)	110.5
C(4)-C(3)-H(3)	110.5	C(2)-C(3)-H(3)	110.5
C(5)-C(4)-C(7)	125.9(3)	C(5)-C(4)-C(3)	120.4(3)
C(7)-C(4)-C(3)	113.7(3)	C(4)-C(5)-P(1)	109.4(2)
C(4)-C(5)-Si(2)	123.2(2)	P(1)-C(5)-Si(2)	125.7(2)
C(2)-C(6)-H(6A)	109.5	C(2)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5	C(2)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5	H(6B)-C(6)-H(6C)	109.5

C(4)-C(7)-H(7A)	109.5	C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5	C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5	H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(13)	120.3(3)	C(9)-C(8)-P(1)	125.9(2)
C(13)-C(8)-P(1)	113.8(2)	C(8)-C(9)-C(10)	119.2(3)
C(8)-C(9)-H(9)	120.4	C(10)-C(9)-H(9)	120.4
C(11)-C(10)-C(9)	120.4(4)	C(11)-C(10)-H(10)	119.8
C(9)-C(10)-H(10)	119.8	C(10)-C(11)-C(12)	120.1(3)
C(10)-C(11)-H(11)	120.0	C(12)-C(11)-H(11)	120.0
C(13)-C(12)-C(11)	119.8(3)	C(13)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1	C(12)-C(13)-C(8)	120.3(3)
C(12)-C(13)-C(3)	125.5(3)	C(8)-C(13)-C(3)	114.1(3)
Si(1)-C(14)-H(14A)	109.5	Si(1)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	Si(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
Si(1)-C(15)-H(15A)	109.5	Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5	Si(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
Si(1)-C(16)-H(16A)	109.5	Si(1)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5	Si(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(16B)-C(16)-H(16C)	109.5
Si(2)-C(17)-H(17A)	109.5	Si(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5	Si(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(17B)-C(17)-H(17C)	109.5
Si(2)-C(18)-H(18A)	109.5	Si(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5	Si(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5	H(18B)-C(18)-H(18C)	109.5
Si(2)-C(19)-H(19A)	109.5	Si(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5	Si(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5	H(19B)-C(19)-H(19C)	109.5
C(21)-C(20)-P(2)	113.9(3)	C(21)-C(20)-H(20A)	108.8
P(2)-C(20)-H(20A)	108.8	C(21)-C(20)-H(20B)	108.8
P(2)-C(20)-H(20B)	108.8	H(20A)-C(20)-H(20B)	107.7
C(20)-C(21)-H(21A)	109.5	C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5	C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5	H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-P(2)	111.8(3)	C(23)-C(22)-H(22A)	109.3
P(2)-C(22)-H(22A)	109.3	C(23)-C(22)-H(22B)	109.3
P(2)-C(22)-H(22B)	109.3	H(22A)-C(22)-H(22B)	107.9
C(22)-C(23)-H(23A)	109.5	C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5	C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5	H(23B)-C(23)-H(23C)	109.5
C(25)-C(24)-P(2)	111.7(3)	C(25)-C(24)-H(24A)	109.3
P(2)-C(24)-H(24A)	109.3	C(25)-C(24)-H(24B)	109.3
P(2)-C(24)-H(24B)	109.3	H(24A)-C(24)-H(24B)	107.9
C(24)-C(25)-H(25A)	109.5	C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5	C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5	H(25B)-C(25)-H(25C)	109.5

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb471bis

atom	U11	U22	U33	U23	U13	U12
Pt(1)	15(1)	18(1)	15(1)	2(1)	4(1)	0(1)
Cl(1)	20(1)	31(1)	62(1)	22(1)	1(1)	4(1)
Cl(2)	23(1)	23(1)	58(1)	2(1)	19(1)	5(1)
P(1)	14(1)	16(1)	16(1)	0(1)	3(1)	0(1)
P(2)	15(1)	19(1)	17(1)	3(1)	4(1)	1(1)
Si(1)	25(1)	36(1)	23(1)	-4(1)	-7(1)	6(1)
Si(2)	23(1)	30(1)	27(1)	-10(1)	4(1)	6(1)
C(1)	17(2)	17(1)	20(2)	-5(1)	2(1)	0(1)
C(2)	15(2)	19(1)	26(2)	-8(1)	3(1)	-1(1)

C(3)	20(2)	19(1)	21(2)	1(1)	7(2)	-5(2)
C(4)	22(2)	17(1)	22(2)	-1(1)	3(1)	-1(1)
C(5)	19(2)	17(1)	21(2)	-1(1)	-1(1)	2(1)
C(6)	18(2)	29(2)	45(2)	-7(2)	7(2)	-4(1)
C(7)	44(2)	18(2)	36(2)	4(2)	7(2)	-3(2)
C(8)	13(1)	17(1)	15(2)	2(1)	2(1)	2(1)
C(9)	18(2)	23(2)	24(2)	2(1)	3(1)	-2(1)
C(10)	27(2)	32(2)	20(2)	-6(2)	1(1)	-5(2)
C(11)	33(2)	32(2)	14(2)	-1(1)	4(2)	-1(2)
C(12)	30(2)	25(2)	23(2)	2(1)	9(2)	-1(2)
C(13)	18(2)	18(1)	22(2)	-1(1)	4(1)	2(1)
C(14)	24(2)	46(2)	39(2)	5(2)	-4(2)	16(2)
C(15)	39(3)	82(3)	22(2)	-5(2)	-2(2)	16(2)
C(16)	68(4)	62(3)	55(3)	-19(3)	-24(3)	-10(3)
C(17)	37(2)	54(3)	62(3)	-36(2)	2(2)	-1(2)
C(18)	28(2)	35(2)	49(3)	-8(2)	3(2)	11(2)
C(19)	74(4)	65(3)	21(2)	-5(2)	17(2)	24(3)
C(20)	26(2)	19(2)	21(2)	5(1)	4(2)	0(1)
C(21)	34(2)	23(2)	41(2)	9(2)	11(2)	-1(2)
C(22)	25(2)	26(2)	22(2)	2(1)	9(1)	3(1)
C(23)	39(2)	42(2)	23(2)	-4(2)	4(2)	11(2)
C(24)	18(2)	30(2)	30(2)	4(2)	-2(2)	-4(1)
C(25)	41(2)	36(2)	25(2)	-6(2)	-3(2)	-6(2)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb471bis

atom	x	y	z	U(eq)
H(3)	5216	4917	4612	24
H(6A)	7074	4749	6117	45
H(6B)	7076	3799	5195	45
H(6C)	7311	3526	6526	45
H(7A)	3027	6697	5526	48
H(7B)	3786	6400	4471	48
H(7C)	4512	6681	5683	48
H(9)	1970	1710	4629	26
H(10)	2108	1523	2657	32
H(11)	3404	2663	1728	31
H(12)	4574	3996	2755	30
H(14A)	7057	1381	8866	56
H(14B)	7396	1758	7637	56
H(14C)	6223	991	7745	56
H(15A)	4164	1893	9103	72
H(15B)	3973	3172	9192	72
H(15C)	5029	2583	10014	72
H(16A)	7058	3775	9542	95
H(16B)	6243	4610	8747	95
H(16C)	7418	4032	8287	95
H(17A)	3148	7253	7359	76
H(17B)	4088	6416	8020	76
H(17C)	2982	6929	8648	76
H(18A)	776	6459	6064	56
H(18B)	305	6531	7306	56
H(18C)	80	5450	6567	56
H(19A)	1374	5055	9138	79
H(19B)	2762	4608	9148	79
H(19C)	1639	3974	8458	79
H(20A)	1764	-974	7619	26

H(20B)	2197	-429	8822	26
H(21A)	361	-1041	9557	48
H(21B)	1072	-2050	9075	48
H(21C)	-117	-1551	8346	48
H(22A)	-400	1864	8854	28
H(22B)	-559	655	9306	28
H(23A)	1461	714	10266	51
H(23B)	662	1700	10683	51
H(23C)	1655	1907	9788	51
H(24A)	-1197	-175	7213	31
H(24B)	-1020	880	6459	31
H(25A)	516	-126	5509	52
H(25B)	-863	-593	5259	52
H(25C)	111	-1183	6163	52

II.13. Crystallographic data for IV-39

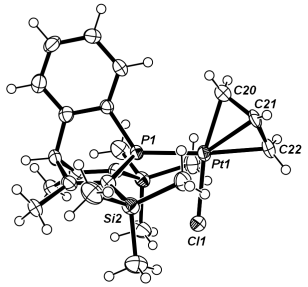


Table 1. Crystal data for mb732

Compound	mb732
Molecular formula	$C_{22}H_{34}ClPPtSi_2$
Molecular weight	616.18
Crystal habit	Colorless Needle
Crystal dimensions(mm)	0.20x0.08x0.02
Crystal system	triclinic
Space group	P -1
a(Å)	10.040(1)
b(Å)	15.536(1)
c(Å)	16.192(1)
α(°)	86.124(1)
β(°)	83.128(1)
γ(°)	89.351(1)
V(Å^3)	2501.8(3)
Z	4
d(g-cm^{-3})	1.636
F(000)	1216
μ(cm^{-1})	5.881
Absorption corrections	multi-scan ; 0.3859 min, 0.8914 max

Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.01
HKL ranges	-14 13 ; -21 21 ; -22 22
Reflections measured	36719
Unique data	14560
Rint	0.0571
Reflections used	10223
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	529
Reflections / parameter	19
wR2	0.1022
R1	0.0407
Weights a, b	0.0381 ; 2.4965
GoF	1.055
difference peak / hole (e Å^{-3})	1.606(0.159) / -1.414(0.159)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb732

atom	x	y	z	U(eq)
Pt(1)	-568(1)	1820(1)	6059(1)	26(1)
Cl(1)	-1703(1)	3167(1)	5983(1)	37(1)
P(1)	722(1)	2332(1)	4893(1)	24(1)
Si(1)	-1914(2)	2237(1)	3838(1)	31(1)
Si(2)	1885(2)	3870(1)	5938(1)	30(1)
C(1)	-146(5)	2573(3)	3972(3)	27(1)
C(2)	691(5)	2957(3)	3334(3)	27(1)
C(3)	2170(5)	3067(3)	3456(3)	28(1)
C(4)	2223(5)	3629(3)	4206(3)	28(1)
C(5)	1633(5)	3354(3)	4942(3)	26(1)
C(6)	2141(5)	1736(3)	4383(3)	23(1)
C(7)	2624(5)	934(3)	4631(3)	32(1)
C(8)	3718(5)	577(4)	4154(4)	36(1)
C(9)	4299(5)	1022(4)	3430(4)	37(1)
C(10)	3840(5)	1835(4)	3191(3)	35(1)
C(11)	2753(5)	2187(3)	3665(3)	28(1)
C(12)	331(6)	3310(4)	2508(3)	36(1)
C(13)	2960(6)	4471(3)	3974(4)	36(1)
C(14)	-3026(6)	3190(4)	3715(5)	49(2)
C(15)	-1790(7)	1587(4)	2900(4)	46(2)
C(16)	-2701(6)	1488(4)	4706(4)	41(1)
C(17)	1561(5)	3104(4)	6879(3)	33(1)
C(18)	830(6)	4853(4)	6059(4)	43(1)
C(19)	3718(6)	4165(4)	5867(4)	45(2)
Pt(2)	6965(1)	8060(1)	-541(1)	30(1)
Cl(2)	6078(2)	6921(1)	-1207(1)	41(1)
P(2)	5801(1)	7509(1)	657(1)	26(1)
Si(3)	2991(2)	8018(1)	-145(1)	34(1)

Si(4)	7622(1)	5719(1)	552(1)	30(1)
C(23)	3953(5)	7480(3)	674(3)	27(1)
C(24)	3388(5)	7053(4)	1365(3)	32(1)
C(25)	4268(5)	6730(3)	2047(3)	30(1)
C(26)	5281(5)	6089(3)	1644(3)	28(1)
C(27)	6153(5)	6387(3)	989(3)	26(1)
C(28)	5818(5)	7969(3)	1672(3)	29(1)
C(29)	6507(5)	8689(4)	1839(4)	34(1)
C(30)	6373(6)	8942(4)	2656(4)	44(2)
C(31)	5585(6)	8497(4)	3278(4)	40(1)
C(32)	4897(5)	7773(4)	3100(3)	36(1)
C(33)	5009(5)	7508(3)	2298(3)	31(1)
C(34)	1933(5)	6795(4)	1595(4)	36(1)
C(35)	5113(6)	5167(4)	1997(3)	37(1)
C(36)	2445(7)	7218(4)	-844(4)	47(2)
C(37)	3949(6)	8900(4)	-791(4)	47(2)
C(38)	1473(6)	8567(4)	394(5)	52(2)
C(39)	7119(7)	4958(4)	-191(4)	46(2)
C(40)	9005(6)	6420(4)	34(4)	48(2)
C(41)	8378(6)	5120(4)	1429(4)	44(2)
C(20)	120(6)	567(4)	6346(4)	40(1)
C(21)	-570(10)	901(7)	7089(7)	31(3)
C(22)	-1890(30)	1170(20)	7080(10)	38(4)
C(20A)	120(6)	567(4)	6346(4)	40(1)
C(21A)	-1150(20)	630(10)	6720(10)	46(5)
C(22A)	-1530(30)	1220(20)	7270(20)	38(4)
C(42)	7924(6)	9162(4)	-232(4)	42(1)
C(43)	8660(10)	8840(10)	-1003(8)	41(4)
C(44)	7920(20)	8760(20)	-1690(20)	40(4)
C(42A)	7924(6)	9162(4)	-232(4)	42(1)
C(43A)	7760(20)	9252(8)	-1080(10)	47(5)
C(44A)	8320(30)	8710(20)	-1560(20)	40(4)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb732

Pt(1)-C(20)	2.100(6)	Pt(1)-C(21)	2.12(1)
Pt(1)-C(21A)	2.12(1)	Pt(1)-C(22)	2.18(3)
Pt(1)-C(22A)	2.22(3)	Pt(1)-P(1)	2.261(1)
Pt(1)-Cl(1)	2.373(1)	P(1)-C(1)	1.830(5)
P(1)-C(6)	1.833(5)	P(1)-C(5)	1.852(5)
Si(1)-C(14)	1.859(6)	Si(1)-C(16)	1.867(6)
Si(1)-C(15)	1.872(6)	Si(1)-C(1)	1.898(5)
Si(2)-C(18)	1.857(6)	Si(2)-C(17)	1.867(5)
Si(2)-C(19)	1.890(6)	Si(2)-C(5)	1.892(5)
C(1)-C(2)	1.360(7)	C(2)-C(12)	1.495(7)
C(2)-C(3)	1.534(7)	C(3)-C(11)	1.514(7)
C(3)-C(4)	1.548(7)	C(3)-H(3)	1.0000
C(4)-C(5)	1.313(7)	C(4)-C(13)	1.513(7)
C(6)-C(7)	1.383(7)	C(6)-C(11)	1.397(7)
C(7)-C(8)	1.397(7)	C(7)-H(7)	0.9500
C(8)-C(9)	1.388(8)	C(8)-H(8)	0.9500
C(9)-C(10)	1.386(8)	C(9)-H(9)	0.9500
C(10)-C(11)	1.387(7)	C(10)-H(10)	0.9500
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800	C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(17)-H(17A)	0.9800

C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800
Pt(2)-C(42)	2.092(5)	Pt(2)-C(43A)	2.12(1)
Pt(2)-C(43)	2.13(1)	Pt(2)-C(44A)	2.21(4)
Pt(2)-C(44)	2.22(3)	Pt(2)-P(2)	2.261(1)
Pt(2)-Cl(2)	2.368(1)	P(2)-C(27)	1.833(5)
P(2)-C(28)	1.839(5)	P(2)-C(23)	1.853(5)
Si(3)-C(36)	1.865(6)	Si(3)-C(37)	1.868(6)
Si(3)-C(23)	1.877(6)	Si(3)-C(38)	1.889(6)
Si(4)-C(40)	1.857(6)	Si(4)-C(39)	1.858(6)
Si(4)-C(41)	1.876(6)	Si(4)-C(27)	1.889(5)
C(23)-C(24)	1.332(7)	C(24)-C(34)	1.515(7)
C(24)-C(25)	1.548(8)	C(25)-C(33)	1.529(7)
C(25)-C(26)	1.537(7)	C(25)-H(25)	1.0000
C(26)-C(27)	1.351(7)	C(26)-C(35)	1.509(7)
C(28)-C(29)	1.380(7)	C(28)-C(33)	1.385(7)
C(29)-C(30)	1.395(8)	C(29)-H(29)	0.9500
C(30)-C(31)	1.358(8)	C(30)-H(30)	0.9500
C(31)-C(32)	1.391(8)	C(31)-H(31)	0.9500
C(32)-C(33)	1.380(7)	C(32)-H(32)	0.9500
C(34)-H(34A)	0.9800	C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800	C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800	C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800	C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800	C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800	C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800	C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800	C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800	C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800	C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800	C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800	C(41)-H(41C)	0.9800
C(20)-C(21)	1.44(1)	C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900	C(21)-C(22)	1.38(3)
C(21)-H(21)	0.9500	C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900	C(21A)-C(22A)	1.34(4)
C(21A)-H(21A)	0.9500	C(22A)-H(22C)	0.9900
C(22A)-H(22D)	0.9900	C(42)-C(43)	1.49(1)
C(42)-H(42A)	0.9900	C(42)-H(42B)	0.9900
C(43)-C(44)	1.43(2)	C(43)-H(43)	0.9500
C(44)-H(44A)	0.9900	C(44)-H(44B)	0.9900
C(43A)-C(44A)	1.27(4)	C(43A)-H(43A)	0.9500
C(44A)-H(44C)	0.9900	C(44A)-H(44D)	0.9900

C(20)-Pt(1)-C(21)	39.9(3)	C(20)-Pt(1)-C(21A)	37.4(4)
C(21)-Pt(1)-C(21A)	27.3(4)	C(20)-Pt(1)-C(22)	68.7(8)
C(21)-Pt(1)-C(22)	37.4(8)	C(21A)-Pt(1)-C(22)	33(1)
C(20)-Pt(1)-C(22A)	66(1)	C(21)-Pt(1)-C(22A)	29(1)
C(21A)-Pt(1)-C(22A)	36(1)	C(22)-Pt(1)-C(22A)	13.3(8)
C(20)-Pt(1)-P(1)	106.7(2)	C(21)-Pt(1)-P(1)	141.9(3)
C(21A)-Pt(1)-P(1)	140.3(4)	C(22)-Pt(1)-P(1)	171.4(7)
C(22A)-Pt(1)-P(1)	170.7(8)	C(20)-Pt(1)-Cl(1)	167.6(2)
C(21)-Pt(1)-Cl(1)	128.8(3)	C(21A)-Pt(1)-Cl(1)	130.7(4)
C(22)-Pt(1)-Cl(1)	98.9(8)	C(22A)-Pt(1)-Cl(1)	102(1)
P(1)-Pt(1)-Cl(1)	85.68(5)	C(1)-P(1)-C(6)	97.5(2)
C(1)-P(1)-C(5)	101.2(2)	C(6)-P(1)-C(5)	96.6(2)
C(1)-P(1)-Pt(1)	116.1(2)	C(6)-P(1)-Pt(1)	123.5(2)
C(5)-P(1)-Pt(1)	117.5(2)	C(14)-Si(1)-C(16)	109.0(3)
C(14)-Si(1)-C(15)	111.2(3)	C(16)-Si(1)-C(15)	104.3(3)
C(14)-Si(1)-C(1)	111.3(2)	C(16)-Si(1)-C(1)	113.7(2)

C(15)-Si(1)-C(1)	107.1(3)	C(18)-Si(2)-C(17)	110.7(3)
C(18)-Si(2)-C(19)	109.9(3)	C(17)-Si(2)-C(19)	105.6(3)
C(18)-Si(2)-C(5)	110.7(3)	C(17)-Si(2)-C(5)	112.5(2)
C(19)-Si(2)-C(5)	107.3(3)	C(2)-C(1)-P(1)	111.2(4)
C(2)-C(1)-Si(1)	122.1(4)	P(1)-C(1)-Si(1)	126.4(3)
C(1)-C(2)-C(12)	127.1(5)	C(1)-C(2)-C(3)	118.3(4)
C(12)-C(2)-C(3)	114.6(4)	C(11)-C(3)-C(2)	108.6(4)
C(11)-C(3)-C(4)	108.7(4)	C(2)-C(3)-C(4)	107.8(4)
C(11)-C(3)-H(3)	110.6	C(2)-C(3)-H(3)	110.6
C(4)-C(3)-H(3)	110.6	C(5)-C(4)-C(13)	127.4(5)
C(5)-C(4)-C(3)	119.3(4)	C(13)-C(4)-C(3)	113.3(4)
C(4)-C(5)-P(1)	111.4(4)	C(4)-C(5)-Si(2)	123.3(4)
P(1)-C(5)-Si(2)	124.8(3)	C(7)-C(6)-C(11)	120.0(5)
C(7)-C(6)-P(1)	127.8(4)	C(11)-C(6)-P(1)	112.1(4)
C(6)-C(7)-C(8)	119.6(5)	C(6)-C(7)-H(7)	120.2
C(8)-C(7)-H(7)	120.2	C(9)-C(8)-C(7)	120.0(5)
C(9)-C(8)-H(8)	120.0	C(7)-C(8)-H(8)	120.0
C(10)-C(9)-C(8)	120.7(5)	C(10)-C(9)-H(9)	119.7
C(8)-C(9)-H(9)	119.7	C(9)-C(10)-C(11)	119.2(5)
C(9)-C(10)-H(10)	120.4	C(11)-C(10)-H(10)	120.4
C(10)-C(11)-C(6)	120.5(5)	C(10)-C(11)-C(3)	123.4(5)
C(6)-C(11)-C(3)	116.1(4)	C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	Si(2)-C(19)-H(19A)	109.5
Si(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(42)-Pt(2)-C(43A)	39.0(4)
C(42)-Pt(2)-C(43)	41.3(4)	C(43A)-Pt(2)-C(43)	30.6(5)
C(42)-Pt(2)-C(44A)	64.6(8)	C(43A)-Pt(2)-C(44A)	34(1)
C(43)-Pt(2)-C(44A)	27.5(7)	C(42)-Pt(2)-C(44)	70.6(7)
C(43A)-Pt(2)-C(44)	35(1)	C(43)-Pt(2)-C(44)	38.2(5)
C(44A)-Pt(2)-C(44)	12.5(8)	C(42)-Pt(2)-P(2)	106.0(2)
C(43A)-Pt(2)-P(2)	139.7(4)	C(43)-Pt(2)-P(2)	142.2(3)
C(44A)-Pt(2)-P(2)	169.7(6)	C(44)-Pt(2)-P(2)	172(1)
C(42)-Pt(2)-Cl(2)	166.8(2)	C(43A)-Pt(2)-Cl(2)	128.4(4)
C(43)-Pt(2)-Cl(2)	126.9(4)	C(44A)-Pt(2)-Cl(2)	102.5(8)
C(44)-Pt(2)-Cl(2)	96.3(7)	P(2)-Pt(2)-Cl(2)	87.10(5)
C(27)-P(2)-C(28)	97.7(2)	C(27)-P(2)-C(23)	101.0(2)
C(28)-P(2)-C(23)	96.8(2)	C(27)-P(2)-Pt(2)	117.1(2)
C(28)-P(2)-Pt(2)	123.9(2)	C(23)-P(2)-Pt(2)	116.0(2)
C(36)-Si(3)-C(37)	109.2(3)	C(36)-Si(3)-C(23)	111.2(3)
C(37)-Si(3)-C(23)	113.2(3)	C(36)-Si(3)-C(38)	109.6(3)
C(37)-Si(3)-C(38)	105.0(3)	C(23)-Si(3)-C(38)	108.4(3)
C(40)-Si(4)-C(39)	109.9(3)	C(40)-Si(4)-C(41)	104.0(3)

C(39)-Si(4)-C(41)	110.7(3)	C(40)-Si(4)-C(27)	110.9(3)
C(39)-Si(4)-C(27)	111.5(3)	C(41)-Si(4)-C(27)	109.6(3)
C(24)-C(23)-P(2)	110.7(4)	C(24)-C(23)-Si(3)	124.2(4)
P(2)-C(23)-Si(3)	125.0(3)	C(23)-C(24)-C(34)	128.5(5)
C(23)-C(24)-C(25)	119.7(5)	C(34)-C(24)-C(25)	111.8(5)
C(33)-C(25)-C(26)	109.8(4)	C(33)-C(25)-C(24)	107.8(4)
C(26)-C(25)-C(24)	106.4(4)	C(33)-C(25)-H(25)	110.9
C(26)-C(25)-H(25)	110.9	C(24)-C(25)-H(25)	110.9
C(27)-C(26)-C(35)	127.1(5)	C(27)-C(26)-C(25)	117.9(5)
C(35)-C(26)-C(25)	114.8(4)	C(26)-C(27)-P(2)	112.0(4)
C(26)-C(27)-Si(4)	121.9(4)	P(2)-C(27)-Si(4)	125.9(3)
C(29)-C(28)-C(33)	121.0(5)	C(29)-C(28)-P(2)	127.2(4)
C(33)-C(28)-P(2)	111.8(4)	C(28)-C(29)-C(30)	118.4(5)
C(28)-C(29)-H(29)	120.8	C(30)-C(29)-H(29)	120.8
C(31)-C(30)-C(29)	121.4(5)	C(31)-C(30)-H(30)	119.3
C(29)-C(30)-H(30)	119.3	C(30)-C(31)-C(32)	119.5(5)
C(30)-C(31)-H(31)	120.3	C(32)-C(31)-H(31)	120.3
C(33)-C(32)-C(31)	120.4(5)	C(33)-C(32)-H(32)	119.8
C(31)-C(32)-H(32)	119.8	C(32)-C(33)-C(28)	119.3(5)
C(32)-C(33)-C(25)	123.7(5)	C(28)-C(33)-C(25)	117.0(4)
C(24)-C(34)-H(34A)	109.5	C(24)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5	C(24)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5	H(34B)-C(34)-H(34C)	109.5
C(26)-C(35)-H(35A)	109.5	C(26)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5	C(26)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5	H(35B)-C(35)-H(35C)	109.5
Si(3)-C(36)-H(36A)	109.5	Si(3)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5	Si(3)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5	H(36B)-C(36)-H(36C)	109.5
Si(3)-C(37)-H(37A)	109.5	Si(3)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5	Si(3)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5	H(37B)-C(37)-H(37C)	109.5
Si(3)-C(38)-H(38A)	109.5	Si(3)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5	Si(3)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5	H(38B)-C(38)-H(38C)	109.5
Si(4)-C(39)-H(39A)	109.5	Si(4)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5	Si(4)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5	H(39B)-C(39)-H(39C)	109.5
Si(4)-C(40)-H(40A)	109.5	Si(4)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5	Si(4)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5	H(40B)-C(40)-H(40C)	109.5
Si(4)-C(41)-H(41A)	109.5	Si(4)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5	Si(4)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5	H(41B)-C(41)-H(41C)	109.5
C(21)-C(20)-Pt(1)	70.8(4)	C(21)-C(20)-H(20A)	116.5
Pt(1)-C(20)-H(20A)	116.5	C(21)-C(20)-H(20B)	116.5
Pt(1)-C(20)-H(20B)	116.5	H(20A)-C(20)-H(20B)	113.5
C(22)-C(21)-C(20)	118(1)	C(22)-C(21)-Pt(1)	74(1)
C(20)-C(21)-Pt(1)	69.3(4)	C(22)-C(21)-H(21)	121.0
C(20)-C(21)-H(21)	121.0	Pt(1)-C(21)-H(21)	127.9
C(21)-C(22)-Pt(1)	69(1)	C(21)-C(22)-H(22A)	116.8
Pt(1)-C(22)-H(22A)	116.8	C(21)-C(22)-H(22B)	116.8
Pt(1)-C(22)-H(22B)	116.8	H(22A)-C(22)-H(22B)	113.8
C(22A)-C(21A)-Pt(1)	76(2)	C(22A)-C(21A)-H(21A)	118.7
Pt(1)-C(21A)-H(21A)	127.0	C(21A)-C(22A)-Pt(1)	68(2)
C(21A)-C(22A)-H(22C)	116.9	Pt(1)-C(22A)-H(22C)	116.9
C(21A)-C(22A)-H(22D)	116.9	Pt(1)-C(22A)-H(22D)	116.9
H(22C)-C(22A)-H(22D)	113.9	C(43)-C(42)-Pt(2)	70.8(4)
C(43)-C(42)-H(42A)	116.5	Pt(2)-C(42)-H(42A)	116.5
C(43)-C(42)-H(42B)	116.5	Pt(2)-C(42)-H(42B)	116.5
H(42A)-C(42)-H(42B)	113.5	C(44)-C(43)-C(42)	117(2)
C(44)-C(43)-Pt(2)	74(1)	C(42)-C(43)-Pt(2)	67.9(4)
C(44)-C(43)-H(43)	121.3	C(42)-C(43)-H(43)	121.3

Pt(2)-C(43)-H(43)	128.7	C(43)-C(44)-Pt(2)	68(1)
C(43)-C(44)-H(44A)	116.9	Pt(2)-C(44)-H(44A)	116.9
C(43)-C(44)-H(44B)	116.9	Pt(2)-C(44)-H(44B)	116.9
H(44A)-C(44)-H(44B)	113.9	C(44A)-C(43A)-Pt(2)	77(2)
C(44A)-C(43A)-H(43A)	120.8	Pt(2)-C(43A)-H(43A)	124.4
C(43A)-C(44A)-Pt(2)	69(2)	C(43A)-C(44A)-H(44C)	116.7
Pt(2)-C(44A)-H(44C)	116.7	C(43A)-C(44A)-H(44D)	116.7
Pt(2)-C(44A)-H(44D)	116.7	H(44C)-C(44A)-H(44D)	113.7

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb732

atom	U11	U22	U33	U23	U13	U12
Pt(1)	29(1)	26(1)	22(1)	2(1)	0(1)	-3(1)
Cl(1)	36(1)	30(1)	42(1)	2(1)	8(1)	4(1)
P(1)	25(1)	22(1)	22(1)	2(1)	-1(1)	-2(1)
Si(1)	32(1)	29(1)	32(1)	1(1)	-7(1)	-4(1)
Si(2)	35(1)	27(1)	30(1)	-3(1)	-6(1)	-3(1)
C(1)	30(3)	27(3)	24(2)	-2(2)	-3(2)	1(2)
C(2)	35(3)	23(3)	23(2)	-1(2)	-4(2)	2(2)
C(3)	30(3)	25(3)	27(3)	2(2)	3(2)	-5(2)
C(4)	30(3)	22(3)	33(3)	1(2)	-3(2)	-2(2)
C(5)	28(3)	24(3)	26(2)	1(2)	-5(2)	-1(2)
C(6)	21(2)	22(2)	27(2)	1(2)	-2(2)	-2(2)
C(7)	36(3)	25(3)	33(3)	6(2)	-1(2)	-4(2)
C(8)	33(3)	27(3)	47(3)	3(3)	1(3)	5(2)
C(9)	26(3)	38(3)	44(3)	-8(3)	6(2)	4(2)
C(10)	33(3)	38(3)	32(3)	-4(3)	3(2)	-6(2)
C(11)	23(2)	31(3)	29(3)	-1(2)	-4(2)	-2(2)
C(12)	44(3)	33(3)	28(3)	6(2)	-1(2)	3(3)
C(13)	40(3)	25(3)	39(3)	8(2)	5(2)	-6(2)
C(14)	34(3)	36(3)	77(5)	6(3)	-17(3)	-1(3)
C(15)	64(4)	41(4)	37(3)	-3(3)	-19(3)	-6(3)
C(16)	38(3)	45(4)	41(3)	0(3)	-3(3)	-14(3)
C(17)	38(3)	35(3)	27(3)	-2(2)	-5(2)	-3(2)
C(18)	51(4)	34(3)	46(4)	-9(3)	-11(3)	5(3)
C(19)	47(3)	37(3)	51(4)	4(3)	-16(3)	-9(3)
Pt(2)	31(1)	27(1)	30(1)	1(1)	2(1)	-4(1)
Cl(2)	60(1)	35(1)	28(1)	0(1)	0(1)	-13(1)
P(2)	26(1)	24(1)	25(1)	-2(1)	0(1)	-2(1)
Si(3)	32(1)	28(1)	43(1)	3(1)	-8(1)	0(1)
Si(4)	33(1)	29(1)	28(1)	-4(1)	-4(1)	4(1)
C(23)	26(2)	26(3)	29(3)	-5(2)	-1(2)	0(2)
C(24)	32(3)	34(3)	31(3)	-12(2)	-1(2)	-5(2)
C(25)	33(3)	33(3)	22(2)	-3(2)	2(2)	0(2)
C(26)	30(3)	31(3)	24(2)	-1(2)	-5(2)	-2(2)
C(27)	31(3)	22(3)	25(2)	0(2)	-3(2)	-1(2)
C(28)	26(2)	31(3)	30(3)	-5(2)	-2(2)	2(2)
C(29)	37(3)	27(3)	40(3)	-2(2)	-6(2)	2(2)
C(30)	43(3)	38(3)	54(4)	-18(3)	-10(3)	7(3)
C(31)	41(3)	45(4)	33(3)	-13(3)	-1(3)	8(3)
C(32)	33(3)	45(4)	29(3)	-8(3)	3(2)	7(3)
C(33)	31(3)	29(3)	34(3)	-7(2)	-3(2)	3(2)
C(34)	28(3)	40(3)	40(3)	-3(3)	-1(2)	-3(2)
C(35)	46(3)	33(3)	32(3)	2(2)	-7(2)	-7(3)
C(36)	58(4)	44(4)	41(3)	6(3)	-23(3)	-8(3)
C(37)	48(4)	36(3)	55(4)	9(3)	-8(3)	5(3)
C(38)	37(3)	41(4)	75(5)	3(4)	-5(3)	5(3)
C(39)	63(4)	37(3)	41(3)	-9(3)	-17(3)	11(3)
C(40)	29(3)	46(4)	65(4)	6(3)	8(3)	8(3)
C(41)	53(4)	42(4)	40(3)	-3(3)	-16(3)	12(3)
C(20)	46(3)	30(3)	41(3)	7(3)	5(3)	4(3)

C(21)	32(6)	34(6)	24(5)	16(4)	-4(4)	-2(5)
C(22)	50(10)	37(5)	30(10)	14(7)	2(6)	-3(8)
C(20A)	46(3)	30(3)	41(3)	7(3)	5(3)	4(3)
C(21A)	60(10)	35(8)	36(8)	15(6)	4(7)	-8(7)
C(22A)	50(10)	37(5)	30(10)	14(7)	2(6)	-3(8)
C(42)	46(3)	32(3)	48(4)	-1(3)	0(3)	-13(3)
C(43)	24(6)	44(8)	53(8)	9(6)	0(5)	-21(6)
C(44)	50(10)	45(5)	30(10)	1(6)	-10(8)	-30(10)
C(42A)	46(3)	32(3)	48(4)	-1(3)	0(3)	-13(3)
C(43A)	60(10)	17(6)	60(10)	11(6)	4(7)	-17(7)
C(44A)	50(10)	45(5)	30(10)	1(6)	-10(8)	-30(10)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb732

atom	x	y	z	U(eq)
H(3)	2680	3347	2942	34
H(7)	2213	627	5121	38
H(8)	4065	32	4326	44
H(9)	5017	765	3094	44
H(10)	4266	2147	2708	42
H(12A)	-631	3230	2487	54
H(12B)	842	3005	2063	54
H(12C)	545	3926	2432	54
H(13A)	2773	4856	4429	54
H(13B)	2657	4744	3466	54
H(13C)	3926	4359	3877	54
H(14A)	-3925.0002	2997	3635	73
H(14B)	-2660	3560	3229	73
H(14C)	-3079	3516	4216	73
H(15A)	-1345	1036	3021	69
H(15B)	-1267	1905	2429	69
H(15C)	-2692	1479	2757	69
H(16A)	-3525	1248	4547	62
H(16B)	-2918	1805	5208	62
H(16C)	-2075	1018	4819	62
H(17A)	2008	3310	7332	50
H(17B)	1911	2532	6745	50
H(17C)	593	3067	7052	50
H(18A)	1007	5244	5558	64
H(18B)	1044	5144	6545	64
H(18C)	-120	4691	6138	64
H(19A)	3858	4740	5583	67
H(19B)	4260	3741	5551	67
H(19C)	3985	4167	6429	67
H(25)	3705	6445	2540	36
H(29)	7059	9005	1408	41
H(30)	6842	9436	2779	53
H(31)	5504	8679	3829	47
H(32)	4348	7458	3533	43
H(34A)	1426	6959	1127	54
H(34B)	1555	7090	2086	54
H(34C)	1877	6169	1719	54
H(35A)	5624	4784	1619	55
H(35B)	4161	5012	2058	55
H(35C)	5443	5108	2544	55
H(36A)	1782	7486	-1179	70
H(36B)	2042	6718	-506	70

H(36C)	3222	7029	-1213	70
H(37A)	4705	8651	-1137	70
H(37B)	4287	9302	-425	70
H(37C)	3356	9209	-1150	70
H(38A)	1741	8892	844	77
H(38B)	807	8132	626	77
H(38C)	1081	8962	-10	77
H(39A)	6741	5283	-649.0001	69
H(39B)	6443	4558	98	69
H(39C)	7906	4632	-416	69
H(40A)	9821	6073	-74	72
H(40B)	9169	6876	398	72
H(40C)	8754	6679	-494.0000	72
H(41A)	7799	4633	1650	67
H(41B)	8459	5509	1872	67
H(41C)	9268	4904	1222	67
H(20A)	-327.0000	91	6111	48
H(20B)	1103	491	6329	48
H(21)	-130	938	7574	37
H(22A)	-2269	1523	7531	46
H(22B)	-2520	740	6919	46
H(20C)	262	184	5879	48
H(20D)	833	516	6720	48
H(21A)	-1807	240	6591	55
H(22C)	-1022	1240	7753	46
H(22D)	-2508.0002	1319	7402	46
H(42A)	7437	9715	-296	51
H(42B)	8385	9103	276	51
H(43)	9587	8692	-1034	49
H(44A)	8334	8402	-2143	48
H(44B)	7461	9282	-1899	48
H(42C)	7378	9549	136	51
H(42D)	8855	9083	-95	51
H(43A)	7238	9711	-1295	57
H(44C)	9297	8614	-1544.9999	48
H(44D)	8046	8713	-2127	48

II.14. Crystallographic data for IV-40

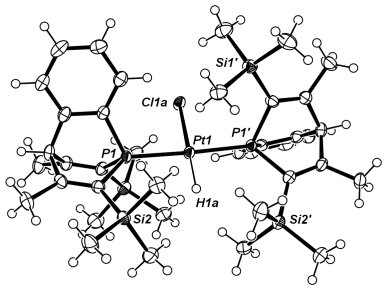


Table 1. Crystal data for mb516

Compound	mb516

Molecular formula	$C_{38}H_{59}ClP_2PtSi_4,4(C_4H_8O)$
Molecular weight	1209.11
Crystal habit	Colorless Needle
Crystal dimensions(mm)	0.20x0.10x0.10
Crystal system	monoclinic
Space group	C2/c
a(Å)	19.770(1)
b(Å)	17.431(1)
c(Å)	17.693(1)
α(°)	90.00
β(°)	100.590(1)
γ(°)	90.00
V(Å^3)	5993.3(6)
Z	4
d(g-cm^{-3})	1.340
F(000)	2512
μ(cm^{-1})	2.559
Absorption corrections	multi-scan ; 0.6286 min, 0.7839 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.02
HKL ranges	-27 26 ; -24 22 ; -17 24
Reflections measured	20562
Unique data	8676
Rint	0.0504
Reflections used	6493
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	310
Reflections / parameter	20
wR2	0.1084
R1	0.0452
Weights a, b	0.0505 ; 0.0000
GoF	0.985
difference peak / hole (e Å^{-3})	1.264(0.147) / -3.161(0.147)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb516

atom	x	y	z	U(eq)
Pt(1)	5000	4725(1)	2500	19(1)
P(1)	3861(1)	4691(1)	1930(1)	19(1)
Si(1)	3486(1)	4092(1)	3569(1)	25(1)
Si(2)	3701(1)	6494(1)	1517(1)	23(1)
Cl(1A)	5000	3340(1)	2500	25(1)
Cl(1B)	5000	6084(5)	2500	25(1)
C(1)	3264(2)	4252(2)	2495(2)	23(1)
C(2)	2651(2)	4122(2)	2054(2)	25(1)
C(3)	2514(2)	4412(3)	1219(2)	26(1)
C(4)	2674(2)	5268(2)	1209(2)	24(1)
C(5)	3314(2)	5511(2)	1513(2)	22(1)
C(6)	3691(2)	4080(2)	1076(2)	22(1)
C(7)	4171(2)	3736(3)	709(2)	29(1)
C(8)	3954(2)	3304(3)	44(2)	32(1)
C(9)	3259(2)	3212(3)	-241(2)	34(1)
C(10)	2775(2)	3550(3)	122(2)	30(1)
C(11)	2992(2)	3989(2)	784(2)	25(1)
C(12)	2058(2)	3675(3)	2280(3)	36(1)
C(13)	2065(2)	5741(3)	841(3)	33(1)
C(14)	4125(2)	4822(3)	4006(2)	31(1)
C(15)	3789(2)	3093(3)	3792(2)	36(1)
C(16)	2724(2)	4278(3)	4036(3)	38(1)
C(17)	3931(2)	6833(3)	2533(2)	36(1)
C(18)	4461(2)	6430(3)	1025(2)	29(1)
C(19)	3121(2)	7228(3)	963(3)	37(1)
O(1)	648(2)	4447(3)	964(4)	98(2)
C(20)	4728(4)	8724(5)	328(6)	103(3)
C(21)	494(4)	3834(6)	484(6)	121(3)
C(22)	136(4)	4523(7)	1387(6)	126(4)
C(23)	4537(5)	9102(7)	988(7)	148(4)
O(2)	3484(3)	2147(4)	1786(4)	123(2)
C(24)	2106(3)	6876(5)	2934(5)	79(2)
C(25)	2053(6)	6187(6)	2943(5)	127(4)
C(26)	1332(6)	5836(5)	2906(8)	170(6)
C(27)	4049(4)	1545(7)	1820(10)	209(8)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb516

Pt(1)-P(1)	2.293(1)	Pt(1)-P(1)#2	2.293(1)
Pt(1)-Cl(1B)	2.370(8)	Pt(1)-Cl(1A)	2.413(2)
Pt(1)-H(1A)	1.68(1)	Pt(1)-H(1B)	1.70(1)
P(1)-C(6)	1.828(4)	P(1)-C(1)	1.847(4)
P(1)-C(5)	1.862(4)	Si(1)-C(14)	1.858(4)
Si(1)-C(15)	1.860(5)	Si(1)-C(16)	1.876(4)
Si(1)-C(1)	1.890(4)	Si(2)-C(17)	1.867(4)
Si(2)-C(19)	1.871(4)	Si(2)-C(18)	1.873(4)
Si(2)-C(5)	1.876(4)	Cl(1A)-H(1B)	0.71(1)
Cl(1B)-H(1A)	0.69(1)	C(1)-C(2)	1.337(5)
C(2)-C(12)	1.521(5)	C(2)-C(3)	1.537(6)
C(3)-C(11)	1.514(6)	C(3)-C(4)	1.525(6)
C(3)-H(3)	1.0000	C(4)-C(5)	1.349(5)
C(4)-C(13)	1.505(5)	C(6)-C(7)	1.382(5)
C(6)-C(11)	1.392(5)	C(7)-C(8)	1.396(6)
C(7)-H(7)	0.9500	C(8)-C(9)	1.383(6)

C(8)-H(8)	0.9500	C(9)-C(10)	1.381(6)
C(9)-H(9)	0.9500	C(10)-C(11)	1.399(6)
C(10)-H(10)	0.9500	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800	C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800	C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800	C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800	C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800	C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800	C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800	O(1)-C(21)	1.36(1)
O(1)-C(22)	1.37(1)	C(20)-C(23)	1.45(1)
C(20)-C(21)#3	1.50(1)	C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900	C(21)-C(20)#3	1.50(1)
C(21)-H(21A)	0.9900	C(21)-H(21B)	0.9900
C(22)-C(23)#3	1.46(1)	C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900	C(23)-C(22)#3	1.46(1)
C(23)-H(23A)	0.9900	C(23)-H(23B)	0.9900
O(2)-C(24)#4	1.428(8)	O(2)-C(27)	1.53(1)
C(24)-C(25)	1.21(1)	C(24)-O(2)#4	1.428(8)
C(24)-H(24A)	0.9900	C(24)-H(24B)	0.9900
C(25)-C(26)	1.54(1)	C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900	C(26)-C(27)#4	1.57(1)
C(26)-H(26A)	0.9900	C(26)-H(26B)	0.9900
C(27)-C(26)#4	1.57(1)	C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900		

P(1)-Pt(1)-P(1)#2	177.03(5)	P(1)-Pt(1)-Cl(1B)	91.48(3)
P(1)#2-Pt(1)-Cl(1B)	91.48(3)	P(1)-Pt(1)-Cl(1A)	88.52(3)
P(1)#2-Pt(1)-Cl(1A)	88.52(3)	Cl(1B)-Pt(1)-Cl(1A)	180.0(1)
P(1)-Pt(1)-H(1A)	91.48(3)	P(1)#2-Pt(1)-H(1A)	91.48(3)
Cl(1B)-Pt(1)-H(1A)	0.000(1)	Cl(1A)-Pt(1)-H(1A)	180.000(2)
P(1)-Pt(1)-H(1B)	88.52(3)	P(1)#2-Pt(1)-H(1B)	88.52(3)
Cl(1B)-Pt(1)-H(1B)	180.000(2	Cl(1A)-Pt(1)-H(1B)	0.0
H(1A)-Pt(1)-H(1B)	180.000(2	C(6)-P(1)-C(1)	99.7(2)
C(6)-P(1)-C(5)	96.6(2)	C(1)-P(1)-C(5)	98.7(2)
C(6)-P(1)-Pt(1)	113.3(1)	C(1)-P(1)-Pt(1)	116.4(1)
C(5)-P(1)-Pt(1)	127.3(1)	C(14)-Si(1)-C(15)	112.7(2)
C(14)-Si(1)-C(16)	103.8(2)	C(15)-Si(1)-C(16)	108.8(2)
C(14)-Si(1)-C(1)	109.3(2)	C(15)-Si(1)-C(1)	110.9(2)
C(16)-Si(1)-C(1)	111.2(2)	C(17)-Si(2)-C(19)	107.8(2)
C(17)-Si(2)-C(18)	113.1(2)	C(19)-Si(2)-C(18)	105.3(2)
C(17)-Si(2)-C(5)	108.7(2)	C(19)-Si(2)-C(5)	114.3(2)
C(18)-Si(2)-C(5)	107.8(2)	Pt(1)-Cl(1A)-H(1B)	0.000(1)
Pt(1)-Cl(1B)-H(1A)	0.000(2)	C(2)-C(1)-P(1)	110.8(3)
C(2)-C(1)-Si(1)	125.5(3)	P(1)-C(1)-Si(1)	123.6(2)
C(1)-C(2)-C(12)	126.4(4)	C(1)-C(2)-C(3)	119.1(3)
C(12)-C(2)-C(3)	114.5(3)	C(11)-C(3)-C(4)	108.6(3)
C(11)-C(3)-C(2)	108.2(3)	C(4)-C(3)-C(2)	109.4(3)
C(11)-C(3)-H(3)	110.2	C(4)-C(3)-H(3)	110.2
C(2)-C(3)-H(3)	110.2	C(5)-C(4)-C(13)	128.1(4)
C(5)-C(4)-C(3)	119.0(4)	C(13)-C(4)-C(3)	112.9(3)
C(4)-C(5)-P(1)	110.5(3)	C(4)-C(5)-Si(2)	129.9(3)
P(1)-C(5)-Si(2)	119.5(2)	C(7)-C(6)-C(11)	119.8(4)
C(7)-C(6)-P(1)	127.1(3)	C(11)-C(6)-P(1)	113.1(3)
C(6)-C(7)-C(8)	119.9(4)	C(6)-C(7)-H(7)	120.0
C(8)-C(7)-H(7)	120.0	C(9)-C(8)-C(7)	120.0(4)
C(9)-C(8)-H(8)	120.0	C(7)-C(8)-H(8)	120.0

C(10)-C(9)-C(8)	120.6(4)	C(10)-C(9)-H(9)	119.7
C(8)-C(9)-H(9)	119.7	C(9)-C(10)-C(11)	119.4(4)
C(9)-C(10)-H(10)	120.3	C(11)-C(10)-H(10)	120.3
C(6)-C(11)-C(10)	120.2(4)	C(6)-C(11)-C(3)	115.2(3)
C(10)-C(11)-C(3)	124.6(4)	C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	Si(2)-C(19)-H(19A)	109.5
Si(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(21)-O(1)-C(22)	108.2(6)
C(23)-C(20)-C(21)#3	101.4(7)	C(23)-C(20)-H(20A)	111.5
C(21)#3-C(20)-H(20A)	111.5	C(23)-C(20)-H(20B)	111.5
C(21)#3-C(20)-H(20B)	111.5	H(20A)-C(20)-H(20B)	109.3
O(1)-C(21)-C(20)#3	108.5(7)	O(1)-C(21)-H(21A)	110.0
C(20)#3-C(21)-H(21A)	110.0	O(1)-C(21)-H(21B)	110.0
C(20)#3-C(21)-H(21B)	110.0	H(21A)-C(21)-H(21B)	108.4
O(1)-C(22)-C(23)#3	107.6(8)	O(1)-C(22)-H(22A)	110.2
C(23)#3-C(22)-H(22A)	110.2	O(1)-C(22)-H(22B)	110.2
C(23)#3-C(22)-H(22B)	110.2	H(22A)-C(22)-H(22B)	108.5
C(20)-C(23)-C(22)#3	108.0(8)	C(20)-C(23)-H(23A)	110.1
C(22)#3-C(23)-H(23A)	110.1	C(20)-C(23)-H(23B)	110.1
C(22)#3-C(23)-H(23B)	110.1	H(23A)-C(23)-H(23B)	108.4
C(24)#4-O(2)-C(27)	113.5(8)	C(25)-C(24)-O(2)#4	104.3(8)
C(25)-C(24)-H(24A)	110.9	O(2)#4-C(24)-H(24A)	110.9
C(25)-C(24)-H(24B)	110.9	O(2)#4-C(24)-H(24B)	110.9
H(24A)-C(24)-H(24B)	108.9	C(24)-C(25)-C(26)	118(1)
C(24)-C(25)-H(25A)	107.7	C(26)-C(25)-H(25A)	107.7
C(24)-C(25)-H(25B)	107.7	C(26)-C(25)-H(25B)	107.7
H(25A)-C(25)-H(25B)	107.1	C(25)-C(26)-C(27)#4	99.6(6)
C(25)-C(26)-H(26A)	111.9	C(27)#4-C(26)-H(26A)	111.9
C(25)-C(26)-H(26B)	111.9	C(27)#4-C(26)-H(26B)	111.9
H(26A)-C(26)-H(26B)	109.6	O(2)-C(27)-C(26)#4	99.4(7)
O(2)-C(27)-H(27A)	111.9	C(26)#4-C(27)-H(27A)	111.9
O(2)-C(27)-H(27B)	111.9	C(26)#4-C(27)-H(27B)	111.9
H(27A)-C(27)-H(27B)	109.6		

Estimated standard deviations are given in the parenthesis.
Symmetry operators ::
1: x, y, z 2: -x, y, -z+1/2 3: x+1/2, y+1/2, z
4: -x+1/2, y+1/2, -z+1/ 5: -x, -y, -z 6: x, -y, z-1/2
7: -x+1/2, -y+1/2, -z 8: x+1/2, -y+1/2, z-1/2

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb516

atom	U11	U22	U33	U23	U13	U12
Pt(1)	17(1)	20(1)	19(1)	0	0(1)	0
P(1)	16(1)	20(1)	18(1)	0(1)	-1(1)	-1(1)
Si(1)	28(1)	27(1)	20(1)	0(1)	4(1)	-3(1)
Si(2)	23(1)	22(1)	24(1)	1(1)	0(1)	3(1)
Cl(1A)	24(1)	16(1)	30(1)	0	-5(1)	0
Cl(1B)	24(1)	16(1)	30(1)	0	-5(1)	0
C(1)	22(2)	23(2)	23(2)	0(2)	4(2)	-5(2)
C(2)	23(2)	28(2)	23(2)	2(2)	3(2)	-1(2)
C(3)	19(2)	33(2)	23(2)	0(2)	-6(2)	-1(2)
C(4)	22(2)	28(2)	20(2)	5(2)	2(2)	6(2)
C(5)	23(2)	23(2)	20(2)	0(2)	3(2)	3(2)
C(6)	22(2)	20(2)	21(2)	1(2)	1(2)	-3(2)
C(7)	30(2)	31(2)	23(2)	1(2)	1(2)	-2(2)
C(8)	41(2)	31(3)	26(2)	-4(2)	6(2)	1(2)
C(9)	48(3)	29(2)	23(2)	-4(2)	-1(2)	-11(2)
C(10)	31(2)	31(2)	25(2)	-1(2)	-2(2)	-8(2)
C(11)	27(2)	25(2)	21(2)	3(2)	-1(2)	-4(2)
C(12)	28(2)	45(3)	34(2)	3(2)	5(2)	-14(2)
C(13)	21(2)	43(3)	34(2)	8(2)	2(2)	7(2)
C(14)	39(2)	32(3)	21(2)	-1(2)	5(2)	-2(2)
C(15)	46(3)	33(3)	27(2)	1(2)	0(2)	-3(2)
C(16)	40(2)	42(3)	34(2)	-3(2)	16(2)	-7(2)
C(17)	35(2)	35(3)	34(2)	-6(2)	-1(2)	3(2)
C(18)	31(2)	32(2)	25(2)	5(2)	7(2)	0(2)
C(19)	31(2)	31(3)	48(3)	10(2)	4(2)	8(2)
O(1)	46(3)	95(4)	145(5)	5(4)	-1(3)	-19(3)
C(20)	77(5)	80(6)	135(8)	-5(6)	-29(5)	-16(4)
C(21)	64(5)	130(10)	150(10)	-52(7)	-17(5)	10(5)
C(22)	67(5)	170(10)	140(10)	-41(8)	8(6)	-33(6)
C(23)	78(6)	190(10)	180(10)	-40(10)	18(7)	-47(7)
O(2)	111(5)	120(5)	138(5)	5(4)	22(4)	-16(4)
C(24)	51(4)	84(6)	104(6)	37(5)	23(4)	27(4)
C(25)	210(10)	107(8)	82(6)	-39(6)	72(7)	-57(8)
C(26)	170(10)	35(5)	260(10)	-15(7)	-70(10)	-30(6)
C(27)	52(5)	120(10)	440(20)	-100(10)	-10(10)	10(6)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb516

atom	x	y	z	U(eq)
H(1A)	5000	5686(6)	2500	29
H(1B)	5000	3748(6)	2500	29
H(3)	2023	4316	974	32
H(7)	4648	3794	908	34
H(8)	4284	3072	-212	39
H(9)	3114	2913	-691	41
H(10)	2298	3485	-76	36
H(12A)	2191	3495	2812	54
H(12B)	1948	3233	1937	54
H(12C)	1654	4008	2239	54
H(13A)	2194	6284	860	50
H(13B)	1685	5664	1120	50
H(13C)	1920	5582	304	50
H(14A)	4532	4793	3765	46

H(14B)	4258	4725	4559	46
H(14C)	3920	5335	3924	46
H(15A)	3450	2731	3518	54
H(15B)	3845	3003	4347	54
H(15C)	4232	3017	3629	54
H(16A)	2454	4703	3774	56
H(16B)	2882	4411	4578	56
H(16C)	2437	3816	4002	56
H(17A)	3510	6922	2737	53
H(17B)	4192	7313	2549	53
H(17C)	4212	6443	2843	53
H(18A)	4783	6043	1282	44
H(18B)	4691	6929	1049	44
H(18C)	4306	6284	486	44
H(19A)	2965	7046	435	56
H(19B)	3371	7711	952	56
H(19C)	2722	7311	1209	56
H(20A)	4510	8972	-159.0000	124
H(20B)	4603	8173	310	124
H(21A)	724	3367	727	145
H(21B)	658	3926	-4	145
H(22A)	20	5071	1434	151
H(22B)	289	4311	1910	151
H(23A)	4390	8717	1337	177
H(23B)	4149	9459	818	177
H(24A)	2105	7064	2406	94
H(24B)	2536	7046	3272	94
H(25A)	2351	5996	3418	153
H(25B)	2243	5981	2504	153
H(26A)	1341	5393	3258	204
H(26B)	1122	5679	2377	204
H(27A)	4468	1684	2190	250
H(27B)	4169	1456	1305	250

II.15. Crystallographic data for IV-41

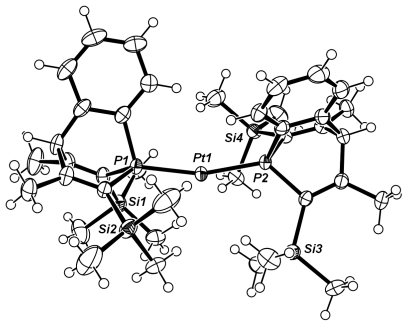


Table 1. Crystal data for mb623

Compound	mb623

Molecular formula	$C_{38}H_{58}P_2PtSi_4$
Molecular weight	884.23
Crystal habit	Colorless Block
Crystal dimensions(mm)	0.20x0.10x0.04
Crystal system	orthorhombic
Space group	Pbca
a(Å)	10.333(1)
b(Å)	18.871(1)
c(Å)	43.480(1)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
V(Å^3)	8478.3(10)
Z	8
d(g-cm^{-3})	1.385
F(000)	3600
μ(cm^{-1})	3.523
Absorption corrections	multi-scan ; 0.5393 min, 0.8719 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	28.28
HKL ranges	-13 11 ; -25 20 ; -57 57
Reflections measured	35911
Unique data	10342
Rint	0.0591
Reflections used	6794
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	422
Reflections / parameter	16
wR2	0.0827
R1	0.0372
Weights a, b	0.0277 ; 7.4025
GoF	0.995
difference peak / hole (e Å^{-3})	1.211(0.114) / -1.378(0.114)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb623

atom	x	y	z	U(eq)
Pt(1)	5264(1)	440(1)	1213(1)	25(1)
P(1)	4296(1)	-54(1)	1622(1)	25(1)
P(2)	6691(1)	694(1)	842(1)	24(1)
Si(1)	3581(1)	1431(1)	1958(1)	32(1)
Si(2)	2023(1)	-711(1)	1212(1)	37(1)

Si(3)	4606(1)	1312(1)	363(1)	30(1)
Si(4)	8185(1)	1722(1)	1311(1)	30(1)
C(1)	3754(4)	445(2)	1967(1)	30(1)
C(2)	3434(4)	10(3)	2202(1)	37(1)
C(3)	3455(4)	-794(2)	2145(1)	34(1)
C(4)	2571(4)	-951(2)	1864(1)	33(1)
C(5)	2852(4)	-647(2)	1592(1)	28(1)
C(6)	5376(4)	-679(2)	1817(1)	29(1)
C(7)	6640(4)	-830(2)	1731(1)	33(1)
C(8)	7364(5)	-1332(3)	1895(1)	43(1)
C(9)	6785(5)	-1681(3)	2143(1)	47(1)
C(10)	5518(5)	-1530(2)	2233(1)	43(1)
C(11)	4820(5)	-1017(2)	2069(1)	33(1)
C(12)	3075(6)	213(3)	2526(1)	58(2)
C(13)	1430(5)	-1426(3)	1938(1)	43(1)
C(14)	3184(4)	1708(2)	1560(1)	41(1)
C(15)	5117(4)	1839(3)	2095(1)	44(1)
C(16)	2183(5)	1724(3)	2203(1)	64(2)
C(17)	1717(5)	195(3)	1062(1)	43(1)
C(18)	412(6)	-1154(5)	1233(2)	106(3)
C(19)	3137(6)	-1200(3)	944(1)	66(2)
C(20)	6336(4)	1074(2)	454(1)	28(1)
C(21)	7399(4)	1093(2)	274(1)	29(1)
C(22)	8682(4)	826(2)	408(1)	31(1)
C(23)	9000(4)	1253(2)	697(1)	29(1)
C(24)	8149(4)	1236(2)	932(1)	26(1)
C(25)	7515(4)	-101(2)	699(1)	27(1)
C(26)	7213(4)	-794(2)	777(1)	33(1)
C(27)	7881(5)	-1348(3)	638(1)	41(1)
C(28)	8874(5)	-1202(3)	434(1)	45(1)
C(29)	9199(5)	-504(3)	358(1)	40(1)
C(30)	8501(4)	49(2)	489(1)	31(1)
C(31)	7488(4)	1326(3)	-57(1)	39(1)
C(32)	10248(4)	1658(2)	678(1)	38(1)
C(33)	3983(4)	1898(2)	675(1)	38(1)
C(34)	4382(5)	1807(3)	-10(1)	50(1)
C(35)	3664(5)	474(2)	335(1)	48(1)
C(36)	6650(4)	2238(2)	1339(1)	34(1)
C(37)	9535(4)	2381(3)	1348(1)	51(1)
C(38)	8319(5)	1062(3)	1630(1)	48(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb623

Pt(1)-P(2)	2.239(1)	Pt(1)-P(1)	2.243(1)
P(1)-C(6)	1.832(4)	P(1)-C(1)	1.858(4)
P(1)-C(5)	1.869(4)	P(2)-C(25)	1.832(4)
P(2)-C(24)	1.863(4)	P(2)-C(20)	1.867(4)
Si(1)-C(14)	1.853(5)	Si(1)-C(15)	1.862(5)
Si(1)-C(1)	1.871(4)	Si(1)-C(16)	1.878(5)
Si(2)-C(17)	1.856(5)	Si(2)-C(18)	1.865(6)
Si(2)-C(5)	1.866(4)	Si(2)-C(19)	1.879(6)
Si(3)-C(35)	1.861(5)	Si(3)-C(33)	1.866(5)
Si(3)-C(20)	1.886(4)	Si(3)-C(34)	1.887(5)
Si(4)-C(36)	1.866(4)	Si(4)-C(38)	1.868(5)
Si(4)-C(37)	1.876(5)	Si(4)-C(24)	1.887(4)
C(1)-C(2)	1.350(6)	C(2)-C(12)	1.510(6)
C(2)-C(3)	1.536(6)	C(3)-C(11)	1.509(6)
C(3)-C(4)	1.556(6)	C(3)-H(3)	1.0000
C(4)-C(5)	1.344(6)	C(4)-C(13)	1.514(6)
C(6)-C(7)	1.388(6)	C(6)-C(11)	1.392(6)
C(7)-C(8)	1.402(6)	C(7)-H(7)	0.9500

C(8)-C(9)	1.396(7)	C(8)-H(8)	0.9500
C(9)-C(10)	1.397(7)	C(9)-H(9)	0.9500
C(10)-C(11)	1.401(6)	C(10)-H(10)	0.9500
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800	C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800
C(20)-C(21)	1.349(5)	C(21)-C(31)	1.508(5)
C(21)-C(22)	1.533(6)	C(22)-C(30)	1.519(6)
C(22)-C(23)	1.528(6)	C(22)-H(22)	1.0000
C(23)-C(24)	1.346(5)	C(23)-C(32)	1.501(6)
C(25)-C(26)	1.387(6)	C(25)-C(30)	1.397(6)
C(26)-C(27)	1.390(6)	C(26)-H(26)	0.9500
C(27)-C(28)	1.385(7)	C(27)-H(27)	0.9500
C(28)-C(29)	1.399(6)	C(28)-H(28)	0.9500
C(29)-C(30)	1.390(6)	C(29)-H(29)	0.9500
C(31)-H(31A)	0.9800	C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800	C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800	C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800	C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800	C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800	C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800	C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800	C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800	C(36)-H(36C)	0.9800
C(37)-H(37A)	0.9800	C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800	C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800	C(38)-H(38C)	0.9800

P(2)-Pt(1)-P(1)	162.62(4)	C(6)-P(1)-C(1)	97.8(2)
C(6)-P(1)-C(5)	97.7(2)	C(1)-P(1)-C(5)	96.8(2)
C(6)-P(1)-Pt(1)	111.3(2)	C(1)-P(1)-Pt(1)	124.3(1)
C(5)-P(1)-Pt(1)	123.4(1)	C(25)-P(2)-C(24)	98.3(2)
C(25)-P(2)-C(20)	95.7(2)	C(24)-P(2)-C(20)	97.9(2)
C(25)-P(2)-Pt(1)	112.1(1)	C(24)-P(2)-Pt(1)	119.9(1)
C(20)-P(2)-Pt(1)	127.1(1)	C(14)-Si(1)-C(15)	111.8(2)
C(14)-Si(1)-C(1)	108.8(2)	C(15)-Si(1)-C(1)	108.8(2)
C(14)-Si(1)-C(16)	106.0(2)	C(15)-Si(1)-C(16)	110.6(3)
C(1)-Si(1)-C(16)	110.7(2)	C(17)-Si(2)-C(18)	106.1(3)
C(17)-Si(2)-C(5)	109.2(2)	C(18)-Si(2)-C(5)	113.3(2)
C(17)-Si(2)-C(19)	109.8(2)	C(18)-Si(2)-C(19)	110.9(4)
C(5)-Si(2)-C(19)	107.4(2)	C(35)-Si(3)-C(33)	111.7(2)
C(35)-Si(3)-C(20)	107.9(2)	C(33)-Si(3)-C(20)	108.3(2)
C(35)-Si(3)-C(34)	107.6(2)	C(33)-Si(3)-C(34)	106.9(2)
C(20)-Si(3)-C(34)	114.6(2)	C(36)-Si(4)-C(38)	111.2(2)
C(36)-Si(4)-C(37)	106.3(2)	C(38)-Si(4)-C(37)	108.8(2)
C(36)-Si(4)-C(24)	107.2(2)	C(38)-Si(4)-C(24)	109.0(2)
C(37)-Si(4)-C(24)	114.3(2)	C(2)-C(1)-P(1)	112.1(3)
C(2)-C(1)-Si(1)	126.7(3)	P(1)-C(1)-Si(1)	121.0(2)
C(1)-C(2)-C(12)	127.8(4)	C(1)-C(2)-C(3)	118.4(4)
C(12)-C(2)-C(3)	113.8(4)	C(11)-C(3)-C(2)	108.9(4)
C(11)-C(3)-C(4)	108.9(3)	C(2)-C(3)-C(4)	107.8(4)
C(11)-C(3)-H(3)	110.4	C(2)-C(3)-H(3)	110.4
C(4)-C(3)-H(3)	110.4	C(5)-C(4)-C(13)	127.4(4)

C(5)-C(4)-C(3)	118.8(4)	C(13)-C(4)-C(3)	113.7(4)
C(4)-C(5)-Si(2)	130.6(3)	C(4)-C(5)-P(1)	111.6(3)
Si(2)-C(5)-P(1)	117.8(2)	C(7)-C(6)-C(11)	120.4(4)
C(7)-C(6)-P(1)	125.5(3)	C(11)-C(6)-P(1)	114.1(3)
C(6)-C(7)-C(8)	120.3(4)	C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9	C(9)-C(8)-C(7)	118.8(5)
C(9)-C(8)-H(8)	120.6	C(7)-C(8)-H(8)	120.6
C(8)-C(9)-C(10)	121.4(5)	C(8)-C(9)-H(9)	119.3
C(10)-C(9)-H(9)	119.3	C(9)-C(10)-C(11)	118.8(5)
C(9)-C(10)-H(10)	120.6	C(11)-C(10)-H(10)	120.6
C(6)-C(11)-C(10)	120.3(5)	C(6)-C(11)-C(3)	115.5(4)
C(10)-C(11)-C(3)	124.3(4)	C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	Si(2)-C(19)-H(19A)	109.5
Si(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(21)-C(20)-P(2)	
112.0(3)			
C(21)-C(20)-Si(3)	130.0(3)	P(2)-C(20)-Si(3)	117.9(2)
C(20)-C(21)-C(31)	127.7(4)	C(20)-C(21)-C(22)	118.3(4)
C(31)-C(21)-C(22)	114.0(3)	C(30)-C(22)-C(23)	110.2(3)
C(30)-C(22)-C(21)	107.4(3)	C(23)-C(22)-C(21)	109.1(3)
C(30)-C(22)-H(22)	110.1	C(23)-C(22)-H(22)	110.1
C(21)-C(22)-H(22)	110.1	C(24)-C(23)-C(32)	128.0(4)
C(24)-C(23)-C(22)	118.0(4)	C(32)-C(23)-C(22)	114.0(4)
C(23)-C(24)-P(2)	112.5(3)	C(23)-C(24)-Si(4)	129.6(3)
P(2)-C(24)-Si(4)	117.8(2)	C(26)-C(25)-C(30)	120.9(4)
C(26)-C(25)-P(2)	125.8(3)	C(30)-C(25)-P(2)	113.3(3)
C(25)-C(26)-C(27)	119.5(4)	C(25)-C(26)-H(26)	120.3
C(27)-C(26)-H(26)	120.3	C(28)-C(27)-C(26)	119.8(5)
C(28)-C(27)-H(27)	120.1	C(26)-C(27)-H(27)	120.1
C(27)-C(28)-C(29)	121.0(4)	C(27)-C(28)-H(28)	119.5
C(29)-C(28)-H(28)	119.5	C(30)-C(29)-C(28)	119.1(5)
C(30)-C(29)-H(29)	120.5	C(28)-C(29)-H(29)	120.5
C(29)-C(30)-C(25)	119.6(4)	C(29)-C(30)-C(22)	124.5(4)
C(25)-C(30)-C(22)	115.8(4)	C(21)-C(31)-H(31A)	109.5
C(21)-C(31)-H(31B)	109.5	H(31A)-C(31)-H(31B)	109.5
C(21)-C(31)-H(31C)	109.5	H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5	C(23)-C(32)-H(32A)	109.5
C(23)-C(32)-H(32B)	109.5	H(32A)-C(32)-H(32B)	109.5
C(23)-C(32)-H(32C)	109.5	H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5	Si(3)-C(33)-H(33A)	109.5
Si(3)-C(33)-H(33B)	109.5	H(33A)-C(33)-H(33B)	109.5
Si(3)-C(33)-H(33C)	109.5	H(33A)-C(33)-H(33C)	109.5

H(33B)-C(33)-H(33C)	109.5	Si(3)-C(34)-H(34A)	109.5
Si(3)-C(34)-H(34B)	109.5	H(34A)-C(34)-H(34B)	109.5
Si(3)-C(34)-H(34C)	109.5	H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5	Si(3)-C(35)-H(35A)	109.5
Si(3)-C(35)-H(35B)	109.5	H(35A)-C(35)-H(35B)	109.5
Si(3)-C(35)-H(35C)	109.5	H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5	Si(4)-C(36)-H(36A)	109.5
Si(4)-C(36)-H(36B)	109.5	H(36A)-C(36)-H(36B)	109.5
Si(4)-C(36)-H(36C)	109.5	H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5	Si(4)-C(37)-H(37A)	109.5
Si(4)-C(37)-H(37B)	109.5	H(37A)-C(37)-H(37B)	109.5
Si(4)-C(37)-H(37C)	109.5	H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5	Si(4)-C(38)-H(38A)	109.5
Si(4)-C(38)-H(38B)	109.5	H(38A)-C(38)-H(38B)	109.5
Si(4)-C(38)-H(38C)	109.5	H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5		

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb623

atom	U11	U22	U33	U23	U13	U12
Pt(1)	24(1)	31(1)	21(1)	3(1)	3(1)	-1(1)
P(1)	28(1)	28(1)	20(1)	2(1)	4(1)	-1(1)
P(2)	26(1)	28(1)	19(1)	2(1)	4(1)	0(1)
Si(1)	35(1)	31(1)	30(1)	-3(1)	7(1)	0(1)
Si(2)	43(1)	38(1)	31(1)	6(1)	-10(1)	-11(1)
Si(3)	29(1)	32(1)	28(1)	0(1)	-2(1)	1(1)
Si(4)	28(1)	33(1)	28(1)	-3(1)	-1(1)	0(1)
C(1)	35(2)	32(2)	22(2)	-4(2)	4(2)	-4(2)
C(2)	43(3)	42(3)	27(3)	-6(2)	5(2)	-7(2)
C(3)	50(3)	32(3)	19(2)	2(2)	6(2)	-8(2)
C(4)	43(3)	30(3)	25(3)	1(2)	4(2)	-5(2)
C(5)	30(2)	29(2)	24(2)	2(2)	1(2)	-3(2)
C(6)	40(3)	26(2)	22(2)	-2(2)	-4(2)	-3(2)
C(7)	36(3)	34(3)	30(3)	-4(2)	-2(2)	-4(2)
C(8)	44(3)	38(3)	47(3)	-5(2)	-18(2)	5(2)
C(9)	64(4)	33(3)	43(3)	-4(2)	-26(3)	7(3)
C(10)	72(4)	32(3)	25(3)	3(2)	-13(2)	-6(3)
C(11)	49(3)	29(2)	21(2)	0(2)	-10(2)	-4(2)
C(12)	99(5)	51(3)	25(3)	-6(2)	18(3)	-11(3)
C(13)	50(3)	41(3)	40(3)	7(2)	5(2)	-15(2)
C(14)	42(3)	38(3)	45(3)	-2(2)	-5(2)	9(2)
C(15)	51(3)	39(3)	43(3)	1(2)	-13(2)	1(2)
C(16)	65(4)	52(4)	74(4)	-5(3)	34(3)	6(3)
C(17)	43(3)	51(3)	36(3)	9(2)	-11(2)	5(3)
C(18)	86(5)	152(8)	80(5)	60(5)	-49(4)	-72(5)
C(19)	104(5)	54(4)	40(4)	-6(3)	-17(3)	19(4)
C(20)	31(2)	33(3)	19(2)	0(2)	-1(2)	1(2)
C(21)	33(2)	28(2)	25(2)	2(2)	4(2)	2(2)
C(22)	26(2)	40(3)	27(3)	4(2)	7(2)	3(2)
C(23)	24(2)	31(2)	31(3)	1(2)	1(2)	3(2)
C(24)	23(2)	28(2)	27(2)	1(2)	-1(2)	0(2)
C(25)	31(2)	30(2)	20(2)	-2(2)	-3(2)	4(2)
C(26)	41(3)	31(3)	26(3)	0(2)	0(2)	-1(2)
C(27)	59(3)	33(3)	31(3)	2(2)	-10(2)	4(2)
C(28)	58(3)	39(3)	37(3)	-9(2)	-3(2)	22(3)
C(29)	47(3)	45(3)	27(3)	-1(2)	5(2)	13(3)
C(30)	31(2)	36(3)	25(2)	-1(2)	1(2)	5(2)
C(31)	43(3)	47(3)	26(3)	10(2)	7(2)	3(2)
C(32)	31(2)	42(3)	40(3)	5(2)	9(2)	-5(2)
C(33)	31(3)	42(3)	43(3)	-5(2)	-2(2)	0(2)
C(34)	45(3)	66(4)	39(3)	13(3)	-9(2)	13(3)

C(35)	43(3)	42(3)	60(4)	-12(3)	-1(2)	-5(3)
C(36)	29(2)	37(3)	37(3)	-5(2)	1(2)	0(2)
C(37)	37(3)	59(4)	56(4)	-18(3)	0(2)	-5(3)
C(38)	58(3)	50(3)	35(3)	1(2)	-8(2)	9(3)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb623

atom	x	y	z	U(eq)
H(3)	3136	-1053	2331	41
H(7)	7016	-591	1561	40
H(8)	8232	-1434	1839	51
H(9)	7264	-2029.0001	2252	56
H(10)	5136	-1769	2402	52
H(12A)	3171	726	2552	87
H(12B)	3646	-33	2671	87
H(12C)	2175	77	2566	87
H(13A)	981	-1553.0001	1747	65
H(13B)	833	-1174	2074	65
H(13C)	1740	-1857	2039	65
H(14A)	3143	2227	1550	62
H(14B)	2344	1509	1500	62
H(14C)	3854	1536	1419	62
H(15A)	5198	1770	2317	67
H(15B)	5111	2347	2048	67
H(15C)	5851	1614	1991	67
H(16A)	1518	1354	2204	95
H(16B)	1817	2162	2119	95
H(16C)	2485	1808	2413	95
H(17A)	1182	458	1209	65
H(17B)	1263	163	864	65
H(17C)	2543	441	1033	65
H(18A)	526	-1650.0001	1294	159
H(18B)	-6.0000	-1135	1030	159
H(18C)	-132	-910	1384	159
H(19A)	3960	-945	928	99
H(19B)	2737	-1232	740	99
H(19C)	3292	-1678	1024	99
H(22)	9390	880	253	37
H(26)	6556	-889	924	39
H(27)	7656	-1825	684	49
H(28)	9342	-1582	344	54
H(29)	9888	-409	220	48
H(31A)	6641	1497	-126	58
H(31B)	7755	924	-185	58
H(31C)	8126	1708	-75	58
H(32A)	10460	1854	880	56
H(32B)	10156	2045	529	56
H(32C)	10943	1339	611	56
H(33A)	4000	1641	871	58
H(33B)	3092	2039	628	58
H(33C)	4529	2320	691	58
H(34A)	4995	2203	-20	75
H(34B)	3495	1990	-22	75
H(34C)	4538	1486	-183	75
H(35A)	3993	189	164	72
H(35B)	2749	584	301	72
H(35C)	3755	206	527	72

H(36A)	6609	2583	1171	52
H(36B)	6623	2488	1537	52
H(36C)	5910	1914	1324	52
H(37A)	10365	2130	1357	76
H(37B)	9417	2658	1537	76
H(37C)	9529	2700	1170	76
H(38A)	7577	738	1622	72
H(38B)	8327	1310	1828	72
H(38C)	9122	791	1606	72

II.16. Crystallographic data for IV-42

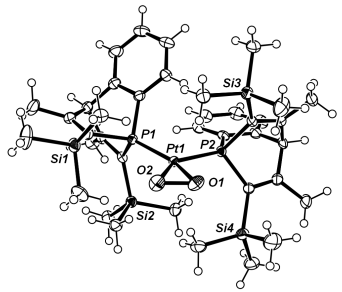


Table 1. Crystal data for mb620

Compound	mb620
Molecular formula	$C_{38}H_{58}O_2P_2PtSi_4$
Molecular weight	916.23
Crystal habit	Pale Brown Block
Crystal dimensions(mm)	0.40x0.40x0.30
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	12.881(1)
b(Å)	17.800(1)
c(Å)	19.600(1)
α(°)	90.00
β(°)	108.536(1)
γ(°)	90.00
V(Å^3)	4260.8(5)
Z	4
d(g-cm^{-3})	1.428
F(000)	1864
μ(cm^{-1})	3.511
Absorption corrections	multi-scan ; 0.3341 min, 0.4190 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite

T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-18 11 ; -24 24 ; -27 26
Reflections measured	27504
Unique data	12316
Rint	0.0232
Reflections used	9977
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	440
Reflections / parameter	22
wR2	0.0842
R1	0.0277
Weights a, b	0.0488 ; 0.0000
GoF	1.054
difference peak / hole (e Å^{-3})	1.183(0.133) / -1.195(0.133)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb620

atom	x	y	z	U(eq)
Pt(1)	7063(1)	2336(1)	2883(1)	16(1)
P(1)	6667(1)	1107(1)	2759(1)	18(1)
P(2)	8904(1)	2388(1)	3207(1)	18(1)
Si(1)	4804(1)	1513(1)	1152(1)	24(1)
Si(2)	5867(1)	1208(1)	4230(1)	24(1)
Si(3)	8959(1)	2157(1)	1582(1)	21(1)
Si(4)	8919(1)	4156(1)	3651(1)	27(1)
O(1)	6342(2)	3348(1)	2829(1)	33(1)
O(2)	5535(2)	2736(1)	2716(1)	31(1)
C(1)	5577(2)	864(2)	1917(2)	20(1)
C(2)	5285(2)	141(2)	1921(2)	23(1)
C(3)	5850(2)	-352(2)	2575(2)	22(1)
C(4)	5695(2)	12(2)	3243(2)	24(1)
C(5)	6050(2)	716(2)	3417(2)	21(1)
C(6)	7596(2)	323(2)	2770(2)	20(1)
C(7)	8703(3)	351(2)	2860(2)	24(1)
C(8)	9286(3)	-313(2)	2870(2)	30(1)
C(9)	8749(3)	-1000(2)	2778(2)	34(1)
C(10)	7636(3)	-1029(2)	2683(2)	30(1)
C(11)	7062(2)	-372(2)	2671(2)	24(1)
C(12)	4420(3)	-277(2)	1342(2)	37(1)
C(13)	5160(3)	-504(2)	3641(2)	34(1)
C(14)	5414(3)	2455(2)	1116(2)	32(1)
C(15)	4710(3)	1083(2)	262(2)	38(1)
C(16)	3414(3)	1665(3)	1249(2)	50(1)
C(17)	4363(3)	1292(2)	4092(2)	45(1)
C(18)	6568(3)	629(2)	5043(2)	34(1)
C(19)	6414(3)	2183(2)	4406(2)	28(1)
C(20)	9665(2)	2110(2)	2590(2)	19(1)
C(21)	10749(2)	2079(2)	2930(2)	24(1)
C(22)	11184(3)	2350(2)	3714(2)	25(1)
C(23)	10760(2)	3150(2)	3760(2)	25(1)
C(24)	9670(2)	3275(2)	3546(2)	23(1)

C(25)	9611(2)	1804(2)	3984(2)	21(1)
C(26)	9127(3)	1370(2)	4386(2)	24(1)
C(27)	9782(3)	976(2)	4978(2)	31(1)
C(28)	10912(3)	1014(2)	5172(2)	36(1)
C(29)	11401(3)	1444(2)	4767(2)	33(1)
C(30)	10747(2)	1844(2)	4183(2)	25(1)
C(31)	11615(3)	1786(2)	2628(2)	34(1)
C(32)	11672(3)	3704(2)	4087(2)	39(1)
C(33)	8264(3)	3091(2)	1444(2)	28(1)
C(34)	7953(3)	1376(2)	1237(2)	26(1)
C(35)	9929(3)	2185(2)	1046(2)	30(1)
C(36)	7979(3)	4494(2)	2770(2)	36(1)
C(37)	8217(3)	3930(2)	4324(2)	30(1)
C(38)	9816(3)	4988(2)	4004(3)	54(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb620

Pt(1)-O(1)	2.014(2)	Pt(1)-O(2)	2.019(2)
Pt(1)-P(1)	2.2428(7	Pt(1)-P(2)	2.2532(8)
P(1)-C(6)	1.834(3)	P(1)-C(1)	1.845(3)
P(1)-C(5)	1.852(3)	P(2)-C(25)	1.829(3)
P(2)-C(20)	1.851(3)	P(2)-C(24)	1.868(3)
Si(1)-C(14)	1.861(3)	Si(1)-C(15)	1.872(3)
Si(1)-C(16)	1.880(4)	Si(1)-C(1)	1.904(3)
Si(2)-C(19)	1.864(3)	Si(2)-C(18)	1.872(3)
Si(2)-C(17)	1.875(3)	Si(2)-C(5)	1.897(3)
Si(3)-C(33)	1.866(3)	Si(3)-C(35)	1.871(3)
Si(3)-C(34)	1.873(3)	Si(3)-C(20)	1.896(3)
Si(4)-C(36)	1.865(4)	Si(4)-C(37)	1.866(3)
Si(4)-C(38)	1.870(4)	Si(4)-C(24)	1.887(3)
O(1)-O(2)	1.473(3)	C(1)-C(2)	1.342(4)
C(2)-C(12)	1.510(4)	C(2)-C(3)	1.533(4)
C(3)-C(11)	1.511(4)	C(3)-C(4)	1.532(4)
C(3)-H(3)	1.0000	C(4)-C(5)	1.340(4)
C(4)-C(13)	1.506(4)	C(6)-C(7)	1.381(4)
C(6)-C(11)	1.398(4)	C(7)-C(8)	1.396(4)
C(7)-H(7)	0.9500	C(8)-C(9)	1.388(5)
C(8)-H(8)	0.9500	C(9)-C(10)	1.387(5)
C(9)-H(9)	0.9500	C(10)-C(11)	1.380(4)
C(10)-H(10)	0.9500	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800	C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800	C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800	C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800	C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800	C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800	C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800	C(20)-C(21)	1.343(4)
C(21)-C(31)	1.511(4)	C(21)-C(22)	1.536(4)
C(22)-C(30)	1.518(4)	C(22)-C(23)	1.537(4)
C(22)-H(22)	1.0000	C(23)-C(24)	1.351(4)
C(23)-C(32)	1.512(4)	C(25)-C(26)	1.385(4)
C(25)-C(30)	1.391(4)	C(26)-C(27)	1.389(4)
C(26)-H(26)	0.9500	C(27)-C(28)	1.384(5)
C(27)-H(27)	0.9500	C(28)-C(29)	1.389(5)
C(28)-H(28)	0.9500	C(29)-C(30)	1.384(4)
C(29)-H(29)	0.9500	C(31)-H(31A)	0.9800

C(31)-H(31B)	0.9800	C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800	C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800	C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800	C(33)-H(33C)	0.9800
C(34)-H(34A)	0.9800	C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800	C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800	C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800	C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800	C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800	C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800	C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800		

O(1)-Pt(1)-O(2)	42.8(1)	O(1)-Pt(1)-P(1)	141.43(7)
O(2)-Pt(1)-P(1)	98.64(7)	O(1)-Pt(1)-P(2)	113.85(7)
O(2)-Pt(1)-P(2)	156.22(6)	P(1)-Pt(1)-P(2)	104.69(3)
C(6)-P(1)-C(1)	98.1(1)	C(6)-P(1)-C(5)	97.4(1)
C(1)-P(1)-C(5)	99.3(1)	C(6)-P(1)-Pt(1)	128.0(1)
C(1)-P(1)-Pt(1)	114.0(1)	C(5)-P(1)-Pt(1)	115.1(1)
C(25)-P(2)-C(20)	99.5(1)	C(25)-P(2)-C(24)	96.7(1)
C(20)-P(2)-C(24)	97.4(1)	C(25)-P(2)-Pt(1)	114.3(1)
C(20)-P(2)-Pt(1)	122.2(1)	C(24)-P(2)-Pt(1)	121.7(1)
C(14)-Si(1)-C(15)	103.7(2)	C(14)-Si(1)-C(16)	107.6(2)
C(15)-Si(1)-C(16)	111.8(2)	C(14)-Si(1)-C(1)	117.0(1)
C(15)-Si(1)-C(1)	110.4(2)	C(16)-Si(1)-C(1)	106.5(2)
C(19)-Si(2)-C(18)	107.6(2)	C(19)-Si(2)-C(17)	105.4(2)
C(18)-Si(2)-C(17)	111.3(2)	C(19)-Si(2)-C(5)	116.4(1)
C(18)-Si(2)-C(5)	107.8(2)	C(17)-Si(2)-C(5)	108.3(2)
C(33)-Si(3)-C(35)	105.6(2)	C(33)-Si(3)-C(34)	111.3(2)
C(35)-Si(3)-C(34)	109.0(1)	C(33)-Si(3)-C(20)	103.9(1)
C(35)-Si(3)-C(20)	113.6(1)	C(34)-Si(3)-C(20)	113.0(1)
C(36)-Si(4)-C(37)	114.0(2)	C(36)-Si(4)-C(38)	103.3(2)
C(37)-Si(4)-C(38)	106.8(2)	C(36)-Si(4)-C(24)	111.8(2)
C(37)-Si(4)-C(24)	106.2(1)	C(38)-Si(4)-C(24)	114.9(2)
O(2)-O(1)-Pt(1)	68.8(1)	O(1)-O(2)-Pt(1)	68.4(1)
C(2)-C(1)-P(1)	110.8(2)	C(2)-C(1)-Si(1)	120.6(2)
P(1)-C(1)-Si(1)	128.4(2)	C(1)-C(2)-C(12)	127.6(3)
C(1)-C(2)-C(3)	119.6(3)	C(12)-C(2)-C(3)	112.8(3)
C(11)-C(3)-C(4)	108.3(2)	C(11)-C(3)-C(2)	108.4(2)
C(4)-C(3)-C(2)	108.4(2)	C(11)-C(3)-H(3)	110.6
C(4)-C(3)-H(3)	110.6	C(2)-C(3)-H(3)	110.6
C(5)-C(4)-C(13)	127.9(3)	C(5)-C(4)-C(3)	119.1(3)
C(13)-C(4)-C(3)	113.0(3)	C(4)-C(5)-P(1)	111.2(2)
C(4)-C(5)-Si(2)	121.4(2)	P(1)-C(5)-Si(2)	127.4(2)
C(7)-C(6)-C(11)	119.5(3)	C(7)-C(6)-P(1)	128.1(2)
C(11)-C(6)-P(1)	112.4(2)	C(6)-C(7)-C(8)	120.0(3)
C(6)-C(7)-H(7)	120.0	C(8)-C(7)-H(7)	120.0
C(9)-C(8)-C(7)	120.0(3)	C(9)-C(8)-H(8)	120.0
C(7)-C(8)-H(8)	120.0	C(10)-C(9)-C(8)	120.1(3)
C(10)-C(9)-H(9)	120.0	C(8)-C(9)-H(9)	120.0
C(11)-C(10)-C(9)	119.8(3)	C(11)-C(10)-H(10)	120.1
C(9)-C(10)-H(10)	120.1	C(10)-C(11)-C(6)	120.6(3)
C(10)-C(11)-C(3)	123.3(3)	C(6)-C(11)-C(3)	116.1(3)
C(2)-C(12)-H(12A)	109.5	C(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5	C(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5	H(12B)-C(12)-H(12C)	109.5
C(4)-C(13)-H(13A)	109.5	C(4)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5	C(4)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5	H(13B)-C(13)-H(13C)	109.5
Si(1)-C(14)-H(14A)	109.5	Si(1)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	Si(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5

Si(1)-C(15)-H(15A)	109.5	Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5	Si(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
Si(1)-C(16)-H(16A)	109.5	Si(1)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5	Si(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(16B)-C(16)-H(16C)	109.5
Si(2)-C(17)-H(17A)	109.5	Si(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5	Si(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(17B)-C(17)-H(17C)	109.5
Si(2)-C(18)-H(18A)	109.5	Si(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5	Si(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5	H(18B)-C(18)-H(18C)	109.5
Si(2)-C(19)-H(19A)	109.5	Si(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5	Si(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5	H(19B)-C(19)-H(19C)	109.5
C(21)-C(20)-P(2)	111.7(2)	C(21)-C(20)-Si(3)	126.7(2)
P(2)-C(20)-Si(3)	119.4(2)	C(20)-C(21)-C(31)	126.9(3)
C(20)-C(21)-C(22)	118.4(3)	C(31)-C(21)-C(22)	114.8(3)
C(30)-C(22)-C(21)	109.4(2)	C(30)-C(22)-C(23)	107.9(3)
C(21)-C(22)-C(23)	109.0(2)	C(30)-C(22)-H(22)	110.2
C(21)-C(22)-H(22)	110.2	C(23)-C(22)-H(22)	110.2
C(24)-C(23)-C(32)	127.9(3)	C(24)-C(23)-C(22)	119.3(3)
C(32)-C(23)-C(22)	112.7(3)	C(23)-C(24)-P(2)	110.5(2)
C(23)-C(24)-Si(4)	128.4(2)	P(2)-C(24)-Si(4)	120.7(2)
C(26)-C(25)-C(30)	119.5(3)	C(26)-C(25)-P(2)	126.5(2)
C(30)-C(25)-P(2)	113.9(2)	C(25)-C(26)-C(27)	119.5(3)
C(25)-C(26)-H(26)	120.2	C(27)-C(26)-H(26)	120.2
C(28)-C(27)-C(26)	120.8(3)	C(28)-C(27)-H(27)	119.6
C(26)-C(27)-H(27)	119.6	C(27)-C(28)-C(29)	119.9(3)
C(27)-C(28)-H(28)	120.1	C(29)-C(28)-H(28)	120.1
C(30)-C(29)-C(28)	119.2(3)	C(30)-C(29)-H(29)	120.4
C(28)-C(29)-H(29)	120.4	C(29)-C(30)-C(25)	121.0(3)
C(29)-C(30)-C(22)	124.1(3)	C(25)-C(30)-C(22)	114.9(3)
C(21)-C(31)-H(31A)	109.5	C(21)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5	C(21)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5	H(31B)-C(31)-H(31C)	109.5
C(23)-C(32)-H(32A)	109.5	C(23)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5	C(23)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5	H(32B)-C(32)-H(32C)	109.5
Si(3)-C(33)-H(33A)	109.5	Si(3)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5	Si(3)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5	H(33B)-C(33)-H(33C)	109.5
Si(3)-C(34)-H(34A)	109.5	Si(3)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5	Si(3)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5	H(34B)-C(34)-H(34C)	109.5
Si(3)-C(35)-H(35A)	109.5	Si(3)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5	Si(3)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5	H(35B)-C(35)-H(35C)	109.5
Si(4)-C(36)-H(36A)	109.5	Si(4)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5	Si(4)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5	H(36B)-C(36)-H(36C)	109.5
Si(4)-C(37)-H(37A)	109.5	Si(4)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5	Si(4)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5	H(37B)-C(37)-H(37C)	109.5
Si(4)-C(38)-H(38A)	109.5	Si(4)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5	Si(4)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5	H(38B)-C(38)-H(38C)	109.5

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb620

atom	U11	U22	U33	U23	U13	U12

Pt(1)	16(1)	14(1)	17(1)	-1(1)	4(1)	0(1)
P(1)	19(1)	16(1)	18(1)	-1(1)	6(1)	-2(1)
P(2)	17(1)	17(1)	18(1)	1(1)	3(1)	-1(1)
Si(1)	22(1)	30(1)	19(1)	0(1)	6(1)	1(1)
Si(2)	23(1)	30(1)	20(1)	-4(1)	10(1)	-5(1)
Si(3)	24(1)	20(1)	21(1)	-2(1)	8(1)	-2(1)
Si(4)	33(1)	19(1)	29(1)	-4(1)	10(1)	-4(1)
O(1)	32(1)	20(1)	43(1)	-4(1)	6(1)	9(1)
O(2)	20(1)	35(1)	34(1)	-4(1)	3(1)	9(1)
C(1)	23(1)	23(1)	16(1)	-3(1)	8(1)	-4(1)
C(2)	26(2)	28(2)	18(1)	-5(1)	9(1)	-6(1)
C(3)	32(2)	17(1)	19(1)	-3(1)	10(1)	-10(1)
C(4)	24(2)	26(2)	21(2)	1(1)	7(1)	-6(1)
C(5)	22(1)	23(1)	18(1)	1(1)	8(1)	-5(1)
C(6)	26(2)	16(1)	18(1)	2(1)	9(1)	3(1)
C(7)	30(2)	21(1)	24(2)	1(1)	12(1)	2(1)
C(8)	30(2)	29(2)	33(2)	3(1)	13(1)	8(1)
C(9)	49(2)	23(2)	33(2)	1(1)	18(2)	10(2)
C(10)	45(2)	19(1)	30(2)	-3(1)	16(2)	-1(1)
C(11)	32(2)	21(1)	18(1)	-2(1)	9(1)	-2(1)
C(12)	45(2)	40(2)	24(2)	-6(2)	9(2)	-23(2)
C(13)	41(2)	36(2)	26(2)	-1(1)	13(2)	-18(2)
C(14)	38(2)	27(2)	25(2)	2(1)	4(2)	6(1)
C(15)	47(2)	39(2)	22(2)	-2(1)	5(2)	-5(2)
C(16)	28(2)	72(3)	51(3)	9(2)	13(2)	7(2)
C(17)	29(2)	63(3)	47(2)	-13(2)	18(2)	-5(2)
C(18)	45(2)	36(2)	20(2)	-1(1)	9(1)	-9(2)
C(19)	35(2)	29(2)	25(2)	-7(1)	15(1)	-3(1)
C(20)	21(1)	17(1)	21(1)	1(1)	8(1)	-1(1)
C(21)	21(1)	21(1)	30(2)	4(1)	8(1)	2(1)
C(22)	16(1)	28(2)	28(2)	3(1)	2(1)	-2(1)
C(23)	26(2)	28(2)	19(1)	-1(1)	5(1)	-5(1)
C(24)	23(1)	19(1)	25(2)	-1(1)	5(1)	-3(1)
C(25)	20(1)	21(1)	19(1)	1(1)	2(1)	1(1)
C(26)	26(2)	21(1)	26(2)	2(1)	9(1)	1(1)
C(27)	41(2)	30(2)	22(2)	7(1)	12(1)	5(2)
C(28)	38(2)	36(2)	27(2)	12(1)	3(2)	8(2)
C(29)	26(2)	36(2)	30(2)	4(2)	1(1)	6(1)
C(30)	21(1)	27(2)	23(2)	1(1)	4(1)	2(1)
C(31)	26(2)	37(2)	40(2)	2(2)	11(2)	7(1)
C(32)	25(2)	47(2)	39(2)	-6(2)	2(2)	-13(2)
C(33)	33(2)	22(1)	26(2)	2(1)	6(1)	1(1)
C(34)	27(2)	26(2)	26(2)	-5(1)	10(1)	-2(1)
C(35)	36(2)	29(2)	28(2)	-4(1)	16(1)	-4(1)
C(36)	43(2)	28(2)	43(2)	9(2)	21(2)	10(2)
C(37)	31(2)	33(2)	25(2)	0(1)	8(1)	2(1)
C(38)	52(3)	33(2)	79(3)	-26(2)	25(2)	-18(2)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb620

atom	x	y	z	U(eq)
H(3)	5536	-871	2505	27
H(7)	9068	820	2915	29
H(8)	10050	-294	2940	36
H(9)	9145	-1451	2779	40
H(10)	7271	-1499	2626	36
H(12A)	3970	82	994	55

H(12B)	3955	-562	1560	55
H(12C)	4774	-624	1096	55
H(13A)	5010	-227	4031	51
H(13B)	5650	-926	3842	51
H(13C)	4471	-695	3308	51
H(14A)	6139	2394	1061	47
H(14B)	5484	2728	1562	47
H(14C)	4940	2737	706	47
H(15A)	4590	1479	-102	56
H(15B)	4097	728	122	56
H(15C)	5392	818	301	56
H(16A)	3495	1890	1719	75
H(16B)	3035	1181	1211	75
H(16C)	2986	2002	868	75
H(17A)	4252	1455	4541	67
H(17B)	4010	803	3949	67
H(17C)	4040	1662	3714	67
H(18A)	7352	599	5104	51
H(18B)	6254	122	4982	51
H(18C)	6465	863	5470	51
H(19A)	7200	2180	4469	42
H(19B)	6294	2376	4843	42
H(19C)	6035	2506	3996	42
H(22)	12003	2345	3886	30
H(26)	8352	1341	4257	29
H(27)	9451	677	5254	37
H(28)	11352	747	5582	43
H(29)	12176	1462	4889	39
H(31A)	11262	1567	2152	51
H(31B)	12052	1401	2951	51
H(31C)	12092	2201	2587	51
H(32A)	11362	4208	4077	59
H(32B)	12185	3703	3809	59
H(32C)	12059	3561	4586	59
H(33A)	8803	3485	1650	42
H(33B)	7699	3096	1681	42
H(33C)	7924	3182	927	42
H(34A)	7426	1370	1503	39
H(34B)	8344	895	1303	39
H(34C)	7564	1455	724	39
H(35A)	9537	2349	554	44
H(35B)	10233	1683	1034	44
H(35C)	10523	2538	1270	44
H(36A)	7566	4929	2850	55
H(36B)	7469	4091	2540	55
H(36C)	8408	4639	2458	55
H(37A)	7853	4381	4423	45
H(37B)	8758	3754	4771	45
H(37C)	7671	3536	4133	45
H(38A)	10199	5127	3662	80
H(38B)	10353	4862	4470	80
H(38C)	9366	5411	4064	80

II.17. Crystallographic data for IV-43

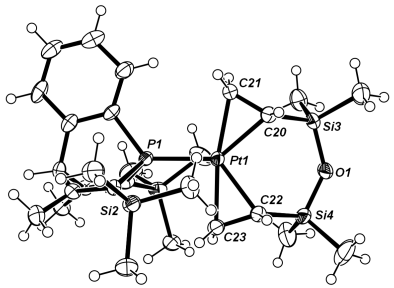


Table 1. Crystal data for mb770

Compound	mb770
Molecular formula	$C_{27}H_{47}OPPtSi_4$
Molecular weight	2904.26
Crystal habit	Colorless Block
Crystal dimensions(mm)	0.33x0.20x0.10
Crystal system	monoclinic
Space group	P 2_1/c
a(Å)	13.039(1)
b(Å)	13.736(1)
c(Å)	20.900(1)
α(°)	90.00
β(°)	118.221(3)
γ(°)	90.00
V(Å^3)	3298.3(4)
Z	1
d(g-cm^{-3})	1.462
F(000)	1464
μ(cm^{-1})	4.466
Absorption corrections	multi-scan ; 0.3204 min, 0.6637 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-16 10 ; -19 11 ; -19 19
Reflections measured	4640
Unique data	3617
Rint	0.0228
Reflections used	2761

Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	307
Reflections / parameter	8
wR2	0.0886
R1	0.0283
Weights a, b	0.0395 ; 0.0000
GoF	1.001
difference peak / hole (e Å^{-3})	0.502(0.090) / -0.754(0.090)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb770

atom	x	y	z	U(eq)
Pt(1)	3969(1)	3287(1)	3797(1)	22(1)
P(1)	2459(3)	4361(1)	3275(2)	23(1)
Si(1)	1937(3)	3728(1)	1633(2)	31(1)
Si(2)	1629(3)	3686(1)	4500(2)	30(1)
Si(3)	6649(3)	2543(1)	4131(2)	29(1)
Si(4)	4740(3)	997(1)	3570(2)	32(1)
O(1)	6024(6)	1473(3)	3853(5)	36(3)
C(1)	1490(10)	4296(4)	2289(8)	25(5)
C(2)	500(10)	4827(5)	2060(10)	23(3)
C(3)	400(10)	5462(4)	2633(7)	32(5)
C(4)	450(10)	4817(4)	3244(7)	23(3)
C(5)	1390(10)	4276(4)	3619(7)	28(4)
C(6)	-490(10)	4879(5)	1330(10)	39(5)
C(7)	-610(10)	4889(5)	3342(8)	45(5)
C(8)	2550(10)	5694(4)	3293(7)	26(5)
C(9)	3570(10)	6239(5)	3586(7)	38(5)
C(10)	3450(10)	7267(5)	3531(8)	42(5)
C(11)	2400(10)	7709(5)	3223(8)	41(5)
C(12)	1380(10)	7153(5)	2927(7)	36(5)
C(13)	1460(10)	6136(4)	2966(8)	28(5)
C(14)	3540(10)	3664(6)	2069(8)	44(5)
C(15)	1540(10)	4530(5)	838(8)	53(6)
C(16)	1230(10)	2502(5)	1314(7)	35(5)
C(17)	3070(10)	3145(5)	5063(8)	32(5)
C(18)	500(10)	2715(5)	4277(7)	36(5)
C(19)	1520(10)	4685(5)	5087(7)	42(5)
C(20)	5810(10)	3296(4)	4463(7)	24(3)
C(21)	5410(10)	4267(4)	4246(7)	29(5)
C(22)	3860(10)	1728(4)	3890(7)	24(3)
C(23)	2733(8)	2112(4)	3425(7)	29(4)
C(24)	8100(10)	2308(5)	4909(8)	47(5)
C(25)	6770(10)	3154(5)	3373(8)	42(5)
C(26)	4980(10)	-218(5)	4020(8)	61(6)
C(27)	4020(10)	854(6)	2574(8)	51(6)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb770

Pt(1)-C(20)	2.13(1)	Pt(1)-C(21)	2.14(1)
Pt(1)-C(23)	2.150(8)	Pt(1)-C(22)	2.161(6)
Pt(1)-P(1)	2.283(3)	P(1)-C(8)	1.834(6)
P(1)-C(1)	1.84(1)	P(1)-C(5)	1.848(6)

Si(1)-C(14)	1.85(1)	Si(1)-C(15)	1.85(1)
Si(1)-C(16)	1.885(8)	Si(1)-C(1)	1.90(1)
Si(2)-C(17)	1.84(1)	Si(2)-C(18)	1.874(8)
Si(2)-C(19)	1.889(8)	Si(2)-C(5)	1.90(1)
Si(3)-O(1)	1.648(6)	Si(3)-C(24)	1.85(1)
Si(3)-C(20)	1.858(7)	Si(3)-C(25)	1.86(1)
Si(4)-O(1)	1.626(6)	Si(4)-C(27)	1.85(1)
Si(4)-C(22)	1.865(7)	Si(4)-C(26)	1.868(8)
C(1)-C(2)	1.36(1)	C(2)-C(6)	1.46(2)
C(2)-C(3)	1.53(1)	C(3)-C(4)	1.53(1)
C(3)-C(13)	1.53(1)	C(3)-H(3)	1.0000
C(4)-C(5)	1.33(1)	C(4)-C(7)	1.49(1)
C(6)-H(6A)	0.9800	C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800	C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800	C(7)-H(7C)	0.9800
C(8)-C(9)	1.39(1)	C(8)-C(13)	1.39(1)
C(9)-C(10)	1.42(1)	C(9)-H(9)	0.9500
C(10)-C(11)	1.35(2)	C(10)-H(10)	0.9500
C(11)-C(12)	1.40(2)	C(11)-H(11)	0.9500
C(12)-C(13)	1.401(8)	C(12)-H(12)	0.9500
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800
C(20)-C(21)	1.42(1)	C(20)-H(20)	1.0000
C(21)-H(21A)	0.9900	C(21)-H(21B)	0.9900
C(22)-C(23)	1.43(1)	C(22)-H(22)	1.0000
C(23)-H(23A)	0.9900	C(23)-H(23B)	0.9900
C(24)-H(24A)	0.9800	C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800	C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800	C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800	C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800	C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800	C(27)-H(27C)	0.9800

C(20)-Pt(1)-C(21)	38.9(3)	C(20)-Pt(1)-C(23)	131.4(3)
C(21)-Pt(1)-C(23)	170.3(3)	C(20)-Pt(1)-C(22)	92.7(3)
C(21)-Pt(1)-C(22)	131.6(4)	C(23)-Pt(1)-C(22)	38.7(4)
C(20)-Pt(1)-P(1)	139.4(2)	C(21)-Pt(1)-P(1)	100.7(2)
C(23)-Pt(1)-P(1)	89.0(2)	C(22)-Pt(1)-P(1)	127.3(3)
C(8)-P(1)-C(1)	94.3(5)	C(8)-P(1)-C(5)	96.3(3)
C(1)-P(1)-C(5)	100.8(5)	C(8)-P(1)-Pt(1)	127.0(4)
C(1)-P(1)-Pt(1)	119.0(2)	C(5)-P(1)-Pt(1)	114.3(3)
C(14)-Si(1)-C(15)	104.0(5)	C(14)-Si(1)-C(16)	112.6(4)
C(15)-Si(1)-C(16)	109.4(6)	C(14)-Si(1)-C(1)	109.1(6)
C(15)-Si(1)-C(1)	110.7(4)	C(16)-Si(1)-C(1)	110.8(3)
C(17)-Si(2)-C(18)	108.4(4)	C(17)-Si(2)-C(19)	104.2(6)
C(18)-Si(2)-C(19)	112.8(4)	C(17)-Si(2)-C(5)	116.3(4)
C(18)-Si(2)-C(5)	108.3(5)	C(19)-Si(2)-C(5)	107.0(4)
O(1)-Si(3)-C(24)	106.5(4)	O(1)-Si(3)-C(20)	110.5(3)
C(24)-Si(3)-C(20)	107.9(6)	O(1)-Si(3)-C(25)	109.1(5)
C(24)-Si(3)-C(25)	111.2(5)	C(20)-Si(3)-C(25)	111.5(4)
O(1)-Si(4)-C(27)	109.8(4)	O(1)-Si(4)-C(22)	110.7(4)
C(27)-Si(4)-C(22)	113.0(5)	O(1)-Si(4)-C(26)	106.3(5)
C(27)-Si(4)-C(26)	110.3(5)	C(22)-Si(4)-C(26)	106.5(4)
Si(4)-O(1)-Si(3)	137.6(3)	C(2)-C(1)-P(1)	114(1)
C(2)-C(1)-Si(1)	123(1)	P(1)-C(1)-Si(1)	123.1(6)

C(1)-C(2)-C(6)	128(1)	C(1)-C(2)-C(3)	117(1)
C(6)-C(2)-C(3)	115.6(8)	C(4)-C(3)-C(2)	109.4(6)
C(4)-C(3)-C(13)	107(1)	C(2)-C(3)-C(13)	107.7(6)
C(4)-C(3)-H(3)	110.8	C(2)-C(3)-H(3)	110.8
C(13)-C(3)-H(3)	110.8	C(5)-C(4)-C(7)	128(1)
C(5)-C(4)-C(3)	118.8(6)	C(7)-C(4)-C(3)	113.4(8)
C(4)-C(5)-P(1)	112.9(7)	C(4)-C(5)-Si(2)	119.6(6)
P(1)-C(5)-Si(2)	126.6(6)	C(2)-C(6)-H(6A)	109.5
C(2)-C(6)-H(6B)	109.5	H(6A)-C(6)-H(6B)	109.5
C(2)-C(6)-H(6C)	109.5	H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5	C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5	H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5	H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5	C(9)-C(8)-C(13)	121.4(6)
C(9)-C(8)-P(1)	126.0(8)	C(13)-C(8)-P(1)	112.6(7)
C(8)-C(9)-C(10)	117(1)	C(8)-C(9)-H(9)	121.3
C(10)-C(9)-H(9)	121.3	C(11)-C(10)-C(9)	122(1)
C(11)-C(10)-H(10)	119.0	C(9)-C(10)-H(10)	119.0
C(10)-C(11)-C(12)	120.3(7)	C(10)-C(11)-H(11)	119.9
C(12)-C(11)-H(11)	119.9	C(11)-C(12)-C(13)	119(1)
C(11)-C(12)-H(12)	120.4	C(13)-C(12)-H(12)	120.4
C(8)-C(13)-C(12)	120(1)	C(8)-C(13)-C(3)	117.0(6)
C(12)-C(13)-C(3)	123(1)	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	Si(2)-C(19)-H(19A)	109.5
Si(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(21)-C(20)-Si(3)	126.3(6)
C(21)-C(20)-Pt(1)	70.7(6)	Si(3)-C(20)-Pt(1)	115.5(6)
C(21)-C(20)-H(20)	112.5	Si(3)-C(20)-H(20)	112.5
Pt(1)-C(20)-H(20)	112.5	C(20)-C(21)-Pt(1)	70.4(5)
C(20)-C(21)-H(21A)	116.6	Pt(1)-C(21)-H(21A)	116.6
C(20)-C(21)-H(21B)	116.6	Pt(1)-C(21)-H(21B)	116.6
H(21A)-C(21)-H(21B)	113.6	C(23)-C(22)-Si(4)	124(1)
C(23)-C(22)-Pt(1)	70.3(4)	Si(4)-C(22)-Pt(1)	115.2(3)
C(23)-C(22)-H(22)	113.3	Si(4)-C(22)-H(22)	113.3
Pt(1)-C(22)-H(22)	113.3	C(22)-C(23)-Pt(1)	71.0(5)
C(22)-C(23)-H(23A)	116.5	Pt(1)-C(23)-H(23A)	116.5
C(22)-C(23)-H(23B)	116.5	Pt(1)-C(23)-H(23B)	116.5
H(23A)-C(23)-H(23B)	113.5	Si(3)-C(24)-H(24A)	109.5
Si(3)-C(24)-H(24B)	109.5	H(24A)-C(24)-H(24B)	109.5
Si(3)-C(24)-H(24C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5	Si(3)-C(25)-H(25A)	109.5
Si(3)-C(25)-H(25B)	109.5	H(25A)-C(25)-H(25B)	109.5
Si(3)-C(25)-H(25C)	109.5	H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5	Si(4)-C(26)-H(26A)	109.5
Si(4)-C(26)-H(26B)	109.5	H(26A)-C(26)-H(26B)	109.5
Si(4)-C(26)-H(26C)	109.5	H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5	Si(4)-C(27)-H(27A)	109.5
Si(4)-C(27)-H(27B)	109.5	H(27A)-C(27)-H(27B)	109.5

Si(4)-C(27)-H(27C)	109.5	H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5		

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb770

atom	U11	U22	U33	U23	U13	U12
Pt(1)	21(1)	21(1)	25(1)	1(1)	12(1)	2(1)
P(1)	24(2)	19(1)	26(4)	0(1)	13(3)	0(1)
Si(1)	35(2)	31(1)	24(4)	-3(1)	12(3)	-8(1)
Si(2)	33(2)	26(1)	39(4)	-3(1)	24(3)	-2(1)
Si(3)	20(2)	30(1)	36(4)	-1(1)	11(3)	2(1)
Si(4)	30(2)	22(1)	49(5)	-2(1)	23(3)	1(1)
O(1)	23(5)	30(2)	50(10)	-12(3)	17(7)	2(2)
C(1)	30(10)	21(3)	10(20)	0(4)	0(10)	-5(3)
C(2)	21(6)	27(2)	10(10)	-2(3)	-3(8)	-1(3)
C(3)	26(8)	22(3)	40(10)	6(4)	10(10)	8(4)
C(4)	21(6)	27(2)	10(10)	-2(3)	-3(8)	-1(3)
C(5)	24(8)	21(3)	40(10)	-2(4)	20(10)	2(3)
C(6)	20(10)	35(4)	30(20)	-3(5)	-10(10)	0(4)
C(7)	40(10)	36(4)	70(10)	0(5)	30(10)	5(4)
C(8)	38(8)	18(3)	20(10)	-4(4)	20(10)	0(3)
C(9)	50(10)	23(3)	50(20)	1(5)	30(10)	-1(4)
C(10)	60(10)	27(3)	40(20)	-5(5)	30(10)	-9(4)
C(11)	60(10)	21(3)	30(20)	1(5)	20(10)	0(4)
C(12)	50(10)	25(3)	20(10)	12(5)	10(10)	17(4)
C(13)	40(10)	22(3)	20(10)	2(4)	20(10)	5(4)
C(14)	40(10)	72(5)	40(20)	-9(6)	30(10)	-14(5)
C(15)	70(10)	46(4)	40(20)	5(6)	20(10)	-7(5)
C(16)	30(10)	36(4)	20(20)	-6(5)	0(10)	-5(4)
C(17)	30(10)	45(4)	20(10)	3(5)	10(10)	7(4)
C(18)	40(10)	35(3)	40(10)	1(5)	20(10)	-8(4)
C(19)	50(10)	40(4)	50(20)	-13(5)	40(10)	-5(4)
C(20)	26(6)	26(2)	20(10)	7(3)	8(8)	0(2)
C(21)	23(8)	25(3)	30(10)	0(4)	10(10)	1(3)
C(22)	26(6)	26(2)	20(10)	7(3)	8(8)	0(2)
C(23)	31(8)	25(3)	40(10)	-3(4)	20(10)	-2(3)
C(24)	40(10)	43(4)	60(20)	7(6)	20(10)	8(4)
C(25)	40(10)	54(5)	40(20)	6(6)	20(10)	8(4)
C(26)	80(10)	32(4)	100(20)	13(6)	60(10)	19(5)
C(27)	40(10)	63(5)	40(20)	-11(7)	10(10)	14(5)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb770

atom	x	y	z	U(eq)
H(3)	-340.0000	5850	2409	38
H(6A)	-464	5501	1107	59
H(6B)	-1215	4829	1356	59
H(6C)	-436	4342	1038	59
H(7A)	-1304	4756	2878	67
H(7B)	-665	5545	3507	67
H(7C)	-560	4412	3704	67
H(9)	4311	5937	3815	46
H(10)	4134	7657	3716	50
H(11)	2352	8399	3208	50
H(12)	641	7462	2702	44

H(14A)	3779	3331	1745	67
H(14B)	3835	3303	2527	67
H(14C)	3865	4325	2168	67
H(15A)	1867	5181	1005	80
H(15B)	690	4576	557	80
H(15C)	1852	4260	532	80
H(16A)	1423	2244	948	53
H(16B)	381	2570	1101	53
H(16C)	1509	2054	1727	53
H(17A)	3224	3115	5569	48
H(17B)	3666	3545	5031	48
H(17C)	3088	2486	4889	48
H(18A)	487	2294	3894	55
H(18B)	-263	3017	4109	55
H(18C)	693	2325	4712	55
H(19A)	1586	4402	5535	63
H(19B)	772	5017	4823	63
H(19C)	2154	5154	5208	63
H(20)	6050	3174	4987	29
H(21A)	5633	4576	3899	34
H(21B)	5460	4712	4631	34
H(22)	3965	1516	4374	29
H(23A)	2166	2095	3614	35
H(23B)	2389	1942	2904	35
H(24A)	8015	1966	5292	70
H(24B)	8505	2928	5098	70
H(24C)	8559	1905	4749	70
H(25A)	7119	2705	3167	63
H(25B)	7259	3735	3556	63
H(25C)	5992	3344	2996	63
H(26A)	5284	-674	3792	92
H(26B)	4233	-466	3966	92
H(26C)	5531	-154	4537	92
H(27A)	3851	1497	2345	76
H(27B)	3295	490	2414	76
H(27C)	4538	498	2436	76

II.17. Crystallographic data for IV-45

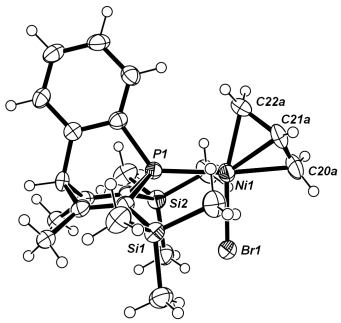


Table 1. Crystal data for mb499

Compound	mb499
Molecular formula	$C_{22}H_{34}BrNiPSi_2$
Molecular weight	524.26
Crystal habit	Red Orange Plate
Crystal dimensions(mm)	0.20x0.16x0.04
Crystal system	triclinic
Space group	P-1
a(Å)	10.039(1)
b(Å)	15.762(1)
c(Å)	16.455(1)
α(°)	100.510(1)
β(°)	93.573(1)
γ(°)	101.637(1)
V(Å^3)	2494.1(3)
Z	4
d(g-cm^{-3})	1.396
F(000)	1088
μ(cm^{-1})	2.546
Absorption corrections	multi-scan ; 0.6300 min, 0.9050 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	26.37
HKL ranges	-12 11 ; -18 19 ; -18 20
Reflections measured	24806
Unique data	10174
Rint	0.0674
Reflections used	6030
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	511
Reflections / parameter	11
wR2	0.1349
R1	0.0545
Weights a, b	0.0510 ; 2.0820
GoF	1.020
difference peak / hole (e Å^{-3})	0.617(0.106) / -0.514(0.106)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb499

atom	x	y	z	U(eq)
Br(1)	3412(1)	7988(1)	-1437(1)	39(1)
Ni(1)	2102(1)	6924(1)	-824(1)	31(1)
P(1)	3345(1)	7417(1)	381(1)	27(1)
Si(1)	2139(2)	9246(1)	515(1)	33(1)
Si(2)	5968(2)	6813(1)	-488(1)	35(1)
C(1)	3338(5)	8572(3)	863(3)	27(1)
C(2)	4296(5)	8888(4)	1516(3)	31(1)
C(3)	5100(5)	8246(3)	1803(3)	28(1)
C(4)	5907(5)	7937(3)	1088(3)	29(1)
C(5)	5207(5)	7472(3)	364(3)	28(1)
C(6)	3186(5)	6943(4)	1319(3)	31(1)
C(7)	4133(5)	7439(3)	1982(3)	28(1)
C(8)	4188(5)	7163(4)	2729(3)	34(1)
C(9)	3344(6)	6394(4)	2830(4)	39(2)
C(10)	2420(6)	5894(4)	2171(4)	41(2)
C(11)	2324(5)	6172(4)	1422(4)	36(1)
C(12)	4702(6)	9825(3)	1990(3)	36(1)
C(13)	7441(5)	8216(4)	1278(4)	37(1)
C(14)	1402(6)	9804(4)	1438(4)	46(2)
C(15)	3011(6)	10093(4)	-32(4)	45(2)
C(16)	619(6)	8523(4)	-154(4)	44(2)
C(17)	6965(6)	7522(4)	-1123(3)	41(2)
C(18)	7127(7)	6211(4)	7(4)	51(2)
C(19)	4641(6)	5938(4)	-1179(4)	51(2)
C(20A)	901(7)	6306(4)	-1916(5)	58(2)
C(21A)	223(8)	6241(5)	-1272(6)	43(2)
C(22A)	768(6)	5904(4)	-570(4)	43(2)
C(20B)	901(7)	6306(4)	-1916(5)	58(2)
C(21B)	930(20)	5780(20)	-1380(20)	43(2)
C(22B)	768(6)	5904(4)	-570(4)	43(2)
Br(2)	2303(1)	1743(1)	6217(1)	38(1)
Ni(2)	1578(1)	3072(1)	6464(1)	31(1)
P(2)	271(1)	2702(1)	5284(1)	28(1)
Si(3)	3075(2)	2900(1)	4304(1)	36(1)
Si(4)	-1638(2)	1108(1)	6012(1)	33(1)
C(23)	1176(5)	2524(4)	4348(3)	34(1)
C(24)	291(6)	2173(4)	3669(3)	34(1)
C(25)	-1242(5)	2029(3)	3743(3)	34(1)
C(26)	-1612(5)	1406(3)	4351(3)	32(1)
C(27)	-1021(5)	1646(3)	5137(3)	32(1)
C(28)	-897(5)	3332(3)	4891(3)	27(1)
C(29)	-1180(5)	4117(4)	5279(4)	34(1)
C(30)	-2140(6)	4475(4)	4898(4)	40(2)
C(31)	-2805(5)	4056(4)	4124(4)	37(1)
C(32)	-2535(5)	3268(4)	3729(3)	32(1)
C(33)	-1580(5)	2908(3)	4114(3)	30(1)
C(34)	650(6)	1844(4)	2793(4)	43(2)
C(35)	-2666(6)	570(4)	3988(4)	38(1)
C(36)	3317(7)	3605(4)	3490(4)	49(2)
C(37)	3966(6)	3615(4)	5292(4)	43(2)
C(38)	3913(6)	1949(4)	4049(4)	52(2)
C(39)	-1092(6)	1888(4)	7031(3)	38(1)
C(40)	-1031(6)	72(4)	6023(4)	41(2)
C(41)	-3572(5)	864(4)	5874(4)	45(2)
C(42A)	1141(6)	4235(4)	6904(4)	44(2)
C(43A)	2490(10)	4190(6)	7243(5)	41(2)
C(44A)	2625(8)	3570(4)	7619(4)	64(2)
C(42B)	1141(6)	4235(4)	6904(4)	44(2)
C(43B)	1660(20)	3810(10)	7610(10)	41(2)
C(44B)	2625(8)	3570(4)	7619(4)	64(2)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb499

Br(1)-Ni(1)	2.335(1)	Ni(1)-C(21B)	1.97(2)
Ni(1)-C(21A)	1.994(7)	Ni(1)-C(22A)	2.000(6)
Ni(1)-C(20A)	2.061(6)	Ni(1)-P(1)	2.198(2)
P(1)-C(6)	1.836(6)	P(1)-C(1)	1.851(5)
P(1)-C(5)	1.856(5)	Si(1)-C(15)	1.851(6)
Si(1)-C(16)	1.864(6)	Si(1)-C(14)	1.882(6)
Si(1)-C(1)	1.885(5)	Si(2)-C(17)	1.857(6)
Si(2)-C(19)	1.862(6)	Si(2)-C(18)	1.879(6)
Si(2)-C(5)	1.883(5)	C(1)-C(2)	1.344(7)
C(2)-C(12)	1.501(7)	C(2)-C(3)	1.536(7)
C(3)-C(7)	1.523(7)	C(3)-C(4)	1.532(7)
C(3)-H(3)	1.0000	C(4)-C(5)	1.349(7)
C(4)-C(13)	1.510(7)	C(6)-C(11)	1.386(7)
C(6)-C(7)	1.401(7)	C(7)-C(8)	1.379(7)
C(8)-C(9)	1.374(8)	C(8)-H(8)	0.9500
C(9)-C(10)	1.387(8)	C(9)-H(9)	0.9500
C(10)-C(11)	1.387(8)	C(10)-H(10)	0.9500
C(11)-H(11)	0.9500	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800	C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800	C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800	C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800	C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800	C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800	C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800	C(20A)-C(21A)	1.30(1)
C(20A)-H(20A)	0.9900	C(20A)-H(20B)	0.9900
C(21A)-C(22A)	1.48(1)	C(21A)-H(21A)	0.9500
C(22A)-H(22A)	0.9900	C(22A)-H(22B)	0.9900
C(21B)-H(21B)	0.9500	Br(2)-Ni(2)	2.329(1)
Ni(2)-C(42A)	1.989(5)	Ni(2)-C(43A)	1.990(8)
Ni(2)-C(43B)	2.01(2)	Ni(2)-C(44A)	2.051(6)
Ni(2)-P(2)	2.190(2)	P(2)-C(28)	1.841(5)
P(2)-C(23)	1.843(6)	P(2)-C(27)	1.858(5)
Si(3)-C(38)	1.859(6)	Si(3)-C(37)	1.859(6)
Si(3)-C(36)	1.889(6)	Si(3)-C(23)	1.889(6)
Si(4)-C(40)	1.858(5)	Si(4)-C(39)	1.868(5)
Si(4)-C(27)	1.875(6)	Si(4)-C(41)	1.892(6)
C(23)-C(24)	1.340(7)	C(24)-C(25)	1.526(8)
C(24)-C(34)	1.530(8)	C(25)-C(33)	1.522(7)
C(25)-C(26)	1.537(8)	C(25)-H(25)	1.0000
C(26)-C(27)	1.343(7)	C(26)-C(35)	1.510(7)
C(28)-C(29)	1.376(7)	C(28)-C(33)	1.395(7)
C(29)-C(30)	1.384(7)	C(29)-H(29)	0.9500
C(30)-C(31)	1.383(8)	C(30)-H(30)	0.9500
C(31)-C(32)	1.380(7)	C(31)-H(31)	0.9500
C(32)-C(33)	1.384(7)	C(32)-H(32)	0.9500
C(34)-H(34A)	0.9800	C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800	C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800	C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800	C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800	C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800	C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800	C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800	C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800	C(39)-H(39C)	0.9800

C(40)-H(40A)	0.9800	C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800	C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800	C(41)-H(41C)	0.9800
C(42A)-C(43A)	1.45(1)	C(42A)-H(42A)	0.9900
C(42A)-H(42B)	0.9900	C(43A)-C(44A)	1.27(1)
C(43A)-H(43A)	0.9500	C(44A)-H(44A)	0.9900
C(44A)-H(44B)	0.9900	C(43B)-H(43B)	0.9500

C(21B)-Ni(1)-C(21A)	32.8(7)	C(21B)-Ni(1)-C(22A)	39.2(8)
C(21A)-Ni(1)-C(22A)	43.3(3)	C(21B)-Ni(1)-C(20A)	38.4(8)
C(21A)-Ni(1)-C(20A)	37.4(3)	C(22A)-Ni(1)-C(20A)	73.0(3)
C(21B)-Ni(1)-P(1)	134.5(8)	C(21A)-Ni(1)-P(1)	138.8(3)
C(22A)-Ni(1)-P(1)	100.8(2)	C(20A)-Ni(1)-P(1)	172.8(2)
C(21B)-Ni(1)-Br(1)	128.0(8)	C(21A)-Ni(1)-Br(1)	124.7(3)
C(22A)-Ni(1)-Br(1)	166.6(2)	C(20A)-Ni(1)-Br(1)	93.6(2)
P(1)-Ni(1)-Br(1)	92.59(5)	C(6)-P(1)-C(1)	98.0(2)
C(6)-P(1)-C(5)	95.6(2)	C(1)-P(1)-C(5)	101.1(2)
C(6)-P(1)-Ni(1)	127.3(2)	C(1)-P(1)-Ni(1)	114.6(2)
C(5)-P(1)-Ni(1)	115.8(2)	C(15)-Si(1)-C(16)	110.3(3)
C(15)-Si(1)-C(14)	109.2(3)	C(16)-Si(1)-C(14)	104.2(3)
C(15)-Si(1)-C(1)	111.8(3)	C(16)-Si(1)-C(1)	111.1(2)
C(14)-Si(1)-C(1)	110.0(2)	C(17)-Si(2)-C(19)	109.6(3)
C(17)-Si(2)-C(18)	109.1(3)	C(19)-Si(2)-C(18)	105.6(3)
C(17)-Si(2)-C(5)	112.4(3)	C(19)-Si(2)-C(5)	112.0(3)
C(18)-Si(2)-C(5)	108.1(3)	C(2)-C(1)-P(1)	111.8(4)
C(2)-C(1)-Si(1)	122.7(4)	P(1)-C(1)-Si(1)	125.5(3)
C(1)-C(2)-C(12)	126.6(5)	C(1)-C(2)-C(3)	118.0(5)
C(12)-C(2)-C(3)	115.4(4)	C(7)-C(3)-C(4)	108.3(4)
C(7)-C(3)-C(2)	110.7(4)	C(4)-C(3)-C(2)	107.2(4)
C(7)-C(3)-H(3)	110.2	C(4)-C(3)-H(3)	110.2
C(2)-C(3)-H(3)	110.2	C(5)-C(4)-C(13)	126.8(5)
C(5)-C(4)-C(3)	118.6(4)	C(13)-C(4)-C(3)	114.6(4)
C(4)-C(5)-P(1)	111.1(4)	C(4)-C(5)-Si(2)	124.6(4)
P(1)-C(5)-Si(2)	123.6(3)	C(11)-C(6)-C(7)	119.4(5)
C(11)-C(6)-P(1)	128.5(4)	C(7)-C(6)-P(1)	112.0(4)
C(8)-C(7)-C(6)	119.8(5)	C(8)-C(7)-C(3)	123.9(5)
C(6)-C(7)-C(3)	116.2(5)	C(9)-C(8)-C(7)	120.9(5)
C(9)-C(8)-H(8)	119.6	C(7)-C(8)-H(8)	119.6
C(8)-C(9)-C(10)	119.4(5)	C(8)-C(9)-H(9)	120.3
C(10)-C(9)-H(9)	120.3	C(11)-C(10)-C(9)	120.6(6)
C(11)-C(10)-H(10)	119.7	C(9)-C(10)-H(10)	119.7
C(6)-C(11)-C(10)	119.8(5)	C(6)-C(11)-H(11)	120.1
C(10)-C(11)-H(11)	120.1	C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5

Si(2)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	Si(2)-C(19)-H(19A)	109.5
Si(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(21A)-C(20A)-Ni(1)	68.5(4)
C(21A)-C(20A)-H(20A)	116.8	Ni(1)-C(20A)-H(20A)	116.8
C(21A)-C(20A)-H(20B)	116.8	Ni(1)-C(20A)-H(20B)	116.8
H(20A)-C(20A)-H(20B)	113.8	C(20A)-C(21A)-C(22A)	120.8(7)
C(20A)-C(21A)-Ni(1)	74.1(5)	C(22A)-C(21A)-Ni(1)	68.5(3)
C(20A)-C(21A)-H(21A)	119.6	C(22A)-C(21A)-H(21A)	119.6
Ni(1)-C(21A)-H(21A)	130.4	C(21A)-C(22A)-Ni(1)	68.1(4)
C(21A)-C(22A)-H(22A)	116.9	Ni(1)-C(22A)-H(22A)	116.9
C(21A)-C(22A)-H(22B)	116.9	Ni(1)-C(22A)-H(22B)	116.9
H(22A)-C(22A)-H(22B)	113.9	Ni(1)-C(21B)-H(21B)	134.2
C(42A)-Ni(2)-C(43A)	42.7(3)	C(42A)-Ni(2)-C(43B)	45.8(6)
C(43A)-Ni(2)-C(43B)	34.5(7)	C(42A)-Ni(2)-C(44A)	71.4(2)
C(43A)-Ni(2)-C(44A)	36.7(3)	C(43B)-Ni(2)-C(44A)	31.6(6)
C(42A)-Ni(2)-P(2)	99.7(2)	C(43A)-Ni(2)-P(2)	136.5(3)
C(43B)-Ni(2)-P(2)	139.6(6)	C(44A)-Ni(2)-P(2)	170.9(2)
C(42A)-Ni(2)-Br(2)	168.5(2)	C(43A)-Ni(2)-Br(2)	127.8(2)
C(43B)-Ni(2)-Br(2)	122.9(6)	C(44A)-Ni(2)-Br(2)	97.2(2)
P(2)-Ni(2)-Br(2)	91.61(4)	C(28)-P(2)-C(23)	97.2(2)
C(28)-P(2)-C(27)	95.6(2)	C(23)-P(2)-C(27)	101.8(3)
C(28)-P(2)-Ni(2)	127.0(2)	C(23)-P(2)-Ni(2)	115.2(2)
C(27)-P(2)-Ni(2)	115.6(2)	C(38)-Si(3)-C(37)	108.1(3)
C(38)-Si(3)-C(36)	110.3(3)	C(37)-Si(3)-C(36)	106.0(3)
C(38)-Si(3)-C(23)	111.8(3)	C(37)-Si(3)-C(23)	112.9(3)
C(36)-Si(3)-C(23)	107.6(3)	C(40)-Si(4)-C(39)	109.9(3)
C(40)-Si(4)-C(27)	112.1(3)	C(39)-Si(4)-C(27)	110.6(3)
C(40)-Si(4)-C(41)	110.1(3)	C(39)-Si(4)-C(41)	106.7(3)
C(27)-Si(4)-C(41)	107.3(2)	C(24)-C(23)-P(2)	111.0(4)
C(24)-C(23)-Si(3)	123.0(4)	P(2)-C(23)-Si(3)	125.6(3)
C(23)-C(24)-C(25)	119.6(5)	C(23)-C(24)-C(34)	126.4(5)
C(25)-C(24)-C(34)	113.9(5)	C(33)-C(25)-C(24)	108.8(4)
C(33)-C(25)-C(26)	107.3(4)	C(24)-C(25)-C(26)	108.9(4)
C(33)-C(25)-H(25)	110.6	C(24)-C(25)-H(25)	110.6
C(26)-C(25)-H(25)	110.6	C(27)-C(26)-C(35)	126.4(5)
C(27)-C(26)-C(25)	119.1(5)	C(35)-C(26)-C(25)	114.5(5)
C(26)-C(27)-P(2)	110.9(4)	C(26)-C(27)-Si(4)	124.3(4)
P(2)-C(27)-Si(4)	123.9(3)	C(29)-C(28)-C(33)	119.5(5)
C(29)-C(28)-P(2)	128.1(4)	C(33)-C(28)-P(2)	112.4(4)
C(28)-C(29)-C(30)	119.8(5)	C(28)-C(29)-H(29)	120.1
C(30)-C(29)-H(29)	120.1	C(31)-C(30)-C(29)	120.4(5)
C(31)-C(30)-H(30)	119.8	C(29)-C(30)-H(30)	119.8
C(32)-C(31)-C(30)	120.4(5)	C(32)-C(31)-H(31)	119.8
C(30)-C(31)-H(31)	119.8	C(31)-C(32)-C(33)	119.1(5)
C(31)-C(32)-H(32)	120.5	C(33)-C(32)-H(32)	120.5
C(32)-C(33)-C(28)	120.8(5)	C(32)-C(33)-C(25)	123.1(5)
C(28)-C(33)-C(25)	116.0(4)	C(24)-C(34)-H(34A)	109.5
C(24)-C(34)-H(34B)	109.5	H(34A)-C(34)-H(34B)	109.5
C(24)-C(34)-H(34C)	109.5	H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5	C(26)-C(35)-H(35A)	109.5
C(26)-C(35)-H(35B)	109.5	H(35A)-C(35)-H(35B)	109.5
C(26)-C(35)-H(35C)	109.5	H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5	Si(3)-C(36)-H(36A)	109.5
Si(3)-C(36)-H(36B)	109.5	H(36A)-C(36)-H(36B)	109.5
Si(3)-C(36)-H(36C)	109.5	H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5	Si(3)-C(37)-H(37A)	109.5
Si(3)-C(37)-H(37B)	109.5	H(37A)-C(37)-H(37B)	109.5
Si(3)-C(37)-H(37C)	109.5	H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5	Si(3)-C(38)-H(38A)	109.5
Si(3)-C(38)-H(38B)	109.5	H(38A)-C(38)-H(38B)	109.5
Si(3)-C(38)-H(38C)	109.5	H(38A)-C(38)-H(38C)	109.5

H(38B)-C(38)-H(38C)	109.5	Si(4)-C(39)-H(39A)	109.5
Si(4)-C(39)-H(39B)	109.5	H(39A)-C(39)-H(39B)	109.5
Si(4)-C(39)-H(39C)	109.5	H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5	Si(4)-C(40)-H(40A)	109.5
Si(4)-C(40)-H(40B)	109.5	H(40A)-C(40)-H(40B)	109.5
Si(4)-C(40)-H(40C)	109.5	H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5	Si(4)-C(41)-H(41A)	109.5
Si(4)-C(41)-H(41B)	109.5	H(41A)-C(41)-H(41B)	109.5
Si(4)-C(41)-H(41C)	109.5	H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5	C(43A)-C(42A)-Ni(2)	68.7(4)
C(43A)-C(42A)-H(42A)	116.8	Ni(2)-C(42A)-H(42A)	116.8
C(43A)-C(42A)-H(42B)	116.8	Ni(2)-C(42A)-H(42B)	116.8
H(42A)-C(42A)-H(42B)	113.8	C(44A)-C(43A)-C(42A)	120(1)
C(44A)-C(43A)-Ni(2)	74.2(5)	C(42A)-C(43A)-Ni(2)	68.6(4)
C(44A)-C(43A)-H(43A)	120.0	C(42A)-C(43A)-H(43A)	120.0
Ni(2)-C(43A)-H(43A)	129.5	C(43A)-C(44A)-Ni(2)	69.1(4)
C(43A)-C(44A)-H(44A)	116.8	Ni(2)-C(44A)-H(44A)	116.8
C(43A)-C(44A)-H(44B)	116.8	Ni(2)-C(44A)-H(44B)	116.8
H(44A)-C(44A)-H(44B)	113.8	Ni(2)-C(43B)-H(43B)	132.7

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb499

atom	U11	U22	U33	U23	U13	U12
Br(1)	43(1)	40(1)	30(1)	8(1)	2(1)	0(1)
Ni(1)	30(1)	33(1)	28(1)	3(1)	1(1)	2(1)
P(1)	26(1)	29(1)	27(1)	6(1)	3(1)	5(1)
Si(1)	36(1)	34(1)	30(1)	9(1)	5(1)	11(1)
Si(2)	32(1)	41(1)	33(1)	5(1)	9(1)	9(1)
C(1)	28(3)	29(3)	26(3)	7(2)	6(2)	4(2)
C(2)	34(3)	35(3)	26(3)	10(3)	9(2)	7(3)
C(3)	30(3)	33(3)	18(3)	0(2)	-1(2)	8(3)
C(4)	25(3)	29(3)	35(3)	14(3)	3(2)	4(2)
C(5)	24(3)	28(3)	33(3)	9(3)	6(2)	4(2)
C(6)	30(3)	32(3)	32(3)	10(3)	4(2)	9(3)
C(7)	26(3)	30(3)	30(3)	6(3)	6(2)	11(2)
C(8)	32(3)	44(4)	28(3)	11(3)	1(3)	12(3)
C(9)	38(3)	50(4)	37(4)	23(3)	7(3)	13(3)
C(10)	35(3)	45(4)	47(4)	23(3)	10(3)	3(3)
C(11)	30(3)	37(3)	39(4)	6(3)	2(3)	3(3)
C(12)	46(3)	31(3)	29(3)	9(3)	1(3)	4(3)
C(13)	35(3)	40(4)	35(4)	13(3)	0(3)	3(3)
C(14)	57(4)	48(4)	39(4)	8(3)	11(3)	26(3)
C(15)	60(4)	37(4)	41(4)	13(3)	7(3)	12(3)
C(16)	37(3)	50(4)	48(4)	5(3)	1(3)	17(3)
C(17)	36(3)	53(4)	30(3)	5(3)	7(3)	5(3)
C(18)	63(4)	56(4)	48(4)	16(3)	24(3)	32(4)
C(19)	40(3)	44(4)	62(5)	-3(3)	4(3)	8(3)
C(20A)	63(4)	42(4)	50(5)	-4(3)	-22(4)	-10(3)
C(21A)	31(4)	42(5)	45(5)	-3(4)	-11(4)	-1(4)
C(22A)	35(3)	39(4)	48(4)	12(3)	0(3)	-9(3)
C(20B)	63(4)	42(4)	50(5)	-4(3)	-22(4)	-10(3)
C(21B)	31(4)	42(5)	45(5)	-3(4)	-11(4)	-1(4)
C(22B)	35(3)	39(4)	48(4)	12(3)	0(3)	-9(3)
Br(2)	39(1)	34(1)	39(1)	3(1)	-4(1)	10(1)
Ni(2)	34(1)	31(1)	26(1)	3(1)	-1(1)	6(1)
P(2)	30(1)	29(1)	25(1)	5(1)	4(1)	6(1)
Si(3)	35(1)	37(1)	36(1)	7(1)	10(1)	7(1)
Si(4)	34(1)	33(1)	30(1)	7(1)	3(1)	5(1)
C(23)	38(3)	36(3)	31(3)	7(3)	9(3)	15(3)
C(24)	43(3)	32(3)	30(3)	9(3)	5(3)	14(3)
C(25)	36(3)	33(3)	28(3)	6(3)	-8(3)	4(3)

C(26)	29(3)	28(3)	35(4)	2(3)	3(3)	5(2)
C(27)	29(3)	28(3)	35(3)	4(3)	-1(3)	5(2)
C(28)	27(3)	29(3)	26(3)	10(2)	7(2)	4(2)
C(29)	34(3)	34(3)	33(3)	6(3)	5(3)	6(3)
C(30)	43(3)	36(3)	45(4)	6(3)	8(3)	17(3)
C(31)	34(3)	38(4)	42(4)	14(3)	4(3)	10(3)
C(32)	30(3)	38(3)	29(3)	12(3)	3(2)	2(3)
C(33)	30(3)	32(3)	31(3)	12(3)	7(2)	7(3)
C(34)	48(4)	48(4)	34(4)	0(3)	9(3)	15(3)
C(35)	39(3)	37(3)	33(4)	4(3)	0(3)	1(3)
C(36)	67(4)	49(4)	31(4)	9(3)	15(3)	5(3)
C(37)	32(3)	49(4)	45(4)	12(3)	7(3)	3(3)
C(38)	38(3)	44(4)	74(5)	10(3)	18(3)	9(3)
C(39)	45(3)	40(4)	29(3)	7(3)	8(3)	8(3)
C(40)	46(3)	40(4)	37(4)	11(3)	4(3)	6(3)
C(41)	42(3)	55(4)	35(4)	11(3)	17(3)	0(3)
C(42A)	60(4)	31(3)	34(4)	-11(3)	-8(3)	17(3)
C(43A)	60(6)	29(5)	27(5)	-4(4)	-7(4)	2(4)
C(44A)	78(5)	56(5)	44(4)	-27(4)	-30(4)	27(4)
C(42B)	60(4)	31(3)	34(4)	-11(3)	-8(3)	17(3)
C(43B)	60(6)	29(5)	27(5)	-4(4)	-7(4)	2(4)
C(44B)	78(5)	56(5)	44(4)	-27(4)	-30(4)	27(4)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb499

atom	x	y	z	U(eq)
H(3)	5740	8551	2310	33
H(8)	4818	7508	3180	41
H(9)	3394	6207	3346	47
H(10)	1848	5356	2235	49
H(11)	1669	5835	979	43
H(12A)	4308	10210	1685	54
H(12B)	5701	10016	2057	54
H(12C)	4364	9862	2539	54
H(13A)	7877	8032	778	55
H(13B)	7737	7938	1723	55
H(13C)	7705	8861	1455	55
H(14A)	653	10055	1245	69
H(14B)	2116	10276	1775	69
H(14C)	1055	9370	1773	69
H(15A)	3385	9805	-517	67
H(15B)	3755	10502	345	67
H(15C)	2354	10421	-212	67
H(16A)	891	8293	-699	67
H(16B)	-77	8867	-225.0000	67
H(16C)	243	8029	108	67
H(17A)	7440	7165	-1507	61
H(17B)	7636	7999	-757	61
H(17C)	6345	7778	-1441	61
H(18A)	6631	5881	386	77
H(18B)	7923	6638	318	77
H(18C)	7433	5799	-426.0000	77
H(19A)	4125	6208	-1546	76
H(19B)	4017	5629	-840	76
H(19C)	5083	5515	-1514	76
H(20A)	640	6692	-2283	69
H(20B)	1121	5757	-2220	69

H(21A)	-631	6412	-1254.9999	52
H(22A)	999	5316	-702.0001	51
H(22B)	341	6011	-45.0000	51
H(20C)	30	6492	-2019	69
H(20D)	1377	6185	-2420	69
H(21B)	1106	5213	-1604	52
H(22C)	1142	5521	-244	51
H(22D)	-128	6016	-414	51
H(25)	-1772	1775	3186	40
H(29)	-716	4412	5807	41
H(30)	-2344	5013	5170	48
H(31)	-3450.9998	4312	3863	45
H(32)	-2998	2976	3200	39
H(34A)	258	2151	2403	65
H(34B)	275	1206	2626	65
H(34C)	1646	1962	2790	65
H(35A)	-2755	176	4387	57
H(35B)	-2376	274	3473	57
H(35C)	-3549	719	3865	57
H(36A)	3916	3382	3094	74
H(36B)	3734	4218	3758	74
H(36C)	2428	3582	3195	74
H(37A)	4052	3250	5707	64
H(37B)	3438	4055	5495	64
H(37C)	4878	3916	5194	64
H(38A)	4891	2168	4019	77
H(38B)	3497	1582	3512	77
H(38C)	3794	1594	4481	77
H(39A)	-1594	1654	7463	57
H(39B)	-1287	2465	6991	57
H(39C)	-109	1955	7173	57
H(40A)	-1377.0001	-351.0000	5501	61
H(40B)	-1367	-184	6491	61
H(40C)	-29	203	6081	61
H(41A)	-3920	258	5563	67
H(41B)	-3878	1279	5567	67
H(41C)	-3920	928	6420	67
H(42A)	1105	4635	6508	52
H(42B)	425	4239	7292	52
H(43A)	3264	4623	7184	50
H(44A)	2097	3514	8102	77
H(44B)	3560	3466	7699	77
H(42C)	1760	4766	6792	52
H(42D)	164	4264	6865	52
H(43B)	1116	3744	8056	50
H(44C)	2703	3137	7975	77
H(44D)	3477	4023	7647	77

II.18. Crystallographic data for IV-50

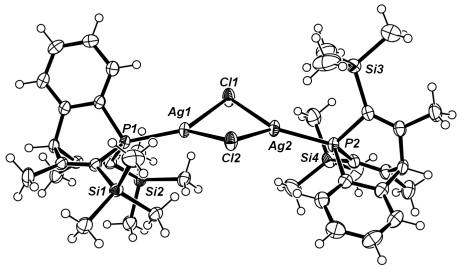


Table 1. Crystal data for mb822

Compound	mb822
Molecular formula	$C_{38}H_{58}Ag_2Cl_2P_2Si_4$
Molecular weight	3903.14
Crystal habit	colorless block
Crystal dimensions(mm)	0.32x0.20x0.16
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	17.321(1)
b(Å)	14.594(1)
c(Å)	21.119(1)
α(°)	90.00
β(°)	120.174(3)
γ(°)	90.00
V(Å^3)	4615.2(5)
Z	1
d(g-cm^{-3})	1.404
F(000)	2000
μ(cm^{-1})	1.162
Absorption corrections	multi-scan ; 0.7074 min, 0.8359 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	28.28
HKL ranges	-23 12 ; -19 17 ; -27 28
Reflections measured	31854
Unique data	11421

Rint	0.0294
Reflections used	8525
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	449
Reflections / parameter	18
wR2	0.0667
R1	0.0297
Weights a, b	0.0251 ; 0.0000
GoF	1.004
difference peak / hole (e Å^{-3})	0.485(0.074) / -0.493(0.074)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb822

atom	x	y	z	U(eq)
Ag(1)	-1817(1)	-4379(1)	-4212(1)	27(1)
Ag(2)	-3362(1)	-5816(1)	-5530(1)	33(1)
Cl(1)	-2389(1)	-5999(1)	-4187(1)	37(1)
Cl(2)	-3206(1)	-4051(1)	-5415(1)	35(1)
P(1)	-481(1)	-3618(1)	-3359(1)	22(1)
P(2)	-4238(1)	-6633(1)	-6627(1)	25(1)
Si(1)	-982(1)	-1874(1)	-4412(1)	26(1)
Si(2)	867(1)	-5167(1)	-3398(1)	27(1)
Si(3)	-5740(1)	-6773(1)	-6178(1)	32(1)
Si(4)	-2863(1)	-8309(1)	-6182(1)	34(1)
C(1)	-273(1)	-2410(1)	-3484(1)	24(1)
C(2)	444(1)	-2075(1)	-2882(1)	25(1)
C(3)	981(1)	-2717(1)	-2227(1)	25(1)
C(4)	1272(1)	-3570(2)	-2480(1)	27(1)
C(5)	646(1)	-4083(1)	-3029(1)	24(1)
C(6)	369(1)	-3044(1)	-1952(1)	24(1)
C(7)	-403(1)	-3495(1)	-2468(1)	22(1)
C(8)	-1008(2)	-3833(1)	-2281(1)	27(1)
C(9)	-844(2)	-3715(2)	-1571(1)	31(1)
C(10)	-79(2)	-3265(2)	-1063(1)	33(1)
C(11)	528(2)	-2928(1)	-1249(1)	27(1)
C(12)	789(2)	-1108(2)	-2756(1)	42(1)
C(13)	2268(2)	-3751(2)	-2047(1)	38(1)
C(16)	-484(2)	-811(1)	-4550(1)	37(1)
C(14)	-2126(2)	-1597(2)	-4596(1)	50(1)
C(15)	-1055(2)	-2757(2)	-5082(1)	35(1)
C(17)	1690(2)	-4951(2)	-3702(1)	41(1)
C(18)	1283(2)	-6070(2)	-2676(1)	46(1)
C(19)	-191(2)	-5564(2)	-4214(1)	33(1)
C(20)	-5397(1)	-6941(1)	-6888(1)	27(1)
C(21)	-5837(1)	-7261(2)	-7577(1)	29(1)
C(22)	-5348(1)	-7359(2)	-8009(1)	30(1)
C(23)	-4504(2)	-7949(1)	-7580(1)	29(1)
C(24)	-3905(1)	-7711(1)	-6887(1)	27(1)
C(25)	-5045(2)	-6415(2)	-8095(1)	30(1)
C(26)	-4483(1)	-5962(2)	-7438(1)	28(1)
C(27)	-4167(2)	-5091(2)	-7437(1)	33(1)
C(28)	-4403(2)	-4677(2)	-8108(1)	44(1)
C(29)	-4944(2)	-5135(2)	-8757(1)	46(1)
C(30)	-5267(2)	-5999(2)	-8753(1)	38(1)
C(31)	-6814(2)	-7511(2)	-8014(1)	43(1)

C(32)	-4425(2)	-8712(2)	-8020(1)	41(1)
C(33)	-6808(2)	-7338(2)	-6403(2)	64(1)
C(34)	-4893(2)	-7326(2)	-5301(1)	68(1)
C(35)	-5806(2)	-5541(2)	-6020(2)	75(1)
C(36)	-1880(2)	-7575(2)	-5965(2)	56(1)
C(37)	-2921(2)	-8471(2)	-5334(1)	47(1)
C(38)	-2697(2)	-9473(2)	-6463(2)	65(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb822

Ag(1)-P(1)	2.3757(5	Ag(1)-Cl(2)	2.5148(5)
Ag(1)-Cl(1)	2.5744(6	Ag(2)-P(2)	2.3574(5)
Ag(2)-Cl(1)	2.4791(5	Ag(2)-Cl(2)	2.5891(6)
P(1)-C(7)	1.826(2)	P(1)-C(5)	1.842(2)
P(1)-C(1)	1.844(2)	P(2)-C(26)	1.829(2)
P(2)-C(20)	1.850(2)	P(2)-C(24)	1.851(2)
Si(1)-C(14)	1.862(3)	Si(1)-C(16)	1.868(2)
Si(1)-C(15)	1.870(2)	Si(1)-C(1)	1.882(2)
Si(2)-C(17)	1.861(3)	Si(2)-C(18)	1.865(2)
Si(2)-C(19)	1.869(2)	Si(2)-C(5)	1.884(2)
Si(3)-C(35)	1.842(3)	Si(3)-C(33)	1.857(3)
Si(3)-C(34)	1.870(3)	Si(3)-C(20)	1.886(2)
Si(4)-C(37)	1.859(3)	Si(4)-C(36)	1.862(3)
Si(4)-C(38)	1.869(3)	Si(4)-C(24)	1.879(2)
C(1)-C(2)	1.346(3)	C(2)-C(12)	1.504(3)
C(2)-C(3)	1.536(3)	C(3)-C(6)	1.520(3)
C(3)-C(4)	1.537(3)	C(3)-H(3)	1.0000
C(4)-C(5)	1.347(3)	C(4)-C(13)	1.516(3)
C(6)-C(11)	1.377(3)	C(6)-C(7)	1.394(3)
C(7)-C(8)	1.385(3)	C(8)-C(9)	1.387(3)
C(8)-H(8)	0.9500	C(9)-C(10)	1.382(3)
C(9)-H(9)	0.9500	C(10)-C(11)	1.384(3)
C(10)-H(10)	0.9500	C(11)-H(11)	0.9500
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800	C(13)-H(13C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800
C(20)-C(21)	1.344(3)	C(21)-C(31)	1.510(3)
C(21)-C(22)	1.531(3)	C(22)-C(25)	1.517(3)
C(22)-C(23)	1.539(3)	C(22)-H(22)	1.0000
C(23)-C(24)	1.346(3)	C(23)-C(32)	1.501(3)
C(25)-C(30)	1.382(3)	C(25)-C(26)	1.398(3)
C(26)-C(27)	1.384(3)	C(27)-C(28)	1.398(3)
C(27)-H(27)	0.9500	C(28)-C(29)	1.383(3)
C(28)-H(28)	0.9500	C(29)-C(30)	1.381(3)
C(29)-H(29)	0.9500	C(30)-H(30)	0.9500
C(31)-H(31A)	0.9800	C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800	C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800	C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800	C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800	C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800	C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800	C(35)-H(35B)	0.9800

C(35)-H(35C)	0.9800	C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800	C(36)-H(36C)	0.9800
C(37)-H(37A)	0.9800	C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800	C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800	C(38)-H(38C)	0.9800

P(1)-Ag(1)-Cl(2)	138.52(2)	P(1)-Ag(1)-Cl(1)	130.70(2)
Cl(2)-Ag(1)-Cl(1)	90.77(2)	P(2)-Ag(2)-Cl(1)	143.22(2)
P(2)-Ag(2)-Cl(2)	125.50(2)	Cl(1)-Ag(2)-Cl(2)	91.23(2)
Ag(2)-Cl(1)-Ag(1)	85.69(2)	Ag(1)-Cl(2)-Ag(2)	84.65(2)
C(7)-P(1)-C(5)	97.5(1)	C(7)-P(1)-C(1)	97.7(1)
C(5)-P(1)-C(1)	99.2(1)	C(7)-P(1)-Ag(1)	111.54(7)
C(5)-P(1)-Ag(1)	123.91(7)	C(1)-P(1)-Ag(1)	121.67(7)
C(26)-P(2)-C(20)	98.3(1)	C(26)-P(2)-C(24)	97.9(1)
C(20)-P(2)-C(24)	99.1(1)	C(26)-P(2)-Ag(2)	112.40(7)
C(20)-P(2)-Ag(2)	118.76(7)	C(24)-P(2)-Ag(2)	125.39(7)
C(14)-Si(1)-C(16)	108.3(1)	C(14)-Si(1)-C(15)	109.3(1)
C(16)-Si(1)-C(15)	108.3(1)	C(14)-Si(1)-C(1)	112.1(1)
C(16)-Si(1)-C(1)	113.4(1)	C(15)-Si(1)-C(1)	105.2(1)
C(17)-Si(2)-C(18)	110.7(1)	C(17)-Si(2)-C(19)	107.4(1)
C(18)-Si(2)-C(19)	109.4(1)	C(17)-Si(2)-C(5)	110.5(1)
C(18)-Si(2)-C(5)	109.3(1)	C(19)-Si(2)-C(5)	109.5(1)
C(35)-Si(3)-C(33)	109.6(2)	C(35)-Si(3)-C(34)	109.3(2)
C(33)-Si(3)-C(34)	104.3(1)	C(35)-Si(3)-C(20)	110.1(1)
C(33)-Si(3)-C(20)	114.3(1)	C(34)-Si(3)-C(20)	109.1(1)
C(37)-Si(4)-C(36)	108.7(1)	C(37)-Si(4)-C(38)	106.3(1)
C(36)-Si(4)-C(38)	109.5(2)	C(37)-Si(4)-C(24)	109.0(1)
C(36)-Si(4)-C(24)	108.9(1)	C(38)-Si(4)-C(24)	114.2(1)
C(2)-C(1)-P(1)	111.5(2)	C(2)-C(1)-Si(1)	129.9(2)
P(1)-C(1)-Si(1)	118.3(1)	C(1)-C(2)-C(12)	127.2(2)
C(1)-C(2)-C(3)	118.8(2)	C(12)-C(2)-C(3)	114.0(2)
C(6)-C(3)-C(2)	108.2(2)	C(6)-C(3)-C(4)	107.0(2)
C(2)-C(3)-C(4)	109.7(2)	C(6)-C(3)-H(3)	110.6
C(2)-C(3)-H(3)	110.6	C(4)-C(3)-H(3)	110.6
C(5)-C(4)-C(13)	127.0(2)	C(5)-C(4)-C(3)	119.2(2)
C(13)-C(4)-C(3)	113.8(2)	C(4)-C(5)-P(1)	111.2(2)
C(4)-C(5)-Si(2)	125.4(2)	P(1)-C(5)-Si(2)	123.3(1)
C(11)-C(6)-C(7)	119.7(2)	C(11)-C(6)-C(3)	125.0(2)
C(7)-C(6)-C(3)	115.3(2)	C(8)-C(7)-C(6)	120.7(2)
C(8)-C(7)-P(1)	125.8(2)	C(6)-C(7)-P(1)	113.5(2)
C(7)-C(8)-C(9)	119.3(2)	C(7)-C(8)-H(8)	120.3
C(9)-C(8)-H(8)	120.3	C(10)-C(9)-C(8)	119.7(2)
C(10)-C(9)-H(9)	120.2	C(8)-C(9)-H(9)	120.2
C(9)-C(10)-C(11)	121.1(2)	C(9)-C(10)-H(10)	119.5
C(11)-C(10)-H(10)	119.5	C(6)-C(11)-C(10)	119.6(2)
C(6)-C(11)-H(11)	120.2	C(10)-C(11)-H(11)	120.2
C(2)-C(12)-H(12A)	109.5	C(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5	C(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5	H(12B)-C(12)-H(12C)	109.5
C(4)-C(13)-H(13A)	109.5	C(4)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5	C(4)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5	H(13B)-C(13)-H(13C)	109.5
Si(1)-C(16)-H(16A)	109.5	Si(1)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5	Si(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(16B)-C(16)-H(16C)	109.5
Si(1)-C(14)-H(14A)	109.5	Si(1)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	Si(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
Si(1)-C(15)-H(15A)	109.5	Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5	Si(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
Si(2)-C(17)-H(17A)	109.5	Si(2)-C(17)-H(17B)	109.5

H(17A)-C(17)-H(17B)	109.5	Si(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(17B)-C(17)-H(17C)	109.5
Si(2)-C(18)-H(18A)	109.5	Si(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5	Si(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5	H(18B)-C(18)-H(18C)	109.5
Si(2)-C(19)-H(19A)	109.5	Si(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5	Si(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5	H(19B)-C(19)-H(19C)	109.5
C(21)-C(20)-P(2)	110.3(2)	C(21)-C(20)-Si(3)	132.3(2)
P(2)-C(20)-Si(3)	117.4(1)	C(20)-C(21)-C(31)	126.7(2)
C(20)-C(21)-C(22)	119.7(2)	C(31)-C(21)-C(22)	113.5(2)
C(25)-C(22)-C(21)	108.4(2)	C(25)-C(22)-C(23)	107.2(2)
C(21)-C(22)-C(23)	110.4(2)	C(25)-C(22)-H(22)	110.3
C(21)-C(22)-H(22)	110.3	C(23)-C(22)-H(22)	110.3
C(24)-C(23)-C(32)	127.2(2)	C(24)-C(23)-C(22)	118.7(2)
C(32)-C(23)-C(22)	113.9(2)	C(23)-C(24)-P(2)	110.9(2)
C(23)-C(24)-Si(4)	130.5(2)	P(2)-C(24)-Si(4)	118.6(1)
C(30)-C(25)-C(26)	119.6(2)	C(30)-C(25)-C(22)	125.5(2)
C(26)-C(25)-C(22)	114.9(2)	C(27)-C(26)-C(25)	120.9(2)
C(27)-C(26)-P(2)	125.9(2)	C(25)-C(26)-P(2)	113.2(2)
C(26)-C(27)-C(28)	118.8(2)	C(26)-C(27)-H(27)	120.6
C(28)-C(27)-H(27)	120.6	C(29)-C(28)-C(27)	120.2(2)
C(29)-C(28)-H(28)	119.9	C(27)-C(28)-H(28)	119.9
C(30)-C(29)-C(28)	120.6(2)	C(30)-C(29)-H(29)	119.7
C(28)-C(29)-H(29)	119.7	C(29)-C(30)-C(25)	119.9(2)
C(29)-C(30)-H(30)	120.1	C(25)-C(30)-H(30)	120.1
C(21)-C(31)-H(31A)	109.5	C(21)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5	C(21)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5	H(31B)-C(31)-H(31C)	109.5
C(23)-C(32)-H(32A)	109.5	C(23)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5	C(23)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5	H(32B)-C(32)-H(32C)	109.5
Si(3)-C(33)-H(33A)	109.5	Si(3)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5	Si(3)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5	H(33B)-C(33)-H(33C)	109.5
Si(3)-C(34)-H(34A)	109.5	Si(3)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5	Si(3)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5	H(34B)-C(34)-H(34C)	109.5
Si(3)-C(35)-H(35A)	109.5	Si(3)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5	Si(3)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5	H(35B)-C(35)-H(35C)	109.5
Si(4)-C(36)-H(36A)	109.5	Si(4)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5	Si(4)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5	H(36B)-C(36)-H(36C)	109.5
Si(4)-C(37)-H(37A)	109.5	Si(4)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5	Si(4)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5	H(37B)-C(37)-H(37C)	109.5
Si(4)-C(38)-H(38A)	109.5	Si(4)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5	Si(4)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5	H(38B)-C(38)-H(38C)	109.5

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb822

atom	U11	U22	U33	U23	U13	U12
Ag(1)	25(1)	28(1)	23(1)	-6(1)	7(1)	-4(1)
Ag(2)	29(1)	36(1)	24(1)	-9(1)	6(1)	-6(1)
Cl(1)	38(1)	28(1)	25(1)	5(1)	1(1)	-6(1)
Cl(2)	34(1)	28(1)	26(1)	4(1)	2(1)	-2(1)
P(1)	24(1)	19(1)	18(1)	-2(1)	8(1)	-1(1)
P(2)	22(1)	25(1)	21(1)	-3(1)	6(1)	-1(1)
Si(1)	29(1)	26(1)	21(1)	2(1)	12(1)	0(1)
Si(2)	28(1)	24(1)	27(1)	-2(1)	13(1)	2(1)
Si(3)	33(1)	33(1)	34(1)	-3(1)	19(1)	-5(1)
Si(4)	26(1)	32(1)	36(1)	5(1)	10(1)	4(1)
C(1)	31(1)	19(1)	21(1)	0(1)	13(1)	-1(1)
C(2)	32(1)	23(1)	21(1)	-1(1)	14(1)	-3(1)
C(3)	25(1)	24(1)	20(1)	-4(1)	7(1)	-4(1)
C(4)	25(1)	31(1)	23(1)	0(1)	12(1)	2(1)
C(5)	24(1)	27(1)	21(1)	0(1)	10(1)	1(1)
C(6)	30(1)	15(1)	22(1)	1(1)	10(1)	3(1)
C(7)	27(1)	17(1)	21(1)	0(1)	10(1)	1(1)
C(8)	30(1)	19(1)	29(1)	0(1)	12(1)	2(1)
C(9)	37(1)	30(1)	34(1)	4(1)	23(1)	5(1)
C(10)	45(2)	33(1)	23(1)	3(1)	19(1)	9(1)
C(11)	31(1)	22(1)	21(1)	-1(1)	8(1)	4(1)
C(12)	55(2)	30(1)	26(1)	-4(1)	9(1)	-15(1)
C(13)	28(1)	46(2)	32(1)	-7(1)	9(1)	2(1)
C(16)	51(2)	29(1)	27(1)	4(1)	18(1)	-3(1)
C(14)	41(2)	64(2)	48(2)	14(1)	24(1)	13(1)
C(15)	46(2)	35(1)	24(1)	-2(1)	18(1)	-10(1)
C(17)	39(2)	46(2)	44(1)	-14(1)	25(1)	-7(1)
C(18)	49(2)	34(2)	46(2)	7(1)	18(1)	9(1)
C(19)	37(1)	30(1)	33(1)	-9(1)	18(1)	2(1)
C(20)	21(1)	25(1)	30(1)	-2(1)	9(1)	-2(1)
C(21)	22(1)	29(1)	29(1)	-1(1)	8(1)	1(1)
C(22)	24(1)	36(1)	22(1)	-8(1)	6(1)	-2(1)
C(23)	28(1)	26(1)	31(1)	-5(1)	13(1)	-1(1)
C(24)	25(1)	26(1)	30(1)	-3(1)	13(1)	-2(1)
C(25)	26(1)	33(1)	25(1)	-1(1)	10(1)	7(1)
C(26)	26(1)	29(1)	28(1)	0(1)	13(1)	4(1)
C(27)	32(1)	30(1)	35(1)	-3(1)	16(1)	1(1)
C(28)	53(2)	32(1)	50(2)	11(1)	27(1)	2(1)
C(29)	58(2)	47(2)	32(1)	13(1)	21(1)	14(1)
C(30)	41(2)	42(2)	24(1)	0(1)	12(1)	8(1)
C(31)	24(1)	54(2)	40(1)	-12(1)	9(1)	-6(1)
C(32)	36(2)	40(2)	38(1)	-13(1)	11(1)	3(1)
C(33)	56(2)	86(2)	61(2)	-7(2)	37(2)	-16(2)
C(34)	57(2)	105(3)	41(2)	13(2)	24(2)	-6(2)
C(35)	133(3)	45(2)	97(3)	-5(2)	94(3)	0(2)
C(36)	29(2)	70(2)	55(2)	17(1)	10(1)	-5(1)
C(37)	40(2)	44(2)	40(1)	7(1)	9(1)	-1(1)
C(38)	70(2)	50(2)	62(2)	8(2)	23(2)	32(2)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb822

atom	x	y	z	U(eq)
H(3)	1513	-2392	-1830	30
H(8)	-1531	-4143	-2634	32
H(9)	-1254.0001	-3944	-1436	37
H(10)	32	-3185	-578	40
H(11)	1050	-2618	-895	32
H(12A)	1383	-1099	-2705	63
H(12B)	828	-869.0001	-2307	63
H(12C)	381	-725	-3172	63
H(13A)	2399	-4333	-2205	57
H(13B)	2464	-3784	-1524	57
H(13C)	2585	-3253	-2131	57
H(16A)	155	-908	-4364	55

H(16B)	-563	-301	-4286	55
H(16C)	-782	-666	-5074	55
H(14A)	-2460	-1287	-5070.0005	75
H(14B)	-2086	-1195	-4209	75
H(14C)	-2435	-2165	-4605	75
H(15A)	-1291	-2474	-5565	52
H(15B)	-1454	-3252	-5111	52
H(15C)	-459.0000	-3006	-4920	52
H(17A)	2243	-4709	-3291.0002	62
H(17B)	1443	-4506	-4103	62
H(17C)	1817	-5527	-3871	62
H(18A)	1351	-6648	-2878.0002	69
H(18B)	855	-6153	-2506	69
H(18C)	1861	-5883	-2263	69
H(19A)	-438	-5069	-4577	50
H(19B)	-623	-5733	-4064	50
H(19C)	-67	-6097	-4431	50
H(22)	-5752	-7636	-8500	36
H(27)	-3797	-4779	-6989	40
H(28)	-4192	-4080	-8117	53
H(29)	-5095.0005	-4853	-9210	55
H(30)	-5641.0005	-6307	-9201	45
H(31A)	-7081	-7460	-7702	64
H(31B)	-6875	-8143	-8192	64
H(31C)	-7121.0005	-7095	-8432	64
H(32A)	-3858	-9035	-7722	62
H(32B)	-4443	-8458	-8457	62
H(32C)	-4921	-9141	-8168	62
H(33A)	-6932	-7235.9995	-6003.9995	97
H(33B)	-6763	-7998	-6466	97
H(33C)	-7294	-7080	-6858	97
H(34A)	-4303	-7062	-5143	102
H(34B)	-4878	-7986	-5378	102
H(34C)	-5054	-7219	-4924	102
H(35A)	-5252	-5238.9995	-5922	113
H(35B)	-5892	-5461	-5598.0005	113
H(35C)	-6311	-5269	-6456	113
H(36A)	-1943	-6983	-5776	84
H(36B)	-1847	-7478	-6409.9995	84
H(36C)	-1333.9999	-7878.9995	-5594	84
H(37A)	-3462	-8817	-5450	70
H(37B)	-2940	-7871	-5133	70
H(37C)	-2394	-8809	-4973	70
H(38A)	-2205	-9783	-6041	98
H(38B)	-2554	-9415	-6854	98
H(38C)	-3246	-9832	-6639	98

II.19. Crystallographic data for IV-50

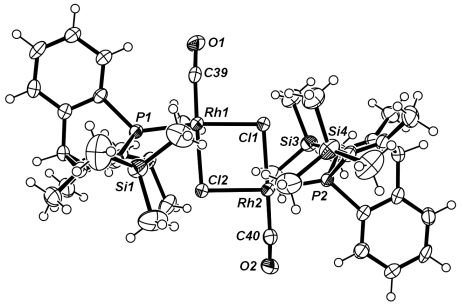


Table 1. Crystal data for mbgo25b

Compound	mbgo25b
Molecular formula	$C_{40}H_{58}Cl_2O_2P_2Rh_2Si_4$,4.5($C_6H_6$)
Molecular weight	1373.37
Crystal habit	Orange Block
Crystal dimensions(mm)	0.22x0.16x0.14
Crystal system	triclinic
Space group	P-1
a(Å)	10.428(1)
b(Å)	16.138(1)
c(Å)	22.217(1)
α(°)	70.996(1)
β(°)	86.645(1)
γ(°)	82.832(1)
V(Å^3)	3506.8(4)
Z	2
d(g-cm^{-3})	1.301
F(000)	1426
μ(cm^{-1})	0.701
Absorption corrections	multi-scan ; 0.8611 min, 0.9083 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	27.47
HKL ranges	-13 13 ; -18 20 ; -28 28
Reflections measured	37438
Unique data	15867

Rint	0.0558
Reflections used	8510
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	728
Reflections / parameter	11
wR2	0.0902
R1	0.0496
Weights a, b	0.0224 ; 0.0000
GoF	0.936
difference peak / hole (e Å^{-3})	0.577(0.085) / -0.488(0.085)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mbgo25b

atom	x	y	z	U(eq)
Rh(1)	154(1)	-780(1)	7925(1)	29(1)
Rh(2)	2115(1)	953(1)	7577(1)	30(1)
Cl(1)	795(1)	369(1)	6996(1)	39(1)
Cl(2)	1213(1)	-55(1)	8520(1)	42(1)
P(1)	-309(1)	-1756(1)	8853(1)	27(1)
P(2)	2657(1)	1837(1)	6630(1)	26(1)
Si(1)	-2167(1)	-164(1)	9210(1)	42(1)
Si(2)	2796(1)	-2514(1)	8937(1)	36(1)
Si(3)	-435(1)	2675(1)	6472(1)	45(1)
Si(4)	4403(1)	126(1)	6368(1)	38(1)
O(1)	-973(4)	-1619(3)	7128(2)	122(2)
O(2)	4017(2)	1434(2)	8300(1)	51(1)
C(1)	-1151(3)	-1272(3)	9435(2)	33(1)
C(2)	-1178(3)	-1878(3)	10012(2)	34(1)
C(3)	-640(3)	-2827(3)	10091(2)	32(1)
C(4)	798(3)	-2851(3)	9895(2)	34(1)
C(5)	1118(3)	-2405(3)	9293(2)	29(1)
C(6)	-1711(4)	-1724(3)	10625(2)	51(1)
C(7)	1693(3)	-3364(3)	10425(2)	48(1)
C(8)	-1363(3)	-3142(3)	9651(2)	29(1)
C(9)	-2070(3)	-3859(3)	9857(2)	36(1)
C(10)	-2750(3)	-4077(3)	9417(2)	41(1)
C(11)	-2725(3)	-3581(3)	8784(2)	41(1)
C(12)	-2007(3)	-2871(3)	8570(2)	34(1)
C(13)	-1312(3)	-2656(2)	9000(2)	27(1)
C(14)	-3808(4)	-381(4)	9564(2)	94(2)
C(15)	-2454(4)	325(4)	8343(2)	65(2)
C(16)	-1489(4)	650(3)	9499(2)	74(2)
C(17)	2762(3)	-2281(3)	8058(2)	54(1)
C(18)	3518(3)	-3693(3)	9253(2)	48(1)
C(19)	3870(3)	-1802(3)	9129(2)	54(1)
C(20)	1247(3)	2465(3)	6147(2)	32(1)
C(21)	1608(3)	2851(3)	5541(2)	36(1)
C(22)	3051(3)	2786(3)	5363(2)	34(1)
C(23)	3564(3)	1824(3)	5496(2)	33(1)
C(24)	3521(3)	1278(3)	6092(2)	29(1)
C(25)	744(3)	3352(3)	4992(2)	55(1)
C(26)	4076(3)	1596(3)	4912(2)	48(1)
C(27)	3770(3)	3150(3)	5782(2)	30(1)
C(28)	4533(3)	3834(3)	5545(2)	38(1)
C(29)	5170(3)	4111(3)	5961(2)	44(1)

C(30)	5027(3)	3733(3)	6610(2)	45(1)
C(31)	4272(3)	3043(3)	6852(2)	37(1)
C(32)	3652(3)	2742(3)	6442(2)	28(1)
C(33)	-1636(3)	2088(3)	6225(2)	56(1)
C(34)	-927(4)	3892(3)	6166(3)	79(2)
C(35)	-503(3)	2393(3)	7351(2)	60(1)
C(36)	3492(4)	-651(3)	6148(2)	51(1)
C(37)	4709(4)	-288(3)	7238(2)	54(1)
C(38)	6059(3)	156(3)	5993(2)	59(1)
C(39)	-554(4)	-1309(3)	7458(2)	57(1)
C(40)	3248(3)	1287(3)	8006(2)	36(1)
C(41)	380(4)	592(3)	5262(2)	56(1)
C(42)	-338(4)	-48(4)	5615(2)	62(2)
C(43)	714(4)	644(3)	4639(2)	59(1)
C(44)	7889(4)	4876(4)	1807(2)	67(2)
C(45)	7596(4)	5602(4)	2000(2)	62(1)
C(46)	8552(4)	6047(4)	2106(2)	63(1)
C(47)	9836(4)	5745(4)	2015(2)	61(1)
C(48)	10141(4)	5030(4)	1816(2)	60(1)
C(49)	9170(5)	4584(4)	1707(2)	64(1)
C(50)	7276(5)	3094(6)	4585(3)	76(2)
C(51)	7385(5)	3938(6)	4362(3)	87(2)
C(52)	8027(6)	4283(5)	3831(4)	120(3)
C(53)	8613(6)	3760(10)	3485(3)	130(5)
C(54)	8492(6)	2837(8)	3739(4)	125(3)
C(55)	7811(5)	2528(5)	4300(4)	88(2)
C(56)	2530(5)	3183(4)	3107(2)	71(2)
C(57)	2351(4)	3884(4)	3318(2)	55(1)
C(58)	3392(4)	4243(3)	3435(2)	55(1)
C(59)	4613(4)	3896(4)	3335(2)	57(1)
C(60)	4805(4)	3190(4)	3124(2)	66(2)
C(61)	3757(6)	2831(4)	3001(2)	81(2)
C(62)	4191(4)	5580(3)	1557(3)	65(1)
C(63)	4940(4)	5875(4)	1017(3)	61(1)
C(64)	5137(4)	6742(4)	778(2)	54(1)
C(65)	4580(3)	7326(3)	1073(2)	49(1)
C(66)	3832(4)	7035(4)	1615(2)	49(1)
C(67)	3621(4)	6179(4)	1856(2)	60(2)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mbgo25b

Rh(1)-C(39)	1.783(4)	Rh(1)-P(1)	2.218(1)
Rh(1)-Cl(1)	2.409(1)	Rh(1)-Cl(2)	2.415(1)
Rh(2)-C(40)	1.794(4)	Rh(2)-P(2)	2.212(1)
Rh(2)-Cl(1)	2.402(1)	Rh(2)-Cl(2)	2.418(1)
P(1)-C(13)	1.827(3)	P(1)-C(5)	1.838(4)
P(1)-C(1)	1.846(3)	P(2)-C(32)	1.820(4)
P(2)-C(24)	1.852(3)	P(2)-C(20)	1.856(4)
Si(1)-C(15)	1.855(4)	Si(1)-C(16)	1.863(4)
Si(1)-C(14)	1.866(4)	Si(1)-C(1)	1.891(4)
Si(2)-C(19)	1.859(4)	Si(2)-C(17)	1.865(4)
Si(2)-C(18)	1.875(4)	Si(2)-C(5)	1.889(3)
Si(3)-C(35)	1.855(4)	Si(3)-C(33)	1.868(4)
Si(3)-C(34)	1.872(5)	Si(3)-C(20)	1.891(3)
Si(4)-C(36)	1.861(4)	Si(4)-C(37)	1.861(4)
Si(4)-C(38)	1.872(3)	Si(4)-C(24)	1.890(4)
O(1)-C(39)	1.144(4)	O(2)-C(40)	1.157(4)
C(1)-C(2)	1.337(5)	C(2)-C(3)	1.521(5)
C(2)-C(6)	1.524(4)	C(3)-C(8)	1.513(4)
C(3)-C(4)	1.536(4)	C(3)-H(3)	1.0000
C(4)-C(5)	1.343(4)	C(4)-C(7)	1.497(5)

C(6)-H(6A)	0.9800	C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800	C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800	C(7)-H(7C)	0.9800
C(8)-C(9)	1.386(5)	C(8)-C(13)	1.403(5)
C(9)-C(10)	1.395(5)	C(9)-H(9)	0.9500
C(10)-C(11)	1.374(5)	C(10)-H(10)	0.9500
C(11)-C(12)	1.385(5)	C(11)-H(11)	0.9500
C(12)-C(13)	1.386(4)	C(12)-H(12)	0.9500
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800
C(20)-C(21)	1.339(5)	C(21)-C(25)	1.502(5)
C(21)-C(22)	1.533(4)	C(22)-C(23)	1.516(5)
C(22)-C(27)	1.523(5)	C(22)-H(22)	1.0000
C(23)-C(24)	1.332(5)	C(23)-C(26)	1.511(4)
C(25)-H(25A)	0.9800	C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800	C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800	C(26)-H(26C)	0.9800
C(27)-C(28)	1.386(5)	C(27)-C(32)	1.404(4)
C(28)-C(29)	1.382(5)	C(28)-H(28)	0.9500
C(29)-C(30)	1.377(5)	C(29)-H(29)	0.9500
C(30)-C(31)	1.388(5)	C(30)-H(30)	0.9500
C(31)-C(32)	1.385(4)	C(31)-H(31)	0.9500
C(33)-H(33A)	0.9800	C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800	C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800	C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800	C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800	C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800	C(36)-H(36C)	0.9800
C(37)-H(37A)	0.9800	C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800	C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800	C(38)-H(38C)	0.9800
C(41)-C(42)	1.356(6)	C(41)-C(43)	1.385(5)
C(41)-H(41)	0.9500	C(42)-C(43)#2	1.369(6)
C(42)-H(42)	0.9500	C(43)-C(42)#2	1.369(6)
C(43)-H(43)	0.9500	C(44)-C(45)	1.369(6)
C(44)-C(49)	1.391(5)	C(44)-H(44)	0.9500
C(45)-C(46)	1.371(6)	C(45)-H(45)	0.9500
C(46)-C(47)	1.393(5)	C(46)-H(46)	0.9500
C(47)-C(48)	1.360(6)	C(47)-H(47)	0.9500
C(48)-C(49)	1.389(6)	C(48)-H(48)	0.9500
C(49)-H(49)	0.9500	C(50)-C(51)	1.307(8)
C(50)-C(55)	1.324(7)	C(50)-H(50)	0.9500
C(51)-C(52)	1.313(8)	C(51)-H(51)	0.9500
C(52)-C(53)	1.38(1)	C(52)-H(52)	0.9500
C(53)-C(54)	1.43(1)	C(53)-H(53)	0.9500
C(54)-C(55)	1.37(1)	C(54)-H(54)	0.9500
C(55)-H(55)	0.9500	C(56)-C(57)	1.348(6)
C(56)-C(61)	1.374(6)	C(56)-H(56)	0.9500
C(57)-C(58)	1.366(5)	C(57)-H(57)	0.9500
C(58)-C(59)	1.361(5)	C(58)-H(58)	0.9500
C(59)-C(60)	1.356(6)	C(59)-H(59)	0.9500
C(60)-C(61)	1.378(6)	C(60)-H(60)	0.9500
C(61)-H(61)	0.9500	C(62)-C(63)	1.375(6)
C(62)-C(67)	1.399(6)	C(62)-H(62)	0.9500
C(63)-C(64)	1.362(7)	C(63)-H(63)	0.9500
C(64)-C(65)	1.369(6)	C(64)-H(64)	0.9500

C(65)-C(66)	1.375(5)	C(65)-H(65)	0.9500
C(66)-C(67)	1.351(6)	C(66)-H(66)	0.9500
C(67)-H(67)	0.9500		

C(39)-Rh(1)-P(1)	94.9(1)	C(39)-Rh(1)-Cl(1)	92.4(1)
P(1)-Rh(1)-Cl(1)	172.62(3)	C(39)-Rh(1)-Cl(2)	176.9(1)
P(1)-Rh(1)-Cl(2)	87.20(3)	Cl(1)-Rh(1)-Cl(2)	85.42(3)
C(40)-Rh(2)-P(2)	95.2(1)	C(40)-Rh(2)-Cl(1)	173.2(1)
P(2)-Rh(2)-Cl(1)	85.09(3)	C(40)-Rh(2)-Cl(2)	94.5(1)
P(2)-Rh(2)-Cl(2)	170.15(3)	Cl(1)-Rh(2)-Cl(2)	85.51(3)
Rh(2)-Cl(1)-Rh(1)	94.25(3)	Rh(1)-Cl(2)-Rh(2)	93.68(3)
C(13)-P(1)-C(5)	97.8(2)	C(13)-P(1)-C(1)	96.1(2)
C(5)-P(1)-C(1)	102.4(2)	C(13)-P(1)-Rh(1)	127.8(1)
C(5)-P(1)-Rh(1)	114.1(1)	C(1)-P(1)-Rh(1)	114.6(1)
C(32)-P(2)-C(24)	96.5(2)	C(32)-P(2)-C(20)	97.1(2)
C(24)-P(2)-C(20)	101.9(2)	C(32)-P(2)-Rh(2)	128.4(1)
C(24)-P(2)-Rh(2)	115.2(1)	C(20)-P(2)-Rh(2)	113.5(1)
C(15)-Si(1)-C(16)	109.2(2)	C(15)-Si(1)-C(14)	103.9(2)
C(16)-Si(1)-C(14)	111.0(2)	C(15)-Si(1)-C(1)	113.5(2)
C(16)-Si(1)-C(1)	112.8(2)	C(14)-Si(1)-C(1)	106.0(2)
C(19)-Si(2)-C(17)	110.3(2)	C(19)-Si(2)-C(18)	109.0(2)
C(17)-Si(2)-C(18)	104.3(2)	C(19)-Si(2)-C(5)	112.1(2)
C(17)-Si(2)-C(5)	111.9(2)	C(18)-Si(2)-C(5)	109.0(2)
C(35)-Si(3)-C(33)	109.1(2)	C(35)-Si(3)-C(34)	104.7(2)
C(33)-Si(3)-C(34)	109.5(2)	C(35)-Si(3)-C(20)	113.2(2)
C(33)-Si(3)-C(20)	112.5(2)	C(34)-Si(3)-C(20)	107.4(2)
C(36)-Si(4)-C(37)	109.9(2)	C(36)-Si(4)-C(38)	110.9(2)
C(37)-Si(4)-C(38)	104.0(2)	C(36)-Si(4)-C(24)	110.3(2)
C(37)-Si(4)-C(24)	113.1(2)	C(38)-Si(4)-C(24)	108.5(2)
C(2)-C(1)-P(1)	110.6(3)	C(2)-C(1)-Si(1)	123.9(3)
P(1)-C(1)-Si(1)	124.0(2)	C(1)-C(2)-C(3)	119.1(3)
C(1)-C(2)-C(6)	126.5(4)	C(3)-C(2)-C(6)	114.4(3)
C(8)-C(3)-C(2)	108.0(3)	C(8)-C(3)-C(4)	109.1(3)
C(2)-C(3)-C(4)	108.7(3)	C(8)-C(3)-H(3)	110.3
C(2)-C(3)-H(3)	110.3	C(4)-C(3)-H(3)	110.3
C(5)-C(4)-C(7)	127.5(3)	C(5)-C(4)-C(3)	118.2(3)
C(7)-C(4)-C(3)	114.2(3)	C(4)-C(5)-P(1)	111.1(2)
C(4)-C(5)-Si(2)	123.6(3)	P(1)-C(5)-Si(2)	125.2(2)
C(2)-C(6)-H(6A)	109.5	C(2)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5	C(2)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5	H(6B)-C(6)-H(6C)	109.5
C(4)-C(7)-H(7A)	109.5	C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5	C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5	H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(13)	119.7(3)	C(9)-C(8)-C(3)	123.8(3)
C(13)-C(8)-C(3)	116.5(3)	C(8)-C(9)-C(10)	119.6(3)
C(8)-C(9)-H(9)	120.2	C(10)-C(9)-H(9)	120.2
C(11)-C(10)-C(9)	120.2(4)	C(11)-C(10)-H(10)	119.9
C(9)-C(10)-H(10)	119.9	C(10)-C(11)-C(12)	120.8(3)
C(10)-C(11)-H(11)	119.6	C(12)-C(11)-H(11)	119.6
C(11)-C(12)-C(13)	119.6(4)	C(11)-C(12)-H(12)	120.2
C(13)-C(12)-H(12)	120.2	C(12)-C(13)-C(8)	120.1(3)
C(12)-C(13)-P(1)	128.8(3)	C(8)-C(13)-P(1)	111.1(2)
Si(1)-C(14)-H(14A)	109.5	Si(1)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	Si(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
Si(1)-C(15)-H(15A)	109.5	Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5	Si(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
Si(1)-C(16)-H(16A)	109.5	Si(1)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5	Si(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(16B)-C(16)-H(16C)	109.5

Si(2)-C(17)-H(17A)	109.5	Si(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5	Si(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(17B)-C(17)-H(17C)	109.5
Si(2)-C(18)-H(18A)	109.5	Si(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5	Si(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5	H(18B)-C(18)-H(18C)	109.5
Si(2)-C(19)-H(19A)	109.5	Si(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5	Si(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5	H(19B)-C(19)-H(19C)	109.5
C(21)-C(20)-P(2)	110.9(2)	C(21)-C(20)-Si(3)	123.3(3)
P(2)-C(20)-Si(3)	125.3(2)	C(20)-C(21)-C(25)	127.2(3)
C(20)-C(21)-C(22)	118.6(3)	C(25)-C(21)-C(22)	114.2(3)
C(23)-C(22)-C(27)	108.0(3)	C(23)-C(22)-C(21)	109.0(3)
C(27)-C(22)-C(21)	108.9(3)	C(23)-C(22)-H(22)	110.3
C(27)-C(22)-H(22)	110.3	C(21)-C(22)-H(22)	110.3
C(24)-C(23)-C(26)	127.1(4)	C(24)-C(23)-C(22)	118.8(3)
C(26)-C(23)-C(22)	114.1(3)	C(23)-C(24)-P(2)	111.2(3)
C(23)-C(24)-Si(4)	124.1(3)	P(2)-C(24)-Si(4)	124.3(2)
C(21)-C(25)-H(25A)	109.5	C(21)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5	C(21)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5	H(25B)-C(25)-H(25C)	109.5
C(23)-C(26)-H(26A)	109.5	C(23)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5	C(23)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5	H(26B)-C(26)-H(26C)	109.5
C(28)-C(27)-C(32)	119.8(3)	C(28)-C(27)-C(22)	123.7(3)
C(32)-C(27)-C(22)	116.5(3)	C(29)-C(28)-C(27)	119.7(3)
C(29)-C(28)-H(28)	120.1	C(27)-C(28)-H(28)	120.1
C(30)-C(29)-C(28)	120.8(3)	C(30)-C(29)-H(29)	119.6
C(28)-C(29)-H(29)	119.6	C(29)-C(30)-C(31)	119.8(3)
C(29)-C(30)-H(30)	120.1	C(31)-C(30)-H(30)	120.1
C(32)-C(31)-C(30)	120.1(3)	C(32)-C(31)-H(31)	119.9
C(30)-C(31)-H(31)	119.9	C(31)-C(32)-C(27)	119.6(3)
C(31)-C(32)-P(2)	129.0(3)	C(27)-C(32)-P(2)	111.3(2)
Si(3)-C(33)-H(33A)	109.5	Si(3)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5	Si(3)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5	H(33B)-C(33)-H(33C)	109.5
Si(3)-C(34)-H(34A)	109.5	Si(3)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5	Si(3)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5	H(34B)-C(34)-H(34C)	109.5
Si(3)-C(35)-H(35A)	109.5	Si(3)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5	Si(3)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5	H(35B)-C(35)-H(35C)	109.5
Si(4)-C(36)-H(36A)	109.5	Si(4)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5	Si(4)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5	H(36B)-C(36)-H(36C)	109.5
Si(4)-C(37)-H(37A)	109.5	Si(4)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5	Si(4)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5	H(37B)-C(37)-H(37C)	109.5
Si(4)-C(38)-H(38A)	109.5	Si(4)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5	Si(4)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5	H(38B)-C(38)-H(38C)	109.5
O(1)-C(39)-Rh(1)	176.0(4)	O(2)-C(40)-Rh(2)	174.6(4)
C(42)-C(41)-C(43)	119.5(4)	C(42)-C(41)-H(41)	120.3
C(43)-C(41)-H(41)	120.3	C(41)-C(42)-C(43)#2	120.2(4)
C(41)-C(42)-H(42)	119.9	C(43)#2-C(42)-H(42)	119.9
C(42)#2-C(43)-C(41)	120.3(4)	C(42)#2-C(43)-H(43)	119.9
C(41)-C(43)-H(43)	119.9	C(45)-C(44)-C(49)	120.2(4)
C(45)-C(44)-H(44)	119.9	C(49)-C(44)-H(44)	119.9
C(44)-C(45)-C(46)	121.0(4)	C(44)-C(45)-H(45)	119.5
C(46)-C(45)-H(45)	119.5	C(45)-C(46)-C(47)	118.7(5)
C(45)-C(46)-H(46)	120.6	C(47)-C(46)-H(46)	120.6
C(48)-C(47)-C(46)	120.9(4)	C(48)-C(47)-H(47)	119.6
C(46)-C(47)-H(47)	119.6	C(47)-C(48)-C(49)	120.3(4)

C(47)-C(48)-H(48)	119.9	C(49)-C(48)-H(48)	119.9
C(48)-C(49)-C(44)	118.9(5)	C(48)-C(49)-H(49)	120.5
C(44)-C(49)-H(49)	120.5	C(51)-C(50)-C(55)	122.9(6)
C(51)-C(50)-H(50)	118.6	C(55)-C(50)-H(50)	118.6
C(50)-C(51)-C(52)	121.6(7)	C(50)-C(51)-H(51)	119.2
C(52)-C(51)-H(51)	119.2	C(51)-C(52)-C(53)	121.0(8)
C(51)-C(52)-H(52)	119.5	C(53)-C(52)-H(52)	119.5
C(52)-C(53)-C(54)	116.7(7)	C(52)-C(53)-H(53)	121.6
C(54)-C(53)-H(53)	121.6	C(55)-C(54)-C(53)	118.7(8)
C(55)-C(54)-H(54)	120.6	C(53)-C(54)-H(54)	120.6
C(50)-C(55)-C(54)	119.1(7)	C(50)-C(55)-H(55)	120.5
C(54)-C(55)-H(55)	120.5	C(57)-C(56)-C(61)	120.3(4)
C(57)-C(56)-H(56)	119.9	C(61)-C(56)-H(56)	119.9
C(56)-C(57)-C(58)	120.1(4)	C(56)-C(57)-H(57)	119.9
C(58)-C(57)-H(57)	119.9	C(59)-C(58)-C(57)	120.1(4)
C(59)-C(58)-H(58)	119.9	C(57)-C(58)-H(58)	119.9
C(60)-C(59)-C(58)	120.3(4)	C(60)-C(59)-H(59)	119.9
C(58)-C(59)-H(59)	119.9	C(59)-C(60)-C(61)	119.7(4)
C(59)-C(60)-H(60)	120.2	C(61)-C(60)-H(60)	120.2
C(56)-C(61)-C(60)	119.5(5)	C(56)-C(61)-H(61)	120.3
C(60)-C(61)-H(61)	120.3	C(63)-C(62)-C(67)	119.4(5)
C(63)-C(62)-H(62)	120.3	C(67)-C(62)-H(62)	120.3
C(64)-C(63)-C(62)	120.3(5)	C(64)-C(63)-H(63)	119.8
C(62)-C(63)-H(63)	119.8	C(63)-C(64)-C(65)	120.1(5)
C(63)-C(64)-H(64)	120.0	C(65)-C(64)-H(64)	120.0
C(64)-C(65)-C(66)	120.0(5)	C(64)-C(65)-H(65)	120.0
C(66)-C(65)-H(65)	120.0	C(67)-C(66)-C(65)	120.7(4)
C(67)-C(66)-H(66)	119.7	C(65)-C(66)-H(66)	119.7
C(66)-C(67)-C(62)	119.6(4)	C(66)-C(67)-H(67)	120.2
C(62)-C(67)-H(67)	120.2		

Estimated standard deviations are given in the parenthesis.
Symmetry operators ::
1: x, y, z 2: -x, -y, -z

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mbgo25b

atom	U11	U22	U33	U23	U13	U12
Rh(1)	34(1)	27(1)	28(1)	-9(1)	2(1)	-11(1)
Rh(2)	36(1)	29(1)	27(1)	-10(1)	4(1)	-13(1)
Cl(1)	56(1)	37(1)	26(1)	-6(1)	-1(1)	-24(1)
Cl(2)	61(1)	43(1)	26(1)	-7(1)	1(1)	-30(1)
P(1)	29(1)	26(1)	28(1)	-9(1)	2(1)	-8(1)
P(2)	30(1)	24(1)	26(1)	-8(1)	4(1)	-7(1)
Si(1)	40(1)	39(1)	50(1)	-21(1)	3(1)	-3(1)
Si(2)	29(1)	35(1)	43(1)	-8(1)	4(1)	-8(1)
Si(3)	30(1)	40(1)	65(1)	-19(1)	4(1)	-4(1)
Si(4)	41(1)	33(1)	44(1)	-18(1)	2(1)	-1(1)
O(1)	226(4)	131(4)	42(2)	-32(2)	17(2)	-142(4)
O(2)	58(2)	66(3)	36(2)	-18(2)	1(1)	-28(2)
C(1)	29(2)	36(3)	40(2)	-20(2)	6(2)	-11(2)
C(2)	31(2)	39(3)	34(2)	-13(2)	6(2)	-13(2)
C(3)	34(2)	37(3)	25(2)	-7(2)	6(2)	-13(2)
C(4)	30(2)	35(3)	35(2)	-8(2)	-4(2)	-9(2)
C(5)	29(2)	27(3)	32(2)	-9(2)	-1(2)	-10(2)
C(6)	63(2)	54(4)	39(2)	-21(2)	16(2)	-15(2)
C(7)	40(2)	62(4)	37(2)	-5(2)	0(2)	-12(2)
C(8)	28(2)	27(3)	32(2)	-8(2)	2(2)	-5(2)
C(9)	33(2)	36(3)	34(2)	-6(2)	9(2)	-10(2)
C(10)	35(2)	35(3)	58(3)	-15(2)	8(2)	-19(2)

C(11)	42(2)	43(3)	42(2)	-16(2)	3(2)	-20(2)
C(12)	35(2)	29(3)	40(2)	-12(2)	0(2)	-9(2)
C(13)	27(2)	19(2)	36(2)	-10(2)	3(2)	-4(2)
C(14)	53(3)	99(6)	111(4)	-24(4)	32(3)	11(3)
C(15)	52(2)	72(4)	68(3)	-30(3)	-17(2)	25(3)
C(16)	96(3)	38(4)	95(4)	-35(3)	-34(3)	16(3)
C(17)	45(2)	58(4)	50(3)	-12(3)	16(2)	7(2)
C(18)	44(2)	44(3)	52(3)	-10(2)	0(2)	-3(2)
C(19)	37(2)	46(4)	73(3)	-9(3)	2(2)	-13(2)
C(20)	33(2)	27(3)	36(2)	-6(2)	-1(2)	-9(2)
C(21)	36(2)	28(3)	40(2)	-5(2)	-6(2)	-7(2)
C(22)	39(2)	35(3)	26(2)	-5(2)	3(2)	-11(2)
C(23)	34(2)	38(3)	33(2)	-17(2)	2(2)	-11(2)
C(24)	29(2)	29(3)	30(2)	-14(2)	0(2)	-4(2)
C(25)	50(2)	49(4)	51(3)	7(3)	-17(2)	-7(2)
C(26)	59(2)	59(4)	34(2)	-24(2)	12(2)	-18(2)
C(27)	31(2)	21(3)	35(2)	-5(2)	6(2)	-5(2)
C(28)	41(2)	36(3)	31(2)	-2(2)	1(2)	-8(2)
C(29)	53(2)	29(3)	47(3)	0(2)	2(2)	-25(2)
C(30)	58(2)	36(3)	44(3)	-12(2)	-5(2)	-21(2)
C(31)	40(2)	34(3)	38(2)	-12(2)	4(2)	-10(2)
C(32)	26(2)	22(3)	36(2)	-8(2)	3(2)	-4(2)
C(33)	37(2)	62(4)	71(3)	-21(3)	0(2)	-14(2)
C(34)	47(3)	52(4)	136(5)	-32(4)	2(3)	6(3)
C(35)	45(2)	77(4)	74(3)	-48(3)	14(2)	-5(2)
C(36)	59(2)	32(3)	70(3)	-27(3)	2(2)	-3(2)
C(37)	62(3)	42(4)	56(3)	-21(3)	-10(2)	17(2)
C(38)	49(2)	60(4)	75(3)	-36(3)	5(2)	-3(2)
C(39)	94(3)	54(4)	29(2)	-8(2)	10(2)	-49(3)
C(40)	39(2)	38(3)	30(2)	-10(2)	7(2)	-12(2)
C(41)	56(3)	68(4)	57(3)	-36(3)	-9(2)	-6(3)
C(42)	64(3)	85(5)	45(3)	-29(3)	1(2)	-21(3)
C(43)	57(3)	65(4)	59(3)	-22(3)	6(2)	-21(3)
C(44)	59(3)	79(5)	72(3)	-38(3)	-24(2)	7(3)
C(45)	53(3)	70(4)	67(3)	-30(3)	-15(2)	9(3)
C(46)	59(3)	65(4)	72(3)	-34(3)	-5(2)	2(3)
C(47)	52(3)	62(4)	71(3)	-24(3)	5(2)	-12(3)
C(48)	64(3)	60(4)	50(3)	-14(3)	7(2)	2(3)
C(49)	85(3)	56(4)	52(3)	-24(3)	-10(3)	11(3)
C(50)	50(3)	93(6)	68(4)	-2(4)	-19(3)	-5(4)
C(51)	56(3)	88(6)	118(6)	-31(5)	-28(4)	3(4)
C(52)	56(4)	121(7)	125(6)	57(6)	-40(4)	-40(4)
C(53)	45(4)	270(10)	43(4)	-3(6)	0(3)	-29(6)
C(54)	65(4)	230(10)	109(7)	-106(8)	-33(4)	21(6)
C(55)	60(3)	87(6)	122(6)	-39(5)	-25(3)	-6(4)
C(56)	83(4)	64(5)	79(4)	-30(3)	-15(3)	-31(3)
C(57)	48(2)	58(4)	59(3)	-18(3)	-3(2)	-9(2)
C(58)	65(3)	41(4)	66(3)	-23(3)	-5(2)	-10(3)
C(59)	49(3)	55(4)	66(3)	-14(3)	-11(2)	-8(3)
C(60)	61(3)	68(5)	54(3)	-10(3)	-5(2)	27(3)
C(61)	131(5)	57(5)	65(4)	-40(3)	-25(3)	18(4)
C(62)	70(3)	32(4)	90(4)	-6(3)	-48(3)	-8(3)
C(63)	54(3)	59(4)	81(4)	-41(4)	-30(3)	20(3)
C(64)	39(2)	71(5)	57(3)	-30(3)	-13(2)	6(3)
C(65)	47(2)	44(4)	62(3)	-21(3)	-9(2)	-7(2)
C(66)	48(2)	59(4)	52(3)	-32(3)	0(2)	-3(2)
C(67)	45(3)	78(5)	53(3)	-8(3)	-14(2)	-22(3)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mbgo25b

atom	x	y	z	U(eq)
H(3)	-750	-3208	10542	39
H(6A)	-1955	-1091	10545	76
H(6B)	-1048	-1940	10951	76
H(6C)	-2473	-2040	10773	76
H(7A)	2586	-3260	10288	72
H(7B)	1608	-3995.0002	10534	72
H(7C)	1472	-3175	10798	72
H(9)	-2092	-4200	10295	43
H(10)	-3231	-4570	9556	50
H(11)	-3204.9998	-3727	8490	49
H(12)	-1992	-2533	8131	41
H(14A)	-3770	-555	10029	140
H(14B)	-4103	-858	9443	140
H(14C)	-4412	155	9406	140
H(15A)	-3143.9998	817	8268	97
H(15B)	-2710	-124	8179	97
H(15C)	-1659.0001	541	8124	97
H(16A)	-669	798	9274	111
H(16B)	-1340	395	9957	111
H(16C)	-2101	1185	9416	111
H(17A)	2421	-1664	7853	81
H(17B)	2205	-2667.9998	7964	81
H(17C)	3640	-2389	7896	81
H(18A)	4181	-3815	8953	72
H(18B)	2839	-4082	9306	72
H(18C)	3910	-3798	9665	72
H(19A)	3787	-1870.0001	9584	81
H(19B)	3622	-1185	8879	81
H(19C)	4769	-1976.9999	9026	81
H(22)	3186	3124	4904	41
H(25A)	943	3113	4641	83
H(25B)	885	3977	4851	83
H(25C)	-161	3295	5128	83
H(26A)	4195	952	5012	72
H(26B)	4906	1830	4779	72
H(26C)	3457	1855	4567	72
H(28)	4618	4112	5098	46
H(29)	5713	4568	5797	53
H(30)	5445	3943	6891	54
H(31)	4180	2778	7299	44
H(33A)	-1508	1458	6470	84
H(33B)	-1518.0001	2164	5770	84
H(33C)	-2513	2332	6306	84
H(34A)	-1747.9999	4032	6369	119
H(34B)	-1033	4079	5704	119
H(34C)	-260	4203	6264	119
H(35A)	-1342.0001	2633	7483	90
H(35B)	190	2646	7488	90
H(35C)	-392	1750	7548	90
H(36A)	2674	-714	6391	77
H(36B)	4008	-1228	6246	77
H(36C)	3313	-421	5692	77
H(37A)	3886	-380	7474	81
H(37B)	5130	145	7356	81
H(37C)	5271	-848	7343	81
H(38A)	6553	-426.0000	6158	88
H(38B)	6501	594	6093	88
H(38C)	5988	316	5529	88
H(41)	652	1001	5440	68

H(42)	-580	-82	6041	74
H(43)	1206	1096	4387	71
H(44)	7215	4572	1741	80
H(45)	6717	5801	2062	74
H(46)	8343	6551	2240	76
H(47)	10508	6043	2092	73
H(48)	11020	4836	1753	72
H(49)	9378	4087	1565	77
H(50)	6792	2876	4968	91
H(51)	6989	4312	4590	105
H(52)	8089	4899	3682	144
H(53)	9073	4005	3098	156
H(54)	8876	2445	3523	150
H(55)	7725	1916	4482	105
H(56)	1804	2931	3032	85
H(57)	1500	4130	3386	66
H(58)	3264	4735	3585	66
H(59)	5334	4149	3414	69
H(60)	5658	2944	3060	80
H(61)	3882	2344	2845	97
H(62)	4062	4974	1727	78
H(63)	5321	5474	809	73
H(64)	5661	6942	407	65
H(65)	4710	7931	903	59
H(66)	3461	7440	1823	59
H(67)	3088	5985	2225	72

II.20. Crystallographic data for IV-51

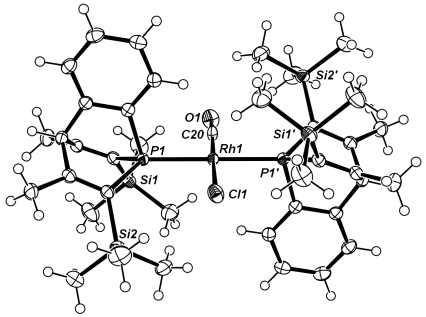


Table 1. Crystal data for mb504

Compound	mb504
Molecular formula	$C_{39}H_{58}ClOP_2RhSi_4, C_7H_8$
Molecular weight	1039.78
Crystal habit	Pale Yellow Plate
Crystal dimensions(mm)	0.26x0.20x0.08
Crystal system	orthorhombic
Space group	Pbca

a(Å)	13.949(1)
b(Å)	17.263(1)
c(Å)	23.168(1)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
V(Å^3)	5578.9(6)
Z	4
d(g-cm^{-3})	1.238
F(000)	2192
μ(cm^{-1})	0.532
Absorption corrections	multi-scan ; 0.8741 min, 0.9587 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-15 19 ; -24 23 ; -31 32
Reflections measured	51032
Unique data	8155
Rint	0.0439
Reflections used	5830
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	241
Reflections / parameter	24
wR2	0.1368
R1	0.0399
Weights a, b	0.0840 ; 0.0000
GoF	1.039
difference peak / hole (e Å^{-3})	0.912(0.097) / -0.698(0.097)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb504

atom	x	y	z	U(eq)
Rh(1)	0	0	5000	17(1)
P(1)	687(1)	1168(1)	5293(1)	18(1)
Si(2)	2802(1)	629(1)	5831(1)	24(1)
Si(1)	-558(1)	1526(1)	6483(1)	24(1)
Cl(1)	-1504(2)	509(2)	5245(1)	31(1)
O(1)	-1904(4)	632(4)	5296(3)	37(1)
C(20)	-1184(7)	376(6)	5172(6)	29(2)
C(7)	258(2)	1582(1)	4120(1)	22(1)
C(2)	540(2)	2553(1)	5775(1)	23(1)
C(6)	613(1)	1793(1)	4655(1)	19(1)
C(1)	168(2)	1835(1)	5835(1)	21(1)
C(9)	625(2)	2859(1)	3758(1)	29(1)
C(13)	3134(2)	2474(1)	5512(1)	32(1)

C(3)	1352(2)	2684(1)	5339(1)	22(1)
C(4)	2166(2)	2110(1)	5451(1)	23(1)
C(11)	966(2)	2540(1)	4742(1)	21(1)
C(5)	1960(2)	1347(1)	5480(1)	21(1)
C(10)	971(2)	3074(1)	4297(1)	26(1)
C(12)	224(2)	3262(1)	6096(1)	33(1)
C(8)	273(2)	2116(1)	3667(1)	26(1)
C(15)	-1835(2)	1826(2)	6427(1)	42(1)
C(14)	-477(2)	464(1)	6594(1)	36(1)
C(18)	3797(2)	346(2)	5339(1)	42(1)
C(16)	-7(2)	1954(2)	7150(1)	42(1)
C(17)	2159(2)	-236(1)	6109(1)	36(1)
C(19)	3297(2)	1089(2)	6496(1)	41(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb504

Rh(1)-C(20)#5	1.82(1)	Rh(1)-C(20)	1.82(1)
Rh(1)-P(1)	2.3341(5	Rh(1)-P(1)#5	2.3341(5)
Rh(1)-Cl(1)	2.343(2)	Rh(1)-Cl(1)#5	2.343(2)
P(1)-C(6)	1.833(2)	P(1)-C(1)	1.851(2)
P(1)-C(5)	1.853(2)	Si(2)-C(17)	1.858(3)
Si(2)-C(18)	1.860(3)	Si(2)-C(19)	1.866(3)
Si(2)-C(5)	1.890(2)	Si(1)-C(14)	1.855(3)
Si(1)-C(15)	1.859(3)	Si(1)-C(16)	1.877(3)
Si(1)-C(1)	1.887(2)	O(1)-C(20)	1.13(1)
C(7)-C(6)	1.384(3)	C(7)-C(8)	1.396(3)
C(7)-H(7)	0.9500	C(2)-C(1)	1.350(3)
C(2)-C(12)	1.498(3)	C(2)-C(3)	1.534(3)
C(6)-C(11)	1.395(3)	C(9)-C(10)	1.389(3)
C(9)-C(8)	1.389(3)	C(9)-H(9)	0.9500
C(13)-C(4)	1.497(3)	C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800	C(13)-H(13C)	0.9800
C(3)-C(11)	1.506(3)	C(3)-C(4)	1.530(3)
C(3)-H(3)	1.0000	C(4)-C(5)	1.349(3)
C(11)-C(10)	1.384(3)	C(10)-H(10)	0.9500
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(8)-H(8)	0.9500
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800	C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9801	C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9801	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800

C(20)#5-Rh(1)-C(20)	180.0(8)	C(20)#5-Rh(1)-P(1)	90.0(4)
C(20)-Rh(1)-P(1)	90.0(4)	C(20)#5-Rh(1)-P(1)#5	90.0(4)
C(20)-Rh(1)-P(1)#5	90.0(4)	P(1)-Rh(1)-P(1)#5	180.0
C(20)#5-Rh(1)-Cl(1)	178.2(4)	C(20)-Rh(1)-Cl(1)	1.8(4)
P(1)-Rh(1)-Cl(1)	88.47(7)	P(1)#5-Rh(1)-Cl(1)	91.53(7)
C(20)#5-Rh(1)-Cl(1)#5	1.8(4)	C(20)-Rh(1)-Cl(1)#5	178.2(4)
P(1)-Rh(1)-Cl(1)#5	91.53(7)	P(1)#5-Rh(1)-Cl(1)#5	88.47(7)
Cl(1)-Rh(1)-Cl(1)#5	180.0(1)	C(6)-P(1)-C(1)	99.2(1)
C(6)-P(1)-C(5)	98.3(1)	C(1)-P(1)-C(5)	96.5(1)
C(6)-P(1)-Rh(1)	104.49(7)	C(1)-P(1)-Rh(1)	125.04(7)
C(5)-P(1)-Rh(1)	127.25(7)	C(17)-Si(2)-C(18)	111.2(1)
C(17)-Si(2)-C(19)	103.5(1)	C(18)-Si(2)-C(19)	110.0(1)
C(17)-Si(2)-C(5)	112.1(1)	C(18)-Si(2)-C(5)	111.9(1)

C(19)-Si(2)-C(5)	107.8(1)	C(14)-Si(1)-C(15)	110.1(1)
C(14)-Si(1)-C(16)	104.4(1)	C(15)-Si(1)-C(16)	109.9(1)
C(14)-Si(1)-C(1)	111.0(1)	C(15)-Si(1)-C(1)	112.3(1)
C(16)-Si(1)-C(1)	108.8(1)	O(1)-C(20)-Rh(1)	177(1)
C(6)-C(7)-C(8)	119.6(2)	C(6)-C(7)-H(7)	120.2
C(8)-C(7)-H(7)	120.2	C(1)-C(2)-C(12)	125.9(2)
C(1)-C(2)-C(3)	119.1(2)	C(12)-C(2)-C(3)	115.0(2)
C(7)-C(6)-C(11)	120.0(2)	C(7)-C(6)-P(1)	126.0(2)
C(11)-C(6)-P(1)	114.0(2)	C(2)-C(1)-P(1)	110.6(2)
C(2)-C(1)-Si(1)	123.2(2)	P(1)-C(1)-Si(1)	125.0(1)
C(10)-C(9)-C(8)	120.3(2)	C(10)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8	C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	C(11)-C(3)-C(4)	108.3(2)
C(11)-C(3)-C(2)	108.5(2)	C(4)-C(3)-C(2)	109.9(2)
C(11)-C(3)-H(3)	110.0	C(4)-C(3)-H(3)	110.0
C(2)-C(3)-H(3)	110.0	C(5)-C(4)-C(13)	126.7(2)
C(5)-C(4)-C(3)	118.9(2)	C(13)-C(4)-C(3)	114.4(2)
C(10)-C(11)-C(6)	120.6(2)	C(10)-C(11)-C(3)	125.0(2)
C(6)-C(11)-C(3)	114.4(2)	C(4)-C(5)-P(1)	110.8(2)
C(4)-C(5)-Si(2)	121.9(2)	P(1)-C(5)-Si(2)	125.9(1)
C(11)-C(10)-C(9)	119.4(2)	C(11)-C(10)-H(10)	120.3
C(9)-C(10)-H(10)	120.3	C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(9)-C(8)-C(7)	120.1(2)
C(9)-C(8)-H(8)	119.9	C(7)-C(8)-H(8)	119.9
Si(1)-C(15)-H(15A)	109.5	Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5	Si(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
Si(1)-C(14)-H(14A)	109.5	Si(1)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	Si(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
Si(2)-C(18)-H(18A)	109.5	Si(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5	Si(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5	H(18B)-C(18)-H(18C)	109.5
Si(1)-C(16)-H(16A)	109.5	Si(1)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5	Si(1)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(16B)-C(16)-H(16C)	109.5
Si(2)-C(17)-H(17A)	109.5	Si(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5	Si(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(17B)-C(17)-H(17C)	109.5
Si(2)-C(19)-H(19A)	109.5	Si(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5	Si(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5	H(19B)-C(19)-H(19C)	109.5

Estimated standard deviations are given in the parenthesis.
Symmetry operators ::
1: x, y, z 2: -x+1/2, -y, z+1/2 3: x+1/2, -y+1/2, -z
4: -x, y+1/2, -z+1/2 5: -x, -y, -z 6: x-1/2, y, -z-1/2
7: -x-1/2, y-1/2, z 8: x, -y-1/2, z-1/2

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb504

atom	U11	U22	U33	U23	U13	U12
Rh(1)	17(1)	15(1)	19(1)	-1(1)	0(1)	-2(1)
P(1)	16(1)	16(1)	20(1)	0(1)	-1(1)	-1(1)
Si(2)	19(1)	23(1)	28(1)	3(1)	-3(1)	1(1)
Si(1)	21(1)	30(1)	21(1)	-3(1)	1(1)	-1(1)

Cl(1)	26(2)	33(2)	32(1)	-11(1)	1(1)	1(1)
O(1)	32(3)	40(3)	39(3)	-9(2)	6(3)	1(3)
C(20)	42(6)	16(4)	30(5)	-5(3)	-9(5)	-6(4)
C(7)	18(1)	23(1)	24(1)	-1(1)	1(1)	1(1)
C(2)	23(1)	22(1)	22(1)	-3(1)	-4(1)	0(1)
C(6)	15(1)	20(1)	22(1)	0(1)	2(1)	2(1)
C(1)	20(1)	23(1)	20(1)	-4(1)	-1(1)	1(1)
C(9)	25(1)	32(1)	29(1)	10(1)	4(1)	1(1)
C(13)	23(1)	25(1)	47(2)	3(1)	-8(1)	-5(1)
C(3)	21(1)	17(1)	28(1)	0(1)	-2(1)	-1(1)
C(4)	18(1)	24(1)	27(1)	0(1)	-3(1)	-1(1)
C(11)	16(1)	22(1)	26(1)	2(1)	0(1)	1(1)
C(5)	16(1)	22(1)	24(1)	0(1)	-1(1)	-1(1)
C(10)	22(1)	22(1)	32(1)	5(1)	4(1)	0(1)
C(12)	40(1)	23(1)	36(1)	-7(1)	-2(1)	1(1)
C(8)	23(1)	34(1)	22(1)	3(1)	-1(1)	1(1)
C(15)	28(1)	51(2)	47(2)	-11(1)	3(1)	4(1)
C(14)	42(2)	37(1)	28(1)	5(1)	5(1)	-2(1)
C(18)	30(1)	46(2)	49(2)	3(1)	7(1)	10(1)
C(16)	44(2)	57(2)	24(1)	-8(1)	0(1)	-10(1)
C(17)	36(1)	30(1)	42(2)	12(1)	-6(1)	-3(1)
C(19)	41(2)	41(1)	41(2)	3(1)	-16(1)	-4(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb504

atom	x	y	z	U(eq)
H(7)	5	1077	4061	26
H(9)	628	3222	3450	34
H(13A)	3149	2794	5861	48
H(13B)	3265	2799	5174	48
H(13C)	3623	2068	5541	48
H(3)	1596	3227	5370	26
H(10)	1210	3582	4359	31
H(12A)	-353	3143	6320	50
H(12B)	81	3677	5820	50
H(12C)	736	3430	6357	50
H(8)	43	1970	3297	31
H(15A)	-2126	1581	6088	62
H(15B)	-1872	2390	6388	62
H(15C)	-2180	1664	6775	62
H(14A)	-818	323	6949	54
H(14B)	198	313	6628	54
H(14C)	-767	196	6265	54
H(18A)	4221	-21	5536	63
H(18B)	4163	807	5229	63
H(18C)	3532	102	4992	63
H(16A)	-280	1703	7492	63
H(16B)	-142	2511	7163	63
H(16C)	687	1870	7143	63
H(17A)	1478	-113	6157	54
H(17B)	2431	-387	6483	54
H(17C)	2229	-665	5835	54
H(19A)	2768	1250	6747	61
H(19B)	3679	1544	6389	61
H(19C)	3703	716	6700	61

II.21. Crystallographic data for IV-54

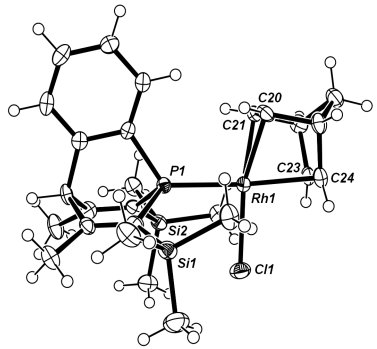


Table 1. Crystal data for mb805

Compound	mb805
Molecular formula	$C_{26}H_{37}ClPRhSi_2$
Molecular weight	575.07
Crystal habit	Orange Block
Crystal dimensions(mm)	0.20x0.08x0.04
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a(Å)	10.642(1)
b(Å)	12.103(1)
c(Å)	20.937(1)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
V(Å^3)	2696.7(4)
Z	4
d(g-cm^{-3})	1.416
F(000)	1192
μ(cm^{-1})	0.893
Absorption corrections	multi-scan ; 0.8416 min, 0.9652 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	27.47
HKL ranges	-13 12 ; -12 15 ; -21 27

Reflections measured	23074
Unique data	6165
Rint	0.0406
Reflections used	5399
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	288
Reflections / parameter	18
wR2	0.0505
R1	0.0280
Flack's parameter	-0.039(17)
Weights a, b	0.0150 ; 0.0000
GoF	1.008
difference peak / hole (e Å^{-3})	0.334(0.064) / -0.394(0.064)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb805

atom	x	y	z	U(eq)
Rh(1)	2121(1)	2988(1)	935(1)	19(1)
Cl(1)	308(1)	1881(1)	1083(1)	31(1)
P(1)	3178(1)	1734(1)	1557(1)	18(1)
Si(1)	2615(1)	-256(1)	514(1)	25(1)
Si(2)	1543(1)	2573(1)	2847(1)	22(1)
C(1)	3107(2)	254(2)	1327(1)	21(1)
C(2)	3632(2)	-399(2)	1774(1)	22(1)
C(3)	4272(3)	147(2)	2351(1)	23(1)
C(4)	3303(2)	832(2)	2713(1)	22(1)
C(5)	2700(3)	1655(2)	2404(1)	21(1)
C(6)	3668(3)	-1636(2)	1777(1)	32(1)
C(7)	3143(3)	493(2)	3399(1)	35(1)
C(8)	5286(3)	913(2)	2097(1)	21(1)
C(9)	6553(3)	774(2)	2220(1)	26(1)
C(10)	7431(3)	1447(2)	1920(1)	28(1)
C(11)	7034(3)	2281(2)	1517(1)	25(1)
C(12)	5760(2)	2444(2)	1402(1)	21(1)
C(13)	4879(2)	1758(2)	1689(1)	19(1)
C(14)	3829(3)	-1249(2)	214(2)	35(1)
C(15)	1063(3)	-962(2)	539(2)	44(1)
C(16)	2587(3)	895(2)	-79(1)	32(1)
C(17)	211(3)	1711(2)	3147(1)	34(1)
C(18)	2374(3)	3230(2)	3540(1)	31(1)
C(19)	839(3)	3721(2)	2374(1)	29(1)
C(20)	3524(3)	3863(2)	423(1)	24(1)
C(21)	3301(2)	4381(2)	1012(1)	21(1)
C(22)	2298(2)	5269(2)	881(1)	26(1)
C(23)	1149(3)	4552(2)	733(1)	25(1)
C(24)	1374(3)	4038(2)	156(1)	26(1)
C(25)	2670(3)	4432(2)	-63(1)	25(1)
C(26)	2664(3)	5628(2)	198(1)	30(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb805

Rh(1)-C(21)	2.108(2)	Rh(1)-C(20)	2.122(2)

Rh(1)-C(23)	2.199(2)	Rh(1)-C(24)	2.215(3)
Rh(1)-P(1)	2.2940(6	Rh(1)-Cl(1)	2.3687(7)
P(1)-C(13)	1.831(3)	P(1)-C(5)	1.849(3)
P(1)-C(1)	1.855(2)	Si(1)-C(15)	1.861(3)
Si(1)-C(16)	1.866(3)	Si(1)-C(14)	1.873(3)
Si(1)-C(1)	1.884(3)	Si(2)-C(19)	1.864(3)
Si(2)-C(17)	1.869(3)	Si(2)-C(18)	1.877(3)
Si(2)-C(5)	1.900(3)	C(1)-C(2)	1.347(3)
C(2)-C(6)	1.498(3)	C(2)-C(3)	1.536(4)
C(3)-C(8)	1.519(3)	C(3)-C(4)	1.524(3)
C(3)-H(3)	1.0000	C(4)-C(5)	1.350(3)
C(4)-C(7)	1.504(4)	C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800	C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800	C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800	C(8)-C(9)	1.382(4)
C(8)-C(13)	1.402(3)	C(9)-C(10)	1.390(4)
C(9)-H(9)	0.9500	C(10)-C(11)	1.381(3)
C(10)-H(10)	0.9500	C(11)-C(12)	1.391(4)
C(11)-H(11)	0.9500	C(12)-C(13)	1.388(3)
C(12)-H(12)	0.9500	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800	C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800	C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800	C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800	C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800	C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800	C(20)-C(21)	1.404(4)
C(20)-C(25)	1.528(4)	C(20)-H(20)	0.9500
C(21)-C(22)	1.540(3)	C(21)-H(21)	0.9500
C(22)-C(23)	1.531(4)	C(22)-C(26)	1.544(4)
C(22)-H(22)	1.0000	C(23)-C(24)	1.379(4)
C(23)-H(23)	0.9500	C(24)-C(25)	1.529(4)
C(24)-H(24)	0.9500	C(25)-C(26)	1.549(3)
C(25)-H(25)	1.0000	C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900		

C(21)-Rh(1)-C(20)	38.8(1)	C(21)-Rh(1)-C(23)	66.8(1)
C(20)-Rh(1)-C(23)	78.7(1)	C(21)-Rh(1)-C(24)	79.1(1)
C(20)-Rh(1)-C(24)	66.0(1)	C(23)-Rh(1)-C(24)	36.4(1)
C(21)-Rh(1)-P(1)	101.18(7)	C(20)-Rh(1)-P(1)	105.80(8)
C(23)-Rh(1)-P(1)	155.49(7)	C(24)-Rh(1)-P(1)	166.71(7)
C(21)-Rh(1)-Cl(1)	158.02(7)	C(20)-Rh(1)-Cl(1)	157.09(8)
C(23)-Rh(1)-Cl(1)	97.40(7)	C(24)-Rh(1)-Cl(1)	97.36(8)
P(1)-Rh(1)-Cl(1)	87.20(2)	C(13)-P(1)-C(5)	97.3(1)
C(13)-P(1)-C(1)	95.4(1)	C(5)-P(1)-C(1)	100.8(1)
C(13)-P(1)-Rh(1)	124.02(8)	C(5)-P(1)-Rh(1)	116.35(8)
C(1)-P(1)-Rh(1)	118.1(1)	C(15)-Si(1)-C(16)	110.3(1)
C(15)-Si(1)-C(14)	109.1(1)	C(16)-Si(1)-C(14)	105.5(1)
C(15)-Si(1)-C(1)	111.8(1)	C(16)-Si(1)-C(1)	111.2(1)
C(14)-Si(1)-C(1)	108.8(1)	C(19)-Si(2)-C(17)	106.9(1)
C(19)-Si(2)-C(18)	106.5(1)	C(17)-Si(2)-C(18)	109.5(1)
C(19)-Si(2)-C(5)	116.0(1)	C(17)-Si(2)-C(5)	109.2(1)
C(18)-Si(2)-C(5)	108.6(1)	C(2)-C(1)-P(1)	111.7(2)
C(2)-C(1)-Si(1)	123.4(2)	P(1)-C(1)-Si(1)	124.2(1)
C(1)-C(2)-C(6)	126.9(3)	C(1)-C(2)-C(3)	118.6(2)
C(6)-C(2)-C(3)	114.6(2)	C(8)-C(3)-C(4)	108.8(2)
C(8)-C(3)-C(2)	107.6(2)	C(4)-C(3)-C(2)	109.0(2)
C(8)-C(3)-H(3)	110.5	C(4)-C(3)-H(3)	110.5
C(2)-C(3)-H(3)	110.5	C(5)-C(4)-C(7)	127.2(2)
C(5)-C(4)-C(3)	119.0(2)	C(7)-C(4)-C(3)	113.8(2)

C(4)-C(5)-P(1)	111.5(2)	C(4)-C(5)-Si(2)	120.4(2)
P(1)-C(5)-Si(2)	128.0(1)	C(2)-C(6)-H(6A)	109.5
C(2)-C(6)-H(6B)	109.5	H(6A)-C(6)-H(6B)	109.5
C(2)-C(6)-H(6C)	109.5	H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5	C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5	H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5	H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5	C(9)-C(8)-C(13)	120.2(2)
C(9)-C(8)-C(3)	123.6(2)	C(13)-C(8)-C(3)	116.0(2)
C(8)-C(9)-C(10)	120.1(2)	C(8)-C(9)-H(9)	120.0
C(10)-C(9)-H(9)	120.0	C(11)-C(10)-C(9)	119.9(3)
C(11)-C(10)-H(10)	120.1	C(9)-C(10)-H(10)	120.1
C(10)-C(11)-C(12)	120.5(3)	C(10)-C(11)-H(11)	119.8
C(12)-C(11)-H(11)	119.8	C(13)-C(12)-C(11)	120.0(2)
C(13)-C(12)-H(12)	120.0	C(11)-C(12)-H(12)	120.0
C(12)-C(13)-C(8)	119.4(2)	C(12)-C(13)-P(1)	127.8(2)
C(8)-C(13)-P(1)	112.7(2)	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	Si(2)-C(19)-H(19A)	109.5
Si(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(21)-C(20)-C(25)	106.5(2)
C(21)-C(20)-Rh(1)	70.1(1)	C(25)-C(20)-Rh(1)	98.2(2)
C(21)-C(20)-H(20)	126.8	C(25)-C(20)-H(20)	126.8
Rh(1)-C(20)-H(20)	99.5	C(20)-C(21)-C(22)	105.8(2)
C(20)-C(21)-Rh(1)	71.1(1)	C(22)-C(21)-Rh(1)	97.6(2)
C(20)-C(21)-H(21)	127.1	C(22)-C(21)-H(21)	127.1
Rh(1)-C(21)-H(21)	99.1	C(23)-C(22)-C(21)	101.2(2)
C(23)-C(22)-C(26)	100.0(2)	C(21)-C(22)-C(26)	100.7(2)
C(23)-C(22)-H(22)	117.3	C(21)-C(22)-H(22)	117.3
C(26)-C(22)-H(22)	117.3	C(24)-C(23)-C(22)	107.1(2)
C(24)-C(23)-Rh(1)	72.4(1)	C(22)-C(23)-Rh(1)	94.2(2)
C(24)-C(23)-H(23)	126.4	C(22)-C(23)-H(23)	126.4
Rh(1)-C(23)-H(23)	101.1	C(23)-C(24)-C(25)	106.2(2)
C(23)-C(24)-Rh(1)	71.2(2)	C(25)-C(24)-Rh(1)	94.4(2)
C(23)-C(24)-H(24)	126.9	C(25)-C(24)-H(24)	126.9
Rh(1)-C(24)-H(24)	101.9	C(20)-C(25)-C(24)	101.3(2)
C(20)-C(25)-C(26)	100.9(2)	C(24)-C(25)-C(26)	100.4(2)
C(20)-C(25)-H(25)	117.1	C(24)-C(25)-H(25)	117.1
C(26)-C(25)-H(25)	117.1	C(22)-C(26)-C(25)	93.7(2)
C(22)-C(26)-H(26A)	113.0	C(25)-C(26)-H(26A)	113.0
C(22)-C(26)-H(26B)	113.0	C(25)-C(26)-H(26B)	113.0
H(26A)-C(26)-H(26B)	110.4		

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb805

atom	U11	U22	U33	U23	U13	U12
Rh(1)	18(1)	20(1)	20(1)	3(1)	-1(1)	0(1)
Cl(1)	21(1)	34(1)	39(1)	0(1)	1(1)	-5(1)
P(1)	20(1)	19(1)	17(1)	1(1)	1(1)	0(1)
Si(1)	28(1)	23(1)	23(1)	-1(1)	-1(1)	-4(1)
Si(2)	25(1)	22(1)	20(1)	0(1)	4(1)	-2(1)
C(1)	21(2)	21(1)	20(2)	1(1)	4(1)	-1(1)
C(2)	23(2)	21(1)	22(2)	5(1)	4(1)	0(1)
C(3)	33(2)	21(1)	14(1)	6(1)	-1(1)	5(1)
C(4)	26(2)	22(1)	18(2)	0(1)	2(1)	1(1)
C(5)	24(2)	21(1)	18(1)	1(1)	1(1)	-5(1)
C(6)	45(2)	22(1)	29(2)	5(1)	3(1)	3(1)
C(7)	52(2)	34(1)	20(2)	8(1)	7(2)	11(1)
C(8)	24(2)	21(1)	16(2)	-4(1)	0(1)	2(1)
C(9)	32(2)	27(1)	19(2)	-2(1)	-4(1)	13(1)
C(10)	21(2)	38(2)	25(2)	-7(1)	-3(1)	8(1)
C(11)	23(2)	28(1)	24(2)	-4(1)	2(1)	1(1)
C(12)	27(2)	19(1)	19(2)	-4(1)	-4(1)	3(1)
C(13)	20(2)	19(1)	17(1)	-4(1)	-3(1)	3(1)
C(14)	49(2)	27(2)	29(2)	-2(1)	7(2)	-2(1)
C(15)	36(2)	39(2)	57(2)	-6(2)	-8(2)	-10(2)
C(16)	45(2)	30(1)	20(2)	-3(1)	-2(1)	5(1)
C(17)	32(2)	35(2)	35(2)	-1(1)	2(1)	-7(1)
C(18)	40(2)	26(1)	27(2)	-2(1)	0(1)	-1(1)
C(19)	30(2)	28(1)	28(2)	-3(1)	5(1)	4(1)
C(20)	28(2)	18(1)	28(2)	5(1)	4(1)	-2(1)
C(21)	21(2)	23(1)	18(2)	5(1)	0(1)	-1(1)
C(22)	30(2)	19(1)	30(2)	-3(1)	4(2)	3(1)
C(23)	24(2)	23(1)	29(2)	10(1)	0(1)	6(1)
C(24)	31(2)	20(1)	26(2)	6(1)	-3(1)	4(1)
C(25)	32(2)	27(1)	15(1)	3(1)	2(1)	4(1)
C(26)	32(2)	25(1)	34(2)	9(1)	5(1)	1(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb805

atom	x	y	z	U(eq)
H(3)	4647	-426.0000	2637	27
H(6A)	3154	-1920	1425	48
H(6B)	3335	-1911	2184	48
H(6C)	4537	-1888.0001	1725	48
H(7A)	3947	567	3624	53
H(7B)	2861	-277	3419	53
H(7C)	2515	969	3603	53
H(9)	6822	219	2509	31
H(10)	8303	1333	1991	33
H(11)	7634	2746	1317	30
H(12)	5493	3023	1128	26
H(14A)	3778	-1938	458	53
H(14B)	4666	-925	265	53
H(14C)	3676	-1404.0001	-239	53
H(15A)	418	-439.0000	681	66
H(15B)	1102	-1585	838	66
H(15C)	851	-1234	111	66
H(16A)	2506	589	-510	48
H(16B)	3369	1319	-48.0000	48
H(16C)	1870	1380	10	48
H(17A)	-529	2179	3211	51

H(17B)	449	1367	3553	51
H(17C)	15	1135	2833	51
H(18A)	3071	3684	3382	46
H(18B)	2703	2654	3823	46
H(18C)	1782	3697	3777	46
H(19A)	451	4257	2664	43
H(19B)	199	3424	2085	43
H(19C)	1498	4087	2124	43
H(20)	4093	3274	342	29
H(21)	3689	4217	1410	25
H(22)	2193	5865	1208	31
H(23)	418	4476	990	30
H(24)	833	3540	-61	31
H(25)	2881	4332	-525	30
H(26A)	3499	5985	178	36
H(26B)	2020	6100	-7.0000	36

II.22. Crystallographic data for IV-55

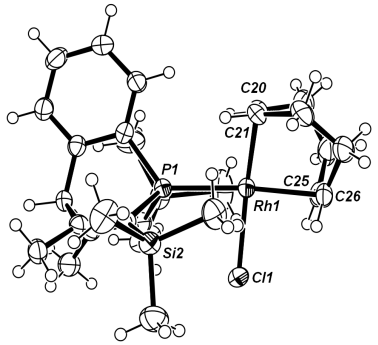


Table 1. Crystal data for mbgo21

Compound	mbgo21
Molecular formula	$C_{27}H_{42}ClPRhSi_2$
Molecular weight	592.12
Crystal habit	Yellow Block
Crystal dimensions(mm)	0.24x0.10x0.06
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	12.029(1)
b(Å)	11.240(1)
c(Å)	24.119(1)
α(°)	90.00
β(°)	118.844(2)
γ(°)	90.00
V(Å^3)	2856.5(4)
Z	4

d(g-cm^{-3})	1.377
F(000)	1236
μ(cm^{-1})	0.845
Absorption corrections	multi-scan ; 0.8229 min, 0.9510 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	27.46
HKL ranges	-15 11 ; -14 13 ; -31 31
Reflections measured	17258
Unique data	6523
Rint	0.0426
Reflections used	4436
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	consrt
Parameters refined	297
Reflections / parameter	14
wR2	0.0977
R1	0.0388
Weights a, b	0.0453 ; 0.0000
GoF	1.010
difference peak / hole (e Å^{-3})	0.659(0.081) / -0.486(0.081)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mbgo21

atom	x	y	z	U(eq)
Rh(1)	-2743(1)	-1971(1)	-4760(1)	31(1)
Cl(1)	-1948(1)	-547(1)	-3932(1)	38(1)
P(1)	-1713(1)	-3349(1)	-3943(1)	27(1)
Si(1)	1011(1)	-2965(1)	-3860(1)	41(1)
Si(2)	-3681(1)	-2922(1)	-3362(1)	33(1)
C(1)	1(3)	-2965(2)	-3452(1)	29(1)
C(2)	578(3)	-3695(3)	-2853(1)	30(1)
C(3)	-215(3)	-4754(3)	-2862(1)	30(1)
C(4)	-1342(3)	-4188(3)	-2831(1)	30(1)
C(5)	-2173(3)	-3501(3)	-3316(1)	29(1)
C(6)	1641(3)	-3418(3)	-2330(1)	43(1)
C(7)	-1397(3)	-4459(3)	-2236(1)	37(1)
C(8)	-698(3)	-5497(3)	-3453(1)	31(1)
C(9)	-438(3)	-6694(3)	-3443(2)	37(1)
C(10)	-1003(3)	-7361(3)	-3995(2)	44(1)
C(11)	-1839(3)	-6829(3)	-4559(2)	41(1)
C(12)	-2090(3)	-5619(3)	-4581(1)	34(1)
C(13)	-1517(3)	-4939(3)	-4032(1)	29(1)
C(14)	2607(3)	-2319(4)	-3322(2)	64(1)
C(15)	288(4)	-1974(4)	-4564(2)	80(2)
C(16)	1277(4)	-4499(3)	-4052(2)	57(1)
C(17)	-4823(3)	-2429(3)	-4176(2)	47(1)
C(18)	-3364(4)	-1654(3)	-2808(2)	52(1)

C(19)	-4483(3)	-4163(3)	-3169(2)	53(1)
C(20)	-3028(4)	-3056(3)	-5540(1)	44(1)
C(21)	-4070(3)	-3153(3)	-5440(1)	40(1)
C(22)	-5342(3)	-2529(3)	-5833(2)	54(1)
C(23)	-5223(3)	-1224(3)	-5953(2)	57(1)
C(24)	-4057(3)	-641(3)	-5432(1)	42(1)
C(25)	-2934(4)	-562(3)	-5433(1)	45(1)
C(26)	-2663(4)	-1055(3)	-5938(2)	60(1)
C(27)	-3056(4)	-2350(3)	-6092(2)	61(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mbgo21

Rh(1)-C(21)	2.116(3)	Rh(1)-C(20)	2.126(3)
Rh(1)-C(25)	2.200(3)	Rh(1)-C(24)	2.211(3)
Rh(1)-P(1)	2.3372(7	Rh(1)-Cl(1)	2.3712(7)
P(1)-C(13)	1.828(3)	P(1)-C(5)	1.852(3)
P(1)-C(1)	1.867(3)	Si(1)-C(16)	1.854(4)
Si(1)-C(15)	1.859(4)	Si(1)-C(14)	1.869(4)
Si(1)-C(1)	1.896(3)	Si(2)-C(17)	1.856(3)
Si(2)-C(18)	1.863(3)	Si(2)-C(19)	1.876(3)
Si(2)-C(5)	1.879(3)	C(1)-C(2)	1.508(4)
C(2)-C(6)	1.330(4)	C(2)-C(3)	1.520(4)
C(3)-C(8)	1.508(4)	C(3)-C(4)	1.530(4)
C(4)-C(5)	1.354(4)	C(4)-C(7)	1.500(4)
C(8)-C(9)	1.379(4)	C(8)-C(13)	1.408(4)
C(9)-C(10)	1.386(4)	C(10)-C(11)	1.379(4)
C(11)-C(12)	1.389(4)	C(12)-C(13)	1.390(4)
C(20)-C(21)	1.389(5)	C(20)-C(27)	1.536(4)
C(21)-C(22)	1.528(4)	C(22)-C(23)	1.515(5)
C(23)-C(24)	1.508(5)	C(24)-C(25)	1.354(5)
C(25)-C(26)	1.511(4)	C(26)-C(27)	1.520(5)

C(21)-Rh(1)-C(20)	38.2(1)	C(21)-Rh(1)-C(25)	96.2(1)
C(20)-Rh(1)-C(25)	81.1(1)	C(21)-Rh(1)-C(24)	81.4(1)
C(20)-Rh(1)-C(24)	89.2(1)	C(25)-Rh(1)-C(24)	35.8(1)
C(21)-Rh(1)-P(1)	97.6(1)	C(20)-Rh(1)-P(1)	99.2(1)
C(25)-Rh(1)-P(1)	157.5(1)	C(24)-Rh(1)-P(1)	165.3(1)
C(21)-Rh(1)-Cl(1)	157.6(1)	C(20)-Rh(1)-Cl(1)	163.6(1)
C(25)-Rh(1)-Cl(1)	89.5(1)	C(24)-Rh(1)-Cl(1)	90.95(8)
P(1)-Rh(1)-Cl(1)	84.43(3)	C(13)-P(1)-C(5)	96.4(1)
C(13)-P(1)-C(1)	97.8(1)	C(5)-P(1)-C(1)	100.2(1)
C(13)-P(1)-Rh(1)	126.5(1)	C(5)-P(1)-Rh(1)	120.3(1)
C(1)-P(1)-Rh(1)	110.8(1)	C(16)-Si(1)-C(15)	113.0(2)
C(16)-Si(1)-C(14)	107.0(2)	C(15)-Si(1)-C(14)	105.8(2)
C(16)-Si(1)-C(1)	111.1(1)	C(15)-Si(1)-C(1)	109.8(2)
C(14)-Si(1)-C(1)	109.9(2)	C(17)-Si(2)-C(18)	108.7(2)
C(17)-Si(2)-C(19)	106.1(2)	C(18)-Si(2)-C(19)	110.1(2)
C(17)-Si(2)-C(5)	111.5(1)	C(18)-Si(2)-C(5)	111.4(2)
C(19)-Si(2)-C(5)	108.9(1)	C(2)-C(1)-P(1)	109.7(2)
C(2)-C(1)-Si(1)	112.5(2)	P(1)-C(1)-Si(1)	117.4(1)
C(6)-C(2)-C(1)	124.7(3)	C(6)-C(2)-C(3)	120.4(3)
C(1)-C(2)-C(3)	114.7(2)	C(8)-C(3)-C(2)	113.5(2)
C(8)-C(3)-C(4)	109.3(2)	C(2)-C(3)-C(4)	103.8(2)
C(5)-C(4)-C(7)	125.9(3)	C(5)-C(4)-C(3)	119.9(2)
C(7)-C(4)-C(3)	114.2(2)	C(4)-C(5)-P(1)	111.7(2)
C(4)-C(5)-Si(2)	122.6(2)	P(1)-C(5)-Si(2)	125.4(2)
C(9)-C(8)-C(13)	119.8(3)	C(9)-C(8)-C(3)	122.9(3)
C(13)-C(8)-C(3)	117.2(3)	C(8)-C(9)-C(10)	120.5(3)
C(11)-C(10)-C(9)	120.0(3)	C(10)-C(11)-C(12)	120.2(3)
C(11)-C(12)-C(13)	120.3(3)	C(12)-C(13)-C(8)	119.1(3)

C(12)-C(13)-P(1)	128.1(2)	C(8)-C(13)-P(1)	112.8(2)
C(21)-C(20)-C(27)	123.1(3)	C(21)-C(20)-Rh(1)	70.5(2)
C(27)-C(20)-Rh(1)	113.5(2)	C(20)-C(21)-C(22)	125.1(3)
C(20)-C(21)-Rh(1)	71.3(2)	C(22)-C(21)-Rh(1)	110.4(2)
C(23)-C(22)-C(21)	113.8(3)	C(24)-C(23)-C(22)	113.4(3)
C(25)-C(24)-C(23)	123.7(3)	C(25)-C(24)-Rh(1)	71.7(2)
C(23)-C(24)-Rh(1)	111.4(2)	C(24)-C(25)-C(26)	125.5(3)
C(24)-C(25)-Rh(1)	72.6(2)	C(26)-C(25)-Rh(1)	110.2(2)
C(25)-C(26)-C(27)	112.7(3)	C(26)-C(27)-C(20)	114.1(3)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mbgo21

atom	U11	U22	U33	U23	U13	U12
Rh(1)	37(1)	27(1)	25(1)	3(1)	13(1)	7(1)
Cl(1)	43(1)	28(1)	36(1)	-3(1)	13(1)	3(1)
P(1)	29(1)	26(1)	24(1)	1(1)	11(1)	2(1)
Si(1)	39(1)	43(1)	49(1)	9(1)	28(1)	8(1)
Si(2)	31(1)	35(1)	33(1)	0(1)	16(1)	2(1)
C(1)	29(2)	25(2)	30(2)	-1(1)	13(1)	1(1)
C(2)	29(2)	29(2)	31(2)	0(1)	13(1)	2(1)
C(3)	32(2)	29(2)	25(2)	5(1)	11(1)	5(1)
C(4)	31(2)	29(2)	26(2)	-2(1)	12(1)	-5(1)
C(5)	29(2)	30(2)	27(2)	0(1)	14(1)	-2(1)
C(6)	38(2)	45(2)	43(2)	0(2)	17(2)	5(2)
C(7)	41(2)	38(2)	32(2)	7(1)	17(1)	1(2)
C(8)	29(2)	29(2)	33(2)	3(1)	15(1)	-1(1)
C(9)	38(2)	32(2)	36(2)	5(2)	14(1)	3(1)
C(10)	50(2)	26(2)	51(2)	0(2)	21(2)	3(2)
C(11)	48(2)	32(2)	37(2)	-6(2)	16(2)	-1(2)
C(12)	36(2)	36(2)	30(2)	1(1)	14(1)	4(1)
C(13)	30(2)	27(2)	32(2)	3(1)	16(1)	2(1)
C(14)	52(2)	59(3)	104(3)	-12(2)	56(2)	-5(2)
C(15)	69(3)	108(4)	94(3)	52(3)	63(3)	29(2)
C(16)	62(2)	62(3)	66(2)	-15(2)	46(2)	-4(2)
C(17)	32(2)	60(2)	46(2)	7(2)	16(2)	11(2)
C(18)	58(2)	55(2)	50(2)	-9(2)	31(2)	4(2)
C(19)	37(2)	51(2)	76(2)	7(2)	31(2)	2(2)
C(20)	62(2)	41(2)	26(2)	2(1)	18(2)	13(2)
C(21)	47(2)	37(2)	22(2)	-1(1)	5(1)	5(2)
C(22)	47(2)	59(2)	34(2)	-4(2)	1(2)	7(2)
C(23)	61(2)	56(2)	38(2)	3(2)	11(2)	30(2)
C(24)	56(2)	37(2)	28(2)	9(1)	15(2)	20(2)
C(25)	69(2)	33(2)	34(2)	13(2)	26(2)	14(2)
C(26)	87(3)	55(2)	45(2)	22(2)	39(2)	27(2)
C(27)	99(3)	55(2)	39(2)	10(2)	41(2)	26(2)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mbgo21

atom	x	y	z	U(eq)
H(1)	13	-2125	-3312	34
H(3)	281	-5261	-2480	36
H(6A)	2307	-3990	-2267	64
H(6B)	1488	-3445	-1966	64
H(6C)	1911	-2615	-2371	64
H(7A)	-1699	-5276	-2255	56

H(7B)	-1980	-3904	-2195	56
H(7C)	-548	-4376	-1870.9999	56
H(9)	132	-7065	-3054.0002	44
H(10)	-815	-8184.0005	-3983	52
H(11)	-2243	-7292	-4935	49
H(12)	-2656	-5255	-4972	41
H(14A)	3069	-2190	-3559	96
H(14B)	3086	-2869.0002	-2971	96
H(14C)	2504	-1557	-3154	96
H(15A)	-455	-2366	-4905	121
H(15B)	911	-1808.9999	-4706	121
H(15C)	27	-1226	-4452	121
H(16A)	1617	-4991	-3669	85
H(16B)	1885	-4483	-4214	85
H(16C)	471	-4835	-4375	85
H(17A)	-4434	-1802	-4308	71
H(17B)	-5590	-2119	-4182	71
H(17C)	-5046	-3105	-4467	71
H(18A)	-4157	-1412.9999	-2818	79
H(18B)	-3021	-983	-2937	79
H(18C)	-2748	-1898	-2377	79
H(19A)	-4348	-4913	-3335	80
H(19B)	-5394	-4000	-3362.9998	80
H(19C)	-4124	-4223	-2709	80
H(20)	-2262	-3443	-5253.0005	53
H(21)	-3983	-3646	-5102	48
H(22A)	-5809.9995	-2940.9998	-6246	65
H(22B)	-5850	-2601	-5612	65
H(23A)	-5200	-1145	-6355.9995	69
H(23B)	-5985	-798	-6001	69
H(24)	-4113	-311	-5084	51
H(25)	-2261	-162	-5087	54
H(26A)	-1744	-983	-5794	71
H(26B)	-3123	-574	-6328	71
H(27A)	-2482	-2741	-6223.0005	73
H(27B)	-3926	-2382	-6455	73

II.23. Crystallographic data for IV-57

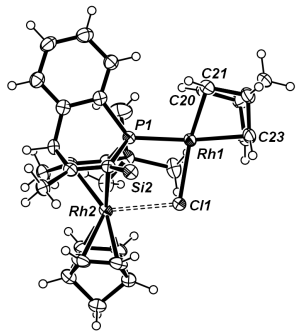


Table 1. Crystal data for mbgo16

Compound	mbgo16
Molecular formula	$C_{33}H_{45}ClPRh_2Si_2F_6P$
Molecular weight	915.08
Crystal habit	Orange Block
Crystal dimensions(mm)	0.12x0.12x0.08
Crystal system	monoclinic
Space group	P 2_1/c
a(Å)	13.898(1)
b(Å)	16.348(1)
c(Å)	21.004(1)
α(°)	90.00
β(°)	131.429(3)
γ(°)	90.00
V(Å^3)	3578.1(4)
Z	4
d(g-cm^{-3})	1.699
F(000)	1848
μ(cm^{-1})	1.209
Absorption corrections	multi-scan ; 0.8685 min, 0.9095 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	27.47
HKL ranges	-18 12 ; -19 21 ; -26 27
Reflections measured	22170
Unique data	8078
Rint	0.0340
Reflections used	5997
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	423
Reflections / parameter	14
wR2	0.0749
R1	0.0330
Weights a, b	0.0297 ; 0.0000
GoF	1.011
difference peak / hole (e Å^{-3})	0.683(0.089) / -0.519(0.089)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mbgo16

atom	x	y	z	U(eq)
Rh(1)	6034(1)	3524(1)	1201(1)	23(1)
Rh(2)	3077(1)	3023(1)	1118(1)	24(1)
Cl(1)	4353(1)	4230(1)	1025(1)	27(1)
P(1)	5009(1)	2404(1)	1127(1)	22(1)

Si(1)	6337(1)	2718(1)	3084(1)	29(1)
Si(2)	2509(1)	2833(1)	-873(1)	26(1)
C(1)	4901(3)	2363(2)	1961(2)	24(1)
C(2)	4066(3)	1741(2)	1794(2)	26(1)
C(3)	3456(3)	1198(2)	1010(2)	26(1)
C(4)	2620(3)	1806(2)	282(2)	24(1)
C(5)	3244(3)	2421(2)	219(2)	22(1)
C(6)	5335(3)	1332(2)	1109(2)	26(1)
C(7)	6320(3)	1025(2)	1165(2)	30(1)
C(8)	6432(3)	181(2)	1144(2)	36(1)
C(9)	5562(3)	-334(2)	1052(2)	37(1)
C(10)	4579(3)	-32(2)	997(2)	32(1)
C(11)	4466(3)	812(2)	1034(2)	27(1)
C(12)	3937(3)	1377(2)	2391(2)	31(1)
C(13)	1235(3)	1570(2)	-377(2)	30(1)
C(14)	6049(3)	2741(2)	3833(2)	41(1)
C(15)	7586(4)	1922(2)	3470(2)	60(1)
C(16)	6955(3)	3749(2)	3138(2)	41(1)
C(17)	1177(3)	3567(2)	-1331(2)	44(1)
C(18)	1912(3)	1934(2)	-1593(2)	41(1)
C(19)	3744(3)	3291(2)	-864(2)	32(1)
C(20)	7897(3)	3088(2)	1837(2)	27(1)
C(21)	7191(3)	3068(2)	963(2)	29(1)
C(22)	7472(3)	3884(2)	743(2)	33(1)
C(23)	6796(3)	4487(2)	883(2)	31(1)
C(24)	7481(3)	4523(2)	1735(2)	29(1)
C(25)	8594(3)	3918(2)	2148(2)	31(1)
C(26)	8878(3)	4015(2)	1561(2)	34(1)
C(27)	3147(3)	3864(2)	1931(2)	34(1)
C(28)	2544(3)	3170(2)	1892(2)	35(1)
C(29)	1102(3)	3308(2)	1183(2)	39(1)
C(30)	1013(3)	3264(2)	421(2)	38(1)
C(31)	1582(3)	3956(2)	436(2)	36(1)
C(32)	2077(3)	4430(2)	1226(2)	38(1)
C(33)	1023(3)	4242(2)	1255(2)	42(1)
P(2)	9698(1)	999(1)	1072(1)	35(1)
F(1)	9599(2)	465(1)	1655(1)	78(1)
F(2)	10562(3)	294(2)	1160(2)	96(1)
F(3)	9825(3)	1514(1)	497(2)	92(1)
F(4)	8867(3)	1684(2)	1011(2)	97(1)
F(5)	8490(2)	552(1)	255(1)	73(1)
F(6)	10948(2)	1435(1)	1897(1)	71(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mbgo16

Rh(1)-C(20)	2.102(3)	Rh(1)-C(21)	2.109(3)
Rh(1)-C(23)	2.232(3)	Rh(1)-C(24)	2.233(3)
Rh(1)-P(1)	2.2611(8	Rh(1)-Cl(1)	2.4062(8)
Rh(2)-C(27)	2.143(3)	Rh(2)-C(31)	2.180(3)
Rh(2)-C(1)	2.188(3)	Rh(2)-C(28)	2.201(3)
Rh(2)-C(30)	2.229(3)	Rh(2)-C(5)	2.273(3)
Rh(2)-C(2)	2.391(3)	Rh(2)-C(4)	2.443(3)
Rh(2)-Cl(1)	2.7439(7	Rh(2)-P(1)	2.8583(8)
P(1)-C(6)	1.818(3)	P(1)-C(1)	1.857(3)
P(1)-C(5)	1.860(3)	Si(1)-C(16)	1.860(3)
Si(1)-C(14)	1.863(3)	Si(1)-C(15)	1.871(4)
Si(1)-C(1)	1.911(3)	Si(2)-C(17)	1.853(3)
Si(2)-C(19)	1.860(3)	Si(2)-C(18)	1.863(3)
Si(2)-C(5)	1.914(3)	C(1)-C(2)	1.402(4)
C(2)-C(12)	1.502(4)	C(2)-C(3)	1.539(4)
C(3)-C(11)	1.509(4)	C(3)-C(4)	1.526(4)

C(3)-H(3)	1.0000	C(4)-C(5)	1.390(4)
C(4)-C(13)	1.498(4)	C(6)-C(7)	1.387(4)
C(6)-C(11)	1.397(4)	C(7)-C(8)	1.391(4)
C(7)-H(7)	0.9500	C(8)-C(9)	1.378(5)
C(8)-H(8)	0.9500	C(9)-C(10)	1.384(4)
C(9)-H(9)	0.9500	C(10)-C(11)	1.398(4)
C(10)-H(10)	0.9500	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800	C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800	C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800	C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800	C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800	C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800	C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800	C(20)-C(21)	1.395(4)
C(20)-C(25)	1.539(4)	C(20)-H(20)	0.9500
C(21)-C(22)	1.545(4)	C(21)-H(21)	0.9500
C(22)-C(23)	1.518(4)	C(22)-C(26)	1.540(4)
C(22)-H(22)	1.0000	C(23)-C(24)	1.363(4)
C(23)-H(23)	0.9500	C(24)-C(25)	1.534(4)
C(24)-H(24)	0.9500	C(25)-C(26)	1.532(4)
C(25)-H(25)	1.0000	C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900	C(27)-C(28)	1.381(4)
C(27)-C(32)	1.531(4)	C(27)-H(27)	0.9500
C(28)-C(29)	1.528(5)	C(28)-H(28)	0.9500
C(29)-C(30)	1.523(5)	C(29)-C(33)	1.546(4)
C(29)-H(29)	1.0000	C(30)-C(31)	1.369(5)
C(30)-H(30)	0.9500	C(31)-C(32)	1.522(4)
C(31)-H(31)	0.9500	C(32)-C(33)	1.537(4)
C(32)-H(32)	1.0000	C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900	P(2)-F(4)	1.551(3)
P(2)-F(3)	1.574(2)	P(2)-F(5)	1.576(2)
P(2)-F(1)	1.582(2)	P(2)-F(2)	1.584(3)
P(2)-F(6)	1.596(2)		

C(20)-Rh(1)-C(21)	38.7(1)	C(20)-Rh(1)-C(23)	78.5(1)
C(21)-Rh(1)-C(23)	65.9(1)	C(20)-Rh(1)-C(24)	66.9(1)
C(21)-Rh(1)-C(24)	78.7(1)	C(23)-Rh(1)-C(24)	35.6(1)
C(20)-Rh(1)-P(1)	102.97(8)	C(21)-Rh(1)-P(1)	104.01(8)
C(23)-Rh(1)-P(1)	162.34(8)	C(24)-Rh(1)-P(1)	160.70(8)
C(20)-Rh(1)-Cl(1)	157.36(8)	C(21)-Rh(1)-Cl(1)	161.49(8)
C(23)-Rh(1)-Cl(1)	102.76(8)	C(24)-Rh(1)-Cl(1)	100.72(8)
P(1)-Rh(1)-Cl(1)	82.73(3)	C(27)-Rh(2)-C(31)	66.2(1)
C(27)-Rh(2)-C(1)	104.7(1)	C(31)-Rh(2)-C(1)	165.2(1)
C(27)-Rh(2)-C(28)	37.0(1)	C(31)-Rh(2)-C(28)	76.7(1)
C(1)-Rh(2)-C(28)	103.4(1)	C(27)-Rh(2)-C(30)	76.7(1)
C(31)-Rh(2)-C(30)	36.2(1)	C(1)-Rh(2)-C(30)	156.5(1)
C(28)-Rh(2)-C(30)	63.2(1)	C(27)-Rh(2)-C(5)	164.5(1)
C(31)-Rh(2)-C(5)	109.5(1)	C(1)-Rh(2)-C(5)	76.0(1)
C(28)-Rh(2)-C(5)	158.4(1)	C(30)-Rh(2)-C(5)	109.0(1)
C(27)-Rh(2)-C(2)	112.6(1)	C(31)-Rh(2)-C(2)	157.9(1)
C(1)-Rh(2)-C(2)	35.3(1)	C(28)-Rh(2)-C(2)	89.9(1)
C(30)-Rh(2)-C(2)	121.9(1)	C(5)-Rh(2)-C(2)	77.2(1)
C(27)-Rh(2)-C(4)	161.4(1)	C(31)-Rh(2)-C(4)	114.6(1)
C(1)-Rh(2)-C(4)	77.9(1)	C(28)-Rh(2)-C(4)	124.4(1)
C(30)-Rh(2)-C(4)	93.6(1)	C(5)-Rh(2)-C(4)	34.0(1)
C(2)-Rh(2)-C(4)	59.1(1)	C(27)-Rh(2)-Cl(1)	84.5(1)
C(31)-Rh(2)-Cl(1)	80.2(1)	C(1)-Rh(2)-Cl(1)	87.42(8)
C(28)-Rh(2)-Cl(1)	121.6(1)	C(30)-Rh(2)-Cl(1)	115.9(1)

C(5)-Rh(2)-Cl(1)	80.00(7)	C(2)-Rh(2)-Cl(1)	121.86(8)
C(4)-Rh(2)-Cl(1)	114.04(7)	C(27)-Rh(2)-P(1)	132.4(1)
C(31)-Rh(2)-P(1)	137.2(1)	C(1)-Rh(2)-P(1)	40.52(8)
C(28)-Rh(2)-P(1)	143.9(1)	C(30)-Rh(2)-P(1)	149.6(1)
C(5)-Rh(2)-P(1)	40.54(7)	C(2)-Rh(2)-P(1)	61.14(7)
C(4)-Rh(2)-P(1)	60.84(7)	Cl(1)-Rh(2)-P(1)	66.83(2)
Rh(1)-Cl(1)-Rh(2)	104.61(2)	C(6)-P(1)-C(1)	99.3(1)
C(6)-P(1)-C(5)	99.8(1)	C(1)-P(1)-C(5)	95.3(1)
C(6)-P(1)-Rh(1)	128.9(1)	C(1)-P(1)-Rh(1)	113.9(1)
C(5)-P(1)-Rh(1)	113.7(1)	C(6)-P(1)-Rh(2)	126.0(1)
C(1)-P(1)-Rh(2)	50.0(1)	C(5)-P(1)-Rh(2)	52.6(1)
Rh(1)-P(1)-Rh(2)	105.10(3)	C(16)-Si(1)-C(14)	106.2(2)
C(16)-Si(1)-C(15)	110.2(2)	C(14)-Si(1)-C(15)	107.7(2)
C(16)-Si(1)-C(1)	114.4(1)	C(14)-Si(1)-C(1)	114.6(1)
C(15)-Si(1)-C(1)	103.6(2)	C(17)-Si(2)-C(19)	110.1(2)
C(17)-Si(2)-C(18)	109.5(2)	C(19)-Si(2)-C(18)	103.8(2)
C(17)-Si(2)-C(5)	114.0(1)	C(19)-Si(2)-C(5)	111.9(1)
C(18)-Si(2)-C(5)	107.0(1)	C(2)-C(1)-P(1)	111.1(2)
C(2)-C(1)-Si(1)	123.0(2)	P(1)-C(1)-Si(1)	118.9(2)
C(2)-C(1)-Rh(2)	80.3(2)	P(1)-C(1)-Rh(2)	89.5(1)
Si(1)-C(1)-Rh(2)	123.7(1)	C(1)-C(2)-C(12)	127.9(3)
C(1)-C(2)-C(3)	117.7(3)	C(12)-C(2)-C(3)	112.3(2)
C(1)-C(2)-Rh(2)	64.4(2)	C(12)-C(2)-Rh(2)	120.2(2)
C(3)-C(2)-Rh(2)	100.2(2)	C(11)-C(3)-C(4)	112.3(2)
C(11)-C(3)-C(2)	111.3(2)	C(4)-C(3)-C(2)	102.2(2)
C(11)-C(3)-H(3)	110.2	C(4)-C(3)-H(3)	110.2
C(2)-C(3)-H(3)	110.2	C(5)-C(4)-C(13)	126.8(3)
C(5)-C(4)-C(3)	117.2(3)	C(13)-C(4)-C(3)	114.8(2)
C(5)-C(4)-Rh(2)	66.3(2)	C(13)-C(4)-Rh(2)	115.9(2)
C(3)-C(4)-Rh(2)	98.5(2)	C(4)-C(5)-P(1)	112.0(2)
C(4)-C(5)-Si(2)	119.8(2)	P(1)-C(5)-Si(2)	122.0(2)
C(4)-C(5)-Rh(2)	79.7(2)	P(1)-C(5)-Rh(2)	86.9(1)
Si(2)-C(5)-Rh(2)	125.2(1)	C(7)-C(6)-C(11)	121.3(3)
C(7)-C(6)-P(1)	126.3(2)	C(11)-C(6)-P(1)	112.3(2)
C(6)-C(7)-C(8)	118.8(3)	C(6)-C(7)-H(7)	120.6
C(8)-C(7)-H(7)	120.6	C(9)-C(8)-C(7)	120.3(3)
C(9)-C(8)-H(8)	119.9	C(7)-C(8)-H(8)	119.9
C(8)-C(9)-C(10)	121.3(3)	C(8)-C(9)-H(9)	119.3
C(10)-C(9)-H(9)	119.3	C(9)-C(10)-C(11)	119.2(3)
C(9)-C(10)-H(10)	120.4	C(11)-C(10)-H(10)	120.4
C(6)-C(11)-C(10)	119.1(3)	C(6)-C(11)-C(3)	117.8(2)
C(10)-C(11)-C(3)	123.1(3)	C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	Si(2)-C(19)-H(19A)	109.5

Si(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(21)-C(20)-C(25)	106.1(3)
C(21)-C(20)-Rh(1)	70.9(2)	C(25)-C(20)-Rh(1)	97.8(2)
C(21)-C(20)-H(20)	127.0	C(25)-C(20)-H(20)	127.0
Rh(1)-C(20)-H(20)	99.1	C(20)-C(21)-C(22)	106.0(3)
C(20)-C(21)-Rh(1)	70.4(2)	C(22)-C(21)-Rh(1)	98.6(2)
C(20)-C(21)-H(21)	127.0	C(22)-C(21)-H(21)	127.0
Rh(1)-C(21)-H(21)	98.9	C(23)-C(22)-C(26)	100.6(3)
C(23)-C(22)-C(21)	101.0(2)	C(26)-C(22)-C(21)	99.9(2)
C(23)-C(22)-H(22)	117.4	C(26)-C(22)-H(22)	117.4
C(21)-C(22)-H(22)	117.4	C(24)-C(23)-C(22)	107.4(3)
C(24)-C(23)-Rh(1)	72.3(2)	C(22)-C(23)-Rh(1)	94.4(2)
C(24)-C(23)-H(23)	126.3	C(22)-C(23)-H(23)	126.3
Rh(1)-C(23)-H(23)	101.1	C(23)-C(24)-C(25)	106.3(3)
C(23)-C(24)-Rh(1)	72.2(2)	C(25)-C(24)-Rh(1)	92.7(2)
C(23)-C(24)-H(24)	126.9	C(25)-C(24)-H(24)	126.9
Rh(1)-C(24)-H(24)	102.4	C(26)-C(25)-C(24)	100.3(2)
C(26)-C(25)-C(20)	100.1(2)	C(24)-C(25)-C(20)	102.3(2)
C(26)-C(25)-H(25)	117.1	C(24)-C(25)-H(25)	117.1
C(20)-C(25)-H(25)	117.1	C(25)-C(26)-C(22)	94.1(2)
C(25)-C(26)-H(26A)	112.9	C(22)-C(26)-H(26A)	112.9
C(25)-C(26)-H(26B)	112.9	C(22)-C(26)-H(26B)	112.9
H(26A)-C(26)-H(26B)	110.3	C(28)-C(27)-C(32)	106.0(3)
C(28)-C(27)-Rh(2)	73.8(2)	C(32)-C(27)-Rh(2)	96.5(2)
C(28)-C(27)-H(27)	127.0	C(32)-C(27)-H(27)	127.0
Rh(2)-C(27)-H(27)	97.9	C(27)-C(28)-C(29)	106.9(3)
C(27)-C(28)-Rh(2)	69.2(2)	C(29)-C(28)-Rh(2)	99.3(2)
C(27)-C(28)-H(28)	126.6	C(29)-C(28)-H(28)	126.6
Rh(2)-C(28)-H(28)	99.3	C(30)-C(29)-C(28)	99.1(3)
C(30)-C(29)-C(33)	100.8(3)	C(28)-C(29)-C(33)	100.5(3)
C(30)-C(29)-H(29)	117.7	C(28)-C(29)-H(29)	117.7
C(33)-C(29)-H(29)	117.7	C(31)-C(30)-C(29)	107.1(3)
C(31)-C(30)-Rh(2)	70.0(2)	C(29)-C(30)-Rh(2)	98.3(2)
C(31)-C(30)-H(30)	126.4	C(29)-C(30)-H(30)	126.4
Rh(2)-C(30)-H(30)	99.6	C(30)-C(31)-C(32)	106.4(3)
C(30)-C(31)-Rh(2)	73.8(2)	C(32)-C(31)-Rh(2)	95.3(2)
C(30)-C(31)-H(31)	126.8	C(32)-C(31)-H(31)	126.8
Rh(2)-C(31)-H(31)	98.9	C(31)-C(32)-C(27)	101.3(2)
C(31)-C(32)-C(33)	100.8(3)	C(27)-C(32)-C(33)	100.5(3)
C(31)-C(32)-H(32)	117.1	C(27)-C(32)-H(32)	117.1
C(33)-C(32)-H(32)	117.1	C(32)-C(33)-C(29)	93.6(2)
C(32)-C(33)-H(33A)	113.0	C(29)-C(33)-H(33A)	113.0
C(32)-C(33)-H(33B)	113.0	C(29)-C(33)-H(33B)	113.0
H(33A)-C(33)-H(33B)	110.4	F(4)-P(2)-F(3)	90.3(2)
F(4)-P(2)-F(5)	92.7(2)	F(3)-P(2)-F(5)	89.6(1)
F(4)-P(2)-F(1)	91.2(2)	F(3)-P(2)-F(1)	178.4(2)
F(5)-P(2)-F(1)	90.7(1)	F(4)-P(2)-F(2)	178.4(2)
F(3)-P(2)-F(2)	91.1(2)	F(5)-P(2)-F(2)	88.2(1)
F(1)-P(2)-F(2)	87.4(2)	F(4)-P(2)-F(6)	89.0(2)
F(3)-P(2)-F(6)	90.0(1)	F(5)-P(2)-F(6)	178.2(2)
F(1)-P(2)-F(6)	89.7(1)	F(2)-P(2)-F(6)	90.1(1)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mbgo16

atom	U11	U22	U33	U23	U13	U12
Rh(1)	21(1)	25(1)	26(1)	1(1)	16(1)	-1(1)
Rh(2)	22(1)	28(1)	23(1)	-1(1)	15(1)	0(1)
Cl(1)	26(1)	26(1)	32(1)	1(1)	21(1)	1(1)
P(1)	21(1)	24(1)	21(1)	0(1)	14(1)	0(1)
Si(1)	24(1)	36(1)	20(1)	-1(1)	12(1)	-2(1)

Si(2)	24(1)	31(1)	20(1)	1(1)	14(1)	0(1)
C(1)	22(2)	27(2)	21(2)	1(1)	13(1)	2(1)
C(2)	24(2)	30(2)	25(2)	3(1)	17(2)	3(1)
C(3)	26(2)	25(2)	25(2)	-2(1)	17(1)	-6(1)
C(4)	23(2)	28(2)	22(2)	-3(1)	15(1)	-1(1)
C(5)	22(2)	25(2)	19(2)	-1(1)	14(1)	1(1)
C(6)	25(2)	29(2)	19(2)	2(1)	13(1)	0(1)
C(7)	30(2)	31(2)	30(2)	4(1)	20(2)	2(1)
C(8)	40(2)	35(2)	38(2)	5(2)	27(2)	8(2)
C(9)	48(2)	24(2)	43(2)	3(1)	32(2)	6(2)
C(10)	38(2)	29(2)	30(2)	2(1)	23(2)	0(2)
C(11)	29(2)	30(2)	19(2)	2(1)	14(1)	1(1)
C(12)	34(2)	36(2)	28(2)	3(1)	23(2)	-2(2)
C(13)	25(2)	33(2)	27(2)	-2(1)	16(2)	-5(1)
C(14)	45(2)	47(2)	24(2)	-4(2)	21(2)	-12(2)
C(15)	34(2)	72(3)	42(2)	0(2)	11(2)	15(2)
C(16)	43(2)	52(2)	26(2)	-14(2)	22(2)	-21(2)
C(17)	43(2)	59(2)	32(2)	16(2)	26(2)	18(2)
C(18)	43(2)	50(2)	34(2)	-10(2)	26(2)	-10(2)
C(19)	34(2)	40(2)	25(2)	0(1)	21(2)	-5(2)
C(20)	25(2)	30(2)	32(2)	5(1)	21(2)	4(1)
C(21)	27(2)	35(2)	29(2)	-2(1)	20(2)	-1(1)
C(22)	32(2)	37(2)	37(2)	4(2)	26(2)	-1(2)
C(23)	22(2)	31(2)	36(2)	5(1)	18(2)	-1(1)
C(24)	26(2)	28(2)	39(2)	-2(1)	24(2)	-4(1)
C(25)	21(2)	35(2)	30(2)	-1(1)	15(2)	-1(1)
C(26)	26(2)	36(2)	45(2)	3(2)	25(2)	1(1)
C(27)	29(2)	44(2)	34(2)	-9(2)	23(2)	-1(2)
C(28)	42(2)	38(2)	40(2)	3(2)	34(2)	7(2)
C(29)	38(2)	38(2)	55(2)	-3(2)	37(2)	-2(2)
C(30)	20(2)	47(2)	39(2)	-8(2)	17(2)	2(2)
C(31)	32(2)	45(2)	38(2)	9(2)	27(2)	13(2)
C(32)	45(2)	29(2)	57(2)	-4(2)	41(2)	-1(2)
C(33)	44(2)	41(2)	57(2)	-2(2)	40(2)	6(2)
P(2)	33(1)	36(1)	30(1)	-1(1)	19(1)	-3(1)
F(1)	94(2)	75(2)	58(2)	9(1)	47(2)	-22(1)
F(2)	77(2)	99(2)	94(2)	-17(2)	49(2)	27(2)
F(3)	148(3)	86(2)	66(2)	-25(1)	81(2)	-63(2)
F(4)	94(2)	90(2)	108(2)	9(2)	68(2)	46(2)
F(5)	60(2)	66(1)	41(1)	-2(1)	11(1)	-25(1)
F(6)	62(2)	88(2)	47(1)	-23(1)	29(1)	-33(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mbgo16

atom	x	y	z	U(eq)
H(3)	2911	765	972	31
H(7)	6906	1384	1218	36
H(8)	7110	-40	1193	44
H(9)	5640	-908	1026	44
H(10)	3987	-395.0000	934	38
H(12A)	4437	871	2634	47
H(12B)	3032	1257	2080	47
H(12C)	4257	1767	2848	47
H(13A)	757	2011	-794	44
H(13B)	884	1476	-104	44
H(13C)	1158	1069	-663	44
H(14A)	6738	3049	4343	61

H(14B)	6035	2180	3992	61
H(14C)	5224	3005	3558	61
H(15A)	8324	2011	4073	91
H(15B)	7863	1960	3146	91
H(15C)	7225	1377	3391	91
H(16A)	6274	4155	2899	62
H(16B)	7230	3748	2813	62
H(16C)	7684	3886	3732	62
H(17A)	722	3653	-1932.9999	66
H(17B)	1525	4089	-1027	66
H(17C)	581	3346	-1275	66
H(18A)	1149	1710	-1716	62
H(18B)	2582	1515	-1317	62
H(18C)	1689	2105	-2123	62
H(19A)	3334	3486	-1435	47
H(19B)	4389	2876	-688	47
H(19C)	4158	3750	-465	47
H(20)	7939	2673	2171	33
H(21)	6648	2639	582	35
H(22)	7273	3915	190	39
H(23)	6036	4784	456	37
H(24)	7303	4858	2017	35
H(25)	9334	3977	2772	37
H(26A)	9462	3588	1650	41
H(26B)	9205	4566	1594	41
H(27)	4044	3969	2316	41
H(28)	2948	2697	2239	42
H(29)	509	2952	1176	46
H(30)	635	2837	13	45
H(31)	1654	4110	33	43
H(32)	2303	5018	1256	46
H(33A)	178	4475	767	50
H(33B)	1259	4408	1796	50

II.24. Crystallographic data for IV-58

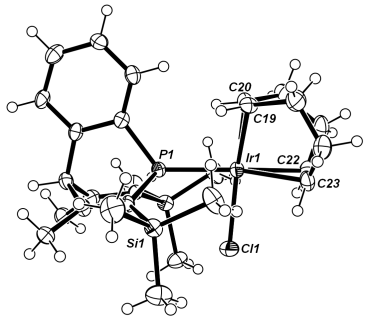


Table 1. Crystal data for mb484

Compound	mb484
Molecular formula	$C_{27}H_{41}ClIrPSi_2$
Molecular weight	864.67

Crystal habit	Orange Block
Crystal dimensions(mm)	0.60x0.30x0.20
Crystal system	triclinic
Space group	P-1
a(Å)	12.016(1)
b(Å)	14.105(1)
c(Å)	19.326(1)
α(°)	95.139(1)
β(°)	91.418(1)
γ(°)	99.813(1)
V(Å^3)	3211.9(4)
Z	4
d(g-cm^{-3})	1.788
F(000)	1760
μ(cm^{-1})	4.398
Absorption corrections	multi-scan ; 0.1778 min, 0.4733 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.01
HKL ranges	-16 16 ; -19 19 ; -27 23
Reflections measured	35860
Unique data	18039
Rint	0.0576
Reflections used	14753
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	594
Reflections / parameter	24
wR2	0.1804
R1	0.0693
Weights a, b	0.0544 ; 60.977
GoF	1.090
difference peak / hole (e Å^{-3})	4.431(0.256) / -3.938(0.256)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb484

atom	x	y	z	U(eq)
Ir(1)	5614(1)	2172(1)	6466(1)	21(1)
Cl(1)	4469(2)	3331(2)	6833(1)	32(1)
P(1)	4139(2)	1052(1)	6820(1)	19(1)
Si(1)	2469(2)	1544(2)	5540(1)	25(1)
Si(2)	4700(2)	2033(2)	8460(1)	24(1)
C(1)	2746(6)	1015(5)	6376(4)	20(1)
C(2)	1909(7)	461(6)	6688(5)	25(2)
C(3)	2238(7)	-94(6)	7297(4)	24(2)

C(4)	2817(8)	648(6)	7880(4)	26(2)
C(5)	3798(7)	1229(5)	7745(4)	20(1)
C(6)	4067(7)	-269(5)	6774(4)	21(1)
C(7)	4828(7)	-820(6)	6511(4)	26(2)
C(8)	4622(8)	-1821(6)	6534(5)	30(2)
C(9)	3640(10)	-2258(6)	6812(5)	31(2)
C(10)	2849(8)	-1728(6)	7074(4)	27(2)
C(11)	671(7)	293(6)	6504(5)	30(2)
C(12)	2212(8)	606(7)	8553(5)	32(2)
C(13)	1720(10)	2597(8)	5700(5)	39(2)
C(14)	3782(8)	1900(10)	5065(5)	40(2)
C(15)	1600(10)	583(8)	4911(6)	45(3)
C(16)	6220(10)	2280(10)	8239(5)	43(3)
C(17)	4160(10)	3191(7)	8650(5)	36(2)
C(18)	4690(10)	1389(8)	9277(6)	40(2)
C(19)	6388(7)	1236(6)	5798(4)	24(2)
C(20)	6859(7)	1277(6)	6486(5)	28(2)
C(21)	8017(8)	1816(7)	6720(6)	37(2)
C(22)	7156(8)	3284(6)	6487(5)	30(2)
C(23)	6553(7)	3244(7)	5859(5)	29(2)
C(24)	6880(10)	2784(7)	5182(5)	38(2)
C(25)	7050(10)	1734(7)	5222(6)	39(2)
C(905)	8236(8)	2873(8)	6573(6)	40(2)
C(997)	3052(7)	-734(6)	7041(4)	23(2)
Ir(2)	10751(1)	3366(1)	1311(1)	21(1)
Cl(2)	9642(2)	2023(1)	1768(1)	26(1)
P(997)	9566(2)	4268(1)	1896(1)	19(1)
Si(3)	10609(2)	3733(2)	3404(1)	28(1)
Si(4)	7391(2)	3138(2)	839(1)	23(1)
C(26)	9538(7)	4201(5)	2849(4)	22(1)
C(27)	8699(7)	4617(6)	3125(4)	24(2)
C(28)	7997(7)	5127(6)	2657(4)	23(2)
C(29)	7397(7)	4381(6)	2078(4)	23(2)
C(30)	8046(6)	3931(6)	1640(4)	21(1)
C(31)	9647(7)	5589(5)	1926(4)	20(1)
C(32)	10411(7)	6258(6)	1618(4)	24(2)
C(33)	10301(8)	7243(6)	1699(5)	28(2)
C(34)	9440(10)	7533(6)	2076(5)	32(2)
C(35)	8684(8)	6866(6)	2395(5)	28(2)
C(36)	8768(7)	5893(6)	2325(4)	22(2)
C(37)	8370(10)	4651(7)	3864(5)	36(2)
C(38)	6132(8)	4265(7)	2060(5)	32(2)
C(39)	11050(10)	4618(8)	4194(5)	40(2)
C(40)	11980(10)	3670(10)	2941(6)	49(3)
C(41)	10010(10)	2544(8)	3705(6)	47(3)
C(42)	6380(10)	3781(7)	388(5)	36(2)
C(43)	8430(10)	2890(10)	178(5)	40(2)
C(44)	6630(10)	1960(7)	1097(6)	37(2)
C(45)	12094(7)	4510(6)	1199(5)	27(2)
C(46)	11358(8)	4365(6)	599(5)	28(2)
C(47)	11650(10)	3880(10)	-104(6)	53(3)
C(48)	11520(20)	2820(10)	-142(7)	79(5)
C(49)	11330(10)	2376(7)	531(5)	35(2)
C(50)	12081(8)	2525(7)	1091(6)	35(2)
C(51)	13240(10)	3170(10)	1120(10)	69(5)
C(52)	13246(8)	4200(8)	1198(8)	48(3)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb484

Ir(1)-C(19)	2.109(8)	Ir(1)-C(20)	2.12(1)
Ir(1)-C(23)	2.18(1)	Ir(1)-C(22)	2.211(8)

Ir(1)-P(1)	2.325(2)	Ir(1)-Cl(1)	2.382(2)
P(1)-C(6)	1.844(8)	P(1)-C(5)	1.849(8)
P(1)-C(1)	1.852(8)	Si(1)-C(14)	1.86(1)
Si(1)-C(13)	1.87(1)	Si(1)-C(1)	1.886(8)
Si(1)-C(15)	1.89(1)	Si(2)-C(16)	1.86(1)
Si(2)-C(17)	1.87(1)	Si(2)-C(18)	1.89(1)
Si(2)-C(5)	1.897(8)	C(1)-C(2)	1.35(1)
C(2)-C(11)	1.50(1)	C(2)-C(3)	1.55(1)
C(3)-C(997)	1.50(1)	C(3)-C(4)	1.53(1)
C(3)-H(3)	1.0000	C(4)-C(5)	1.36(1)
C(4)-C(12)	1.50(1)	C(6)-C(7)	1.38(1)
C(6)-C(997)	1.41(1)	C(7)-C(8)	1.40(1)
C(7)-H(7)	0.9500	C(8)-C(9)	1.38(1)
C(8)-H(8)	0.9500	C(9)-C(10)	1.39(1)
C(9)-H(9)	0.9500	C(10)-C(997)	1.39(1)
C(10)-H(10)	0.9500	C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800	C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800	C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(19)-C(20)	1.43(1)
C(19)-C(25)	1.53(1)	C(19)-H(19)	0.9500
C(20)-C(21)	1.50(1)	C(20)-H(20)	0.9500
C(21)-C(905)	1.52(1)	C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900	C(22)-C(23)	1.39(1)
C(22)-C(905)	1.52(1)	C(22)-H(22)	0.9500
C(23)-C(24)	1.50(1)	C(23)-H(23)	0.9500
C(24)-C(25)	1.53(1)	C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900	C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900	C(905)-H(90A)	0.9900
C(905)-H(90B)	0.9900	Ir(2)-C(45)	2.109(8)
Ir(2)-C(46)	2.110(8)	Ir(2)-C(49)	2.17(1)
Ir(2)-C(50)	2.17(1)	Ir(2)-P(997)	2.316(2)
Ir(2)-Cl(2)	2.375(2)	P(997)-C(31)	1.844(8)
P(997)-C(30)	1.850(8)	P(997)-C(26)	1.854(8)
Si(3)-C(41)	1.86(1)	Si(3)-C(39)	1.88(1)
Si(3)-C(26)	1.896(8)	Si(3)-C(40)	1.91(1)
Si(4)-C(43)	1.86(1)	Si(4)-C(44)	1.87(1)
Si(4)-C(42)	1.88(1)	Si(4)-C(30)	1.896(8)
C(26)-C(27)	1.35(1)	C(27)-C(37)	1.49(1)
C(27)-C(28)	1.53(1)	C(28)-C(36)	1.50(1)
C(28)-C(29)	1.54(1)	C(28)-H(28)	1.0000
C(29)-C(30)	1.35(1)	C(29)-C(38)	1.50(1)
C(31)-C(32)	1.39(1)	C(31)-C(36)	1.42(1)
C(32)-C(33)	1.41(1)	C(32)-H(32)	0.9500
C(33)-C(34)	1.38(1)	C(33)-H(33)	0.9500
C(34)-C(35)	1.39(1)	C(34)-H(34)	0.9500
C(35)-C(36)	1.39(1)	C(35)-H(35)	0.9500
C(37)-H(37A)	0.9800	C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800	C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800	C(38)-H(38C)	0.9800
C(39)-H(39A)	0.9800	C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800	C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800	C(40)-H(40C)	0.9800
C(41)-H(41A)	0.9800	C(41)-H(41B)	0.9800
C(41)-H(41C)	0.9800	C(42)-H(42A)	0.9800

C(42)-H(42B)	0.9800	C(42)-H(42C)	0.9800
C(43)-H(43A)	0.9800	C(43)-H(43B)	0.9800
C(43)-H(43C)	0.9800	C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800	C(44)-H(44C)	0.9800
C(45)-C(46)	1.42(1)	C(45)-C(52)	1.52(1)
C(45)-H(45)	0.9500	C(46)-C(47)	1.54(1)
C(46)-H(46)	0.9500	C(47)-C(48)	1.47(2)
C(47)-H(47A)	0.9900	C(47)-H(47B)	0.9900
C(48)-C(49)	1.50(2)	C(48)-H(48A)	0.9900
C(48)-H(48B)	0.9900	C(49)-C(50)	1.37(1)
C(49)-H(49)	0.9500	C(50)-C(51)	1.53(1)
C(50)-H(50)	0.9500	C(51)-C(52)	1.45(2)
C(51)-H(51A)	0.9900	C(51)-H(51B)	0.9900
C(52)-H(52A)	0.9900	C(52)-H(52B)	0.9900

C(19)-Ir(1)-C(20)	39.4(3)	C(19)-Ir(1)-C(23)	81.5(3)
C(20)-Ir(1)-C(23)	96.3(3)	C(19)-Ir(1)-C(22)	89.8(4)
C(20)-Ir(1)-C(22)	80.3(3)	C(23)-Ir(1)-C(22)	36.9(3)
C(19)-Ir(1)-P(1)	99.0(2)	C(20)-Ir(1)-P(1)	96.4(2)
C(23)-Ir(1)-P(1)	160.2(2)	C(22)-Ir(1)-P(1)	161.7(3)
C(19)-Ir(1)-Cl(1)	159.7(2)	C(20)-Ir(1)-Cl(1)	160.5(3)
C(23)-Ir(1)-Cl(1)	88.4(3)	C(22)-Ir(1)-Cl(1)	92.6(3)
P(1)-Ir(1)-Cl(1)	84.63(8)	C(6)-P(1)-C(5)	96.9(3)
C(6)-P(1)-C(1)	96.1(4)	C(5)-P(1)-C(1)	101.8(4)
C(6)-P(1)-Ir(1)	126.5(3)	C(5)-P(1)-Ir(1)	115.4(3)
C(1)-P(1)-Ir(1)	115.7(2)	C(14)-Si(1)-C(13)	110.2(5)
C(14)-Si(1)-C(1)	112.6(4)	C(13)-Si(1)-C(1)	111.0(4)
C(14)-Si(1)-C(15)	103.0(5)	C(13)-Si(1)-C(15)	110.1(5)
C(1)-Si(1)-C(15)	109.5(5)	C(16)-Si(2)-C(17)	110.6(6)
C(16)-Si(2)-C(18)	104.5(5)	C(17)-Si(2)-C(18)	109.3(5)
C(16)-Si(2)-C(5)	111.7(4)	C(17)-Si(2)-C(5)	110.6(4)
C(18)-Si(2)-C(5)	109.9(4)	C(2)-C(1)-P(1)	111.6(6)
C(2)-C(1)-Si(1)	121.3(6)	P(1)-C(1)-Si(1)	126.8(4)
C(1)-C(2)-C(11)	127.5(8)	C(1)-C(2)-C(3)	118.1(7)
C(11)-C(2)-C(3)	114.4(7)	C(997)-C(3)-C(4)	109.6(7)
C(997)-C(3)-C(2)	108.5(7)	C(4)-C(3)-C(2)	108.2(7)
C(997)-C(3)-H(3)	110.2	C(4)-C(3)-H(3)	110.2
C(2)-C(3)-H(3)	110.2	C(5)-C(4)-C(12)	128.3(8)
C(5)-C(4)-C(3)	118.3(7)	C(12)-C(4)-C(3)	113.4(7)
C(4)-C(5)-P(1)	111.4(6)	C(4)-C(5)-Si(2)	121.8(6)
P(1)-C(5)-Si(2)	126.7(4)	C(7)-C(6)-C(997)	119.1(7)
C(7)-C(6)-P(1)	129.1(6)	C(997)-C(6)-P(1)	111.8(6)
C(6)-C(7)-C(8)	120.3(8)	C(6)-C(7)-H(7)	119.8
C(8)-C(7)-H(7)	119.8	C(9)-C(8)-C(7)	119.6(8)
C(9)-C(8)-H(8)	120.2	C(7)-C(8)-H(8)	120.2
C(8)-C(9)-C(10)	121.7(8)	C(8)-C(9)-H(9)	119.1
C(10)-C(9)-H(9)	119.1	C(9)-C(10)-C(997)	118.4(8)
C(9)-C(10)-H(10)	120.8	C(997)-C(10)-H(10)	120.8
C(2)-C(11)-H(11A)	109.5	C(2)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5	C(2)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5	H(11B)-C(11)-H(11C)	109.5
C(4)-C(12)-H(12A)	109.5	C(4)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5	C(4)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5	H(12B)-C(12)-H(12C)	109.5
Si(1)-C(13)-H(13A)	109.5	Si(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5	Si(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5	H(13B)-C(13)-H(13C)	109.5
Si(1)-C(14)-H(14A)	109.5	Si(1)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	Si(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
Si(1)-C(15)-H(15A)	109.5	Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5	Si(1)-C(15)-H(15C)	109.5

H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
Si(2)-C(16)-H(16A)	109.5	Si(2)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5	Si(2)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(16B)-C(16)-H(16C)	109.5
Si(2)-C(17)-H(17A)	109.5	Si(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5	Si(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(17B)-C(17)-H(17C)	109.5
Si(2)-C(18)-H(18A)	109.5	Si(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5	Si(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5	H(18B)-C(18)-H(18C)	109.5
C(20)-C(19)-C(25)	122.0(8)	C(20)-C(19)-Ir(1)	70.6(5)
C(25)-C(19)-Ir(1)	114.0(6)	C(20)-C(19)-H(19)	119.0
C(25)-C(19)-H(19)	119.0	Ir(1)-C(19)-H(19)	85.6
C(19)-C(20)-C(21)	124(1)	C(19)-C(20)-Ir(1)	70.0(5)
C(21)-C(20)-Ir(1)	113.6(6)	C(19)-C(20)-H(20)	118.0
C(21)-C(20)-H(20)	118.0	Ir(1)-C(20)-H(20)	86.5
C(20)-C(21)-C(905)	114.4(8)	C(20)-C(21)-H(21A)	108.6
C(905)-C(21)-H(21A)	108.6	C(20)-C(21)-H(21B)	108.6
C(905)-C(21)-H(21B)	108.6	H(21A)-C(21)-H(21B)	107.6
C(23)-C(22)-C(905)	124(1)	C(23)-C(22)-Ir(1)	70.2(5)
C(905)-C(22)-Ir(1)	112.9(6)	C(23)-C(22)-H(22)	117.9
C(905)-C(22)-H(22)	117.9	Ir(1)-C(22)-H(22)	86.9
C(22)-C(23)-C(24)	124(1)	C(22)-C(23)-Ir(1)	72.9(5)
C(24)-C(23)-Ir(1)	111.2(6)	C(22)-C(23)-H(23)	117.9
C(24)-C(23)-H(23)	117.9	Ir(1)-C(23)-H(23)	85.9
C(23)-C(24)-C(25)	112.9(8)	C(23)-C(24)-H(24A)	109.0
C(25)-C(24)-H(24A)	109.0	C(23)-C(24)-H(24B)	109.0
C(25)-C(24)-H(24B)	109.0	H(24A)-C(24)-H(24B)	107.8
C(19)-C(25)-C(24)	113.6(8)	C(19)-C(25)-H(25A)	108.8
C(24)-C(25)-H(25A)	108.8	C(19)-C(25)-H(25B)	108.8
C(24)-C(25)-H(25B)	108.8	H(25A)-C(25)-H(25B)	107.7
C(22)-C(905)-C(21)	112.9(8)	C(22)-C(905)-H(90A)	109.0
C(21)-C(905)-H(90A)	109.0	C(22)-C(905)-H(90B)	109.0
C(21)-C(905)-H(90B)	109.0	H(90A)-C(905)-H(90B)	107.8
C(10)-C(997)-C(6)	120.8(8)	C(10)-C(997)-C(3)	122.7(7)
C(6)-C(997)-C(3)	116.4(7)	C(45)-Ir(2)-C(46)	39.3(4)
C(45)-Ir(2)-C(49)	94.5(4)	C(46)-Ir(2)-C(49)	81.4(4)
C(45)-Ir(2)-C(50)	81.1(3)	C(46)-Ir(2)-C(50)	92.4(4)
C(49)-Ir(2)-C(50)	36.8(4)	C(45)-Ir(2)-P(997)	97.5(2)
C(46)-Ir(2)-P(997)	97.9(2)	C(49)-Ir(2)-P(997)	159.8(3)
C(50)-Ir(2)-P(997)	162.0(3)	C(45)-Ir(2)-Cl(2)	160.3(3)
C(46)-Ir(2)-Cl(2)	159.9(3)	C(49)-Ir(2)-Cl(2)	89.0(3)
C(50)-Ir(2)-Cl(2)	90.4(3)	P(997)-Ir(2)-Cl(2)	85.06(7)
C(31)-P(997)-C(30)	97.0(4)	C(31)-P(997)-C(26)	96.2(4)
C(30)-P(997)-C(26)	101.4(4)	C(31)-P(997)-Ir(2)	126.4(3)
C(30)-P(997)-Ir(2)	115.6(3)	C(26)-P(997)-Ir(2)	115.7(3)
C(41)-Si(3)-C(39)	108.3(5)	C(41)-Si(3)-C(26)	111.6(5)
C(39)-Si(3)-C(26)	109.4(4)	C(41)-Si(3)-C(40)	110.8(6)
C(39)-Si(3)-C(40)	104.4(5)	C(26)-Si(3)-C(40)	112.1(5)
C(43)-Si(4)-C(44)	109.0(5)	C(43)-Si(4)-C(42)	105.2(5)
C(44)-Si(4)-C(42)	110.0(5)	C(43)-Si(4)-C(30)	113.7(4)
C(44)-Si(4)-C(30)	109.9(4)	C(42)-Si(4)-C(30)	109.0(4)
C(27)-C(26)-P(997)	111.2(6)	C(27)-C(26)-Si(3)	122.4(6)
P(997)-C(26)-Si(3)	126.2(5)	C(26)-C(27)-C(37)	126.5(8)
C(26)-C(27)-C(28)	119.0(7)	C(37)-C(27)-C(28)	114.5(7)
C(36)-C(28)-C(27)	109.3(7)	C(36)-C(28)-C(29)	108.3(7)
C(27)-C(28)-C(29)	108.6(7)	C(36)-C(28)-H(28)	110.2
C(27)-C(28)-H(28)	110.2	C(29)-C(28)-H(28)	110.2
C(30)-C(29)-C(38)	127.6(8)	C(30)-C(29)-C(28)	118.0(7)
C(38)-C(29)-C(28)	114.4(7)	C(29)-C(30)-P(997)	111.8(6)
C(29)-C(30)-Si(4)	120.7(6)	P(997)-C(30)-Si(4)	127.4(4)
C(32)-C(31)-C(36)	120.3(7)	C(32)-C(31)-P(997)	128.8(6)
C(36)-C(31)-P(997)	110.9(6)	C(31)-C(32)-C(33)	119.2(8)

C(31)-C(32)-H(32)	120.4	C(33)-C(32)-H(32)	120.4
C(34)-C(33)-C(32)	120.4(8)	C(34)-C(33)-H(33)	119.8
C(32)-C(33)-H(33)	119.8	C(33)-C(34)-C(35)	120.4(8)
C(33)-C(34)-H(34)	119.8	C(35)-C(34)-H(34)	119.8
C(36)-C(35)-C(34)	121(1)	C(36)-C(35)-H(35)	119.7
C(34)-C(35)-H(35)	119.7	C(35)-C(36)-C(31)	119.0(8)
C(35)-C(36)-C(28)	124.1(8)	C(31)-C(36)-C(28)	116.9(7)
C(27)-C(37)-H(37A)	109.5	C(27)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5	C(27)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5	H(37B)-C(37)-H(37C)	109.5
C(29)-C(38)-H(38A)	109.5	C(29)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5	C(29)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5	H(38B)-C(38)-H(38C)	109.5
Si(3)-C(39)-H(39A)	109.5	Si(3)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5	Si(3)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5	H(39B)-C(39)-H(39C)	109.5
Si(3)-C(40)-H(40A)	109.5	Si(3)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5	Si(3)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5	H(40B)-C(40)-H(40C)	109.5
Si(3)-C(41)-H(41A)	109.5	Si(3)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5	Si(3)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5	H(41B)-C(41)-H(41C)	109.5
Si(4)-C(42)-H(42A)	109.5	Si(4)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5	Si(4)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5	H(42B)-C(42)-H(42C)	109.5
Si(4)-C(43)-H(43A)	109.5	Si(4)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5	Si(4)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5	H(43B)-C(43)-H(43C)	109.5
Si(4)-C(44)-H(44A)	109.5	Si(4)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5	Si(4)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5	H(44B)-C(44)-H(44C)	109.5
C(46)-C(45)-C(52)	123(1)	C(46)-C(45)-Ir(2)	70.4(5)
C(52)-C(45)-Ir(2)	113.2(6)	C(46)-C(45)-H(45)	118.8
C(52)-C(45)-H(45)	118.8	Ir(2)-C(45)-H(45)	86.5
C(45)-C(46)-C(47)	123(1)	C(45)-C(46)-Ir(2)	70.3(5)
C(47)-C(46)-Ir(2)	113.2(6)	C(45)-C(46)-H(46)	118.3
C(47)-C(46)-H(46)	118.3	Ir(2)-C(46)-H(46)	86.5
C(48)-C(47)-C(46)	115(1)	C(48)-C(47)-H(47A)	108.6
C(46)-C(47)-H(47A)	108.6	C(48)-C(47)-H(47B)	108.6
C(46)-C(47)-H(47B)	108.6	H(47A)-C(47)-H(47B)	107.5
C(47)-C(48)-C(49)	116(1)	C(47)-C(48)-H(48A)	108.2
C(49)-C(48)-H(48A)	108.2	C(47)-C(48)-H(48B)	108.2
C(49)-C(48)-H(48B)	108.2	H(48A)-C(48)-H(48B)	107.4
C(50)-C(49)-C(48)	125(1)	C(50)-C(49)-Ir(2)	71.8(5)
C(48)-C(49)-Ir(2)	111.1(7)	C(50)-C(49)-H(49)	117.4
C(48)-C(49)-H(49)	117.4	Ir(2)-C(49)-H(49)	87.0
C(49)-C(50)-C(51)	125(1)	C(49)-C(50)-Ir(2)	71.4(5)
C(51)-C(50)-Ir(2)	111.4(7)	C(49)-C(50)-H(50)	117.7
C(51)-C(50)-H(50)	117.7	Ir(2)-C(50)-H(50)	87.1
C(52)-C(51)-C(50)	116(1)	C(52)-C(51)-H(51A)	108.3
C(50)-C(51)-H(51A)	108.3	C(52)-C(51)-H(51B)	108.3
C(50)-C(51)-H(51B)	108.3	H(51A)-C(51)-H(51B)	107.4
C(51)-C(52)-C(45)	116(1)	C(51)-C(52)-H(52A)	108.2
C(45)-C(52)-H(52A)	108.2	C(51)-C(52)-H(52B)	108.2
C(45)-C(52)-H(52B)	108.2	H(52A)-C(52)-H(52B)	107.4

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb484

atom	U11	U22	U33	U23	U13	U12
Ir(1)	21(1)	22(1)	21(1)	3(1)	3(1)	1(1)
Cl(1)	33(1)	29(1)	38(1)	3(1)	7(1)	12(1)

P(1)	19(1)	21(1)	17(1)	2(1)	1(1)	3(1)
Si(1)	24(1)	31(1)	19(1)	5(1)	-1(1)	5(1)
Si(2)	27(1)	27(1)	18(1)	0(1)	0(1)	5(1)
C(1)	18(3)	22(3)	21(4)	8(3)	6(3)	1(3)
C(2)	22(4)	28(4)	24(4)	5(3)	2(3)	3(3)
C(3)	22(4)	26(4)	22(4)	3(3)	5(3)	1(3)
C(4)	33(4)	25(4)	21(4)	4(3)	8(3)	8(3)
C(5)	23(4)	21(3)	17(3)	4(3)	2(3)	4(3)
C(6)	26(4)	22(3)	15(3)	2(3)	0(3)	2(3)
C(7)	24(4)	31(4)	20(4)	2(3)	2(3)	0(3)
C(8)	30(4)	29(4)	33(5)	4(3)	10(4)	9(3)
C(9)	45(5)	23(4)	26(4)	5(3)	2(4)	3(3)
C(10)	34(4)	23(4)	23(4)	10(3)	7(3)	0(3)
C(11)	20(4)	31(4)	39(5)	4(4)	-1(3)	5(3)
C(12)	34(5)	31(4)	29(5)	4(3)	11(4)	6(3)
C(13)	49(6)	48(6)	27(5)	7(4)	-1(4)	22(5)
C(14)	28(5)	67(7)	24(5)	6(4)	1(4)	3(4)
C(15)	44(6)	50(6)	37(6)	-4(5)	-8(5)	1(5)
C(16)	29(5)	73(8)	26(5)	5(5)	3(4)	0(5)
C(17)	47(6)	28(4)	34(5)	-2(4)	3(4)	11(4)
C(18)	41(6)	48(6)	31(5)	8(4)	-8(4)	5(4)
C(19)	30(4)	28(4)	16(4)	3(3)	4(3)	10(3)
C(20)	22(4)	28(4)	33(5)	5(3)	2(3)	1(3)
C(21)	22(4)	42(5)	46(6)	6(4)	-3(4)	1(4)
C(22)	30(4)	25(4)	32(5)	1(3)	2(4)	-5(3)
C(23)	19(4)	34(4)	33(5)	10(4)	1(3)	-1(3)
C(24)	40(5)	40(5)	32(5)	9(4)	5(4)	-2(4)
C(25)	44(6)	39(5)	35(5)	4(4)	11(4)	6(4)
C(905)	26(5)	42(5)	48(6)	9(5)	-3(4)	-7(4)
C(997)	26(4)	23(3)	18(4)	6(3)	1(3)	0(3)
Ir(2)	20(1)	22(1)	21(1)	4(1)	5(1)	4(1)
Cl(2)	27(1)	25(1)	29(1)	7(1)	9(1)	4(1)
P(997)	21(1)	20(1)	16(1)	3(1)	2(1)	3(1)
Si(3)	34(1)	28(1)	22(1)	5(1)	-4(1)	4(1)
Si(4)	23(1)	25(1)	19(1)	3(1)	0(1)	1(1)
C(26)	25(4)	21(3)	20(4)	6(3)	0(3)	4(3)
C(27)	33(4)	22(3)	17(4)	4(3)	5(3)	4(3)
C(28)	25(4)	28(4)	17(4)	2(3)	4(3)	5(3)
C(29)	23(4)	24(4)	21(4)	3(3)	4(3)	4(3)
C(30)	18(3)	26(4)	19(4)	2(3)	1(3)	3(3)
C(31)	22(4)	18(3)	20(4)	2(3)	-3(3)	3(3)
C(32)	28(4)	23(4)	20(4)	3(3)	-2(3)	3(3)
C(33)	32(4)	27(4)	25(4)	10(3)	-1(3)	2(3)
C(34)	44(5)	24(4)	29(5)	6(3)	-3(4)	8(4)
C(35)	40(5)	26(4)	21(4)	2(3)	-2(3)	13(3)
C(36)	28(4)	21(3)	19(4)	2(3)	-2(3)	7(3)
C(37)	43(5)	34(5)	31(5)	3(4)	15(4)	8(4)
C(38)	25(4)	38(5)	36(5)	10(4)	5(4)	9(3)
C(39)	47(6)	44(5)	24(5)	-2(4)	-8(4)	-1(4)
C(40)	41(6)	71(8)	36(6)	3(5)	-6(5)	14(5)
C(41)	63(7)	33(5)	43(6)	7(4)	-14(5)	3(5)
C(42)	39(5)	39(5)	31(5)	7(4)	-7(4)	6(4)
C(43)	34(5)	57(6)	27(5)	-2(4)	-1(4)	6(4)
C(44)	37(5)	30(4)	38(6)	-1(4)	-4(4)	-4(4)
C(45)	19(4)	27(4)	35(5)	6(3)	6(3)	2(3)
C(46)	30(4)	29(4)	27(4)	12(3)	15(3)	4(3)
C(47)	70(8)	49(6)	35(6)	9(5)	20(6)	-4(6)
C(48)	150(20)	60(10)	34(7)	19(6)	40(10)	50(10)
C(49)	43(5)	30(4)	34(5)	-1(4)	15(4)	10(4)
C(50)	24(4)	33(4)	50(6)	8(4)	10(4)	11(3)
C(51)	34(6)	42(6)	140(10)	17(8)	23(8)	9(5)
C(52)	22(4)	40(5)	80(10)	10(6)	4(5)	5(4)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb484

atom	x	y	z	U(eq)
H(3)	1550	-492.0000	7469	29
H(7)	5496	-518	6312	31
H(8)	5155	-2199	6360	36
H(9)	3508	-2939.0002	6825	38
H(10)	2183	-2037	7271	32
H(11A)	518	741	6168	44
H(11B)	253	401	6924	44
H(11C)	430	-374	6298	44
H(12A)	2566	1145	8885	47
H(12B)	2260	-7.0000	8744	47
H(12C)	1417	652	8467	47
H(13A)	2210	3118	5989	59
H(13B)	1022	2397	5941	59
H(13C)	1535	2828	5255	59
H(14A)	3583	2073	4603	60
H(14B)	4197	1359	5015	60
H(14C)	4257	2458	5326	60
H(15A)	1103	881	4621	67
H(15B)	1143	103	5171	67
H(15C)	2105	265	4615	67
H(16A)	6307	2679	7850	65
H(16B)	6470	1662	8107	65
H(16C)	6672	2613	8644	65
H(17A)	4573	3562	9056	55
H(17B)	3351	3049	8744	55
H(17C)	4261	3569	8247	55
H(18A)	4578	690	9151	61
H(18B)	4072	1544	9564	61
H(18C)	5411	1599	9538	61
H(19)	5644	891	5692	29
H(20)	6414	943	6818	34
H(21A)	8589	1486	6486	45
H(21B)	8121	1782	7227	45
H(22)	6874	3587	6888	36
H(23)	5889	3526	5858	35
H(24A)	7597	3166	5041	45
H(24B)	6292	2799	4820	45
H(25A)	6804	1361	4769	47
H(25B)	7862	1724	5302	47
H(90A)	8710	3258	6960	48
H(90B)	8664	2936	6143	48
H(28)	7429	5421	2934	28
H(32)	11001	6057	1355	29
H(33)	10825	7708	1494	34
H(34)	9355	8194	2116	38
H(35)	8106	7077	2665	34
H(37A)	8760	4213	4110	53
H(37B)	7554	4450	3884	53
H(37C)	8593	5310	4086	53
H(38A)	5899	4841	1896	48
H(38B)	5861	4180	2529	48
H(38C)	5809	3696	1745	48
H(39A)	10534	4457	4569	60
H(39B)	11011	5274	4075	60

H(39C)	11821	4582	4346	60
H(40A)	12564	3571	3276	74
H(40B)	12223	4274	2732	74
H(40C)	11853	3129	2576	74
H(41A)	10604	2299	3958	71
H(41B)	9729	2086	3301	71
H(41C)	9392	2619	4013	71
H(42A)	6635	3899	-79	54
H(42B)	6343	4398	656	54
H(42C)	5624	3379	351	54
H(43A)	8033	2521	-234	60
H(43B)	8966	2526	373	60
H(43C)	8845	3509	46	60
H(44A)	6291	1553	682	55
H(44B)	6029	2079	1412	55
H(44C)	7161	1630	1333	55
H(45)	11859	4813	1615	32
H(46)	10650	4578	633	34
H(47A)	11153	4053	-473	63
H(47B)	12437	4146	-202.0000	63
H(48A)	12206	2629	-343	94
H(48B)	10874	2542	-469	94
H(49)	10630	1956	572	42
H(50)	11864	2204	1491	42
H(51A)	13699	3007	1509	83
H(51B)	13626	3016	685	83
H(52A)	13674	4493	817	57
H(52B)	13659	4471	1641	57

II.25. Crystallographic data for IV-62

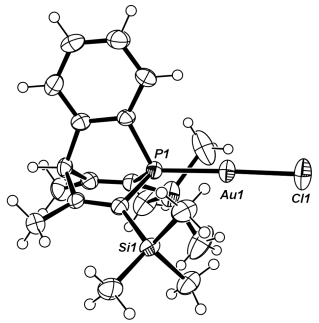


Table 1. Crystal data for mb708

Compound	mb708
Molecular formula	$2(C_{19}H_{29}AuClPSi_2),C_7H_8$
Molecular weight	1246.11

Crystal habit	Colorless Plate
Crystal dimensions(mm)	0.26x0.20x0.18
Crystal system	orthorhombic
Space group	$Pca2_1$
a(Å)	20.048(1)
b(Å)	12.533(1)
c(Å)	20.768(1)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
V(Å^3)	5218.2(6)
Z	4
d(g-cm^{-3})	1.586
F(000)	2456
μ(cm^{-1})	5.900
Absorption corrections	multi-scan ; 0.3091 min, 0.4164 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	29.95
HKL ranges	-28 19 ; -17 15 ; -23 29
Reflections measured	29978
Unique data	11692
Rint	0.0557
Reflections used	9301
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	513
Reflections / parameter	18
wR2	0.1012
R1	0.0405
Flack's parameter	0.016(6)
Weights a, b	0.0496 ; 0.0000
GoF	1.042
difference peak / hole (e Å^{-3})	2.114(0.135) / -1.948(0.135)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb708

atom	x	y	z	U(eq)
Au(1)	2376(1)	10358(1)	632(1)	36(1)
Cl(1)	1472(1)	11442(2)	502(1)	62(1)
P(1)	3280(1)	9341(1)	698(1)	27(1)
Si(1)	3381(1)	9710(2)	-820(1)	31(1)
Si(2)	2409(1)	7472(2)	1299(1)	46(1)
C(1)	3747(3)	9155(5)	-53(3)	27(1)
C(2)	4307(3)	8582(5)	55(3)	27(1)

C(3)	4446(3)	8193(5)	747(3)	31(1)
C(4)	3852(3)	7534(5)	985(3)	32(1)
C(5)	3244(3)	7967(5)	1011(3)	32(2)
C(6)	4827(3)	8280(7)	-430(4)	39(2)
C(7)	4044(4)	6396(6)	1182(4)	47(2)
C(8)	3951(3)	9835(6)	1207(3)	29(1)
C(9)	3936(4)	10744(6)	1575(3)	35(2)
C(10)	4511(4)	11020(7)	1920(4)	46(2)
C(11)	5070(4)	10392(7)	1890(4)	43(2)
C(12)	5076(3)	9465(6)	1512(4)	38(2)
C(13)	4510(3)	9177(6)	1173(3)	30(1)
C(14)	3335(4)	11206(6)	-740(4)	45(2)
C(15)	3859(4)	9403(7)	-1568(4)	50(2)
C(16)	2534(4)	9109(6)	-929(5)	45(2)
C(17)	2125(6)	8360(8)	1970(6)	81(4)
C(18)	2437(4)	6086(7)	1636(5)	58(2)
C(19)	1823(4)	7475(8)	590(7)	77(3)
Au(2)	184(1)	5550(1)	3559(1)	42(1)
Cl(2)	263(2)	6855(2)	2798(1)	77(1)
P(2)	213(1)	4361(1)	4345(1)	29(1)
Si(10)	-458(1)	2589(2)	3467(1)	48(1)
Si(99)	1794(1)	4748(2)	4274(1)	38(1)
C(20)	1048(3)	4121(5)	4686(3)	31(1)
C(21)	1011(3)	3476(5)	5201(4)	32(2)
C(22)	325(3)	3054(6)	5386(4)	36(2)
C(23)	-5(3)	2450(6)	4829(4)	35(2)
C(24)	-101(3)	2987(6)	4271(4)	38(2)
C(25)	1559(3)	3136(6)	5639(5)	48(2)
C(26)	-194(4)	1313(6)	4972(5)	48(2)
C(27)	-220(3)	4743(6)	5066(4)	31(2)
C(28)	-617(3)	5630(6)	5184(4)	39(2)
C(29)	-880(4)	5819(7)	5789(4)	46(2)
C(30)	-741(4)	5118(8)	6288(4)	48(2)
C(31)	-363(4)	4197(8)	6180(4)	45(2)
C(32)	-108(3)	4011(6)	5574(4)	35(1)
C(33)	1741(4)	6228(7)	4349(5)	57(2)
C(34)	2603(4)	4290(10)	4619(6)	71(3)
C(35)	1787(5)	4413(7)	3402(4)	60(3)
C(36)	179(5)	2800(10)	2826(4)	62(3)
C(37)	-739(4)	1179(8)	3418(6)	72(3)
C(38)	-1210(5)	3440(10)	3310(6)	86(4)
C(39)	3646(5)	1750(10)	3553(6)	81(3)
C(40)	3196(5)	2080(10)	3006(5)	64(3)
C(41)	3264(6)	3063(8)	2692(6)	80(3)
C(42)	2890(10)	3380(10)	2216(6)	109(6)
C(43)	2380(10)	2730(20)	1994(6)	130(10)
C(44)	2282(6)	1770(10)	2263(6)	95(5)
C(45)	2698(5)	1400(10)	2775(5)	69(3)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb708

Au(1)-P(1)	2.220(2)	Au(1)-Cl(1)	2.282(2)
P(1)-C(8)	1.820(7)	P(1)-C(1)	1.834(7)
P(1)-C(5)	1.841(7)	Si(1)-C(15)	1.865(8)
Si(1)-C(16)	1.872(7)	Si(1)-C(14)	1.885(8)
Si(1)-C(1)	1.886(7)	Si(2)-C(17)	1.87(1)
Si(2)-C(18)	1.87(1)	Si(2)-C(5)	1.882(7)
Si(2)-C(19)	1.88(1)	C(1)-C(2)	1.35(1)
C(2)-C(6)	1.50(1)	C(2)-C(3)	1.54(1)
C(3)-C(13)	1.52(1)	C(3)-C(4)	1.53(1)
C(4)-C(5)	1.34(1)	C(4)-C(7)	1.53(1)

C(8)-C(9)	1.37(1)	C(8)-C(13)	1.39(1)
C(9)-C(10)	1.40(1)	C(10)-C(11)	1.37(1)
C(11)-C(12)	1.40(1)	C(12)-C(13)	1.38(1)
Au(2)-P(2)	2.210(2)	Au(2)-Cl(2)	2.280(3)
P(2)-C(27)	1.797(8)	P(2)-C(24)	1.841(8)
P(2)-C(20)	1.841(7)	Si(10)-C(37)	1.86(1)
Si(10)-C(36)	1.86(1)	Si(10)-C(38)	1.87(1)
Si(10)-C(24)	1.884(8)	Si(99)-C(35)	1.86(1)
Si(99)-C(34)	1.86(1)	Si(99)-C(33)	1.86(1)
Si(99)-C(20)	1.895(7)	C(20)-C(21)	1.34(1)
C(21)-C(25)	1.49(1)	C(21)-C(22)	1.52(1)
C(22)-C(32)	1.53(1)	C(22)-C(23)	1.53(1)
C(23)-C(24)	1.35(1)	C(23)-C(26)	1.50(1)
C(27)-C(28)	1.39(1)	C(27)-C(32)	1.41(1)
C(28)-C(29)	1.38(1)	C(29)-C(30)	1.39(1)
C(30)-C(31)	1.40(1)	C(31)-C(32)	1.38(1)
C(39)-C(40)	1.51(1)	C(40)-C(45)	1.40(1)
C(40)-C(41)	1.40(1)	C(41)-C(42)	1.30(2)
C(42)-C(43)	1.39(3)	C(43)-C(44)	1.34(2)
C(44)-C(45)	1.43(2)		

P(1)-Au(1)-Cl(1)	176.29(8)	C(8)-P(1)-C(1)	99.2(3)
C(8)-P(1)-C(5)	98.2(3)	C(1)-P(1)-C(5)	101.6(3)
C(8)-P(1)-Au(1)	116.4(2)	C(1)-P(1)-Au(1)	115.9(2)
C(5)-P(1)-Au(1)	121.8(2)	C(15)-Si(1)-C(16)	106.4(4)
C(15)-Si(1)-C(14)	107.7(4)	C(16)-Si(1)-C(14)	111.5(4)
C(15)-Si(1)-C(1)	115.3(3)	C(16)-Si(1)-C(1)	107.8(3)
C(14)-Si(1)-C(1)	108.1(3)	C(17)-Si(2)-C(18)	106.4(5)
C(17)-Si(2)-C(5)	108.2(4)	C(18)-Si(2)-C(5)	113.5(4)
C(17)-Si(2)-C(19)	112.9(6)	C(18)-Si(2)-C(19)	108.2(4)
C(5)-Si(2)-C(19)	107.8(4)	C(2)-C(1)-P(1)	110.5(5)
C(2)-C(1)-Si(1)	131.2(5)	P(1)-C(1)-Si(1)	118.3(3)
C(1)-C(2)-C(6)	127.0(6)	C(1)-C(2)-C(3)	118.1(6)
C(6)-C(2)-C(3)	114.9(5)	C(13)-C(3)-C(4)	108.4(5)
C(13)-C(3)-C(2)	107.5(5)	C(4)-C(3)-C(2)	109.3(5)
C(5)-C(4)-C(3)	120.3(6)	C(5)-C(4)-C(7)	126.5(6)
C(3)-C(4)-C(7)	113.2(6)	C(4)-C(5)-P(1)	109.3(5)
C(4)-C(5)-Si(2)	133.7(6)	P(1)-C(5)-Si(2)	117.1(4)
C(9)-C(8)-C(13)	122.5(6)	C(9)-C(8)-P(1)	126.1(5)
C(13)-C(8)-P(1)	111.4(5)	C(8)-C(9)-C(10)	118.1(7)
C(11)-C(10)-C(9)	120.5(8)	C(10)-C(11)-C(12)	120.6(7)
C(13)-C(12)-C(11)	119.6(7)	C(12)-C(13)-C(8)	118.7(7)
C(12)-C(13)-C(3)	125.1(6)	C(8)-C(13)-C(3)	116.1(6)
P(2)-Au(2)-Cl(2)	173.4(1)	C(27)-P(2)-C(24)	98.8(3)
C(27)-P(2)-C(20)	99.4(3)	C(24)-P(2)-C(20)	100.9(3)
C(27)-P(2)-Au(2)	115.0(2)	C(24)-P(2)-Au(2)	124.1(3)
C(20)-P(2)-Au(2)	114.7(2)	C(37)-Si(10)-C(36)	107.9(5)
C(37)-Si(10)-C(38)	106.6(5)	C(36)-Si(10)-C(38)	110.2(6)
C(37)-Si(10)-C(24)	114.6(5)	C(36)-Si(10)-C(24)	109.5(4)
C(38)-Si(10)-C(24)	108.0(4)	C(35)-Si(99)-C(34)	108.2(5)
C(35)-Si(99)-C(33)	107.8(4)	C(34)-Si(99)-C(33)	108.9(5)
C(35)-Si(99)-C(20)	109.9(4)	C(34)-Si(99)-C(20)	112.6(4)
C(33)-Si(99)-C(20)	109.3(3)	C(21)-C(20)-P(2)	110.8(5)
C(21)-C(20)-Si(99)	130.8(5)	P(2)-C(20)-Si(99)	118.4(4)
C(20)-C(21)-C(25)	128.2(6)	C(20)-C(21)-C(22)	117.4(6)
C(25)-C(21)-C(22)	114.3(6)	C(21)-C(22)-C(32)	107.7(6)
C(21)-C(22)-C(23)	111.7(6)	C(32)-C(22)-C(23)	109.6(5)
C(24)-C(23)-C(26)	127.1(7)	C(24)-C(23)-C(22)	117.5(6)
C(26)-C(23)-C(22)	115.4(7)	C(23)-C(24)-P(2)	110.2(5)
C(23)-C(24)-Si(10)	132.9(6)	P(2)-C(24)-Si(10)	116.8(5)
C(28)-C(27)-C(32)	118.6(7)	C(28)-C(27)-P(2)	129.6(6)
C(32)-C(27)-P(2)	111.8(5)	C(29)-C(28)-C(27)	121.1(8)

C(28)-C(29)-C(30)	119.5(8)	C(29)-C(30)-C(31)	120.9(8)
C(32)-C(31)-C(30)	119.1(8)	C(31)-C(32)-C(27)	120.8(7)
C(31)-C(32)-C(22)	125.1(7)	C(27)-C(32)-C(22)	114.1(6)
C(45)-C(40)-C(41)	117(1)	C(45)-C(40)-C(39)	121(1)
C(41)-C(40)-C(39)	122(1)	C(42)-C(41)-C(40)	125(2)
C(41)-C(42)-C(43)	119(2)	C(44)-C(43)-C(42)	120(1)
C(43)-C(44)-C(45)	121(2)	C(40)-C(45)-C(44)	118(1)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb708

atom	U11	U22	U33	U23	U13	U12
Au(1)	28(1)	34(1)	45(1)	6(1)	1(1)	5(1)
Cl(1)	43(1)	65(1)	78(2)	14(1)	1(1)	24(1)
P(1)	25(1)	23(1)	33(1)	1(1)	0(1)	-1(1)
Si(1)	33(1)	30(1)	31(1)	2(1)	-7(1)	-4(1)
Si(2)	35(1)	36(1)	67(2)	18(1)	4(1)	-4(1)
C(1)	28(3)	22(3)	32(4)	1(3)	-4(3)	-2(2)
C(2)	25(3)	26(3)	31(3)	-3(3)	-4(3)	-2(2)
C(3)	28(3)	28(3)	38(4)	3(3)	-3(3)	7(2)
C(4)	36(3)	23(4)	36(4)	0(3)	-4(3)	1(3)
C(5)	33(3)	23(4)	39(4)	1(3)	0(3)	-6(3)
C(6)	35(4)	41(4)	40(4)	-3(3)	2(3)	4(3)
C(7)	52(4)	29(4)	59(5)	5(4)	-2(4)	8(3)
C(8)	28(3)	26(3)	32(3)	-3(3)	-1(3)	-6(3)
C(9)	45(4)	27(4)	33(4)	-2(3)	4(3)	-2(3)
C(10)	49(4)	43(5)	45(5)	-10(4)	-1(4)	-7(4)
C(11)	44(4)	54(5)	32(4)	-1(3)	-11(3)	-9(4)
C(12)	29(3)	51(5)	33(4)	6(4)	-1(3)	-1(3)
C(13)	34(3)	24(3)	33(4)	2(3)	-3(3)	-5(3)
C(14)	54(4)	33(4)	49(5)	5(4)	-15(4)	-5(3)
C(15)	52(5)	73(6)	27(4)	0(4)	-3(3)	5(4)
C(16)	43(4)	32(4)	61(5)	8(4)	-16(4)	-9(3)
C(17)	81(7)	47(6)	110(10)	13(6)	50(7)	13(5)
C(18)	53(5)	46(5)	75(7)	26(5)	-8(4)	-17(4)
C(19)	40(4)	76(7)	120(10)	49(7)	-18(6)	-25(4)
Au(2)	58(1)	35(1)	32(1)	2(1)	-4(1)	13(1)
Cl(2)	140(2)	46(1)	43(1)	11(1)	-10(1)	19(1)
P(2)	30(1)	25(1)	33(1)	1(1)	-1(1)	4(1)
Si(10)	40(1)	48(1)	55(2)	-16(1)	-12(1)	5(1)
Si(99)	34(1)	32(1)	48(1)	-1(1)	9(1)	1(1)
C(20)	32(3)	27(3)	35(4)	-7(3)	1(3)	1(3)
C(21)	32(3)	23(3)	42(4)	5(3)	3(3)	1(3)
C(22)	39(3)	30(4)	37(4)	6(3)	-2(3)	1(3)
C(23)	29(3)	26(3)	51(5)	4(3)	-1(3)	6(3)
C(24)	34(3)	36(4)	44(5)	-12(3)	-4(3)	7(3)
C(25)	44(4)	48(5)	51(5)	9(5)	-8(5)	4(3)
C(26)	43(4)	31(4)	72(6)	1(4)	3(4)	-3(3)
C(27)	29(3)	27(4)	38(4)	0(3)	2(3)	-3(3)
C(28)	29(3)	35(4)	53(5)	-7(4)	0(3)	-2(3)
C(29)	39(4)	40(4)	59(6)	-16(4)	14(4)	-6(3)
C(30)	46(4)	59(6)	40(5)	-14(4)	14(4)	-17(4)
C(31)	48(4)	47(5)	39(4)	-4(4)	9(4)	-8(4)
C(32)	37(3)	33(4)	34(4)	1(3)	5(3)	-8(2)
C(33)	51(5)	38(5)	82(7)	-5(5)	11(5)	-4(4)
C(34)	33(4)	78(8)	100(10)	19(7)	-7(5)	-7(4)
C(35)	65(5)	62(6)	52(6)	-14(4)	26(4)	8(4)
C(36)	80(6)	82(8)	24(4)	-22(5)	1(4)	-14(5)
C(37)	50(5)	63(6)	100(10)	-42(6)	-3(5)	-4(4)
C(38)	75(6)	71(7)	110(10)	-22(7)	-43(7)	17(6)
C(39)	88(7)	92(8)	64(6)	-2(7)	2(7)	20(6)
C(40)	75(7)	62(7)	55(6)	9(5)	23(5)	24(5)

C(41)	108(8)	51(6)	80(8)	1(6)	45(7)	35(6)
C(42)	180(20)	100(10)	54(8)	19(7)	40(10)	90(10)
C(43)	160(10)	200(20)	42(7)	20(10)	16(8)	140(20)
C(44)	68(7)	160(10)	64(8)	-20(10)	18(6)	24(8)
C(45)	70(6)	81(8)	58(6)	6(6)	27(5)	9(6)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb708

atom	x	y	z	U(eq)
H(3)	4865	7760	762	37
H(6A)	4737	8648	-837	58
H(6B)	4816	7507	-500	58
H(6C)	5269	8487	-270	58
H(7A)	4391	6423	1514	70
H(7B)	4211	6009	806	70
H(7C)	3650	6028	1354	70
H(9)	3546	11174	1595	42
H(10)	4514	11646	2177	55
H(11)	5457	10585	2127	52
H(12)	5467	9037	1488	45
H(14A)	3103	11505	-1114	68
H(14B)	3788	11500	-717	68
H(14C)	3091	11391	-346	68
H(15A)	3943	8633	-1592	76
H(15B)	4286	9785	-1560	76
H(15C)	3601	9628	-1944	76
H(16A)	2227	9410	-609	68
H(16B)	2561	8335	-871	68
H(16C)	2370	9270	-1362	68
H(17A)	1885	8974	1791	121
H(17B)	2513	8611	2214	121
H(17C)	1826	7961	2256	121
H(18A)	2560	5583	1295	87
H(18B)	1997	5897	1807	87
H(18C)	2768	6053	1983	87
H(19A)	1731	8213	461	116
H(19B)	1405	7124	710	116
H(19C)	2028	7091	230	116
H(22)	370	2566	5765	43
H(25A)	1973	3494	5514	72
H(25B)	1618	2361	5607	72
H(25C)	1445	3327	6082	72
H(26A)	-476	1289	5357	73
H(26B)	210	891	5044	73
H(26C)	-440	1017	4605	73
H(28)	-709	6114	4844	47
H(29)	-1154	6426	5863	55
H(30)	-905	5265	6707	58
H(31)	-283	3705	6520	54
H(33A)	1756	6427	4805	85
H(33B)	1321	6478	4160	85
H(33C)	2117	6557	4123	85
H(34A)	2970	4538	4347	106
H(34B)	2608	3509	4639	106
H(34C)	2655	4582	5054	106
H(35A)	2174	4741	3191	90
H(35B)	1376	4684	3204	90

H(35C)	1807	3637	3349	90
H(36A)	543	2290	2879	93
H(36B)	357	3531	2860	93
H(36C)	-28.0000	2709	2403	93
H(37A)	-974	1063	3010	108
H(37B)	-1042	1025	3777	108
H(37C)	-352	704	3441	108
H(38A)	-1070	4177	3236	129
H(38B)	-1508	3410	3684	129
H(38C)	-1445	3170	2929	129
H(39A)	3864	2380	3732	122
H(39B)	3985	1251	3393	122
H(39C)	3380	1398	3888	122
H(41)	3605	3531	2838	95
H(42)	2969	4058	2020	131
H(43)	2101	2958	1652	158
H(44)	1930	1329	2112	114
H(45)	2638	704	2953	83

II.26. Crystallographic data for IV-63

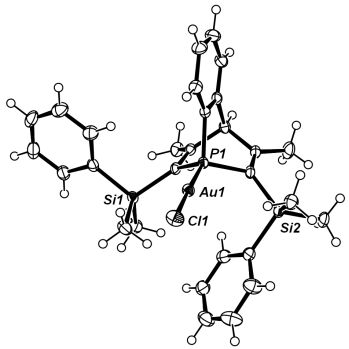


Table 1. Crystal data for mb452

Compound	mb452
Molecular formula	$C_{29}H_{33}AuClPSi_2$
Molecular weight	701.12
Crystal habit	colorless block
Crystal dimensions(mm)	0.24x0.20x0.20
Crystal system	triclinic
Space group	P -1
a(Å)	10.958(1)
b(Å)	11.069(1)
c(Å)	12.221(1)
α(°)	84.408(1)
β(°)	79.109(1)
γ(°)	75.365(1)

V(Å^3)	1406.5(2)
Z	2
d(g-cm^{-3})	1.656
F(000)	692
μ(cm^{-1})	5.483
Absorption corrections	multi-scan ; 0.3528 min, 0.4068 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.00
HKL ranges	-15 15 ; -15 15 ; -17 15
Reflections measured	16677
Unique data	8172
Rint	0.0426
Reflections used	7451
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	313
Reflections / parameter	23
wR2	0.0643
R1	0.0266
Weights a, b	0.0324 ; 0.0000
GoF	1.017
difference peak / hole (e Å^{-3})	1.818(0.128) / -2.066(0.128)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb452

atom	x	y	z	U(eq)
Au(1)	2376(1)	9788(1)	2069(1)	18(1)
Cl(1)	1937(1)	11790(1)	1306(1)	29(1)
P(1)	2669(1)	7861(1)	2856(1)	16(1)
Si(1)	5813(1)	7269(1)	2317(1)	20(1)
Si(2)	1237(1)	7267(1)	1011(1)	19(1)
C(1)	4249(2)	6838(2)	2921(2)	18(1)
C(2)	4142(2)	5736(2)	3461(2)	19(1)
C(3)	2794(2)	5531(2)	3926(2)	20(1)
C(4)	2035(2)	5704(2)	2957(2)	19(1)
C(5)	1900(2)	6778(2)	2341(2)	18(1)
C(6)	1987(2)	7761(2)	4324(2)	18(1)
C(7)	1394(2)	8763(3)	4998(2)	24(1)
C(8)	900(3)	8505(3)	6116(2)	28(1)
C(9)	981(3)	7288(3)	6523(2)	30(1)
C(10)	1586(3)	6291(3)	5849(2)	26(1)
C(11)	2102(2)	6538(2)	4747(2)	19(1)
C(12)	5232(3)	4641(3)	3627(2)	26(1)
C(13)	1516(3)	4598(3)	2848(3)	33(1)
C(14)	6925(3)	5987(3)	1474(2)	28(1)
C(15)	5563(3)	8732(3)	1414(2)	30(1)
C(16)	6527(2)	7553(3)	3527(2)	22(1)

C(17)	7853(3)	7236(3)	3515(2)	28(1)
C(18)	8372(3)	7532(3)	4384(2)	34(1)
C(19)	7580(3)	8144(3)	5277(2)	35(1)
C(20)	6273(3)	8476(3)	5310(2)	35(1)
C(21)	5758(3)	8174(3)	4447(2)	30(1)
C(22)	569(3)	6076(3)	510(2)	28(1)
C(23)	-55(3)	8745(3)	1167(2)	26(1)
C(24)	2648(3)	7472(3)	-67(2)	23(1)
C(25)	3889(3)	6791(3)	10(2)	31(1)
C(26)	4935(3)	6927(4)	-802(2)	39(1)
C(27)	4745(3)	7744(3)	-1715(3)	40(1)
C(28)	3519(3)	8416(3)	-1829(3)	43(1)
C(29)	2496(3)	8288(3)	-1009(2)	35(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb452

Au(1)-P(1)	2.2243(7	Au(1)-Cl(1)	2.2885(7)
P(1)-C(6)	1.812(2)	P(1)-C(1)	1.826(3)
P(1)-C(5)	1.844(2)	Si(1)-C(15)	1.860(3)
Si(1)-C(14)	1.870(3)	Si(1)-C(16)	1.884(3)
Si(1)-C(1)	1.890(2)	Si(2)-C(22)	1.860(3)
Si(2)-C(23)	1.872(3)	Si(2)-C(24)	1.878(3)
Si(2)-C(5)	1.882(3)	C(1)-C(2)	1.351(4)
C(2)-C(12)	1.500(4)	C(2)-C(3)	1.544(3)
C(3)-C(11)	1.526(3)	C(3)-C(4)	1.541(3)
C(3)-H(3)	1.0000	C(4)-C(5)	1.334(4)
C(4)-C(13)	1.502(4)	C(6)-C(11)	1.385(4)
C(6)-C(7)	1.394(3)	C(7)-C(8)	1.401(4)
C(7)-H(7)	0.9500	C(8)-C(9)	1.376(4)
C(8)-H(8)	0.9500	C(9)-C(10)	1.392(4)
C(9)-H(9)	0.9500	C(10)-C(11)	1.388(3)
C(10)-H(10)	0.9500	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800	C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(16)-C(21)	1.396(4)
C(16)-C(17)	1.403(4)	C(17)-C(18)	1.396(4)
C(17)-H(17)	0.9500	C(18)-C(19)	1.376(5)
C(18)-H(18)	0.9500	C(19)-C(20)	1.379(5)
C(19)-H(19)	0.9500	C(20)-C(21)	1.390(4)
C(20)-H(20)	0.9500	C(21)-H(21)	0.9500
C(22)-H(22A)	0.9800	C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800	C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800	C(23)-H(23C)	0.9800
C(24)-C(25)	1.394(4)	C(24)-C(29)	1.401(4)
C(25)-C(26)	1.396(4)	C(25)-H(25)	0.9500
C(26)-C(27)	1.379(5)	C(26)-H(26)	0.9500
C(27)-C(28)	1.387(5)	C(27)-H(27)	0.9500
C(28)-C(29)	1.382(4)	C(28)-H(28)	0.9500
C(29)-H(29)	0.9500		

P(1)-Au(1)-Cl(1)	176.29(2)	C(6)-P(1)-C(1)	98.4(1)
C(6)-P(1)-C(5)	98.9(1)	C(1)-P(1)-C(5)	100.1(1)
C(6)-P(1)-Au(1)	115.0(1)	C(1)-P(1)-Au(1)	123.1(1)
C(5)-P(1)-Au(1)	117.1(1)	C(15)-Si(1)-C(14)	108.6(1)
C(15)-Si(1)-C(16)	107.9(1)	C(14)-Si(1)-C(16)	110.7(1)
C(15)-Si(1)-C(1)	111.7(1)	C(14)-Si(1)-C(1)	110.8(1)
C(16)-Si(1)-C(1)	107.1(1)	C(22)-Si(2)-C(23)	107.6(1)

C(22)-Si(2)-C(24)	107.1(1)	C(23)-Si(2)-C(24)	111.8(1)
C(22)-Si(2)-C(5)	114.3(1)	C(23)-Si(2)-C(5)	111.1(1)
C(24)-Si(2)-C(5)	104.9(1)	C(2)-C(1)-P(1)	110.4(2)
C(2)-C(1)-Si(1)	125.0(2)	P(1)-C(1)-Si(1)	124.5(2)
C(1)-C(2)-C(12)	125.7(2)	C(1)-C(2)-C(3)	119.0(2)
C(12)-C(2)-C(3)	115.3(2)	C(11)-C(3)-C(4)	107.6(2)
C(11)-C(3)-C(2)	108.3(2)	C(4)-C(3)-C(2)	108.8(2)
C(11)-C(3)-H(3)	110.7	C(4)-C(3)-H(3)	110.7
C(2)-C(3)-H(3)	110.7	C(5)-C(4)-C(13)	128.1(2)
C(5)-C(4)-C(3)	118.7(2)	C(13)-C(4)-C(3)	113.2(2)
C(4)-C(5)-P(1)	111.0(2)	C(4)-C(5)-Si(2)	131.3(2)
P(1)-C(5)-Si(2)	117.3(1)	C(11)-C(6)-C(7)	121.0(2)
C(11)-C(6)-P(1)	112.6(2)	C(7)-C(6)-P(1)	126.4(2)
C(6)-C(7)-C(8)	118.4(3)	C(6)-C(7)-H(7)	120.8
C(8)-C(7)-H(7)	120.8	C(9)-C(8)-C(7)	120.3(2)
C(9)-C(8)-H(8)	119.8	C(7)-C(8)-H(8)	119.8
C(8)-C(9)-C(10)	121.0(2)	C(8)-C(9)-H(9)	119.5
C(10)-C(9)-H(9)	119.5	C(11)-C(10)-C(9)	119.0(3)
C(11)-C(10)-H(10)	120.5	C(9)-C(10)-H(10)	120.5
C(6)-C(11)-C(10)	120.1(2)	C(6)-C(11)-C(3)	115.7(2)
C(10)-C(11)-C(3)	124.1(2)	C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	C(21)-C(16)-C(17)	116.8(3)
C(21)-C(16)-Si(1)	120.9(2)	C(17)-C(16)-Si(1)	122.1(2)
C(18)-C(17)-C(16)	121.4(3)	C(18)-C(17)-H(17)	119.3
C(16)-C(17)-H(17)	119.3	C(19)-C(18)-C(17)	120.0(3)
C(19)-C(18)-H(18)	120.0	C(17)-C(18)-H(18)	120.0
C(18)-C(19)-C(20)	120.0(3)	C(18)-C(19)-H(19)	120.0
C(20)-C(19)-H(19)	120.0	C(19)-C(20)-C(21)	119.8(3)
C(19)-C(20)-H(20)	120.1	C(21)-C(20)-H(20)	120.1
C(20)-C(21)-C(16)	121.9(3)	C(20)-C(21)-H(21)	119.0
C(16)-C(21)-H(21)	119.0	Si(2)-C(22)-H(22A)	109.5
Si(2)-C(22)-H(22B)	109.5	H(22A)-C(22)-H(22B)	109.5
Si(2)-C(22)-H(22C)	109.5	H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5	Si(2)-C(23)-H(23A)	109.5
Si(2)-C(23)-H(23B)	109.5	H(23A)-C(23)-H(23B)	109.5
Si(2)-C(23)-H(23C)	109.5	H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5	C(25)-C(24)-C(29)	116.8(3)
C(25)-C(24)-Si(2)	121.8(2)	C(29)-C(24)-Si(2)	121.4(2)
C(24)-C(25)-C(26)	121.8(3)	C(24)-C(25)-H(25)	119.1
C(26)-C(25)-H(25)	119.1	C(27)-C(26)-C(25)	119.7(3)
C(27)-C(26)-H(26)	120.2	C(25)-C(26)-H(26)	120.2
C(26)-C(27)-C(28)	120.0(3)	C(26)-C(27)-H(27)	120.0
C(28)-C(27)-H(27)	120.0	C(29)-C(28)-C(27)	119.7(3)
C(29)-C(28)-H(28)	120.2	C(27)-C(28)-H(28)	120.2
C(28)-C(29)-C(24)	122.1(3)	C(28)-C(29)-H(29)	119.0
C(24)-C(29)-H(29)	119.0		

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb452

atom	U11	U22	U33	U23	U13	U12

Au(1)	19(1)	16(1)	20(1)	-2(1)	-2(1)	-6(1)
Cl(1)	34(1)	20(1)	32(1)	2(1)	-2(1)	-6(1)
P(1)	14(1)	16(1)	18(1)	-3(1)	-2(1)	-5(1)
Si(1)	15(1)	24(1)	21(1)	-5(1)	0(1)	-6(1)
Si(2)	17(1)	22(1)	21(1)	-4(1)	-5(1)	-6(1)
C(1)	13(1)	21(1)	20(1)	-5(1)	-3(1)	-3(1)
C(2)	17(1)	21(1)	19(1)	-5(1)	-4(1)	-3(1)
C(3)	17(1)	18(1)	24(1)	-1(1)	-4(1)	-4(1)
C(4)	15(1)	19(1)	23(1)	-5(1)	-3(1)	-4(1)
C(5)	15(1)	19(1)	22(1)	-5(1)	-4(1)	-6(1)
C(6)	15(1)	21(1)	19(1)	-3(1)	-2(1)	-6(1)
C(7)	20(1)	24(1)	26(1)	-6(1)	-4(1)	-2(1)
C(8)	25(1)	34(2)	23(1)	-10(1)	0(1)	-2(1)
C(9)	25(1)	42(2)	21(1)	1(1)	0(1)	-7(1)
C(10)	20(1)	33(2)	24(1)	1(1)	-3(1)	-8(1)
C(11)	14(1)	22(1)	22(1)	-2(1)	-4(1)	-5(1)
C(12)	21(1)	24(1)	31(1)	-5(1)	-7(1)	0(1)
C(13)	41(2)	27(2)	39(2)	1(1)	-16(1)	-19(1)
C(14)	20(1)	37(2)	28(1)	-11(1)	1(1)	-7(1)
C(15)	24(1)	36(2)	29(1)	2(1)	1(1)	-12(1)
C(16)	21(1)	21(1)	24(1)	1(1)	-4(1)	-9(1)
C(17)	25(1)	30(2)	30(1)	0(1)	-5(1)	-10(1)
C(18)	34(2)	35(2)	41(2)	4(1)	-16(1)	-17(1)
C(19)	55(2)	31(2)	32(2)	2(1)	-19(1)	-23(2)
C(20)	49(2)	28(2)	28(1)	-5(1)	-6(1)	-12(1)
C(21)	30(2)	30(2)	30(1)	-6(1)	-3(1)	-5(1)
C(22)	28(1)	33(2)	30(1)	-9(1)	-8(1)	-14(1)
C(23)	24(1)	27(2)	28(1)	-2(1)	-7(1)	-5(1)
C(24)	25(1)	25(1)	22(1)	-6(1)	-2(1)	-10(1)
C(25)	25(1)	45(2)	23(1)	-3(1)	-4(1)	-8(1)
C(26)	22(1)	68(3)	28(1)	-10(2)	-2(1)	-13(2)
C(27)	41(2)	47(2)	33(2)	-11(1)	9(1)	-22(2)
C(28)	52(2)	36(2)	32(2)	6(1)	5(1)	-9(2)
C(29)	34(2)	32(2)	33(2)	4(1)	-1(1)	-3(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb452

atom	x	y	z	U(eq)
H(3)	2852	4678	4300	23
H(7)	1327	9600	4708	28
H(8)	507	9173	6595	34
H(9)	617	7127	7276	36
H(10)	1646	5454	6139	31
H(12A)	5362	4053	3042	39
H(12B)	5033	4221	4359	39
H(12C)	6012	4933	3589	39
H(13A)	964	4799	2278	49
H(13B)	1017	4393	3565	49
H(13C)	2227	3879	2629	49
H(14A)	6427	5563	1121	42
H(14B)	7422	5385	1963	42
H(14C)	7507	6341	897	42
H(15A)	6394	8900	1080	45
H(15B)	5055	9431	1864	45
H(15C)	5108	8638	820	45
H(17)	8408	6812	2903	33
H(18)	9272	7310	4359	41

H(19)	7932	8338	5872	42
H(20)	5727	8909	5921	41
H(21)	4856	8398	4484	36
H(22A)	-186	5958	1043	42
H(22B)	1217	5281	443	42
H(22C)	324	6361	-220	42
H(23A)	-525	8869	542	39
H(23B)	329	9453	1171	39
H(23C)	-644.9999	8686	1870	39
H(25)	4027	6218	631	37
H(26)	5773	6459	-726	47
H(27)	5454	7847	-2266	47
H(28)	3383	8962	-2468	51
H(29)	1663	8769	-1087	42

II.27. Crystallographic data for IV-65

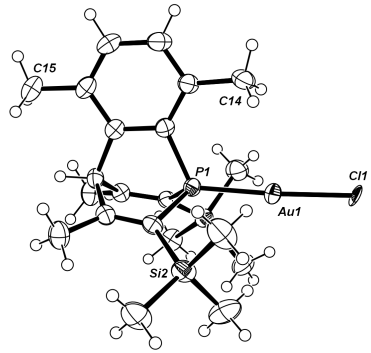


Table 1. Crystal data for mb823

Compound	mb823
Molecular formula	$C_{21}H_{33}AuBr_{0.40}Cl_{0.60}PSi_2$
Molecular weight	622.82
Crystal habit	Colorless Block
Crystal dimensions(mm)	0.20x0.20x0.10
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	11.741(1)
b(Å)	16.567(1)
c(Å)	15.795(1)
α(°)	90.00
β(°)	124.649(4)

γ(°)	90.00
V(Å^3)	2527.5(3)
Z	4
d(g-cm^{-3})	1.637
F(000)	1221
μ(cm^{-1})	6.678
Absorption corrections	multi-scan ; 0.3485 min, 0.5548 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-16 11 ; -20 23 ; -21 22
Reflections measured	25123
Unique data	7349
Rint	0.0525
Reflections used	5562
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	254
Reflections / parameter	21
wR2	0.0628
R1	0.0295
Weights a, b	0.0227 ; 0.0000
GoF	0.991
difference peak / hole (e Å^{-3})	0.683(0.112) / -1.097(0.112)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb823

atom	x	y	z	U(eq)
Au(1)	4730(1)	-3520(1)	6633(1)	29(1)
Cl(1)	6900(10)	-4021(8)	7550(10)	32(1)
Br(1)	7064(6)	-4020(4)	7468(5)	34(1)
P(1)	2584(1)	-3027(1)	5805(1)	25(1)
Si(1)	3926(1)	-1270(1)	6033(1)	31(1)
Si(2)	1819(1)	-4174(1)	3926(1)	38(1)
C(1)	2384(3)	-1935(2)	5604(2)	26(1)
C(2)	1048(3)	-1735(2)	5135(2)	27(1)
C(3)	-20(3)	-2408(2)	4823(2)	29(1)
C(4)	60(3)	-3045(2)	4154(2)	29(1)
C(5)	1271(3)	-3398(2)	4507(2)	28(1)
C(6)	459(3)	-900(2)	4942(3)	40(1)
C(7)	-1307(3)	-3225(2)	3165(3)	44(1)
C(8)	326(3)	-2816(2)	5804(2)	28(1)
C(9)	1636(3)	-3173(2)	6396(2)	27(1)
C(10)	2081(3)	-3573(2)	7312(3)	32(1)
C(11)	1186(4)	-3579(2)	7621(3)	40(1)
C(12)	-119(3)	-3225(2)	7028(3)	40(1)
C(13)	-584(3)	-2847(2)	6110(3)	35(1)

C(14)	3451(4)	-4019(2)	7957(3)	48(1)
C(15)	-2024(3)	-2492(2)	5463(3)	47(1)
C(16)	5004(3)	-1187(3)	7458(3)	47(1)
C(17)	3432(3)	-237(2)	5468(3)	41(1)
C(18)	4965(4)	-1732(2)	5598(3)	43(1)
C(19)	3270(5)	-3751(3)	3918(4)	65(1)
C(20)	432(4)	-4420(3)	2565(3)	58(1)
C(21)	2344(4)	-5105(2)	4716(3)	56(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for mb823

Au(1)-P(1)	2.2313(7	Au(1)-Cl(1)	2.26(1)
Au(1)-Br(1)	2.415(6)	P(1)-C(1)	1.827(3)
P(1)-C(9)	1.830(3)	P(1)-C(5)	1.834(3)
Si(1)-C(16)	1.856(4)	Si(1)-C(17)	1.863(4)
Si(1)-C(18)	1.870(3)	Si(1)-C(1)	1.887(3)
Si(2)-C(19)	1.849(4)	Si(2)-C(21)	1.855(4)
Si(2)-C(20)	1.860(4)	Si(2)-C(5)	1.892(3)
C(1)-C(2)	1.341(4)	C(2)-C(6)	1.499(4)
C(2)-C(3)	1.535(4)	C(3)-C(8)	1.518(4)
C(3)-C(4)	1.534(4)	C(3)-H(3)	1.0000
C(4)-C(5)	1.331(4)	C(4)-C(7)	1.501(4)
C(6)-H(6A)	0.9800	C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800	C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800	C(7)-H(7C)	0.9800
C(8)-C(9)	1.398(4)	C(8)-C(13)	1.401(4)
C(9)-C(10)	1.395(4)	C(10)-C(11)	1.388(5)
C(10)-C(14)	1.519(5)	C(11)-C(12)	1.392(5)
C(11)-H(11)	0.9500	C(12)-C(13)	1.376(5)
C(12)-H(12)	0.9500	C(13)-C(15)	1.511(4)
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800	C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800	C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800	C(21)-H(21C)	0.9800

P(1)-Au(1)-Cl(1)	176.7(2)	P(1)-Au(1)-Br(1)	177.1(2)
Cl(1)-Au(1)-Br(1)	6.0(4)	C(1)-P(1)-C(9)	99.4(1)
C(1)-P(1)-C(5)	101.2(1)	C(9)-P(1)-C(5)	99.0(1)
C(1)-P(1)-Au(1)	117.1(1)	C(9)-P(1)-Au(1)	117.6(1)
C(5)-P(1)-Au(1)	118.9(1)	C(16)-Si(1)-C(17)	109.0(2)
C(16)-Si(1)-C(18)	109.8(2)	C(17)-Si(1)-C(18)	106.9(2)
C(16)-Si(1)-C(1)	109.4(2)	C(17)-Si(1)-C(1)	113.0(1)
C(18)-Si(1)-C(1)	108.8(2)	C(19)-Si(2)-C(21)	111.4(2)
C(19)-Si(2)-C(20)	106.2(2)	C(21)-Si(2)-C(20)	109.5(2)
C(19)-Si(2)-C(5)	108.4(2)	C(21)-Si(2)-C(5)	108.2(2)
C(20)-Si(2)-C(5)	113.2(2)	C(2)-C(1)-P(1)	109.6(2)
C(2)-C(1)-Si(1)	129.5(2)	P(1)-C(1)-Si(1)	120.9(2)
C(1)-C(2)-C(6)	126.9(3)	C(1)-C(2)-C(3)	118.9(3)
C(6)-C(2)-C(3)	114.0(3)	C(8)-C(3)-C(4)	108.1(2)
C(8)-C(3)-C(2)	107.5(2)	C(4)-C(3)-C(2)	111.2(2)
C(8)-C(3)-H(3)	110.0	C(4)-C(3)-H(3)	110.0
C(2)-C(3)-H(3)	110.0	C(5)-C(4)-C(7)	127.1(3)

C(5)-C(4)-C(3)	118.9(3)	C(7)-C(4)-C(3)	113.9(3)
C(4)-C(5)-P(1)	109.9(2)	C(4)-C(5)-Si(2)	132.2(3)
P(1)-C(5)-Si(2)	117.9(2)	C(2)-C(6)-H(6A)	109.5
C(2)-C(6)-H(6B)	109.5	H(6A)-C(6)-H(6B)	109.5
C(2)-C(6)-H(6C)	109.5	H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5	C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5	H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5	H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5	C(9)-C(8)-C(13)	121.2(3)
C(9)-C(8)-C(3)	115.2(3)	C(13)-C(8)-C(3)	123.6(3)
C(10)-C(9)-C(8)	121.0(3)	C(10)-C(9)-P(1)	127.9(2)
C(8)-C(9)-P(1)	111.1(2)	C(11)-C(10)-C(9)	117.1(3)
C(11)-C(10)-C(14)	119.1(3)	C(9)-C(10)-C(14)	123.8(3)
C(10)-C(11)-C(12)	121.6(3)	C(10)-C(11)-H(11)	119.2
C(12)-C(11)-H(11)	119.2	C(13)-C(12)-C(11)	121.8(3)
C(13)-C(12)-H(12)	119.1	C(11)-C(12)-H(12)	119.1
C(12)-C(13)-C(8)	117.2(3)	C(12)-C(13)-C(15)	120.7(3)
C(8)-C(13)-C(15)	122.1(3)	C(10)-C(14)-H(14A)	109.5
C(10)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
C(10)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(1)-C(17)-H(17A)	109.5
Si(1)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
Si(1)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(1)-C(18)-H(18A)	109.5
Si(1)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
Si(1)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	Si(2)-C(19)-H(19A)	109.5
Si(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	Si(2)-C(20)-H(20A)	109.5
Si(2)-C(20)-H(20B)	109.5	H(20A)-C(20)-H(20B)	109.5
Si(2)-C(20)-H(20C)	109.5	H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5	Si(2)-C(21)-H(21A)	109.5
Si(2)-C(21)-H(21B)	109.5	H(21A)-C(21)-H(21B)	109.5
Si(2)-C(21)-H(21C)	109.5	H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5		

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mb823

atom	U11	U22	U33	U23	U13	U12
Au(1)	26(1)	28(1)	34(1)	1(1)	17(1)	5(1)
Cl(1)	15(2)	44(1)	45(2)	8(1)	22(1)	9(1)
Br(1)	19(1)	40(1)	51(1)	0(1)	24(1)	5(1)
P(1)	26(1)	23(1)	27(1)	1(1)	16(1)	4(1)
Si(1)	28(1)	32(1)	32(1)	-3(1)	17(1)	-4(1)
Si(2)	49(1)	32(1)	33(1)	-5(1)	23(1)	6(1)
C(1)	29(2)	24(2)	27(2)	3(1)	17(1)	3(1)
C(2)	29(2)	22(2)	28(2)	-1(1)	15(1)	1(1)
C(3)	24(1)	28(2)	31(2)	4(1)	14(1)	3(1)
C(4)	29(2)	26(2)	30(2)	3(1)	15(1)	-3(1)
C(5)	33(2)	23(2)	25(2)	2(1)	15(1)	-1(1)
C(6)	36(2)	27(2)	50(2)	0(2)	20(2)	3(1)
C(7)	32(2)	42(2)	45(2)	-7(2)	14(2)	-3(2)
C(8)	30(2)	23(2)	33(2)	-3(1)	19(1)	-2(1)
C(9)	31(2)	23(2)	30(2)	-3(1)	19(1)	2(1)

C(10)	38(2)	29(2)	31(2)	2(1)	21(2)	5(1)
C(11)	50(2)	41(2)	37(2)	4(2)	30(2)	2(2)
C(12)	44(2)	44(2)	50(2)	-3(2)	37(2)	0(2)
C(13)	30(2)	36(2)	43(2)	-7(2)	23(2)	-5(1)
C(14)	57(2)	56(3)	38(2)	18(2)	32(2)	23(2)
C(15)	35(2)	52(2)	61(3)	-1(2)	32(2)	3(2)
C(16)	41(2)	61(3)	37(2)	-6(2)	20(2)	-10(2)
C(17)	42(2)	32(2)	48(2)	-6(2)	25(2)	-7(2)
C(18)	43(2)	43(2)	54(2)	3(2)	34(2)	-1(2)
C(19)	79(3)	71(3)	71(3)	-16(3)	58(3)	0(2)
C(20)	75(3)	48(2)	40(2)	-9(2)	27(2)	16(2)
C(21)	71(3)	37(2)	42(2)	-5(2)	22(2)	12(2)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mb823

atom	x	y	z	U(eq)
H(3)	-973	-2173	4445	34
H(6A)	1215	-507	5299	60
H(6B)	-126	-857	5200	60
H(6C)	-98	-789	4202	60
H(7A)	-1768	-2718	2821	66
H(7B)	-1891	-3529.9998	3312	66
H(7C)	-1154	-3545	2716	66
H(11)	1470	-3831	8253	48
H(12)	-704	-3244	7264	48
H(14A)	3514	-4285	8536	72
H(14B)	4215	-3634.0002	8219	72
H(14C)	3508	-4425	7531	72
H(15A)	-1961	-1908	5402	71
H(15B)	-2509	-2602	5790	71
H(15C)	-2535.0002	-2737	4776	71
H(16A)	5204	-1729.0001	7761	71
H(16B)	4502	-877	7676	71
H(16C)	5874	-913.0001	7689	71
H(17A)	3150	85	5840	61
H(17B)	2660	-274	4741	61
H(17C)	4225	20	5527	61
H(18A)	5568	-1321	5602	64
H(18B)	4339	-1945	4899	64
H(18C)	5531	-2172	6065	64
H(19A)	3624	-4163	3678	98
H(19B)	4011	-3581	4615	98
H(19C)	2944	-3283.9998	3455	98
H(20A)	116	-3923	2155	86
H(20B)	-346	-4674	2531	86
H(20C)	797	-4791	2291	86
H(21A)	2694	-5501.0005	4457	84
H(21B)	1542	-5330	4676	84
H(21C)	3072	-4975	5434	84