STUDIES OF ISOMERIC PHOSPHOLES: SYNTHESIS AND APPLICATION IN TRANSITION-METAL AND ORGANIC CATALYSIS

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My thanks are extended to the staff of NTU who have assisted my research in any way, and more importantly to those who made countless efforts in soothing all the graduate matters – Celine and Gladys.

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Ana Ciric

December 2011

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ABSTRACT

The work described herein encompasses a few topics related to the studies of isomeric phospholes. Phospholes have been explored thoroughly over the past many years. They are now accepted as only weakly aromatic: the aromatic stabilization resulting from electronic delocalization of phosphole's planar state is not sufficient enough to overcome its intrinsically high inversion barrier of phosphorus. This results in their pyramidal structure when in ground state and a very poor orbital overlap between the phosphorus lone pair n_p and the π orbitals of the diene unit. Therefore, they seem to resemble more cyclopentadienes than their nitrogen analogues – pyrroles. Though, only recently has the attention been shifted to the phosphole's isomeric form – phospholene. Due to phosphole's low aromaticity, there lies the opportunity to switch from slightly aromatic to slightly antiaromatic character of these heterocycles, which in turn changes the chemistry of this species.

The first chapter describes the synthesis and exploration of the first phosphole-annulated 1,2-dithiole-3-thione. Many analogues of this compound have found uses in different kinds of industries, one of which is biological activity with regards to chemoprevention. Characterization, properties and preliminary biological activity studies are discussed.

The second chapter encompasses the study of 3-aminophospholes and their properties that led to unexpected yet interesting transformations into phosphirene analogues.

The last chapter deals with the studies and synthetic tuning of isomeric phosphole ligands and their use in catalysis.

LIST OF PUBLICATIONS

"Boosting the Nucleophilicity of Phosphole Lone Pairs by Isomerization"*
Ana Ciric, Francois Mathey
Organometallics, **2010**, *29*, 4785-4786
*Invited for the Special Edition dedicated to the former Chief Editor of *Organometallics*, Professor Dietmar Seyferth

"The Chemistry of 3-Aminophospholes"
Wei Luo, Ana Ciric, Rongqiang Tian, Francois Mathey
Organometallics, **2010**, *29*, 1862-1864

"An Unexpected Sequence: From Phosphole Sulfide to Phosphole- and Thiophene-Annulated 1,2-Dithiole-3-thiones"
Ana Ciric, Francois Mathey
Organometallics, **2009**, *28*, 4621-4623

I Introduction

Basics of Phospholes and Phospholenes

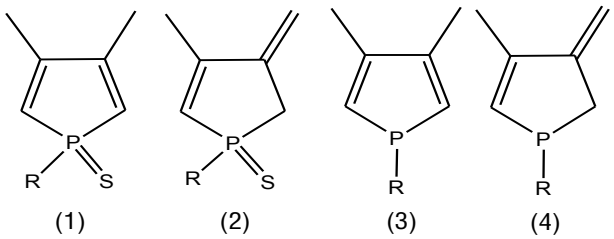
Phospholes and their chemistry have been studied in extensive detail over the past few decades. They are now accepted as only weakly aromatic: the aromatic stabilization resulting from electronic delocalization of phosphole's planar state is not sufficient enough to overcome its intrinsically high inversion barrier of phosphorus. This results in their pyramidal structure when in ground state and a very poor orbital overlap between the phosphorus lone pair n_p and the π orbitals of the diene unit. Therefore, they seem to resemble more cyclopentadienes than their nitrogen analogues – pyrroles. However, their low aromaticity arises from the interaction of the diene π-system with the exocyclic σ(P-R) bond in the form of hyperconjugation. This particular characteristic allows for [1,5] sigmatropic shift, which is the most distinctive feature of phosphole chemistry.[1]

Phospholes have versatile roles in carbon-phosphorus heterocyclic chemistry: they have been used as pre-cursors to phosphinines, phosphinidene complexes, 1-phosphanorbornadienes and as ligands in catalysis (e. g. hydroformylation of olefins, hydrogenation of C=C and C=O double bonds, asymmetric catalysis and so on).[2]

Phospholes have been explored thoroughly over the past many years. Though, only recently has the attention been shifted to the phosphole's isomeric form – phospholene. Due to phosphole's low aromaticity, there lies the opportunity to switch from slightly aromatic to slightly antiaromatic character of these heterocycles.[3] When R = Me, aromatic tricovalent phosphole **3** is more stable than its isomeric phospholene **4** by 3.5 kcal mol^{-1}. But the trend for their pentacovalent species is inverted: upon oxidation, phosphole sulfide **1** becomes slightly antiaromatic and it tends to isomerize

[1] Phosphorus: The Carbon Copy, ed. K. B. Dillon, F. Mathey, J. F. Nixon, Wiley, **1998**
[2] Mathey, F.; Fischer, J.; Nelson, J. H. *Struc. Bonding* **1983**, *55*, 153; Kollar, L.; Keglevich, G. *Chem. Rev.* **2010,** 110, 4257–4302
[3] Reau, R.; Nyulaszi, L.; Holloczki, O.; Lescop, C.; Hissler, M. *Org. Biomol. Chem*., **2006**, *4*, 996–998

into its respective isomer **2** that contains an exocyclic double bond (Scheme 1).



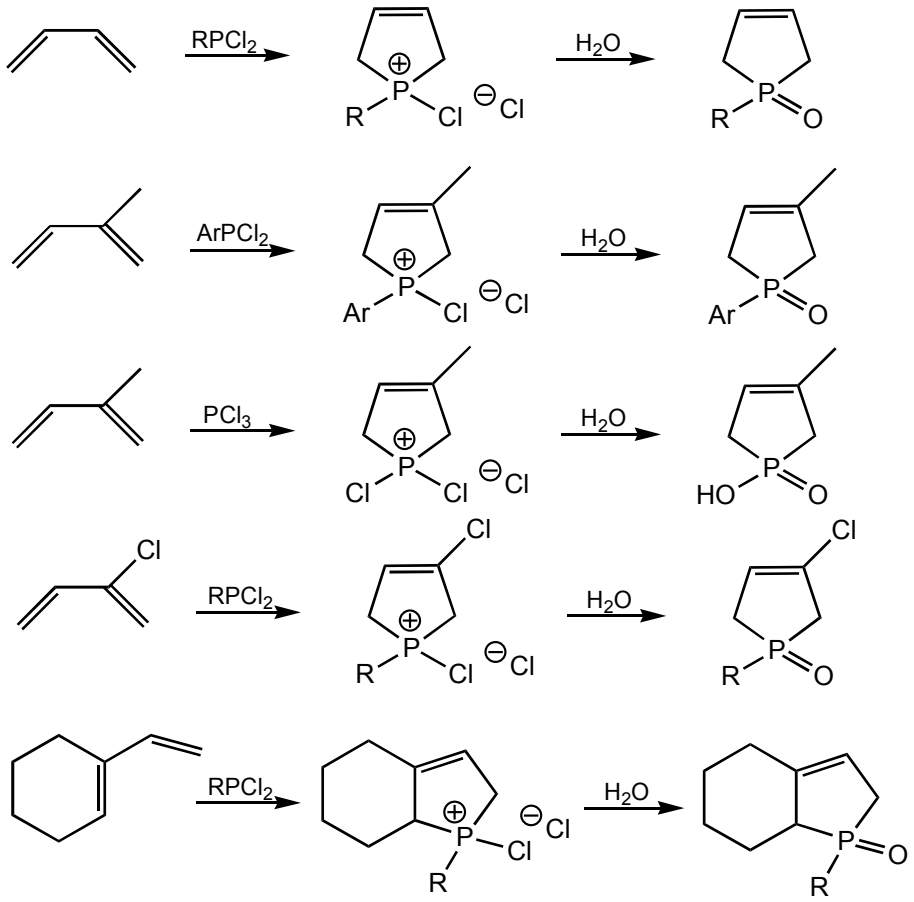
Scheme 1.

This antiaromatic character of the pentacovalent species could be explained using the electronegativities of atoms bonded to the phosphorus center: the more electronegative the atom on phosphorus is (e.g. oxygen or sulfur), the more electron deficient the phosphorus atom will be. This lowers the energy of all orbitals at phosphorus as well as the interaction of endocyclic π system with the empty orbitals of phosphorus. The result is antiaromaticity and decrease in stability of the molecule. This analogy is parallel to the one of cyclopentadiene cation.[3] Independently, some computational studies of this methodology have been proposed (ISE, isomerization stabilization energy) as the means for describing the total energy differences between a methyl derivative of an aromatic system and its nonaromatic exocyclic isomer.[4] This unique yet vaguely explored trait offers a wide potential in the field of phospholes.

[4] P. v. R. Schleyer and F. Puhlhofer, *Org. Lett.*, **2002**, *4(17)*, 2873-2876

Synthesis of Phospholenes

2- and 3-phospholenes are most commonly obtained through the synthesis by McCormack reaction: cycloaddition of trivalent phosphorus halides with dienes, followed by hydrolysis, generates phosphorus oxides (Scheme 2).[5]

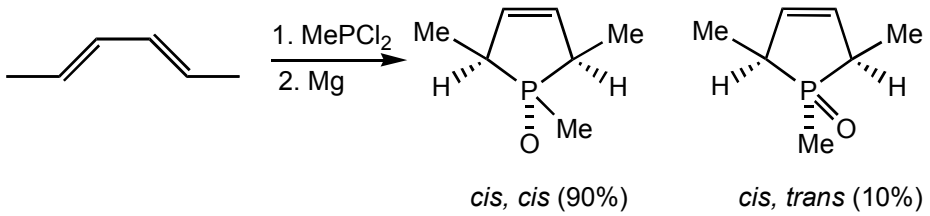


Scheme 2.

A mixture of regioisomers can be obtained but it is usually dominated by only one and the isomers can be easily separated. If R = iPr, the reaction proceeds very slowly, and if R = tBu, there is no reaction at all. Another limitation is the reaction of dienes with a disubstituted terminal carbon – it fails to react. Both of these two limitations are due to sterics. When a commercially obtained mixture of *trans*- and *cis*-1,3-pentadiene (72% and 27%, respectively) is used

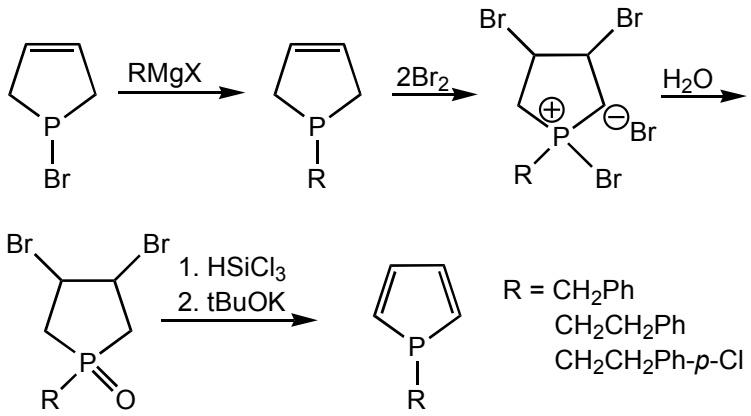
[5] Phosphorous-Carbon Heterocyclic Chemistry: The Rise of a New Domain, ed. F. Mathey, Pergamon, Oxford, **2001**

in the cycloaddition, only the *trans* isomer reacts.[6] Also, in the case of *trans,trans*-2,4-hexadiene, the 3-phospholene oxide with the two methyls *cis*-oriented is formed exclusively, proving that the addition is concerted and disrotatory and, thus, a cheletropic process, as evident below (Scheme 3):



Scheme 3.

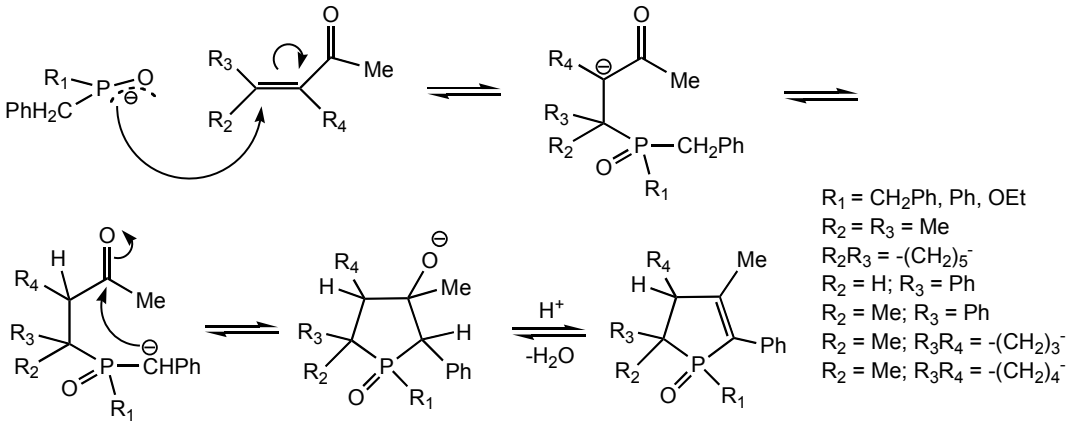
The branched-chain substituents can be obtained by the reaction of P-halophospholene with organometallic reagents, and further transformed into their phosphole forms (Scheme 4).[7]



Scheme 4.

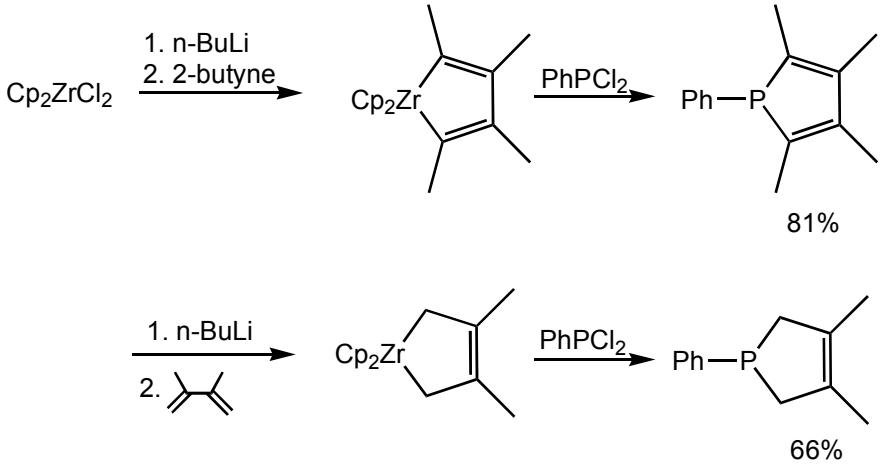
McCormack reaction is superior for its simplicity and versatility; however, another reported method allows 2,2-disubstitution that cannot be obtained through the McCormack approach (Scheme 5)[8]:

[6] Quin, L. D.; Barket, T. P. *J. Am. Chem. Soc.* **1970**, *92(14)*, 4303
[7] Quin, L. D.; Borleske, S. G.; Engel, J. F. *J. Org. Chem.* **1973**, *38(10)*, 1858
[8] Bodalski, R.; Pietrusiewicz, K. M.; Koszuk, J. *Tetrahedron* **1975**, *31*, 1907



Scheme 5.

Phospholes and phospholenes can also be derived via zirconium metallacycles (Scheme 6)[9]:

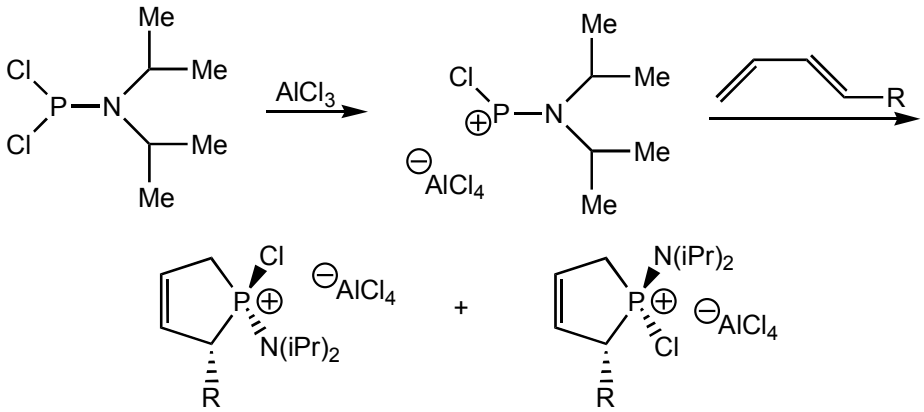


Scheme 6.

The cheletropic cycloaddition of $[ClP(NiPr)_2]^+AlCl_4^-$ with 1-substituted dienes yields the 1-(*N, N*-diisopropylamino)-1-chloro-2-alkyl-δ^3-phospholenium tetrachloroaluminates (Scheme 7)[10]:

[9] Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880

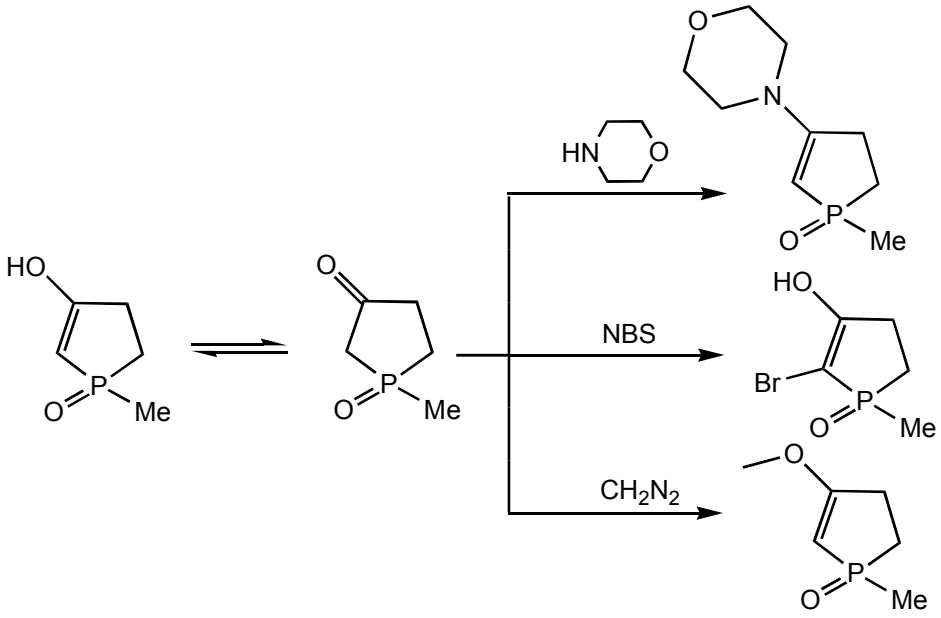
[10] Polniaszek, R. P. *J. Org. Chem.* **1992**, *57*, 5189


Me
Cl
Me
P
N
Cl
Me
Me
AlCl3
Cl
Me
P
N
Me
AlCl4
Me
R
Cl
AlCl4
P
N(iPr)2
R
+
N(iPr)2
P
AlCl4
Cl
R

Scheme 7.

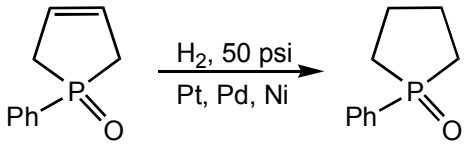
Phospholene Chemistry

The double bond in 2-phospholene oxides is activated by the phosphoryl group, so the nucleophilic additions are then plausible with such reactants such as ^{-}OH, RO^{-}, ^{-}CN, RNH_2, $(RO)_2P(O)H$, and so on. The activating effect also makes it possible to perform Diels-Alder[11] and permits the easy displacement of the leaving group from the 3-position by the means of a nucleophilic attack[12] (Scheme 8):



Scheme 8.

Phospholene oxides serve as great starting point for the synthesis of phospholane oxides, by simple hydrogenation techniques (Scheme 9)[13]:

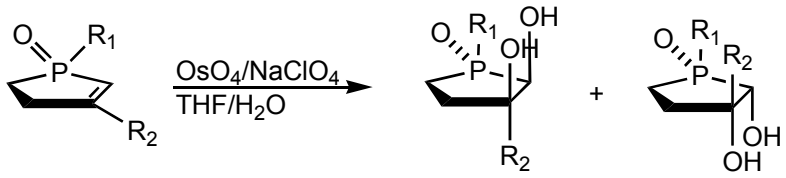


Scheme 9.

[11] Can J Chem, **1971**, 49, 530
[12] Quin, L.D.; Stocks, R. C. *J. Org. Chem.* **1974**, *39*,(5) 686
[13] Marsi, K. L.; Burns, F. B.; Clark, R. T. *J. Org. Chem.* **1972**, *37(2)*, 238

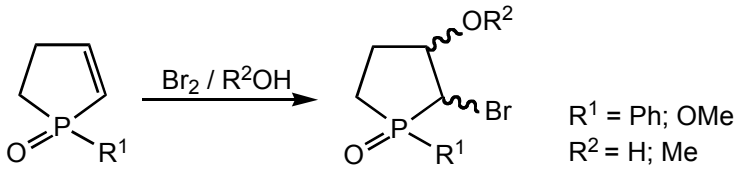
Furthermore, they can also be reduced to their phosphine form by the use of silanes as reducing agents (e.g. $HSiCl_3$). In case of tricovalent 3-phospholenes (with 2- and 2,5-substituents), the total of three chiral centers are produced, including the preserved stereochemistry at the phosphorus after the oxide reduction (due to the high barrier to pyramidal inversion).

2- and 3-phospholenes have also been used as starting materials for the synthesis of phosphanyl sugars, analogs of sugars that have phosphorus in place of the ring oxygen. Catalytic *cis*-dihydroxylation of 2- and 3-phospholene-1-oxide derivatives with osmium(VIII) oxide in the presence of a co-oxidant affords 3- and 1-deoxy-tetrafuranose-type phosphanyl sugar derivatives, respectively (Scheme 10)[14]:



Scheme 10.

Reactions of 1-phenyl- and 1-methoxy-2-phospholene oxides with Br_2 in aqueous organic solvents afford 2-bromo-3-hydroxy or 2-bromo-3-methoxy phospholane oxides in high yields (Scheme 11)[15]:



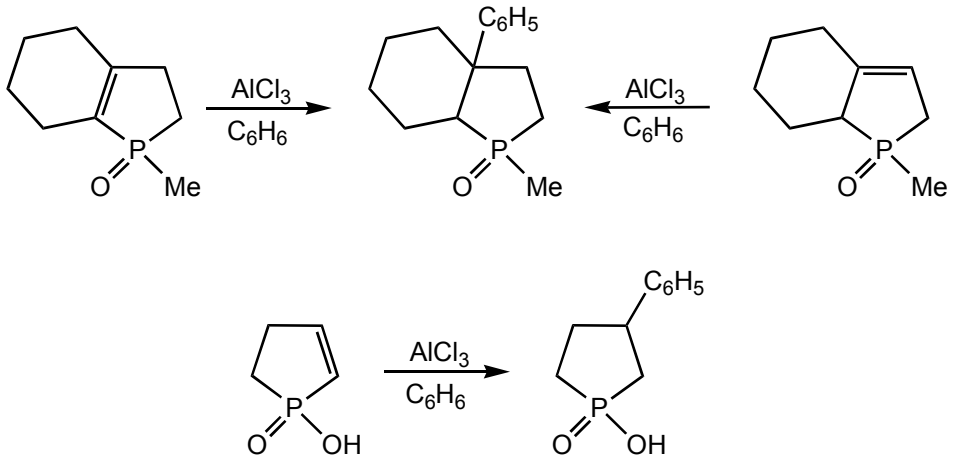
Scheme 11.

Phospholene oxides as well as phosphinic acids undergo the arylation reaction under Friedel-Crafts conditions, with significant ease (Scheme 12)[16]:

[14] Yamashita, M.; Yabui, A.; Suzuki, K.; Kato, Y.; Uchimura, M.; Iida, A.; Mizuno, H.; Ikai, K.; Oshikawa, T.; Parkanayi, L.; Clardy, J. *J. Carbohydrate Chem.* **1997**, *16(4&5)*, 499

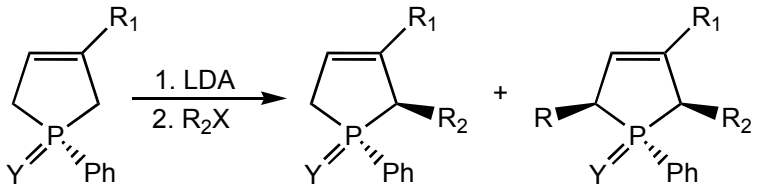
[15] Yamashita, M.; Iida, A.; Mizuno, H.; Miyamoto, Y.; Morishita, T.; Sata, N.; Kiguchi, K.; Yabui, A.; Oshikawa, T. *Heteroatom Chem.* **1993**, *4(6)*, 553

[16] MacDiarmid, J. E.; Quin, L. D. *J. Org. Chem.* **1981**, *46*, 1451



Scheme 12.

Pakulski et al. have also shown that easily accessible 1-phenyl-3-phospholene and its derivatives can serve as precursors to the more substituted monocyclic and bicyclic systems.[17] Their deprotonation with LDA, followed by alkylation occurs exclusively with the *anti* selectivity of the incoming electrophile in relation to the P-R group. 2- and 2,5-substitutions are observed despite the steric crowding (Scheme 13):

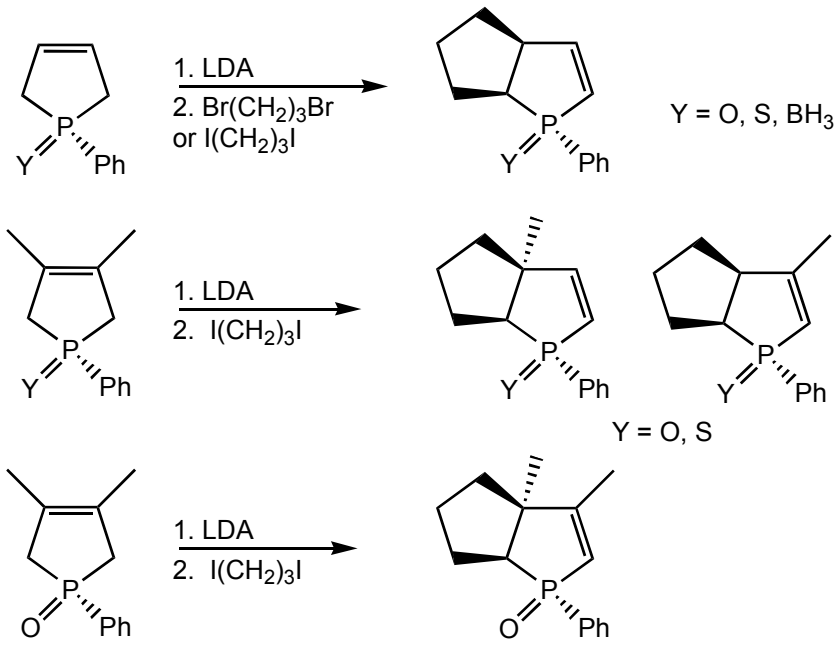


R_1 = H, Me
Y = O, S

Scheme 13.

The alkylation of unsubstituted, 3-substituted and 3,4-disubstituted phospholenes with propylene dihalides yielded cyclopentane-annulated phospholene oxides with high regio- and stereoselectivities (Scheme 14)[17]:

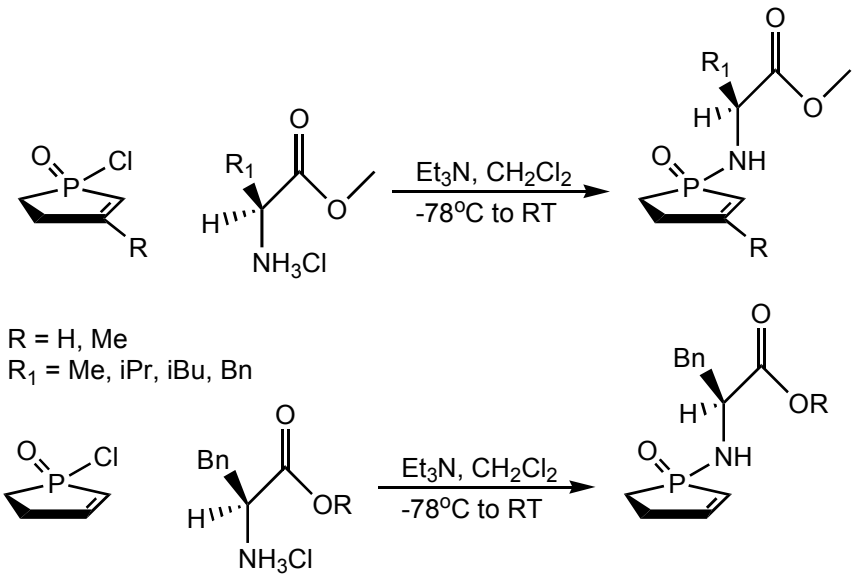
[17] Pakulski, Z.; Kwiatosz, R.; Pietrusiewicz, K. M. *Tetrahedron* **2005**, *61*, 1481



Scheme 14.

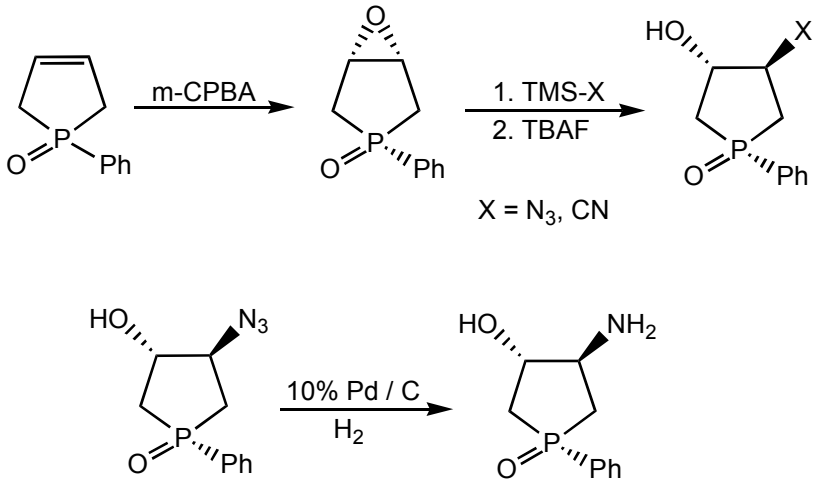
Amino phosphonic acids that have been isolated from several organisms and human beings have proved to be a biologically active class of compounds.[18] Thus, the group of Yamashita saw the potential in the structural activity of amino acid derivatives of phospholene oxides, and reported their unprecedented synthesis (Scheme 15). [18] By reacting P-chloro-2-phospholenes with amino acid esters, they were able to obtain the corresponding 1-*L*-α-amino acid derivatives as chiral P-N phospholenes.

[18] Haritha, B.; Reddy, V. K.; Takahashi, M.; Yamashita, M. *Tetrahedron Lett*. **2004**, *45*, 5339



Scheme 15.

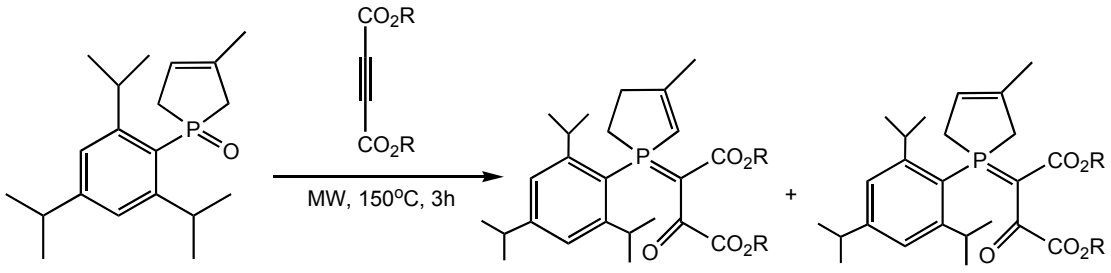
Asymmetric opening of phospholene epoxides by azide and cyanide nuclophiles in the presence of a chiral Lewis acid catalyst ($Ti(O–iPr)_4$ itself and $Ti(O–iPr)_4$ in the presence of TADDOL, or salen–Al complex) has also been achieved.[19] Both targets can find use as intermediates in the synthesis of phosphasugars (Scheme 16). The azide group can be easily reduced to enantioenriched phospholane derivative possessing versatile 1,2-aminoalcohol functionality.



Scheme 16.

[19] Pakulski, Z.; Pietrusiewicz, K. M. *Tetrahedron: Asymm*. **2004**, *15*, 41

A reaction of phospholene oxide and dialkyl acetylenedicarboxylates (DAAD) resulted in formation of P=C and C=O bonds.[20] Under microwave conditions, this novel reaction produces corresponding ß-oxophosphoranes, which can be regarded as stabilized phosphonium ylides, making it the inverse Wittig-type reaction (Scheme 17).

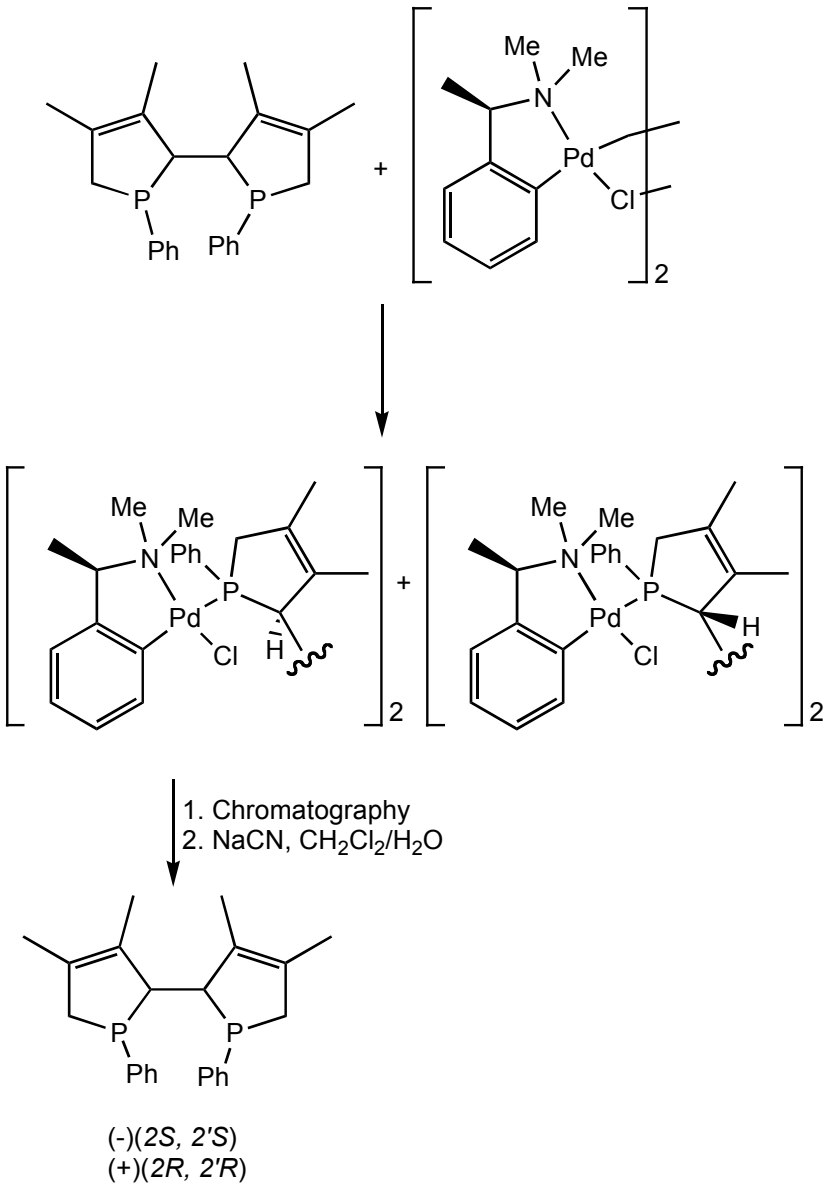


Scheme 17.

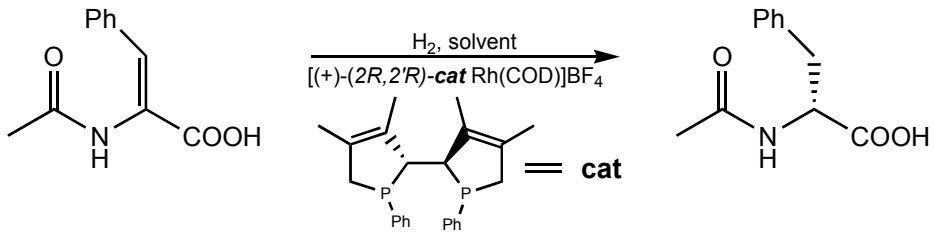
Phospholes and phospholenes have also made major contribution in enantioselective catalysis. These phosphacyclic ligands and their metal complexes have been used to prepare numerous intermediates and building blocks on commercial scales.

Mathey reported the enantiopure 2,2'-biphospholene that was complexed to palladium and purified by chromatographic separation of the diastereomers (Scheme 18). The initial experiments in the rhodium-catalyzed assymetric hydrogenation of α-acetamidocinnamic acid showed strong activity and enantioselectivities up to 75% (Scheme 19)[21]:

[20] Keglevich, G.; Dudas, E.; Sipos, M.; Lengyel, D.; Ludanyi, K. *Synthesis* **2006**, *8*, 1365
[21] Beinewald, F.; Ricard, L.; Mercier, F.; Mathey, F. *Tetrahedron: Asymm*. **1999**, *10*, 4701



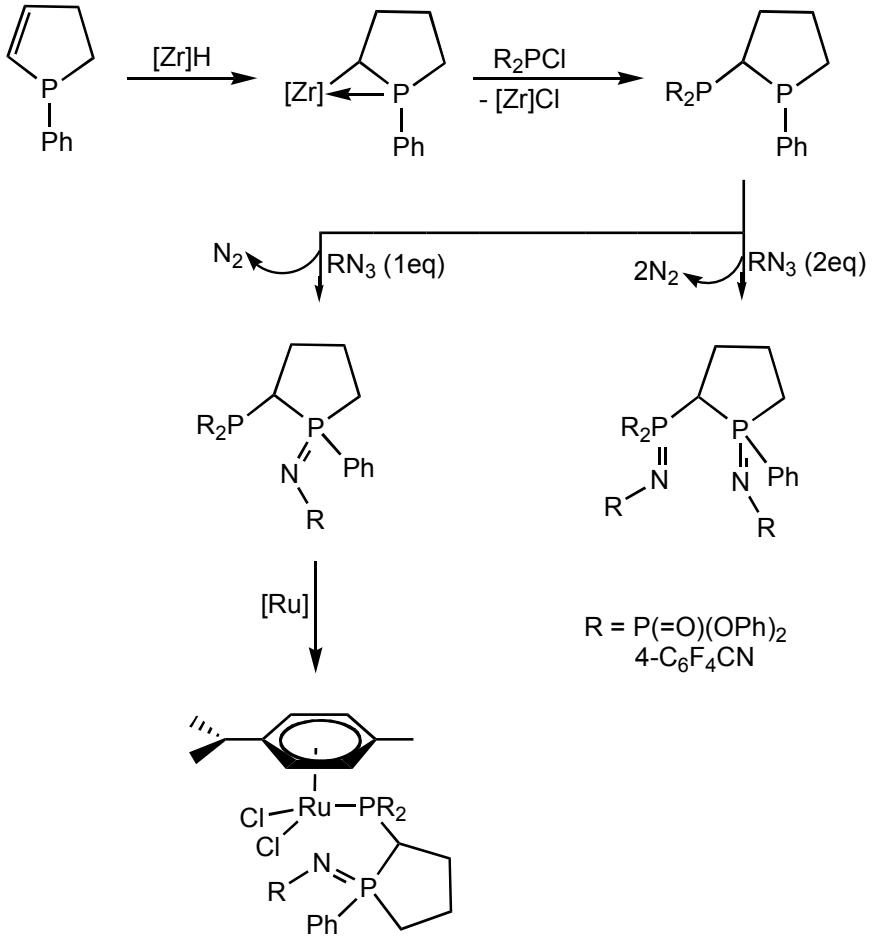
Scheme 18.



Scheme 19.

Optically active 1-phenyl-2-phospholene was used for the synthesis 1-phenyl-2-diphenylphosphino phospholane via the hydrozirconation and

subsequent transmetallation with chlorophosphines (Scheme 20).[22] These phospholanes were then transformed into imino-phosphorane-phosphines (nitrogen analogues of phosphorus ylides) and complexed to ruthenium(II) chloro-bridged dimer [{RuCl(μ-Cl)(Z6-p-cymene)}2] for their examination in catalysis. More specifically, they were assessed in asymmetric Diels-Alder cycloaddition reactions however, only with moderate diestereo- and enantioselectivities.

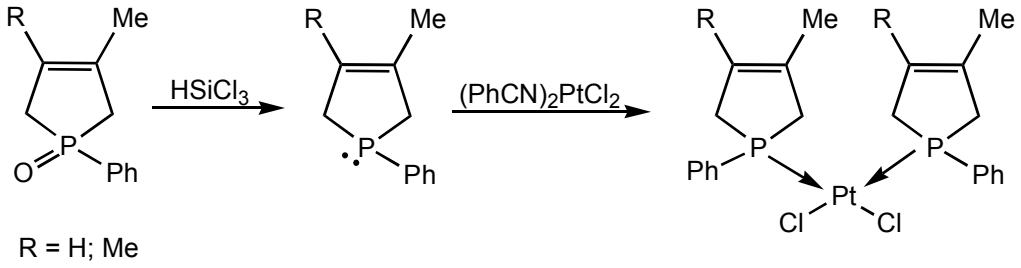


Scheme 20.

Several phospholene platinum (II) complexes were synthesized recently with the potential in homogeneous catalysis, such as hydroformylation and hydrogenation reactions (Scheme 21).[23]

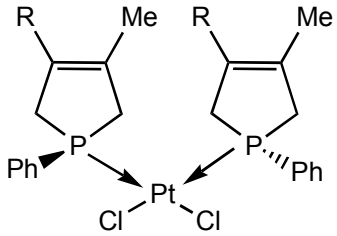
[22] Diaz-Alvarez, A. E.; Crochet, P.; Zablocka, M.; Cadierno, V.; Duhayon, C.; Gimeno, J.; Majoral, J.-P. *New J. Chem.* **2006**, *30*, 1295

[23] Kerenyi, A.; Kovacs, V.; Kortvelyesi, T.; Ludanyi, K.; Drahos, L.; Keglevich, G. *Heteroat. Chem.* **2010**, *21(2)*, 63



Scheme 21.

The formation of the *cis*-Pt(ligand)$_2$Cl$_2$ complexes was favored in all cases. The optically active of 1-phenyl-3-phospholene oxide was available by resolution using TADDOL derivatives, and then consequently converted to the corresponding platinum complex (R,R) (Scheme 22).



Scheme 22.

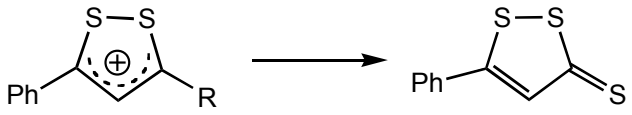
Chapter I

1.1 Introduction

1,2-Dithiole-3-thiones have proven numerous uses; against various fungi, as pesticides, additives for lubricating oils, vulcanization accelerators, detergents, and when in mixtures with t-butyl hydroperoxides, for slime control in paper making.[1] They also have diverse biological activities, in part due to their antioxidant properties. They have been investigated in treatment of cancers,[2] Parkinsons,[3] and cardiovascular diseases.[4] Oltipraz is a well-established chemopreventive agent.[5]

1.2 Synthesis

The early chemistry (year 1965-1980) of 3*H*-1,2-dithiole-3-thiones and their synthesis have been described in great detail by C. Pedersen.[1] The 1,2-dithiole-3-thiones are obtained from decomposition of dithiolylium salts during their reaction with elemental sulfur or tertiary amines, without the formation of tetrathiafulvalenes (Scheme 1.1). In similar fashion, 3-chloro-1,2-dithiolylium salts form 1,2-dithiol-3-ones with carboxylic acids.

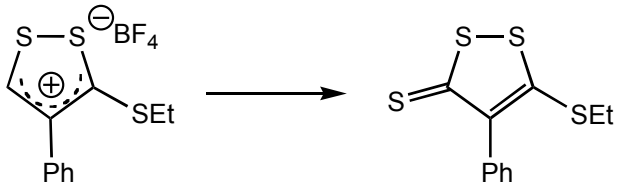


Scheme 1.1.

When reacted with sulfur, 3-Ethylthio-1,2-dithiolylium fluoroborates give 5-ethylthio-1,2-dithiole-3-thiones (Scheme 1.2).

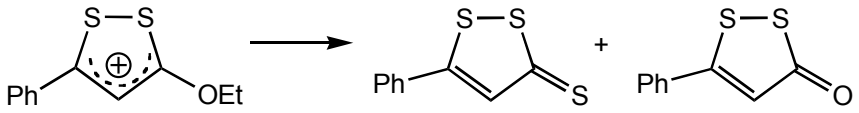
---

[1] Pedersen, C. T. Advances in Heterocyclic Chemistry, Vol 31.63-113; Pedersen, C. T. *Sulfur Rep*. **1995**, *16*, 173-221.
[2] Huang, Y.; Yan, J.; Lubet, R.; Kensler, T. W.; Sutter, T. R. *Physiological Genomics* **2006**, *24*, 144-153.
[3] Jia, Z.; Zhu, H.; Misra, H. P.; Li, Y. *Brain Research* **2008**, *1197*, 159-169; Burton, N. C.; Kensler, T. W.; Guilarte, T. R. *Nerotoxicology* **2006**, *27*, 1094-1100.
[4] Cao, Z.; Li, Y. *Cardiovascular Toxicology* **2004**, *4*, 339-353.
[5] Velayutham, M.; Villamena, F. A.; Navamal, M.; Fishbein, J. C.; Zweier, J. L. *Chem. Res. Toxicol.* **2005**, *18*, 970-975



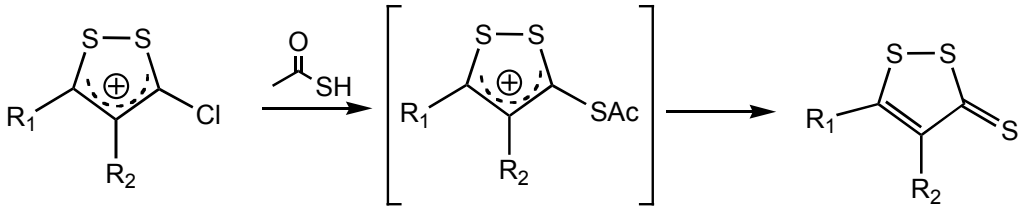
Scheme 1.2.

With water-pyridine mixtures, the related 3-ethoxy-1,2-dithilylium salts produce a mixture of 1,2-dithiole-3-thiones and 1,2-dithiol-3-ones (Scheme 1.3).



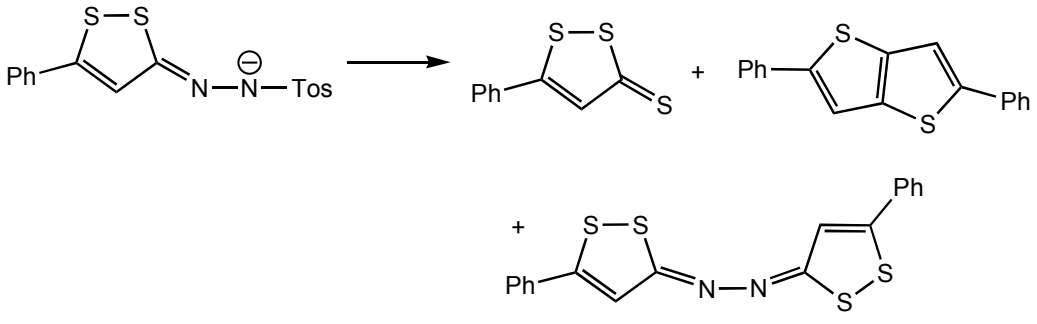
Scheme 1.3.

If reacted with thioacetic acid, 3-chloro-1,2-dithiolylium chlorides are converted into 1,2-dithiole-3-thiones with the speculated intermediate shown in Scheme 1.4.



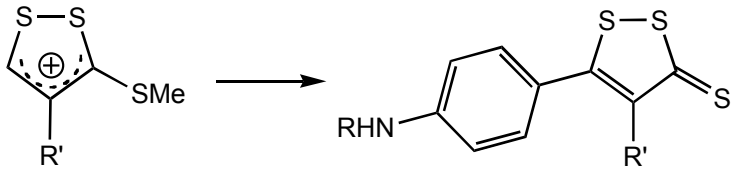
Scheme 1.4.

1,2-Dithiol-3-one tosylhydrazones undergoing Stevens-Bamford reaction did not yield 1,2-dithiolyl carbenes, nor any species derived from those. Among other products, they also gave 1,2-dithiole-3-thiones (Scheme 1.5).



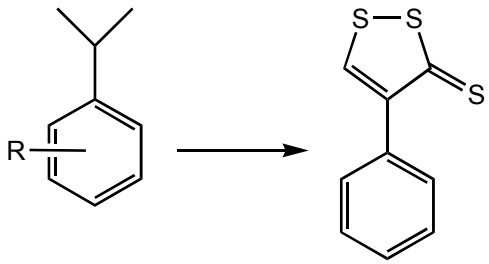
Scheme 1.5.

3-Methylthio-1,2-dithiolylium salts having a free 5-position react with aryl amines to form a 1,2-dithiole-3-thiones with arylated 5-position (Scheme 1.6).



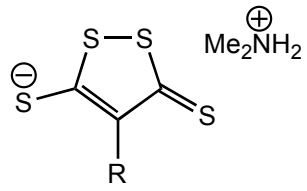
Scheme 1.6.

1,2-Dithiole-3-thiones can also be synthesized from compounds that do not contain the 1,2-dithiole rings, such as alkanes, alkenes, ketones, aldehydes and so on. Starting from alkanes, the first step towards the 1,2-dithiole-3-thiones is assumed to be dehydrogenation of the alkane to form the corresponding alkene, which then reacts with sulfur to yield the target. However, no mechanistic studies have been reported of such postulation. One main example involves the transformation of isopropyl benzene type (Scheme 1.7).

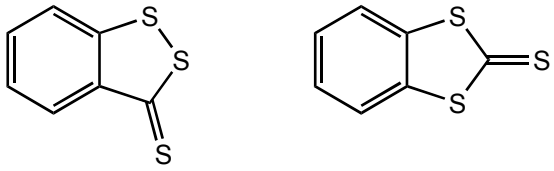


Scheme 1.7.

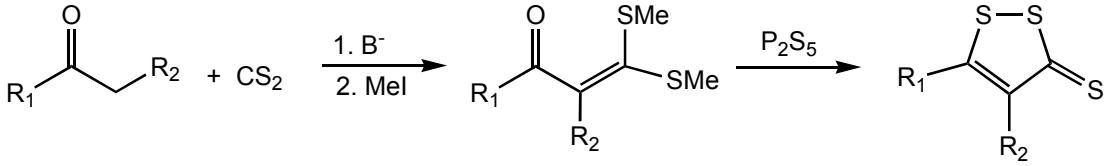
Thiation reaction of aromatic and aliphatic alkenes in dimethylformamide resulted in the formation of dimethyl ammonium salts of the thiolates of the type shown below:



Both 1,2- and 1,3-benzodithiolethione (see below) can be formed from benzynes: when phthalic anhydride and carbon disulfide are passed through a tube filled with Vycor chips at 700^0C.

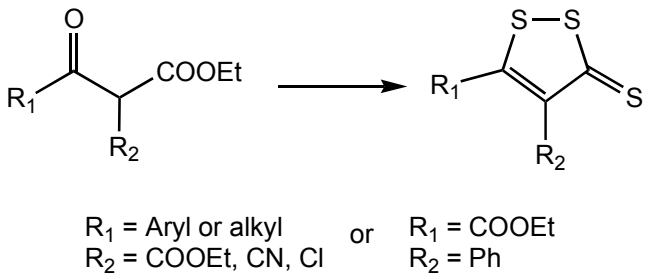


Ketones can also be transformed by the use of carbon disulfide and a base (Scheme 1.8).



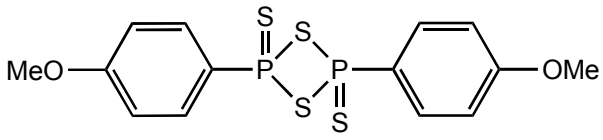
Scheme 1.8.

1,2-dithiole-3-thiones can be also synthesized via the sulfurization of ß-ketoesters with phosphorus pentasulfide alone or in a mixture with elemental sulfur. Depending on the substitution of the ß-ketoester itself, different substitutions are obtained on the final dithiolethione. For instance, 1,2-dithiole-3-thiones with cyano, chloro and ester groups on the 4-position and ester groups on the 5-position have been prepared (Scheme 1.9).

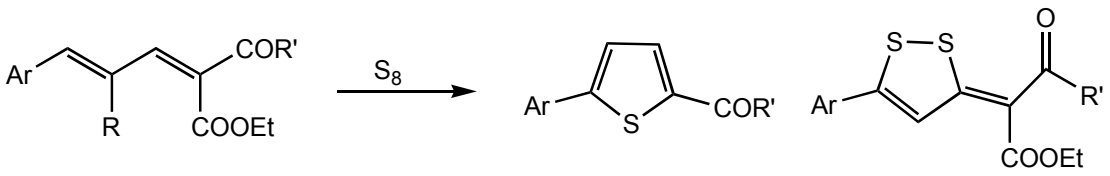


Scheme 1.9.

Lawesson's reagent (below) has also been shown to give high yields of 1,2-dithiole-3-thiones as a sulfurizing reagent when reacted with ß-ketoesters, but only when used on small scale reactions (0.1 mol).



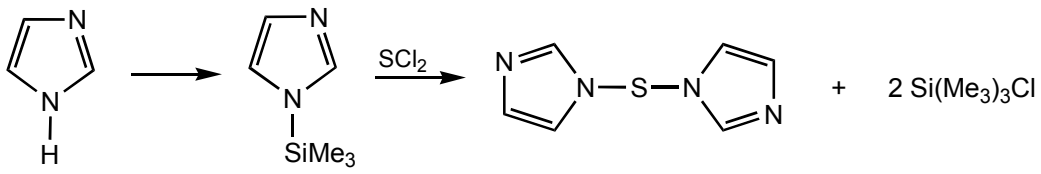
Scheme 1.10 shows the reaction of ketones with elemental sulfur. Depending on the R group, different mixtures of products are obtained. If R = H, the reaction yields thiophene and 1,2-dithiole-3-ylidine ketones. In contrast, when R = R' = Me, the resulting product is 1,2-dithiole-3-thione.



Scheme 1.10.

1.3 Results and Discussion

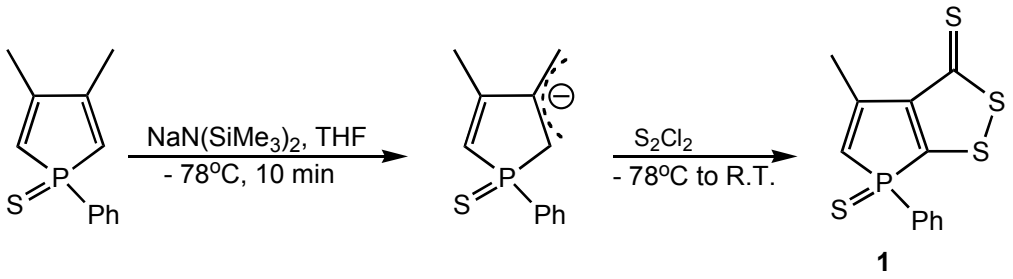
Our initial attempts were to synthesize two phosphole units linked by a sulfur atom, with the ultimate goal of forming a sulfur-bridged phosphaferrocene. The first choice of reagent was going to be SCl_2, or its more stable and reactive imidazole derivative[6] (Scheme 1.11).



Scheme 1.11.

[6] Feher, F.; Degen, B. *Angew. Chem. Int. Ed.* **1967**, *6*(8), 703-704

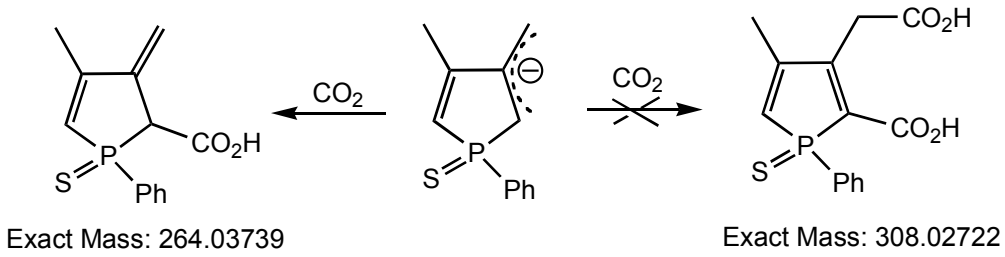
However, the discontinuation of SCl_2 reagent by all chemical companies in the U.S., we decided to try out the more easily obtainable dichloro disulfide (S_2Cl_2). The initial reaction was carried out using sodium bis(trimethylsilys)amide as a bulky base for the formation of phosphole sulfide's delocalized anion, followed by the reaction with freshly distilled S_2Cl_2. After quenching with a 3N aqueous HCl solution and purification by column chromatography, only one bright red product gave a ^{31}P NMR signal. The mass, $^{1}H/^{13}C$ NMR, and ultimately the X-ray crystallography confirmed the structure of compound **1** (Scheme 1.12).[7]



Scheme 1.12.

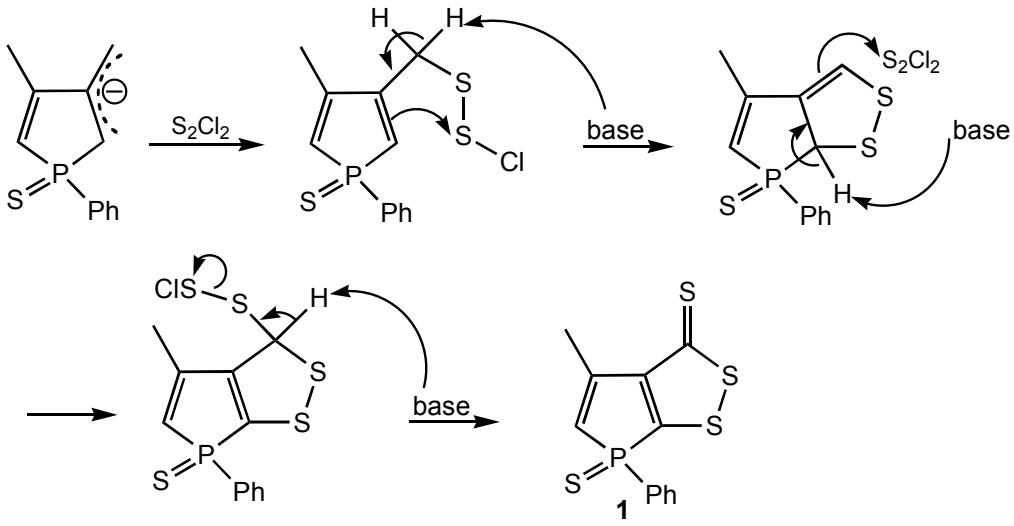
The yields of **1** were initially extremely low, thus we had to optimize the synthesis. In order to determine what changes were to be undertaken, we had to understand the mechanism for transforming our phosphole sulfide into a phosphole-annulated 1,2-dithiole-3-thione **1**. The first step was to test the nature of the anion and determine whether the attack on S_2Cl_2 was arising from a dianion instead.[8] After reacting our phosphole sulfide with one equivalent of sodium hexamethyldisilazide and then purging it with a constant flow of CO_2, the mass found (M^+ = 265.0447) revealed that only a mono-substituted phosphole sulfide was obtained (Scheme 1.13).

[7] Ciric, A.; Mathey, F. *Organometallics* **2009**, *28*(15), 4621-4623
[8] Melaimi, M.; Ricard, L.; Mathey, F.; Le Floch, P. *Org. Lett.* **2002**, *4*(8), 1245-1247



Scheme 1.13.

This suggested a stepwise mechanism for the observed transformation (Scheme 1.14):



Scheme 1.14.

Based on the proposed mechanism it seemed evident that we needed a strong non-nucleophilic base to generate the anion and the first C-S link, then three additional equivalents of a weaker base which will serve to close the dithiole ring and create the thiocarbonyl group, without activating the S-Cl bond. We proceeded to test a few other bases. When LDA was used instead of the bulky sodium bis(trimethylsilyl)amide (Scheme 1.12), no target was seen, only the isomeric phosphole sulfide. With tBuLi, a large mixture of organic products was obtained but none of compound **1**. Then we decided to use a different base for the last three steps and to carry out the addition of both bases and S_2Cl_2 in a step-wise manner. Therefore, following our mechanistic analysis: we added one equivalent of $NaN(SiMe_3)_2$ and S_2Cl_2 at -78 ^oC, warmed the reaction

to O ^{o}C, added two equivalents of triethylamine, second equivalent of S_2Cl_2 at -78 ^{o}C and the third equivalent of NEt_3 at O ^{0}C, all stepwise. Seemingly complicated, this new route fortunately provided us with a reproducible 10% yield, along with some oligomers.

When the same reaction was attempted using t-BuLi as the initial base, the reaction failed, giving only a mixture of products with major one being the isomeric phosphole. Another method reported by Klingsberg[9] using elemental sulfur and a guanidine base in boiling toluene was attempted however, it resulted in no reaction in our case.

DFT calculations (B3LYP/6-311+G(d,p) level) were performed on the model compound below (Figure 1.1).

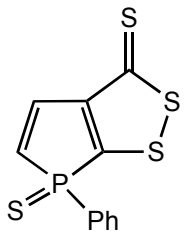


Figure 1.1.

The computed structure is corresponding to the structure obtained by X-ray crystallography. The calculations further reveal that the HOMO is largely localized on the dithiolethione ring excluding the participation of phosphorus (Figure 1.2). Participation of phosphorus is more significant in the LUMO. The high coefficient at C=S sulfur indicate that it will be a reactive site towards electrophiles. In addition, according to the nucleus-independent chemical shift, NICS(1), which gives -5.1 value, the dithiole ring is only weakly aromatic. (Benzene has a value of -13.4)

[9] Klingsberg, E. *Synthesis* **1971**, 213

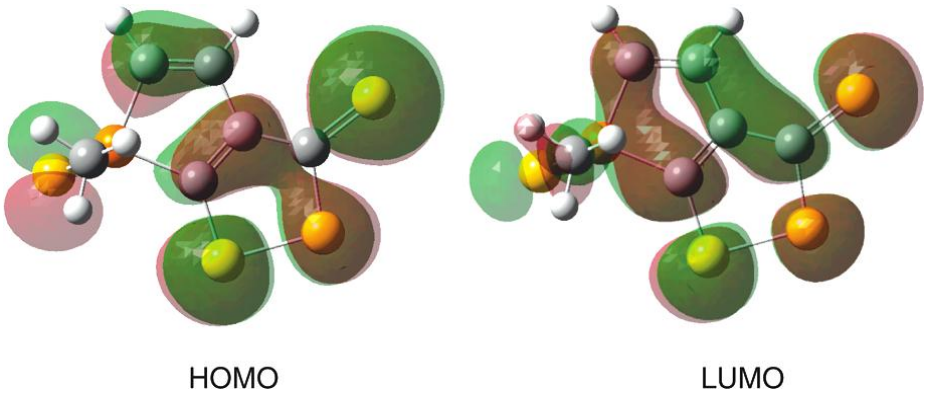


Figure 1.2.

The UV-vis data (Figure 1.13) shows a band at 483 nm (ε 8339), which occurs at 410 nm (ε 6400) in the parent dithiolethione[10] and corresponds to the $\pi^* \leftarrow \pi$ transition. The slight decrease in energy (3.02 eV to 2.57 eV) seems to indicate that the phosphole annulation has slightly increased the delocalization within the dithiolethione ring.

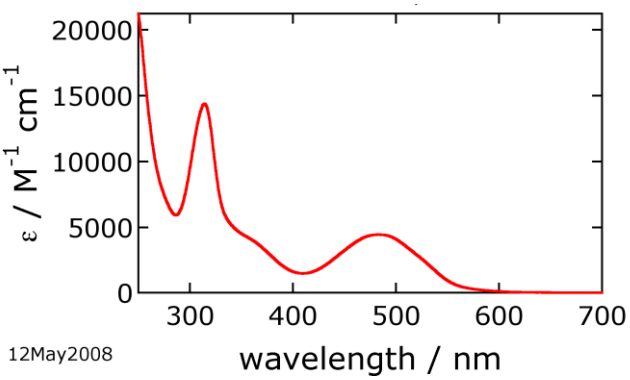
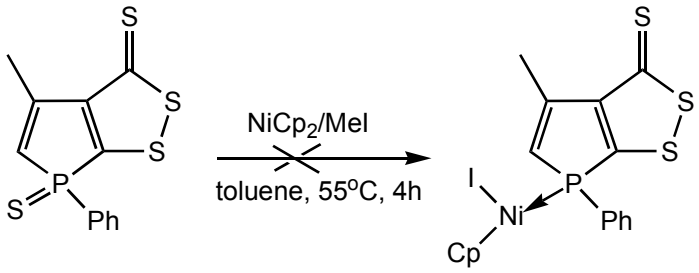


Figure 1.3.

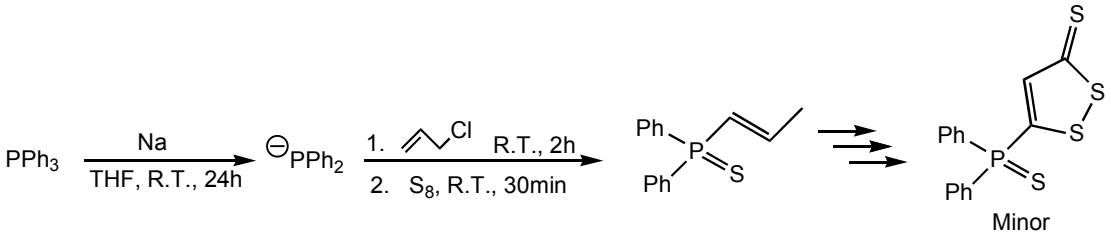
In order to confirm the theoretical prediction, we decided to investigate the reduction of **1**. We chose a mild and selective method relying on complexation-reduction of P=S bonds by $NiCp_2$/MeI [11] (Scheme 1.15). Unfortunately, it produced only a mixture of decomposed products. This indicated that the calculations might have predicted the reactive site correctly (C=S and not P=S).

[10] Gonbeau, D.; Guimon, C.; Pfister-Guillouzo, G. *Tetrahedron* **1973**, *29*, 3599
[11] Mathey, F. *J. Organomet. Chem.* **1975**, *87*, 371; Mathey, F. *J. Organomet. Chem.* **1976**, *105*, 73



Scheme 1.15.

Having discovered a novel method for dithiolethione synthesis, we were prompted to see if this method could be generalized. So we used the relatively inexpensive and commercially available triphenyl phosphine. Scheme 1.16 describes the synthesis of *trans*-diphenylpropenyl[12] phosphine sulfide in 49 % yield,[13] which was to be used later as a precursor to dithiolethione. Following the same steps as in Scheme 14 seems to have achieved the target compound only as a minor product, which was easily oxidized during handling, and to a lot of unreacted starting material.

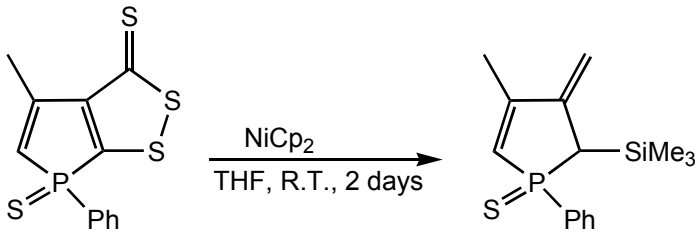


Scheme 1.16.

Our next efforts were focused on the complexation of **1** to a transition metal in order to establish its preferential complexation site (P=S or C=S). Initially, we attempted the same reaction as in Scheme 15, but excluded methyl iodide. The reaction product obtained was the unanticipated mono-silyl phospholene (Scheme 1.17). In order to understand the formation of this major product, we postulated that this was the result of a radical intermediate reacting with glass surface. However, after changing the $NaN(SiMe_3)_2$ to LDA in the synthesis of **1**, and carrying out the complexation reaction in quartz and glass flasks, side by side, none of the isolated products were the mono-silyl

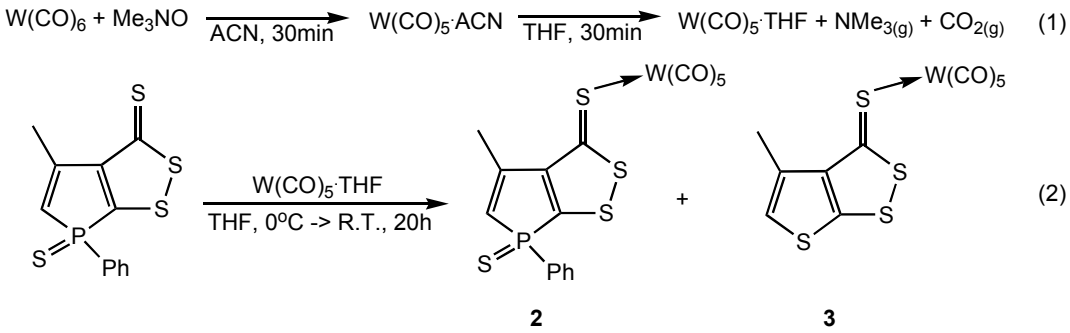
[12] Duncan, M.; Gallagher, M. J. *Org. Magn. Res.* **1981**, *15*, 37
[13] Ashby, E. C.; Gurumurthy, R.; Ridlehuber, R. W. *J. Org. Chem.* **1993**, *58*, 5832-5837

phospholene. This experiment confirmed that there was no reaction with glass surface; instead, bulky $NaN(SiMe_3)_2$ was probably not completely removed during the column chromatography leaving some of the silyl groups available during the subsequent steps.



Scheme 1.17.

We decided to investigate the complexation of **1** to tungsten pentacarbonyl.[14] When **1** was added to the solution of $W(CO)_5$ made *in situ*, and left to stir over night, the color of the crude turned dark blue. The two products isolated by column chromatography were left to crystalize over night in test tubes. Their structures were confirmed by X-ray crystallography (Scheme 1.18):



Scheme 1.18.

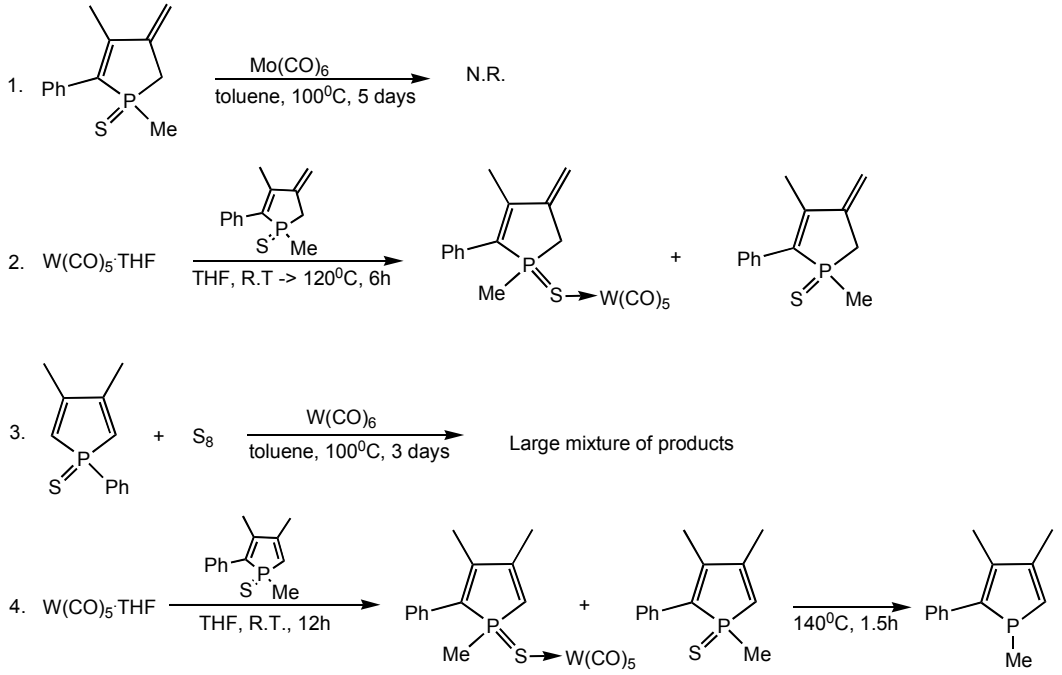
As the calculations predicted, the C=S was indeed the preferred coordination site, as shown in **2**. However, the more intriguing product was the thiophene-annulated dithiolethione **3**, produced as a result of the unprecedented transformation of a phosphole ring into a thiophene ring. The main structural difference between **2** and **3** is the co-planarity of the two rings: the phosphole

[14] Raubenheimer, H. G.; Kruger, G. J.; Marais, C. F. *J. Chem Soc., Chem. Commun.* **1984**, 634

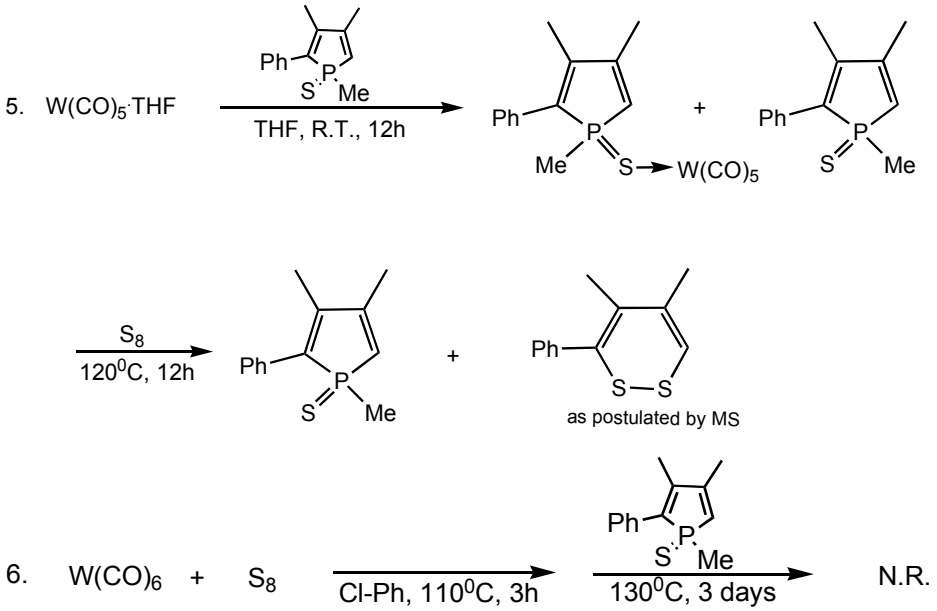
and dithiolethione rings have the 6.5° P-C-C-C(S) dihedral angle, whereas the thiophene and dithiolethione rings are strictly co-planar.

Undoubtedly, we decided to carry out several test reactions in attempt to elucidate the observed transformation (Scheme 1.19). Firstly, if we were going to transform phosphole into its thiophene derivative, we had to choose one that was going to give a product that can be isolated. 3,4-Dimethyl-2-phenylthiophene was known[15] and so we made a α-phenyl phosphole sulfide. We also chose to put a smaller methyl substituent on the phosphorus center rather than the usual bulky phenyl.

The first two reactions shown involve the use of isomeric phosphole sulfide, which gives the more reactive trivalent phosphole. Even under harsh conditions, the reaction with molybdenum resulted in no change and the reaction with tungsten gave only the starting material complexed to the metal center. Third reaction was a test reaction using equimolar amounts of elemental sulfur and catalytic amounts of tungsten hexacarbonyl however, it resulted in a mixture of products impossible to purify. Fourth and fifth reactions are similar: when we obtained the desulfurized product in the first, we decided to have sulfur source in the latter after the complex was formed.



[15] Sekiya, H. *et al. J. Phys. Chem. A* **2003**, *107*, 5384

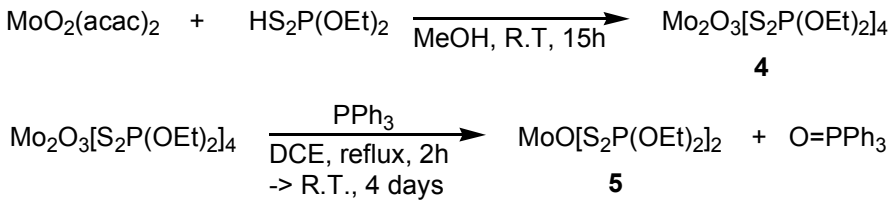


Scheme 1.19.

As the amounts obtained during the column chromatography were too small to work with, only the liquid chromatography mass spectrometer (LCMS) was able to give us a hint towards one product, which did not produce a ^{31}P NMR signal. And according to this mass, we postulated the structure based on a few examples known in the literature.[16] In the last reaction we attempted to create catalytic W-S as the source of sulfur first, then react it with phosphole sulfide. Unfortunately, this approach was unsuccessful as well.

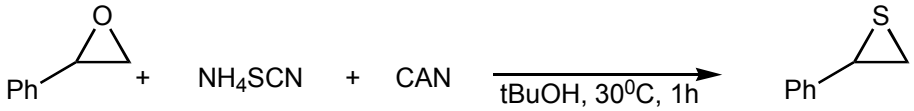
At that point we needed a better source of sulfur. We came across an article describing episulfidation of alkenes and allenes using molybdenum oxo complexes and phenylthiirane (and elemental sulfur) as sulfur donors.[17] Scheme 1.20 describes the synthesis the dithiophosphate molybdenum oxo complex in 46% yield.

[16] Harpp, D. N. *et al. J. Am. Chem. Soc.* **2006**, *128*, 291
[17] a. Adam, W.; Bargon, R. M.; Schenk, W. A. *J. Am. Chem. Soc.* **2003**, *125*, 3871-3876; b. Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*(11), 2612-2615



Scheme 1.20.

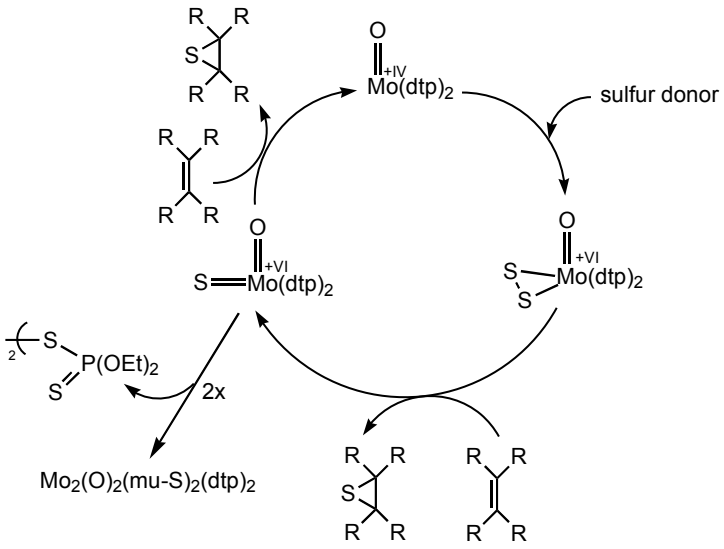
The most efficient synthesis of phenylthiirane (40% yield) that we tried is described in Scheme 1.21.[18]



Scheme 1.21.

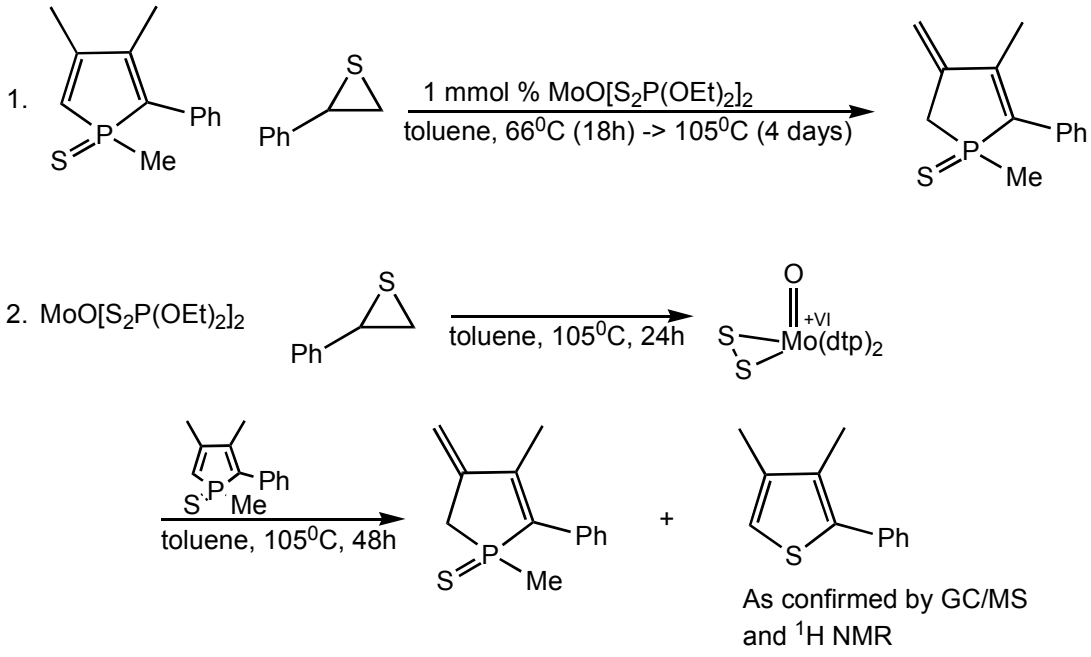
The suggested catalytic cycle of the generation of the molybdenum oxo-disulfur complex and the sulfurization of alkenes is shown in Scheme 1.22.[16a] The molybdenum oxo complex reacts with a sulfur source (phenylthiirane or S_8) to generate the disulfur complex, which is the active sulfur-transferring species. The disulfur complex then transfers both sulfur atoms to two alkene molecules. During the sulfur transfer, the oxo complex is regenerated and the catalytic cycle is sustained through its sulfuration.

[18] Iranpoor, N.; Kazemi, F. *Synthesis* **1996**, 821-822



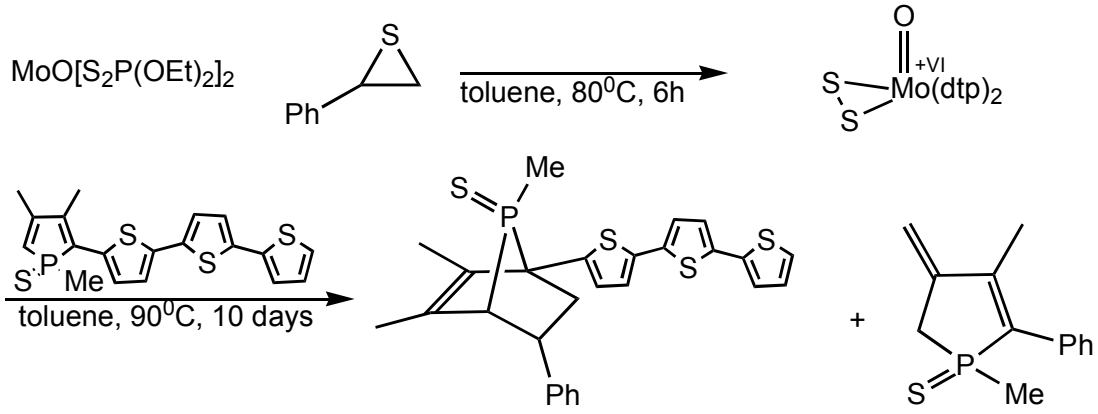
Scheme 1.22.

Following the same procedure, our initial trials had promising results. The first reaction in Scheme 1.23 produced only the isomeric phosphole sulfide. The second reaction differed slightly in that we attempted to create the active catalyst prior to adding the phosphole sulfide that is supposed to be transformed into its thiophene analogue. The major product was still the isomerized phosphole sulfide however, there were trace amounts of oily product that seemed to be our desired thiophene target.



Scheme 1.23.

In order to increase the quantitative yield for analytical purposes, we substituted the α-phenyl group with something more bulky, α-terthiophene. Scheme 1.24 shows that the 4+2 cycloaddition was preferred instead of 4+1 as we anticipated. This was most likely due to the presence of styrene, which could be produced as a result of sulfur extraction from thiirane by the molybdenum oxo catalyst.



Scheme 1.24.

1.4 Biological Studies (work done by Dr. Barbara Merk, UVA)

Lastly, samples of **1** were sent to University of Virginia to be tested for potential biological activities and the results are discussed below.

Cytotoxicity Studies

Addition of 1,2-dithiole-3-thione to the growth medium at concentrations up to 100 μM did not appear to have any adverse effects on any of the cell lines. There was no indication that treated cells were undergoing apoptosis, growing more slowly or otherwise impacted by the presence of the compound. Visually, no difference was seen between treated cells and the DMSO-only control.

^{3}H-Thymidine Incorporation

The cell proliferation assay was done to confirm the lack of adverse effects seen visually. Treatment of U-1242MG and U-87MG cells with 1,2-dithiole-3-thione at concentrations up to 100 μM did not significantly alter their uptake of ^{3}H-thymidine, suggesting that their rates of proliferation were unchanged.

Cell Signaling/Signal Transduction

No effects were observed on either the JAK/STAT or the MAPK signaling pathways when the compound was added to cells prior to growth factor treatment. 1,2-dithiole-3-thione by itself also did not induce signaling via these pathways.

Discussion

It is hard to say whether the 1,2-dithiole-3-thione truly does not affect the parameters studied above, or whether it simply is unable to enter cells from the growth medium. Cell membranes selectively take up some compounds and not others; it is entirely possible that **1** never made it into the cells and that this was the reason for the lack of effects seen here. It would be interesting to see whether common DNA transfection methods, including electroporation, would effectively induce cellular uptake of the compound and whether this in turn would result in biological activity.

1.5 Experimental

1,2-Dithiole-3-thione (**1**). To a solution of 1-phenyl-3,4-dimethylphosphole sulfide (0.5 g, 2.27 mmol) in 10 mL of THF at -80 ^{0}C and under argon was added sodium bis(trimethylsilyl)amide (2.4 mL of 1 M solution in THF) via syringe. The color immediately turned from pale yellow to dark red. This solution was stirred for 5 min, after which freshly distilled S_2Cl_2 (0.2 mL, 2.4 mmol) was added via syringe and the solution was warmed to 0 ^{0}C and stirred for 20 min. At this point the color of the solution turned lighter red. Still at 0 ^{0}C, triethylamine (0.97 mL, 6.96 mmol) was added to the mixture followed by another equivalent of S_2Cl_2 (0.2 mL, 2.4 mmol). The color turned brown. The solution was then warmed to room temperature. The reaction was monitored by ^{31}P NMR and TLC (50:50 petroleum ether/CH_2Cl_2), proving the presence of the red compound **1**. The solvent was removed *in vacuo*, and the mixture was purified by column chromatography on silica gel using 75:25 petroleum ether/methylene chloride as the eluent, yielding 73 mg (10.3%) of **1**. Black crystals were formed spontaneously overnight.
^{1}H NMR (CD_2Cl_2): δ 2.61 (dd, 3H, $^4J_{PH}$=1.7 Hz, $^4J_{HH}$=1.1 Hz, Me), 6.19 (dd, 1H, $^2J_{PH}$ = 32.2 Hz, $^4J_{HH}$ = 1.1 Hz, =CH-P), 7.56 (m, 2H, Ph meta H), 7.64 (m, 1H, Ph para H), 7.87 (m, 2H, Ph ortho H). ^{13}C NMR (CD_2Cl_2): δ 18.90 (d, $^3J_{PC}$ = 16.2 Hz, Me), 126.94 (d, $^1J_{PC}$ = 83.7 Hz, Ph ipso C), 128.03 (d, $^1J_{PC}$ = 83.3 Hz, =CH-P), 129.87 (d, $^3J_{PC}$ = 14.4 Hz, Ph meta CH), 131.34 (d, $^2J_{PC}$ = 12.7 Hz, Ph ortho CH), 133.95 (s, Ph para CH), 150.24 (d, $^2J_{PC}$ = 28.7 Hz, Me-C=), 153.65 (s, =C-C=S), 175.75(d, $^1J_{PC}$ = 64.8 Hz, P-C-S), 209.61 (d, $^3J_{PC}$ = 16.6 Hz, C=S). ^{31}P NMR (CD_2Cl_2): δ 31.6. Mass spectrum: m/z 312.9398 (MH^+, 100%). Anal. Calculated for $C_{12}H_9PS_4$: C, 46.13; H, 2.90. Found: C, 46.21; H, 3.00.

Complexation of **1** by Tungsten Pentacarbonyl. Tungsten pentacarbonyl was made *in situ* by dissolving 86 mg (0.24 mmol) of tungsten hexacarbonyl in 12 mL of acetonitrile, then adding 27 mg (0.24 mmol) of trimethylamine-N-oxide dihydrate as a solid. The solution turned bright yellow immediately and was stirred for 30 min. Acetonitrile was removed *in vacuo*, and the remaining bright yellow solid was then redissolved in 10 mL of dry THF. This solution

was stirred for 20 min and cooled to 0 ^{O}C, and the 24 mM solution of **1** (76 mg in 10 mL of THF) was added dropwise via a syringe. The mixture was stirred overnight, and in the morning, the solution appeared dark blue. One pink and one blue spot were observed by TLC (50:50 petroleum ether/dichloromethane). The crude mixture was initially filtered quickly through silica gel, after which it was further purified using silica gel column chromatography (100% petroleum ether -> 100% dichloromethane). The pink fraction (**3**) was eluted with a 70:30 solvent mixture in 2.3% yield (3 mg), and the blue fraction (**2**) with a 50:50 solvent mixture in 1% yield (1.6 mg). Both fractions were left overnight in test tubes, and pink and blue crystals were obtained spontaneously. Elemental analyses were not obtained for **4** and **5** due to insufficient quantities of products.

Complex **3**: ^{1}H NMR (CD_2Cl_2): δ 2.66 (dd, 3H, $^{4}J_{PH} \approx {}^{4}J_{HH}$ = 1.8 Hz, Me), 6.29 (dd, 1H, $^{2}J_{PH}$ = 32.0 Hz, $^{4}J_{HH}$ = 1.8 Hz, =CH-P), 7.55 (m, 2H, Ph meta H), 7.64 (m, 1H, Ph para H), 7.87 (m, 2H, Ph ortho H). ^{13}C NMR (CD_2Cl_2): δ 19.79 (d, $^{3}J_{PC}$=16.1 Hz, Me), 125.57 (d, $^{1}J_{PC}$ = 84.2 Hz, Ph ipso C), 129.32 (d, $^{1}J_{PC}$ = 83 Hz, =CH-P), 129.64 (d, $^{3}J_{PC}$ = 13.4 Hz, Ph meta CH), 130.93 (d, $^{2}J_{PC}$ = 12.0 Hz, Ph ortho CH), 133.87 (s, Ph para CH), 151.49 (s, =C-C=S), 196.91 (s, cis-CO), 201.04 (s, trans-CO), 207.70 (d, $^{3}J_{PC}$ = 13.4 Hz, C=S). ^{31}P NMR ($CDCl_3$): δ 38.0.

Complex **2**: ^{1}H NMR ($CDCl_3$): δ 2.62 (s, Me), 7.09 (s, =CH-S). ^{13}C NMR ($CDCl_3$): δ 15.67 (s, Me), 128.23 (s, =CH-S), 134.92 (s, Me-C=), 197.26 (s, cis-CO), 201.08 (s, trans-CO), 207.11 (s, C=S). Mass spectrum: m/z 203.94 (base peak). Anal. Calculated for M-W(CO)5: 203.92.

(Procedure described hereon was done by Dr. Barbara Merk)

Preparation of Sterile Stock Solution

1,2-dithiole-3-thione was initially dissolved in sterile dimethyl sulfoxide (DMSO) to make a 100 mM stock solution. (Note: there was a dramatic color change to red/orange as soon as the compound was added to the DMSO)

The stock solution was filtered (pore size: 0.2 microns) to sterilize it, divided into aliquots and stored at -20 ^{O}C.

Cell Culture

Cell lines used in this study included 4 established Glioblastoma (GBM) cell lines (U-1242MG, U-87MG, U-251MG and A172), one breast cancer cell line (MCF-7) and non-malignant human fetal astrocytes ("normal human astrocytes, NHA). The U-1242MG and U-251MG cell lines were originally supplied by Dr. A.J. Yates (Ohio State University) and Dr. D.D. Bigner (Duke University), respectively. Both cell lines were isolated from characterized GBM tumors and have been extensively described elsewhere (Hussaini et al., 2000). The U-87MG cell line was obtained from the American Type Culture Collection (Manassas, VA), and the A172 cell line was supplied by Dr. R. Abounader (University of Virginia).

All four GBM cell lines were cultured in minimal essential medium-α (MEM-α) supplemented with 10% fetal bovine serum (FBS) Hyclone, Logan, Utah) and 1% penicillin/streptomycin (Invitrogen) at 37 ^{0}C in 4.8% CO_2, 90% relative humidity, and passed every 4-6 days.

NHA cells were cultured in a growth medium containing 25 μg/ml bovine insulin, 20 ng/ml Epidermal Growth Factor (EGF), 5% fetal bovine serum, 20 ng/ml progesterone, and 50 μg/ml transferring at 37 ^{0}C in 4.8% CO_2, 90% relative humidity.

MCF-7 cells were obtained from Dr. C. Silva (University of Virginia) and cultured in high glucose Dulbecco's Modified Eagle Medium (DMEM) with 10% FBS and 1% penicillin/streptomycin at 37° C in 4.8% CO_2, 90% relative humidity. They were passed every 6-7 days.

Cytotoxicity Studies

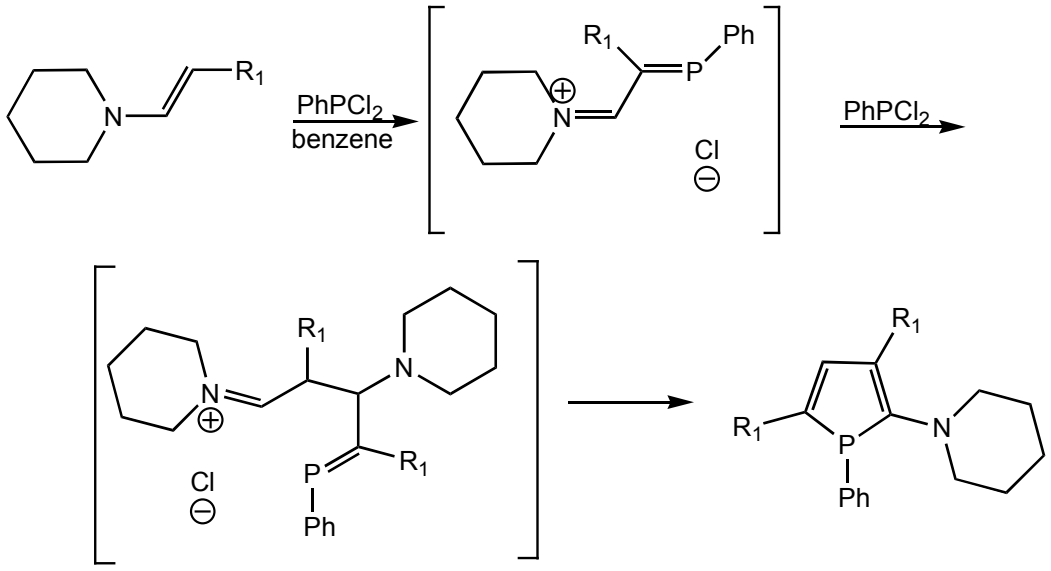
Initial experiments looked for any potential cytotoxicity of the compound when added to cells in culture. The 100mM stock solution of 1,2-dithiole-3-thione was added to fresh cell culture medium and thereby diluted to final concentrations ranging from 100 nM to 100 μM. Cytotoxicity studies were performed on all 6 cell lines.

Cells were trypsinized, counted and plated in 6-well culture plates and allowed to grow to 40-50% confluence. The medium was removed, and cells

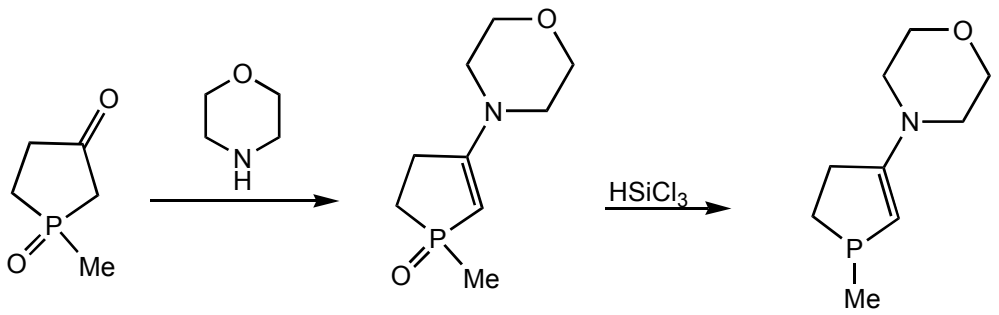
Chapter II

2.1 Introduction

The synthesis of aminophospholes is very limited to this day and their chemistry has not been well explored. Foucaud[1] and Quin[2] reported the syntheses of 2-aminophosphole (Scheme 2.1) and 3-aminophospholene (Scheme 2.2), respectively, however the latter one is the phosphole derivative that does not possess the dienic system within the ring.



Scheme 2.1.



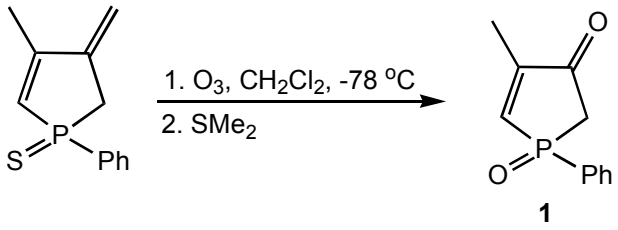
Scheme 2.2.

[1] Tan, W. H.-L. W.; Foucaud, A. *Tetrahedron Lett* **1988**, *29*, 4581
[2] Quin, L. D.; Stocks, R. C. *J. Org. Chem.* **1974**, *39*(5), 686

Taking into account the poor aromaticity of phospholes, an electron-donating substituent such as amine on the beta position seemed like a good candidate for the disruption of phosphole's dienic system. We expected that such a substitution would have a strong effect on the phosphorus lone pair by increasing its basicity. The experimental data indeed showed the effects of the morpholine substituent but in quite unexpected way.

2.2 Results and Discussion

The synthesis of our 3-aminophosphole begins with the transformation of easily accessible 2-phospholene sulfide into 3-oxophosphol-4-ene oxide in 78% yield (Scheme 2.3).[3] We used ozonolysis reaction to cleave the exocyclic C=C double bond in order to form the ketone **1**.

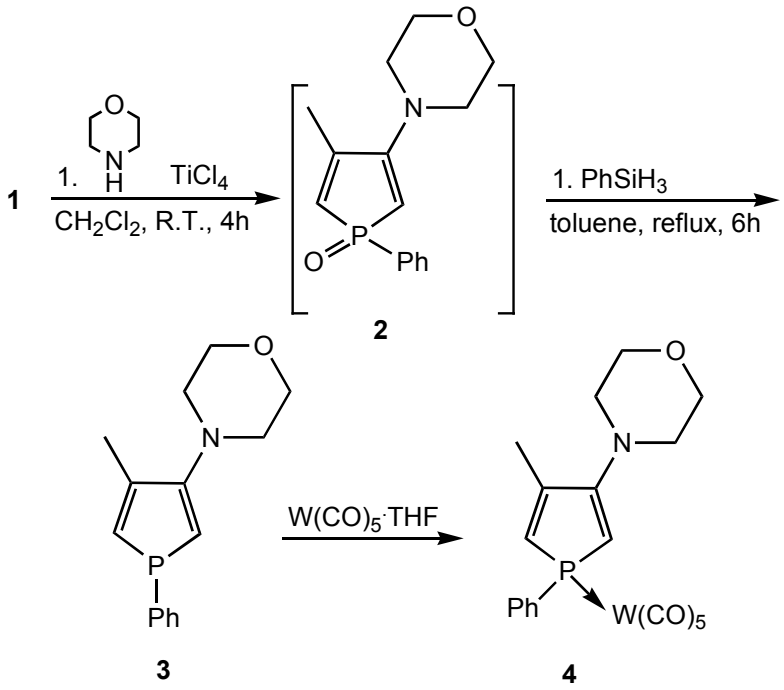


1

Scheme 2.3.

When **1** was reacted with morpholine in the presence of $TiCl_4$ catalyst, the corresponding 3-amino phosphole oxide **2** was then reduced *in situ* by phenylsilane (Scheme 2.4). The tricovalent phosphole **3** was prone to hydrolysis and oxidation, so the full characterization of **3** was carried out on its P-$W(CO)_5$ complex **4**. Crystal structures of other metal complexes of **3** were also attempted using $PdCl_2$, $PdCl_2(CH_3CN)_2$, CuCl but to no avail.

[3] Luo, W.; Ciric, A.; Tian, R.; Mathey, F. *Organometallics* **2010**, *29*, 1862



Scheme 2.4.

P-W coupling is directly correlated to the electron donation of P lone pair: the higher the coupling value, the lower the donation.[4] The measured P-W value of **4** was 219 Hz, which is higher than the value of 215 Hz for the 1-phenyl-3,4-dimethylphosphole P-$W(CO)_5$ complex. This discovery contradicted our initial presumptions, proving that the amino substituent had no significant effect on the basicity of phosphorus lone pair. The calculations that we subsequently conducted supported the experimental findings. Figure 2.1 depicts the LUMO, HOMO, and HOMO-1 for 1,3,4-trimethylphosphole (**A**) and 3-aminophosphole (**B**). The LUMO of **B** has higher energy than **A** by 0.13 eV but without major modifications in shape. The HOMO of **A** seems to be localized mainly over the diene unit however, it spreads over the P and N lone pairs in **B**. And HOMO-1, which corresponds to the lone pair on phosphorus, does not show any substantial increase in energy. These values support our observations in the P-$W(CO)_5$ complex.

[4] Schumann, H.; Kroth, H.-J. *Z. Naturforsch*. **1977**, *32b*, 768; Mercier, F.; Mathey, F.; Afiong-Akpan, C.; Nixon, J. F. *J. Organomet. Chem.* **1988**, *348*, 361

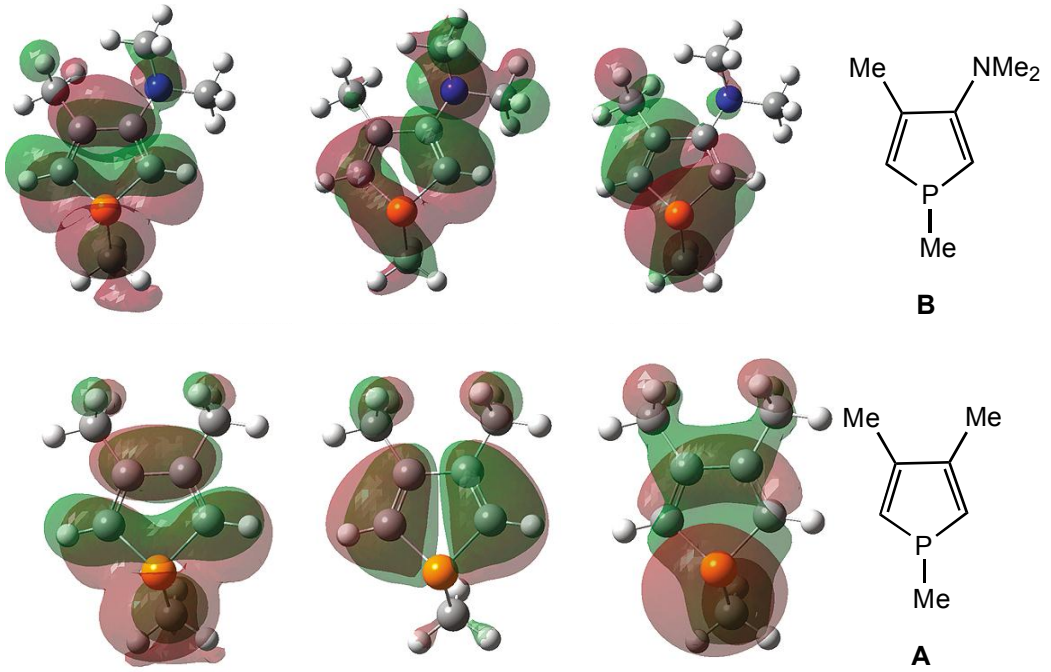


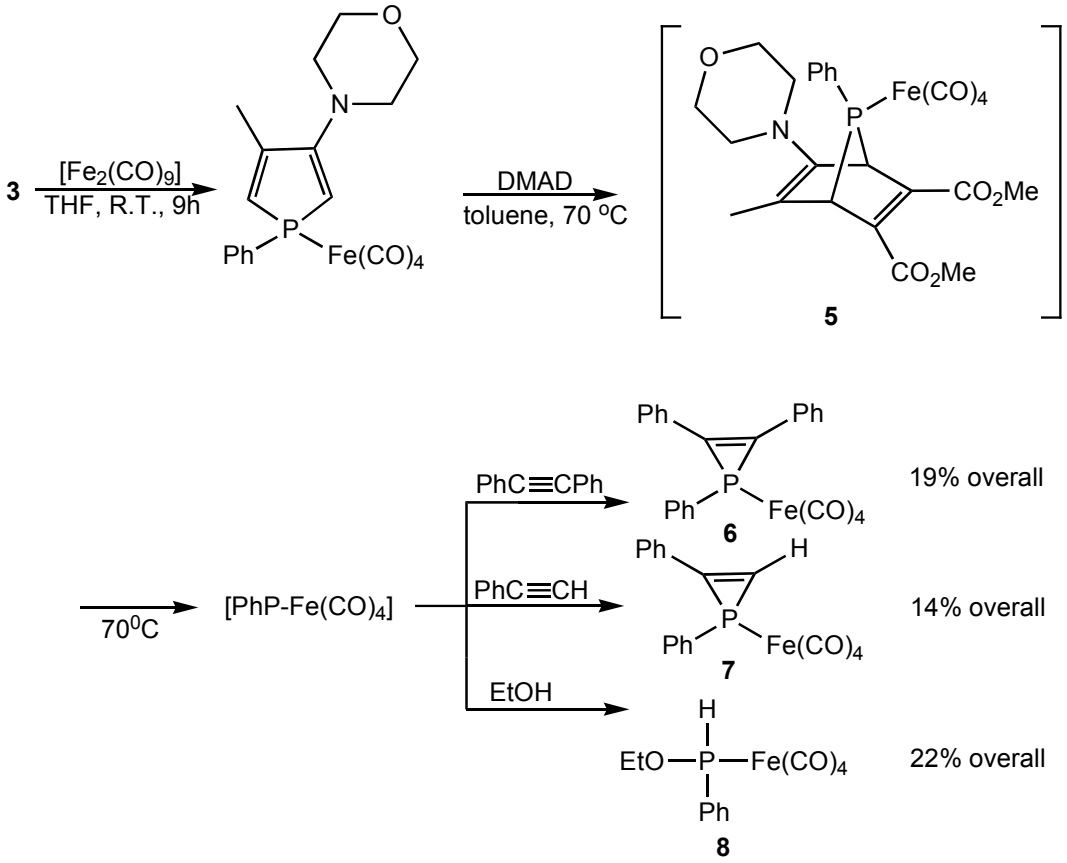
Figure 2.1. LUMO, HOMO, and HOMO-1 of model compounds A and B

Since the main effect of β-amino substitution is enhanced reactivity of the dienic system, we decided to use this property for the synthesis of 7-phosphanorbornadienes, known mainly as precursors to terminal phosphinidine complexes.[5] Lammertsma has also done research with [iPr_2N-P-$Fe(CO)_4$] complex, synthesized from the Collman's regent iPr_2N-PCl_2 and $Na_2Fe(CO)_4$, in addition to the more commonly used substituents Co, Mo, and $W(CO)_5$.[6] We wanted to explore whether our compound **3** is able to produce such a P-$Fe(CO)_4$ complex, which would not have to be limited to the amino substituent as previously mentioned.

Scheme 2.5 shows the synthetic route to the phosphirene complexes. Compound **3** was transformed into its iron complex in high yields and purity thus, it was used without further purification in the reaction with dimethyl acetylenedicarboxylate (DMAD). This reaction occurs readily however, the resulting bicyclic structure **5** is thermodynamically unstable even at mild conditions. Therefore, we decided to follow the same protocol reported for

[5] Lammertsma, K.; Vlaar, M. J. M. *Eur. J. Org. Chem.* **2002**, 1127
[6] Borst, M. L. G.; van der Riet, N.Lemmens, R. H.; de Kanter, F. J. J.; Schakel, M.; Ehlers, A. W.; Mills, A. M.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Chem. Eur. J.* **2005**, *11*, 3631

the generation and trapping of [ClP-W(CO)$_5$].[7] We used DMAD and trapping reagents (diphenyl acetylene, phenylacetylene) simultaneously while heating the reaction mixture overnight. Complexes **6** and **7** were obtained from their respective alkynes, and the secondary phosphinite complex **8** was obtained from ethanol. 2,4-Dimethyl-1,4-butadiene trapping reagent resulted in no reaction. In contrast to **3**, 1-phenyl-3,4-dimethylphosphole cannot be reacted in the same way, indicating the enhanced reactivity of the diene system upon β-amino substitution.



Scheme 2.5.

[7] Duffy, M. D.; Mathey, F. *J. Am. Chem. Soc.* **2009**, *131*, 7534

2.3 Experimental

Isomeric Phosphole Sulfide. To a solution of 1-phenyl-3,4-dimethylphosphole sulfide (2.0 g, 9.1 mmol) in 30 mL of THF at -78 ^{0}C and under argon was added sodium bis(trimethylsilyl)amide (5 mL of a 2 M solution in THF) via a syringe. After stirring for about 10 min, 4 mL of 3 N HCl was added via a syringe; the mixture was stirred for another 10 min at -78 ^{0}C, then slowly warmed to room temperature. After extraction, the organic layer was dried with $MgSO_4$. The residue was chromatographed with CH_2Cl_2/hexane (70:30). Yield: 1.4 mg, 70%. ^{31}P NMR (162 MHz, $CDCl_3$): δ 49.2. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.10 (s, 3H, CH_3), 3.11-3.21 (m, 2H, P-CH_2), 5.24 (d, J = 1.84 Hz, 1H, =CH_2), 5.40 (s, 1H, =CH_2), 6.06 (d, J = 25.64 Hz, 1H, P-CH), 7.40-7.47 (m, 3H, Ph), 7.75-7.81 (m, 2H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.53 (d, J = 17.2 Hz, CH_3), 40.36 (d, J = 60.35 Hz, P-CH_2), 113.04 (d, J = 13.42 Hz, =CH_2), 127.52 (d, J = 78.55 Hz, P-CH), 128.61 (d, J = 12.46, Ph), 130.93 (d, J = 11.49 Hz, Ph), 131.76 (d, J = 28.7 Hz, Ph), 132.81 (d, J = 79.52, Ph), 145.48 (d, J = 9.58 Hz), 156.70 (d, J = 12.46 Hz).

4-Ketophospholene (**1**). A 2.0 g (9.1 mmol) amount of isomeric phosphole sulfide was dissolved in 50 mL of CH_2Cl_2. A stream of ozone was bubbled through the solution at -78 ^{0}C. Ozone treatment was terminated when the mixture turned blue. A stream of O_2 removed the excess ozone; then an excess of dimethyl sulfide was added. The mixture was slowly warmed to room temperature and stirred overnight. After removal of the solvent, the product was purified by column chromatography with CH_2Cl_2/EtOH (40:1). Yield: 1.46 mg, 78%. ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.12. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 3H, CH_3), 2.79-2.99 (m, 2H, CH_2), 7.22 (d, J = 16.48 Hz, 1H, P-CH), 7.48-7.56 (m, 5H, Ph). ^{13}C NMR (100MHz, $CDCl_3$): δ 13.82 (d, J = 16.11 Hz, CH_3), 37.78 (d, J = 73.64 Hz, P-CH_2), 129.21 (d, J = 12.65 Hz, Ph), 130.76 (d, J = 10.36 Hz, Ph), 132.84 (d, J = 2.3 Hz, Ph), 143.42 (d, J = 82.84 Hz, P-CH), 158.03 (d, J = 5.75 Hz), 197.12 (d, J = 19.56, C=O).

3-Aminophosphole (**3**). A 0.2 g (0.97 mmol) amount of **1** was dissolved in 10

mL of CH_2Cl_2, followed by 1 mL (excess) of morpholine. Then 0.4 mL of $TiCl_4$ (1 M in toluene) was added slowly at 0 ^{0}C. The mixture was slowly warmed to room temperature, stirred for 4 h, and then filtered. The solvent was evaporated, and the residue was dissolved in 10 mL of toluene. $PhSiH_3$ (0.2 mL, excess) was added to the solution, which was refluxed for 6 h. The solvent was evaporated, and phosphole **3** was extracted with hexane. ^{31}P NMR (162 MHz, $CDCl_3$): δ -7.6. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 (dd, J = 1.4 and 2.7 Hz, 3H, CH_3), 2.85-3.04 (dm, 4H, NCH_2), 3.78-3.84 (m, 4H, OCH_2), 5.75 (dd, J = 2.7, 30 Hz, 1H, P-CH), 6.59 (dm, J = 35.26 Hz, 1H, P-CH), 7.23-7.47 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.45 (s, CH_3), 51.75 (s, NCH_2), 67.02 (s, OCH_2), 109.09 (s, P-CH=), 145.77 (s, Me-C=), 160.76 (d, J = 10.5 Hz, =C-N).

3-Aminophosphole Tungsten Complex (**4**). Phosphole **3** was made from 0.2 g of **1** starting material as described before. Then 0.5 mmol of $[W(CO)_5(THF)]$ in 10 mL of THF was added to the phosphole **3**, and the mixture was stirred overnight at room temperature. Complex **4** was recrystallized from CH_2Cl_2. Yield: 169.6 mg, 30% overall. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 4.73 ($J_{P\text{-}W}$ = 219.1 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.21 (s, 3H, CH_3), 2.93-3.04 (dm, 4H, NCH_2), 3.77-3.79 (m, 4H, OCH_2), 5.67 (d, J = 32.28 Hz, 1H, P-CH), 6.63 (d, J = 33.44 Hz, 1H, P-CH), 7.37-7.38 (m, 3H, Ph), 7.49-7.54 (m, 2H, Ph). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 17.06 (d, J = 11.5 Hz, CH_3), 51.40 (d, J = 2.87 Hz, NCH_2), 66.48 (d, J = 1.92 Hz, OCH_2), 107.1 (d, J = 49.8 Hz, P-CH=), 128.74 (d, J = 10.54 Hz, Ph), 130.3 (s, Ph), 131.11 (d, J = 12,46 Hz, Ph), 132.17 (d, J = 40.29 Hz, P-C(Ph)), 133.21 (d, J = 41.68 Hz, P-CH=), 147.78 (d, J = 5.75 Hz, C-Me), 161.05 (d, J = 15.33 Hz, N-C), 199.56 (d, J = 18.2 Hz, *trans* C=O), 196.59 (d, J=6.71 Hz, cis C=O). Most of the resonances are double due to the presence of two almost undistinguishable enantiomers. Exact mass: calculated for $C_{20}H_{18}NO_6P^{183}W$, 582.0374; found, 582.0372.

Triphenylphosphirene Iron Complex (**6**). Phosphole **3** was obtained from 0.2 g of **1** starting material. The phosphole was dissolved in 10 mL of THF, $Fe_2(CO)_9$ (0.3 g, 0.82 mmol) was added, the mixture was stirred for 2 h at room temperature and monitored by ^{31}P, and the peak at -7 shifted to 61 ppm.

The solvent was removed under vacuum, the residue was dissolved in 10 mL of toluene, and an excess of dimethylacetylenedicarboxylate and diphenylacetylene were added. The reaction mixture was then heated under argon at 70 ^{0}C overnight. After removal of the solvent, the product was purified by chromatography with hexane-CH_2Cl_2 (40:3). Yield: 83 mg, 18.9% (overall). ^{31}P NMR (162 MHz, $CDCl_3$): δ -90.3. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.88 (m, 15H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.02 (d, J = 5.73 Hz, Ph), 128.42 (d, J = 8.59 Hz, Ph), 129.55 (s, Ph), 128.77 (d, J = 11.45 Hz), 130.47 (d, J=5.72 Hz, Ph), 130.62 (d, J = 6.68 Hz, Ph), 131.07 (s, Ph), 131.71 (s, Ph), 132 (d, J = 14.31 Hz), 135.98 (d, J = 17.18 Hz, P-C(Ph)), 213.22 (d, J = 22.9, C=O). Exact mass: calculated for $C_{24}H_{16}O_4PFe$, 455.0136; found, 455.0145.

1,2-Diphenylphosphirene Iron Complex (**7**). The same experiment as for **9** was conducted, with phenylacetylene instead of diphenylacetylene. The product was purified by chromatography with hexane-CH_2Cl_2 (35:5). Yield: 50 mg, 13.6% (overall). ^{31}P NMR (162 MHz, $CDCl_3$): δ -85.5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, J = 19.68, 1H, =CH-), 7.39-7.72 (m, 10H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 120.20 (d, J = 4.77 Hz, P-CH=), δ 125.65 (d, J = 6.68 Hz, Ph), 128.62 (d, J = 11.45 Hz), 129.43 (s, Ph), 130.43 (d, J = 4.77, Ph), 131.13 (s, Ph), 131.81 (d, J = 6.67 Hz, Ph), 131.99 (s, Ph), 136.94 (d, J = 18.3 Hz, P-C(Ph)), 141.84 (d, J = 9.54 Hz), 213.15 (d, J = 22.9 Hz, C=O). Exact mass: calculated for $C_{18}H_{12}O_4PFe$, 378.9823; found, 378.9821.

Secondary Phosphinite Iron Complex (**8**). The same experiment as for **7** was conducted, with EtOH instead of diphenylacetylene. The product was purified by chromatography with hexane-CH_2Cl_2 (35:5). Yield: 70 mg, 21.8% (overall). ^{31}P NMR (162 MHz, $CDCl_3$): δ 153.34. ^{31}P{1H} NMR: δ 153.36 (d, J_{P-H} =390). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (t, J = 6.88 Hz, 3H, CH_3), 3.84 (q, J = 8.72 Hz, 2H, CH_2), 7.92 (d, J_{P-H} = 391.4, 1H, P-H), 7.54 (s, 3H, Ph), 7.70-7.75 (m, 2H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.12 (d, J = 7.66 Hz, CH_3), 67.14 (d, J = 11.5 Hz, CH_2), 129.14 (d, J = 10.54 Hz, Ph), 130.42 (d, J = 10.54 Hz, Ph), 132.19 (d, J = 1.91 Hz, Ph), 134.33 (d, J = 52.69 Hz, P-C(Ph)), 212.37 (d, J = 22.04 Hz, C=O). Exact mass: calculated for $C_{12}H_{12}O_5PFe$, 322.9772; found, 322.9778.

were washed briefly with sterile phosphate buffered saline (PBS) buffer. Fresh medium containing the compound was added (2 ml/well), after which cells were returned to the incubator and visually monitored for any adverse reaction every 4-6 hours.

^{3}H-Thymidine Incorporation

The relative rate of cell proliferation was determined by the measurement of ^{3}H-thymidine incorporation into DNA, as previously described (Hussaini et al., 2000). Briefly, cells were counted and plated in 24-well plates at a density of 1.5 x 10^{4} cells/well (U-1242MG) or 5x10^{5} cells/well (U-87MG). After 24 hours, cells were washed and treated with 1,2-dithiole-3-thione (50-100 μM) or DMSO (control) in their normal growth medium. After another 48 hours, cells were pulsed with ^{3}H-thymidine (1 μCi/ml) for 4 hours. Cells were then washed 3 times with cold PBS, fixed with 10% trichloroacetic acid (TCA), washed again with room temperature PBS, and permeabilized in 1N NaOH overnight. The pH was neutralized with an equal volume of 1M HCl and the solution was transferred into scintillation vials containing Ready-Safe scintillation fluid (10ml). A Beckman Liquid Scintillation Counter was used to quantify ^{3}H-thymidine uptake by the cells. All samples were run in triplicate, and each assay was repeated three times.

Cell Signaling/Signal Transduction

Cells were plated in 6-well plates and grown to 80-90% confluence. 1,2-dithiole-3-thione was added to the medium 12 hours prior to addition of any growth factors or chemokines.

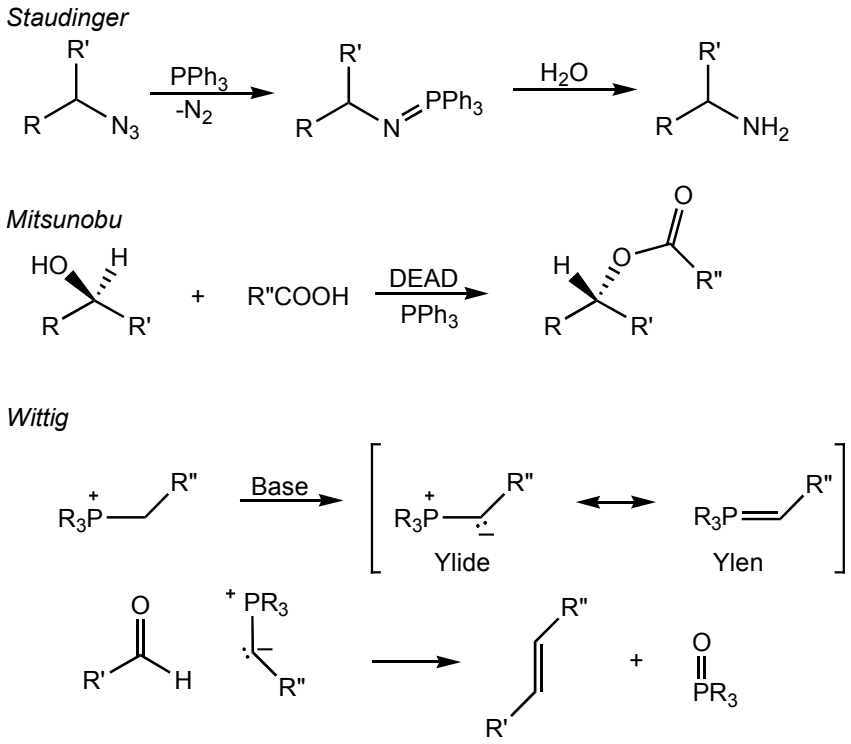
Individual wells were then treated with Epidermal Growth Factor (EGF), Platelet-Derived Growth Factor (PDGF), or Hepatocyte Growth Factor/Scatter Factor (HGF/SF) for 10, 30 or 60 minutes before cells were lysed. Subsequent Western blots assessed the effects of 1,2-dithiole-3-thione on the JAK/STAT and MAPK signaling pathways. As a control, some wells were treated with only 1,2-dithiole-3-thione to ensure that the compound does not by itself induce the activation of intracellular signaling pathways.

Chsapter III

3.1 Introduction

Phosphorus ligands have undoubtedly acquired much attention for their use in homogeneous organometallic catalysis.[1] Careful manipulation of these ligands can lead to high activity and stereoselectivity under relatively mild conditions. Whereas heterogeneous catalysis has found more use in chemical industries, in which the catalyst can be easily separated from the product phase, homogeneous catalysis has found applications in pharmaceutical and agricultural sectors.

Tricoordinated organophosphorus compounds have a wide range of applications in organic synthesis as well.[2] They are well known as agents in Staudinger, Mitsunobu and Wittig reactions (Scheme 3.1).



Scheme 3.1.

[1] Mathey, F. *P-C Heterocyclic Chemistry: The Rise of a New Domain*; Pergamon Press: Oxford, U. K. 2001.; Klein Gebbink, R. J. M. *et al*, *Chem. Eur. J.* **2011**, *17*, 42-57; Allen, D. W. *Organophosphorus Chemistry: Phosphines and Related P-C Compounds* **2011**, *40*, 1-51; Kollar, L.; Keglevich, G. *Chem. Rev.* **2010***, 110*, 4257-4302

[2] Methot, J.L; Roush, W. R. *Science of Synthesis* **2009,** *42*, 469-501

Due to their nucleophilicity and high inversion barrier, acyclic electron-rich phosphines have also become useful as ligands for asymmetric organocatalysis.[2] Chemists find them superior to amines in part due to their inversion barrier, which allows acyclic phosphines to exist in their enantiopure forms, and in part due to their nonbasic character, which permits the use of Lewis or Bronsted acids as co-catalysts. These properties enable phosphines to be used in Morita-Baylis-Hillman reactions, Michael addition, acylation, alcohol-resolution and many other reactions.

The two most widely accepted parameters that affect the strength of phosphorus – transition metal bond, are the sterics and electronics. Steric factors, sometimes quantified by Tolman cone angle and CO stretching frequencies in $(CO)_nM\text{-}PR_3$, are related to the ability of a ligand to find best overlap between the orbital of the phosphorus lone pair and the metal. Electronic factors are related to the P → M σ-donation involving the phosphorus lone pair, and the M → P π-back donation, which involves antisymmetric hybridization of phosphorus 3d and P-R σ^* orbitals.[3] However, once the phosphorus center is incorporated into a ring, the resulting rigidity affects both the sterics (Tolman angle) and the electronics through the modification in the intracyclic R-P-R angle. This allows better control of the space around the catalytic center, which proves to be of enormous influence in enantioselective catalysis. Therefore, the field of phosphorus heterocyclic chemistry has boomed and expanded substantially in the last few decades.

The connection between steric and electronic effects is important. A relatively recent review covers a detailed examination of transition metal phosphine complexes, and how even subtle changes in the ligand structure can affect the reactivity of certain processes and ultimately the catalytic activity of the entire system.[4] The authors also discuss the correlation between the rates of the oxidative addition and catalytic activity in cross-coupling reactions; while these two seem to be directly proportional in the case of R-X activation of alkyl halides, the opposite was found for the aryl halides. Numerous examples suggest that in both cases an electron rich

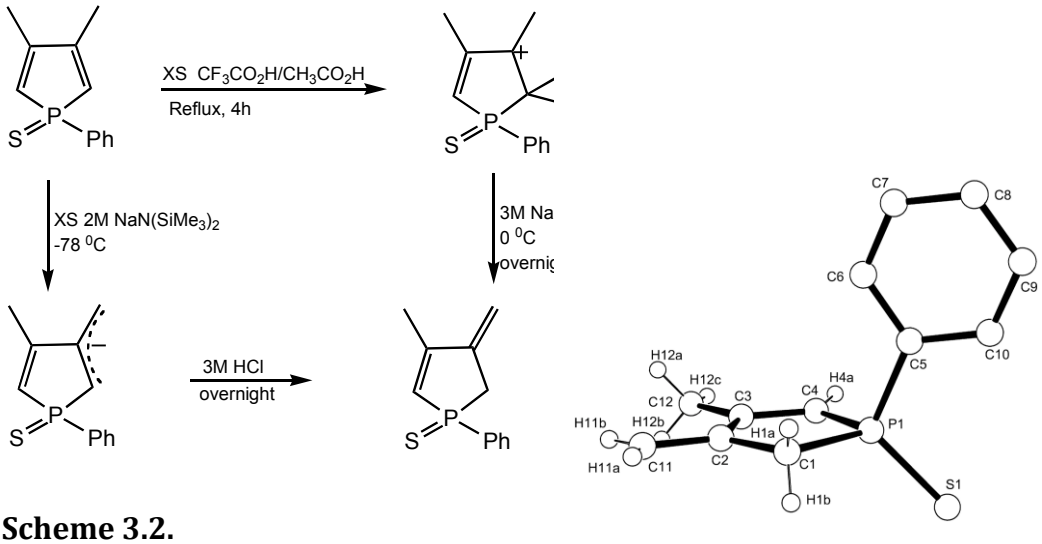
[3] Orpen, A. G.; Connely, N. G. *J. Chem. Soc., Chem. Comm.* **1985**, 1310; Pacchioni, G.; Bagus, P. S. *Inorg. Chem.* **1992**, *31*, 4391-4398
[4] Frew, J. J. R.; Clarke, M. L. *Organomet. Chem.* **2009**, *35*, 19-46

phosphine is required however, once the threshold of donor strength has been passed, it comes down to the more subtle steric effects to determine if the certain oxidative addition will progress readily. The authors also report on the less study of stereo-electronic effects on the transmetallation step, specifically for Stille coupling reaction. In this case, the electron-donating effects are also dependent on the concentration, presence of salts, and also whether the ligand was mono- or bidentate.

3.2 Results and Discussion

The aim of our research was to make a new class of ultrabasic phospholes that would rely on a novel approach, which entails the energy boost of phosphorus lone pair by destabilizing its overlap with the diene system.

As discussed in the Introduction, phospholes can be easily isomerized so that one of the double bonds is shifted to the exocyclic position. There are two ways to carry this process as shown in Scheme 3.2. Both pathways give the same high yield (70-80 %) and they both do not go to completion and yield some of the starting material as well.



Scheme 3.2.

The initial DFT calculations done at the B3LYP/6-311 +G(d,p) level show that phospholene sulfide, the isomeric form, is more stable than the

slightly antiaromatic phosphole sulfide by 2.4 kcal/mol. As a ligand though, our phospholene sulfide had to be converted to its trivalent form, which is 3.5 kcal/mol less stable than its slightly aromatic parent phosphole. Further calculations revealed that isomerization shifts the lone pair on phosphorus to higher energy by 0.49 eV; this destabilization seems to be a consequence of the antibonding overlap of phosphorus lone pair with the HOMO of the diene unit (Figure 3.1).[5]

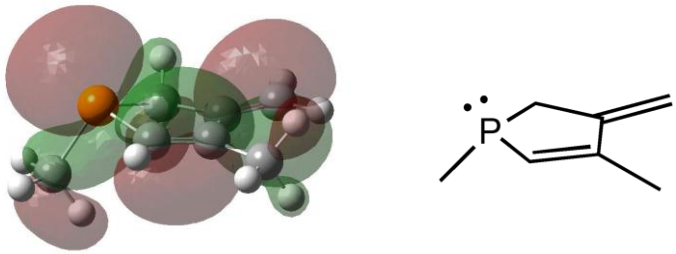
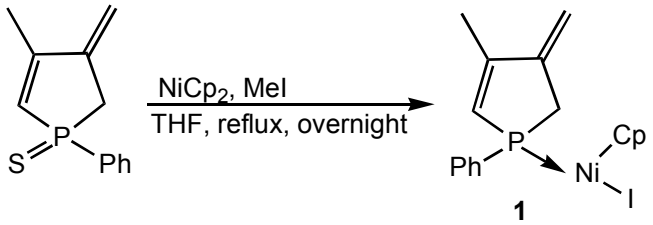


Figure 3.1.

There are a few methods which can be used for desulfurization of P=S bonds[6] however, reagents that we attempted to use (trimethyl phosphite, 1,2-bis(diphenylphosphino)ethane and 1-methylimidazole) produced a large mixture of products that made it quite difficult to identify and isolate the target. Therefore, we decided to apply a mild method that has been described in literature before, using nickelocene and methyl iodide for the reduction/complexation to nickel metal center (Scheme 3.3).[7]



Scheme 3.3.

[5] Ciric, A.; Mathey, F. *Organometallics* **2010**, *29*, 4785
[6] Matano, Y. *et al*. *Organometallics* **2009**, *28*, 6213; Daran, J.-C. . *et al*. *Eur. J. Org. Chem.* **2002**, *4*, 675; Deschamps, E.; Ricard, L.; Mathey, F. *Organometallics* **2001**, *20*, 1499; Mathey, F. *Tetrahed. Lett.* **1979**, *20*, 1753; Santini, C.; Mathey, F. *J. Org. Chem.* **1985**, *50*, 467; van Eis. *et al*. *J. Am. Chem. Soc.* **2000**, *122*, 3386
[7] Mathey, F. *Tetrahedron* **1972**, *28*, 4171; Mathey, F. *J. Organomet. Chem.* **1975**, *87*, 371; Mathey, F. *J. Organomet. Chem* **1979**, *177*, 255

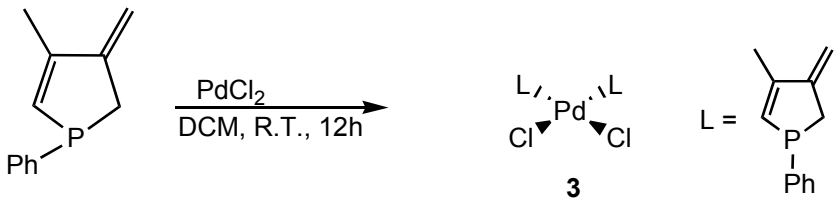
The exact mechanism of this reaction has not been studied in detail. We can only presume that one of the anionic cyclopentadienyl ligands oscillates between η^5 and η^1 coordination so when it takes the η^1 form, the P=S bond coordinates to nickel via the sulfur atom; this results in the weakened P=S bond which facilitates its reduction. Furthermore, one major advantage to this approach is the selectivity: even if some of the phosphole sulfide was present in the reaction mixture, only the phospholene sulfide ended up being reduced.

The following step is the ligand decomplexation using potassium cyanide.[8] This method requires the presence of water, which proved to have other undesired effects, such as oxidation of air-sensitive trivalent species (Scheme 3.4). Thus, certain preventive measures had to be undertaken each time: de-oxygenation of solvents via freeze-thaw-degas technique, use of argon instead of nitrogen, and careful handling during the washings of the crude with deoxygenated brine, the step required to remove excess potassium cyanide (XS KCN). The rate of this particular step can also be increased by heating it in a closed pressure tube at ~70 ^{0}C, which shortens the reaction time to a few hours, as monitored by ^{31}P NMR.

Scheme 3.4.

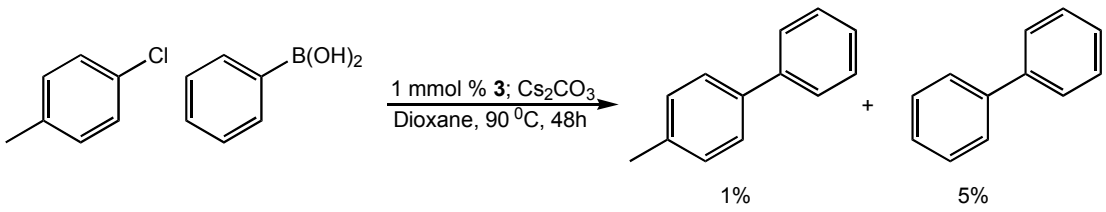
The decomplexed ligand made *in situ* is then reacted with palladium dichloride at room temperature and stirred overnight. The resulting product is a monomeric single isomer, *cis*-PdL_2Cl_2 type of complex (Scheme 3.5).

[8] Pullarkat, S.; Cheow, Y. L.; Li, Y.; Leung, P.-H. *Inorg. Chem.* **2009**, *16*, 2375



Scheme 3.5.

Keeping in mind that this phosphole should be very nucleophilic, we decided to investigate the potential of its palladium catalyst through activating aryl halides, and more specifically in Suzuki cross-coupling reaction. Phenyl iodide, phenyl bromide and phenyl chloride are all useful synthons for making of numerous compounds.[9] Their Ph-X bond dissociation energies are 65 kcal/mol, 81 kcal/mol, and 96 kcal/mol, respectively. So even though phenyl chlorides may be low cost substrates existing in wide variety, they seem to have the most difficult bond to activate. In order to accomplish this step during the oxidative addition, a very nucleophilic ligand is needed to increase the electron richness of palladium metal center. Therefore, we ran the reaction shown in Scheme 3.6, which can be considered a representative reaction for Suzuki cross-coupling.[10]

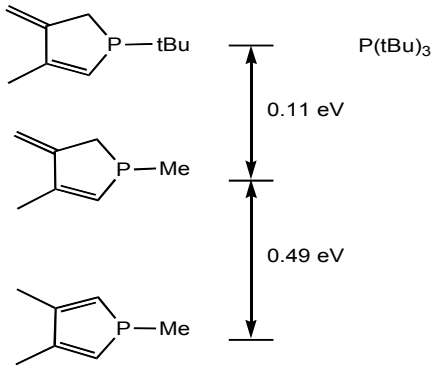


Scheme 3.6.

The yield of the cross-coupled product was low, as determined by gas chromatography mass spectrometer and *n*-dodecane as an internal standard (see Experimental). In addition, an unexpected homo-coupled product was observed as well. Looking back at the structure of our ligand, we realized that perhaps small tuning could change its properties and increase the energy of the phosphorus lone pair making it more basic. The calculations below show that in addition to isomerization, which boosts the energy of P lone pair by

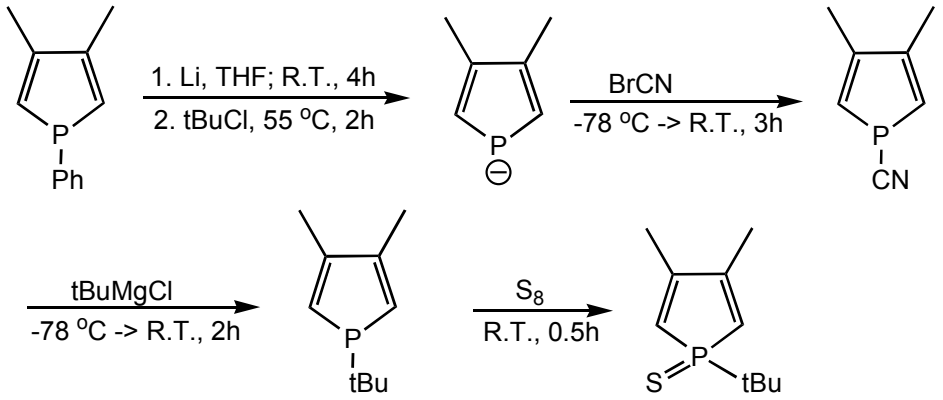
[9] Fu, G.C.; Littke, A. F. *Angew. Chem. Int. Ed.* **2002**, *41*, 4176
[10] Littke, A. F.; Fu, G. C. *Angew. Chem. Int. Ed.* **1998**, *37*, 3387; Kirchhoff, J. H.; Dai, C.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 1945

0.49 eV, the change of phosphorus substituent increases the energy further by another 0.11 eV (Scheme 3.7). Interestingly, this energy level is the same as for $P(tBu)_3$ which is well known for its catalytic potential.[10,11]



Scheme 3.7.

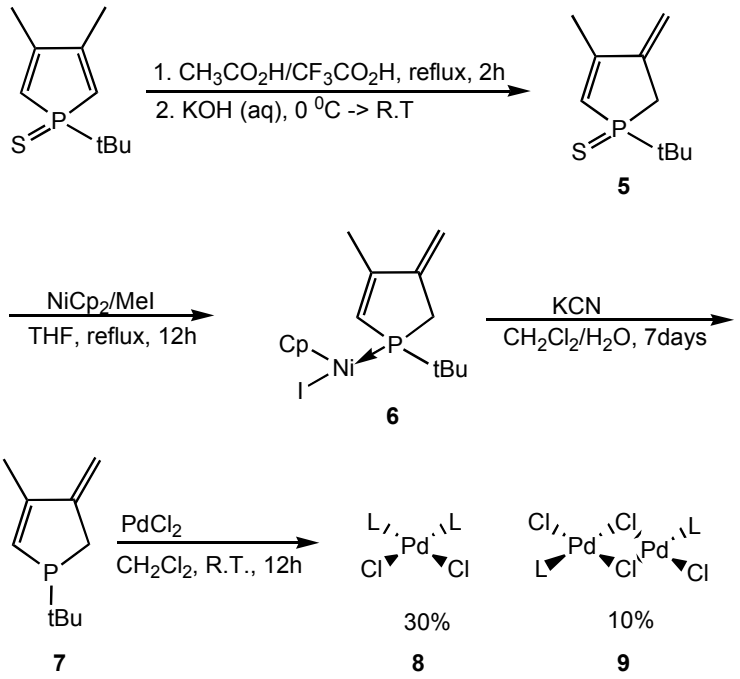
So our next goal was to exchange the phenyl group by a sterically more bulky *tert*-butyl group. In order to achieve this substitution, we had to make the phosphorus center electrophilic, which was done by forming a P-CN bond; so the SN2 substitution by a nucleophile became possible. This reaction was later simplified by the use of tBuLi, which can do nucleophilic substitution (SN2) directly on 1-phenyl-3,4-dimethyl phosphole.[12]

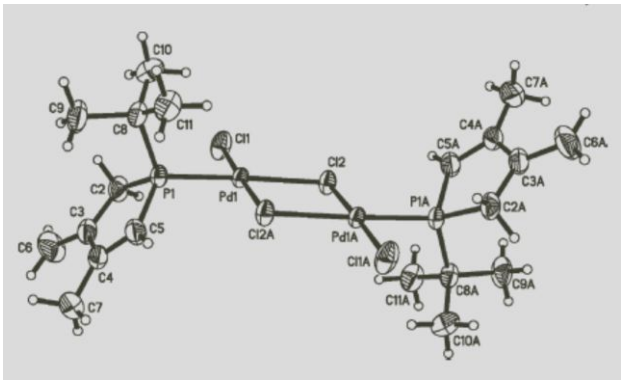


Scheme 3.8.

Once we had **4**, the rest of the synthetic route followed the previously described steps (Scheme 3.9).

[11] Littke, A. F.; Fu, G. C. *J. Org. Chem.* **1999**, *64*, 10; Fu, G. C. *Accts. Chem Res.* **2008**, *41*, 1555
[12] Mathey, F. *Tetrahedron* **1972**, *28*, 4171

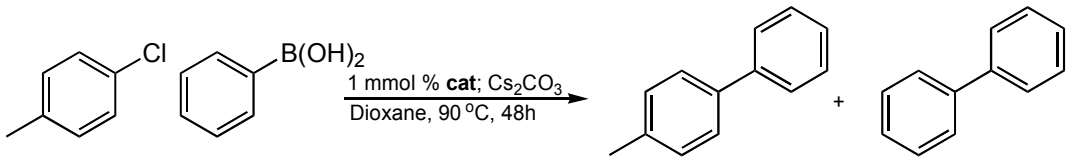




Scheme 3.9.

The yields of all intermediate products were relatively high (50-60%), and X-ray crystal structures were obtained for **6**, **8** and **9**. The ratios for the monomeric and dimeric palladium complexes can be changed easily by using lesser amounts of $PdCl_2$, i.e., when the estimated ratio of ligand to Pd is closer to 1:1.

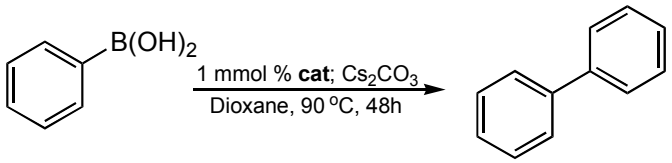
The two new catalysts were also tested in aforementioned Suzuki cross-coupling (Scheme 3.10).



Cat = 8:	8%	3%
9:	41%	44%

Scheme 3.10.

The monomeric complex **8** had much poorer catalytic activity compared to **9**, which gave an interesting ratio of cross- and homo-coupled products in high yields. The reaction we saw here was, in fact, well known.[13] Deboronation homocoupling of aryl boronic acids is a useful synthetic method for deriving symmetric biaryls, which are present in pharmaceutical, optical, electronic and other materials. Therefore, we carried the same reaction without the presence of aryl chloride (Scheme 3.11), in order to see the full potential of our catalysts in the homocoupling reaction.

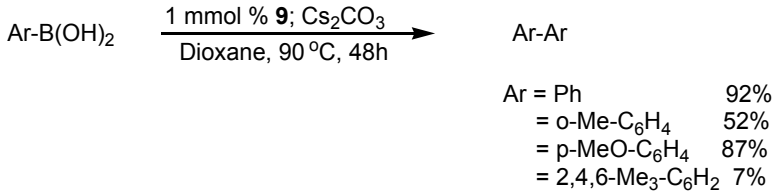


Cat = 3:	12%
8:	43%
9:	92%

Scheme 3.11.

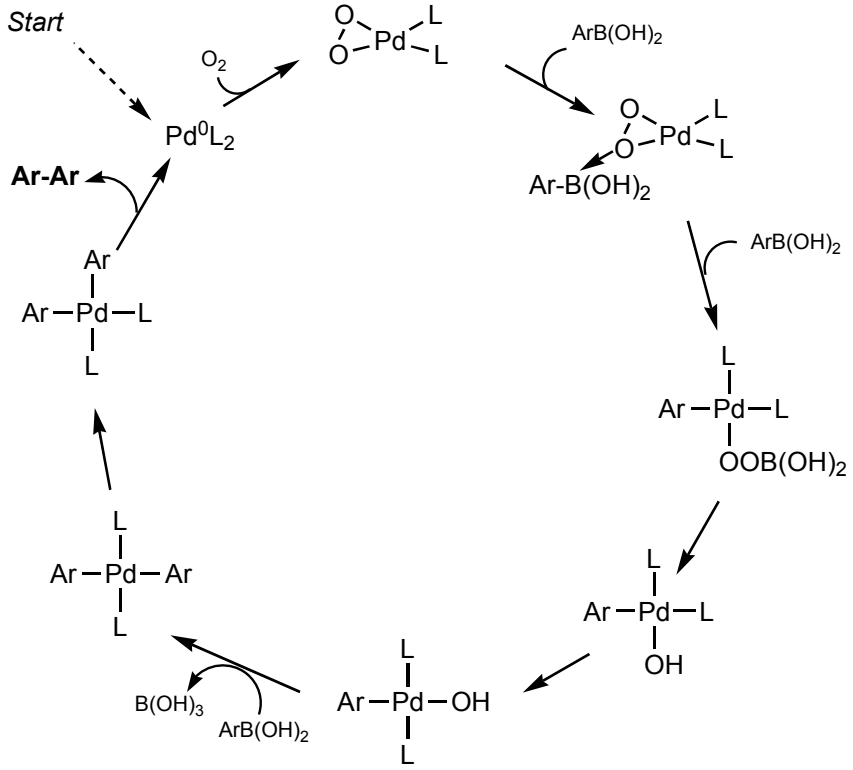
As seen in Scheme above, catalyst **9** showed decent activity, which prompted us to explore other, more bulky and electron rich boronic acids (Scheme 3.12). The homo-coupling of *para*-methoxy phenyl boronic acid gave 87% yield. *Ortho*-methyl was homo-coupled in 52% yield, and even the sterically massive 2,4,6-trimethyl was made in 7% yield. Regarding this last example, only the deboronated boronic acid has been observed by others.[13]

[13] Jin, Z.; Guo, S.-X.; Gu, X.-P.; Qiu, L.-L.; Song, H.-B.; Fang, J.-X. *Adv. Synth. Catal.* **2009**, *351*, 1575



Scheme 3.12.

The mechanism for this transformation[14] has been studied in-depth by the group of Lakmini. They proposed a cycle as shown in Scheme 3.13.



Scheme 3.13.

The palladium peroxo complex was established to have a main role in the catalytic homocoupling of aryl boronic acids. Coordination of Ar-$B(OH)_2$ via the Lewis acid-base interaction between boron and (peroxo) oxygen is thought to be the first step of the mechanism; the bond lengths are consistent with the literature values for boron-ligand distances of known boronated complexes. The subsequent step was experimentally demonstrated to be

[14] Adamo, C.; Amatore, C.; Ciofini, I.; Jutand, A.; Lakmini, H. *J. Am. Chem. Soc.* **2006**, *128*, 6829; Lakmini, H. Ciofini, I.; Jutand, A.; Amatore, C.; Adamo, C. *J. Phys. Chem. A* **2008**, *112*, 12896

trimolecular (with the second order in aryl boronic acid) and thus, upon the formation of Lewis acid-base adduct, the second molecule of aryl boronic acid comes and transfers the aryl group to the palladium coordination sphere in a concerted step. The proposed four-center transition state is depicted in Figure 3.2.

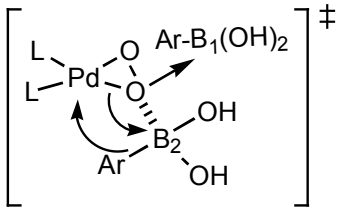
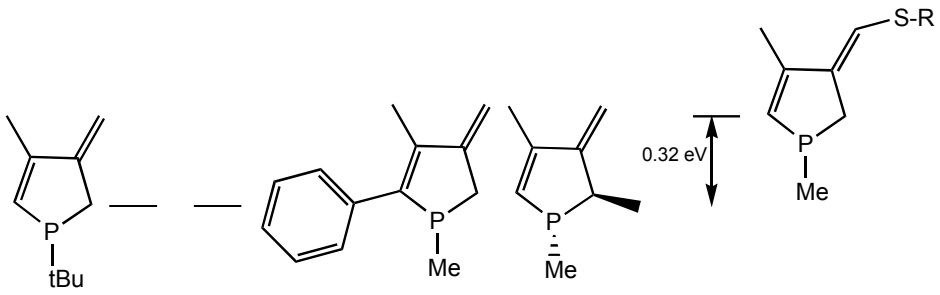


Figure 3.2.

The following transformations consist of hydrolysis of the peroxo complex and *cis-trans* isomerization, leading to the trans $PdL_2(OH)R$ complex that has been characterized experimentally. The cycle is finished by transmetallation and elimination of symmetric biaryls. Our attempts to synthesize a peroxo complex, by purging a DCM solution of **3** with O_2 for a week, resulted in no reaction.

We then decided to investigate, computationally and synthetically, the possibility of modifying the ligand **7** in order to further enhance the overall catalytic activity of its palladium complex. As it can be seen in Scheme 3.14, we designed three new targets that belong to the same class of phospholenes.

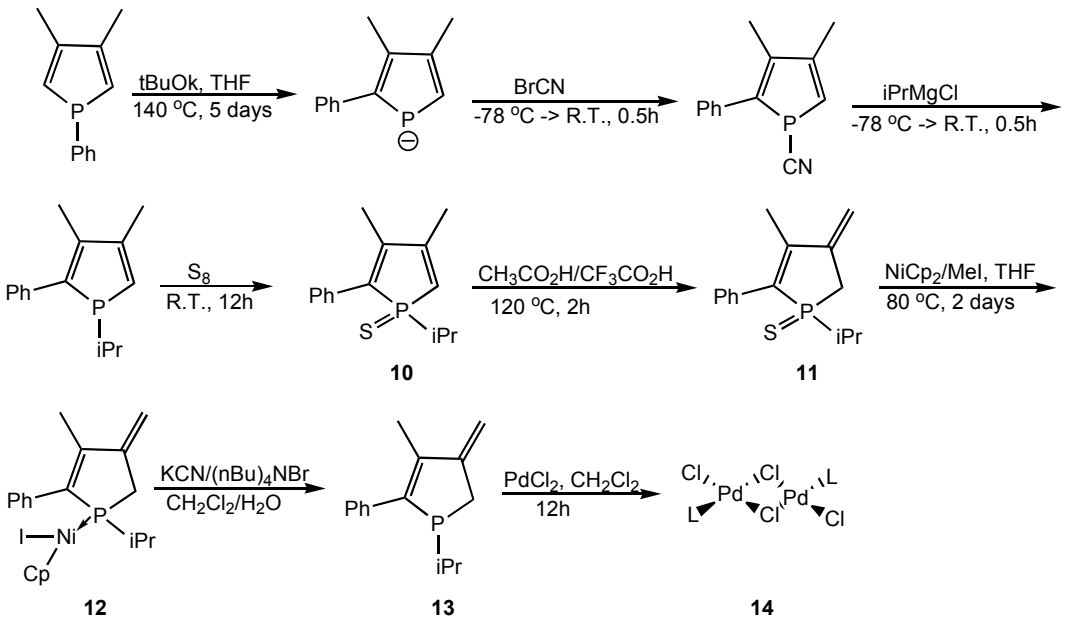


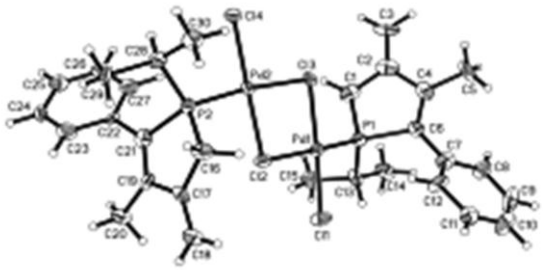
Scheme 3.14.

The first two targets are, in fact, of same energy when compared to our phospholene **7**, suggesting that they won't be more basic than **7**. However,

they do have more steric bulk, which was expected to hinder the phosphorus lone pair more effectively. In addition, the second target possesses a chiral carbon center that could be useful in asymmetric catalysis. The last target was computed to be significantly more basic than **7**, by 0.32 eV rise in P lone pair energy. The synthetic route of these targets was based on some of the substitution methods observed in phosphole chemistry in the past.[15]

The synthesis of α-phenyl phospholene was done as depicted below (Scheme 3.15).





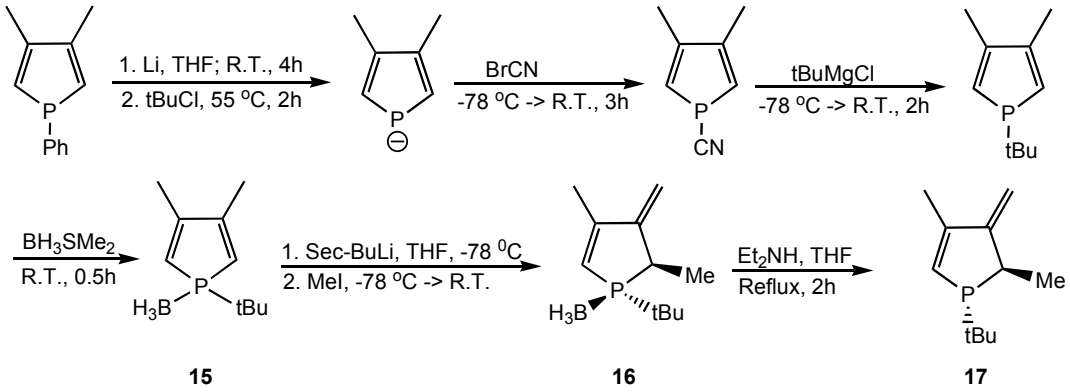
Scheme 3.15.

The first step involves a 1,5-sigmatropic shift, a well-established approach to functionalizing the slightly aromatic phospholes.[15a] After the formation of P-CN bond, we used isopropyl Grignard reagent instead, simply

[15] a) Mathey, M.; Mercier, F.; Charrier, C.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1981**, *103*, 4595; Bachrach, S. H. *J. Org. Chem.* **1993**, *58*, 5414; Mathey, F. *Acc. Chem. Res.* **1992**, *25*, 90; Holland, S.; Jeanjean, M.; Mathey, F. *Angew. Chem. Int. Ed.* **1997**, *36*, 98. b) Tran Huy, N. H.; Mathey, F. *Organometallics* **1994**, *13*, 925.

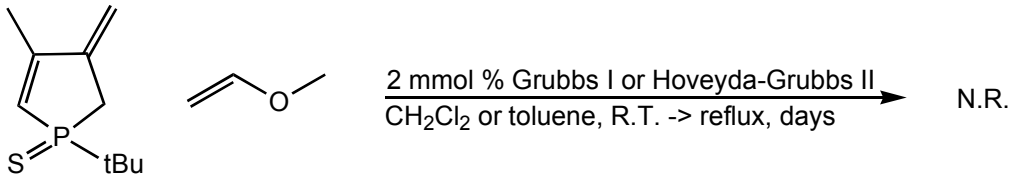
because the tert-butyl was giving poor yields. After sulfurization, **10** was converted into its isomeric form **11**. This product was then reduced following the same method as described earlier, which produced **12** in 30-40% yield. Decomplexation from nickel gave **13**, which was reacted with $W(CO)_5$ and to palladium to give the dimeric PdL_2Cl_4 complex **14**. $J_{(P-W)}$ was 236 Hz, which confirms a slight decrease in basicity compared to our ligand **5**. Unluckily, when this catalyst was used in the same cross-coupling reaction as described in Scheme 10, only 13% of the cross-coupled product was obtained and 23% of the homocoupled product.

Scheme 3.16 describes the synthesis of our second target. One-pot reaction leading to **15** resulted in 64% yield however, the next step gave a mixture of both **16** and **15**. These two could be only slightly purified by extractions with cold n-pentane. After deboronation with diethylamine, both the expected phospholene **17** and its phosphole isomer were obtained in 5:1 ratio. The result of this mixture of isomers is the mixture of two palladium complexes which are not separable by column chromatography nor by extractions. Therefore, we were never able to obtain full characterization of our target phospholene-palladium complex. Since re-crystallization was also unsuccessful, conducting any cross-coupling reaction with a mixture of products was not feasible either. Ligand **17** was reacted with $W(CO)_5$·THF in order to obtain the P-W coupling constant. Since $J_{(P-W)}$ value of **17**-$W(CO)_5$ was 230 Hz, we could say that the basicity of the ligand supports the computational prediction in terms of expected basicity. Moreover, if there were a way to isolate its paladium complex in high purity, the imprinted chirality coupled with the level of basicity could be very useful.



Scheme 3.16.

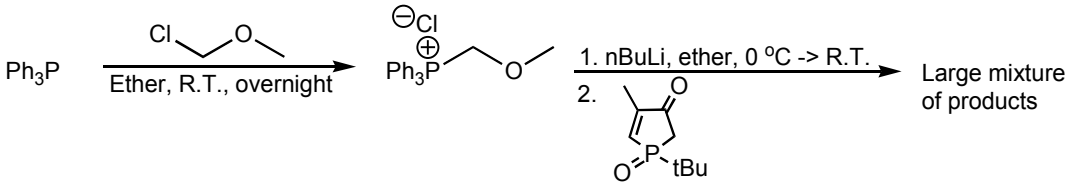
Our last target (see Scheme 3.14), which we hoped would have a significant boost in the energy of the phosphorus lone pair was synthesized as described below. But first, it is worthy mentioning the hopelessness in creating the ~O-R donating group instead of ~S-R. Attempts were made using Grubbs metathesis with our isomeric phospholene **5** and vinylethylether (Scheme 3.17). Taking into account that P=S bond could be interfering with the catalyst, we attempted the same reaction using P-BH_3 adduct,[16] as well as P=O, but to no avail.



Scheme 3.17.

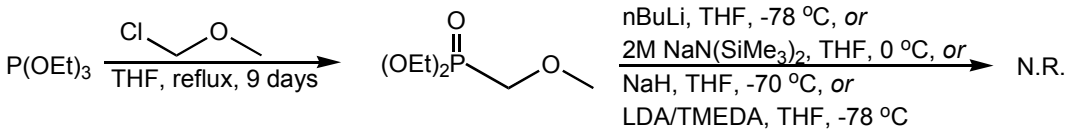
Next attempt involved the use of Wittig reagent. Even though the phosphonium salt was easily made, it was unclear if the ylide was synthesized successfully, because upon addition of our 4-ketophospholene, there was only a large mixture of products.

[16] Schuman, M.; Trevitt, M.; Redd, A.; Gouverneur, V. *Angew. Chem. Int. Ed.* **2000**, *39*, 2491



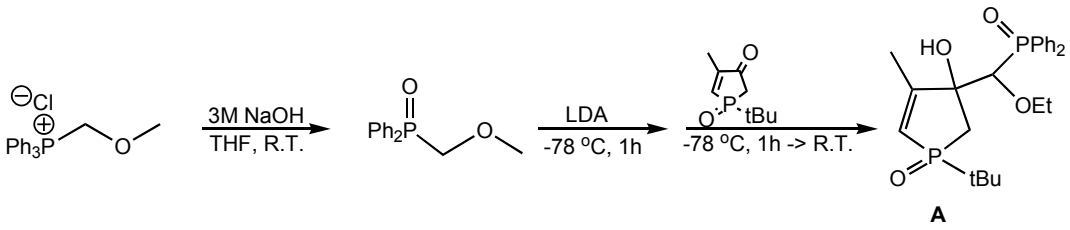
Scheme 3.18.

We also attempted Michaelis-Arbuzov reaction with triethyl phosphite and chloromethyl ethyl ether. The alkyl phosphonate was again successfully made, although the corresponding ylide cold not be obtained with a few different bases (Scheme 3.19). [17]



Scheme 19.

One more method[18] of Wittig-Horner reaction was attempted (Scheme 3.20), in which compound **A** was supposed to be obtained and subsequently deprotonated with tBuOK to yield the desired γ-substituted phospholene (and $Ph_2P(O)OH$ by-product). However, this intermediate was not observed, only a decomposition of products.



Scheme 3.20.

Hence, we focused on creating a sulfur-alkyl substituent (Target **24**, Scheme 3.21), which according to the calculations should have the same electron-donating effects on the phosphorus lone pair as oxygen was supposed to.

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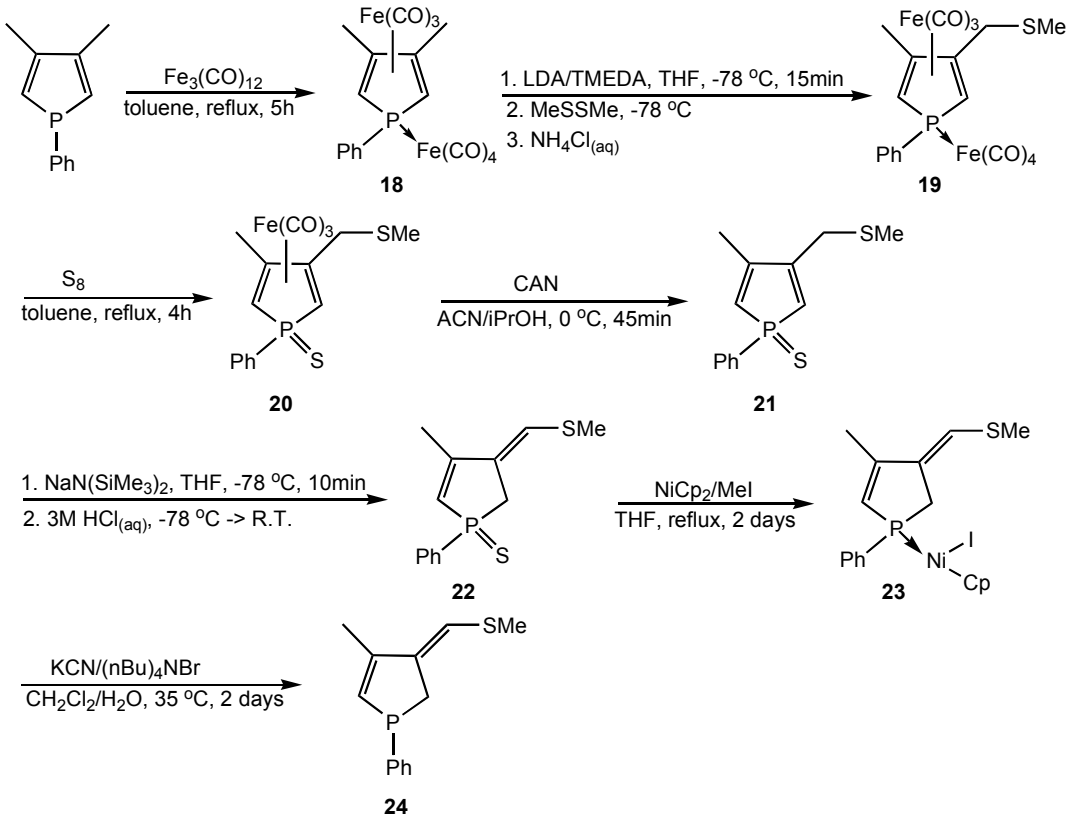
[17] Vo-Quang, Y.; Carniato, D.; Vo-Quang, L.; Le Goffic, F. *J. Chem. Soc., Chem Commun.* **1983**, 1505; Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863; Clayden, J.; Warren, S. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 241

[18] Ley, S. V.; Lygo, B.; Organ, H. M.; Wonnacott, A. *Tetrahedron* **1985**, *41*(18), 3825; Watanabe, M.; Morimoto, H.; Tomoda, M.; Iwanaga, U. *Synthesis* **1994**, 1083



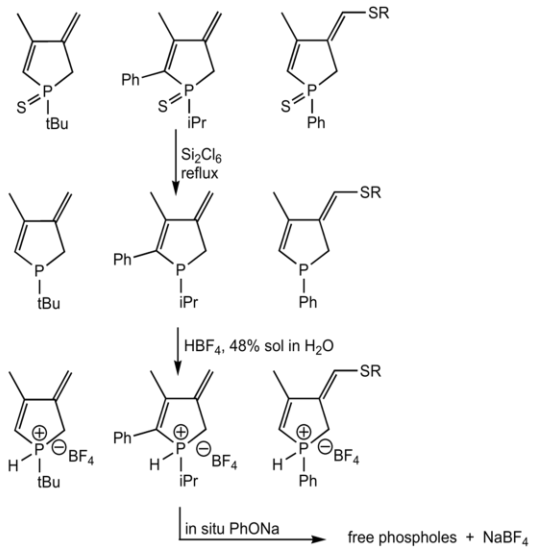
Scheme 3.21.

When we tried to react the delocalized anion of phosphole sulfide directly with MeS-SMe electrophile, both mono- and bi-functionalized phospholes were obtained, most likely due to reaction taking place at both γ and α positions. Thus we had to "lock" phosphole's π system by complexation to $Fe(CO)_3$ (see **18**).[19] In order to functionalize **18**, we had to use LDA as a base; the commonly used $NaN(SiMe_3)_2$ has been shown to add to the carbonyl of $Fe(CO)_3$ in pseudo-Peterson reaction way, resulting in conversion of C=O to C=N.[20] Target **19** was always obtained in good yields, but the following two steps had to be done quickly in order to avoid hydrolysis. In addition, sulfurization had to be the first step so as to prevent oxidation of phosphorus center by cerium ammonium nitrate (CAN). Other methods[21] for **20** -> **21** transformation were also attempted, but they resulted in no reaction. Once we had **21**, isomerization (**22**), reduction/complexation (**23**) and

[19] Mathey, F.; *J. Organomet. Chem.* **2001**, *624*, 105; *J. Organomet. Chem.* **1977**, *136*, 241
[20] Semmelhack, M. F.; Fewkes, E. J. *Tetrahedron Lett* **1987**, *28*, 1497
[21] Knolker, H.-J.; Cammerer, S. *Tetrahedron Lett.* **2000**, *41*, 5035

decomplexation (**24**) all proceed in relatively decent yields. However, at every attempt to react **24** either with $W(CO)_5$ or $PdCl_2$, it was found to be oxidized.

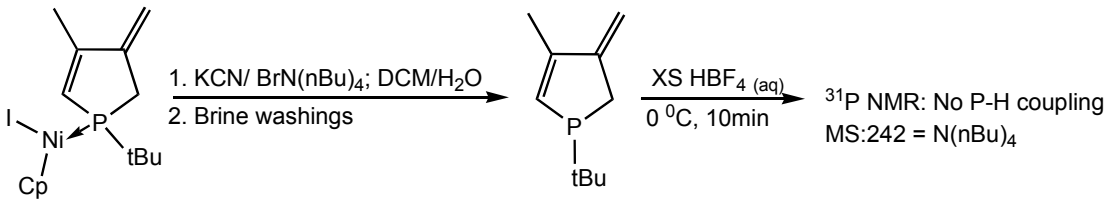
Realizing the difficulties of handling oxygen-sensitive compunds, we looked for an alternative and found a reportedly interesting new route to the active trivalent phospholene species (Scheme 3.22).[22] Formation of phosphonium salt, found to be extremely air- and moisture-stable, and *in situ* deprotonation seemed like an ideal solution to our obstacle.



Scheme 3.22.

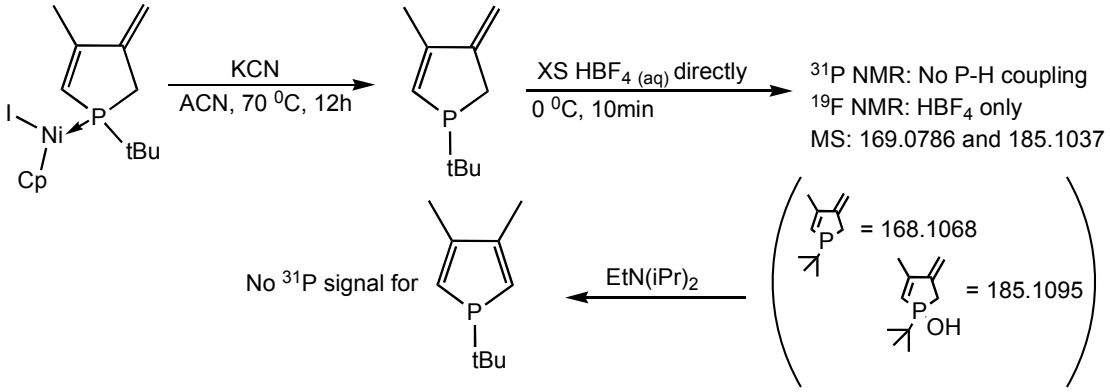
The first reaction was done with our ligand **7**. Since decomplexation with KCN was a long reaction (up to several days), we added some of tetrabutylammonium bromide to have a role of a phase-transfer agent (PTA). With this PTA, the reaction time was shortened to 12h. Excess KCN was removed with brine washings, after which excess aqueous tetrafluoroboric acid was added. As a result, the crude mixture did not produce P-H coupled signal in ^{31}P NMR. It was clear that our target was preceded by the oxidation of **7** (Scheme 3.23).

[22] Netherton, M. R.; Fu, G. C. *Org. Lett.* **2001**, *3*, 4295



Scheme 3.23.

Similar reaction was conducted under slightly different conditions (Scheme 3.24). To avoid the use of PTA, which was found as the major isolated product above, but to still keep the reaction time short, experiment was run in acetonitrile at high temperatures, and excess HBF_4 was added directly to the crude, without removal of excess KCN. Similarly though, no P-H coupling was observed and only one peak was seen in ^{19}F NMR, which corresponded to the reagent used. The two peaks in the mass spectrum indicated the starting ligand **7** as well as the oxidized equivalent of **7**. In order to confirm non existance of our desired target, we reacted the crude with a base, but it did not yield **7**, proving no P-H bond was formed in the first place.

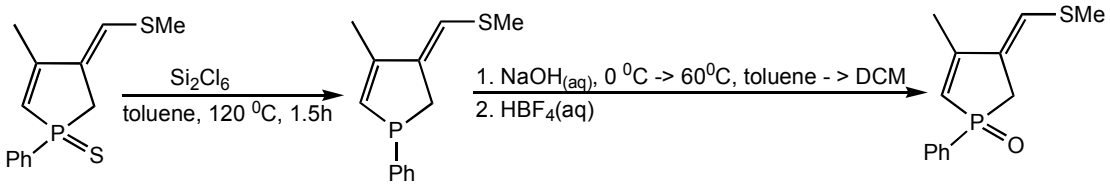


Scheme 3.24.

Similarly to the experiment above, we also did an experiment with ether solution of HBF_4 in order to avoid possible oxidation by water. Unfortunately, even this reagent did not provide us with our target.

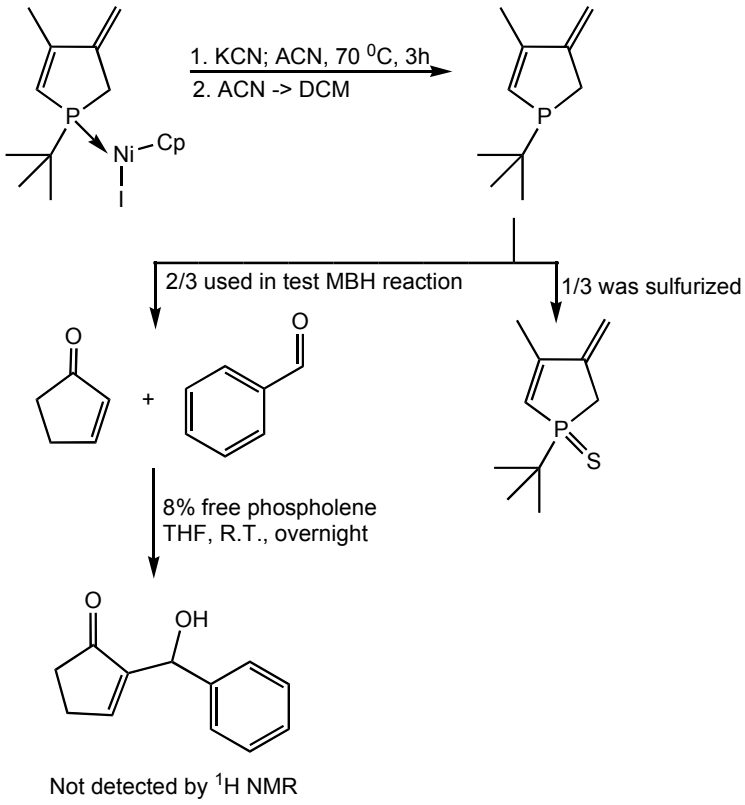
The aforementioned methods for the formation of trivalent species seemed to be highly sensitive to oxidation, so we tried another method used

for reducing P=S bonds.[23] Scheme 3.25 describes our yet another attempt, however, we ran into the same problem as before. Even when starting with the less basic compund **11**, the same phospholene oxide is produced.



Scheme 3.25.

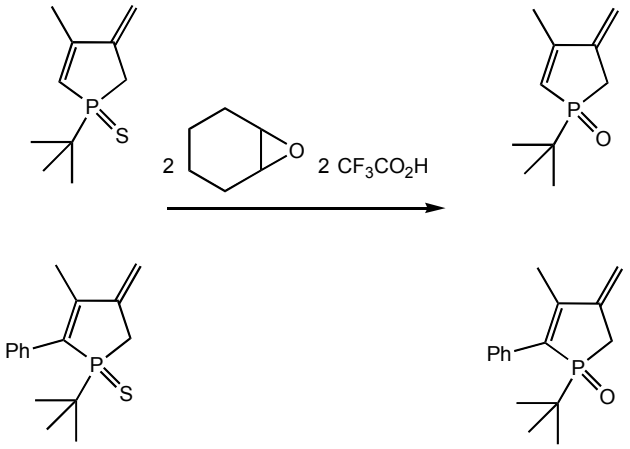
We even attempted to use the trivalent species *in situ* for Morita-Baylis-Hilman reaction. The amount of phospholene used was determined by taking 1/3 of the solution, sulfurizing and quantifying it. The other 2/3 were used directly in a representative MBH reaction (Scheme 3.26). Unfortunately, the expected alcohol was not detected by NMR, implying the oxidation of **7**.



Scheme 3.26.

[23] Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012; Tang, W.; Zhang, X. *Angew. Chem. Int. Ed.* **2002**, *41*, 1612

The highly oxidizable ligands indeed indicate the highly basic/nucleophilic nature of these phospholenes. Even though we were unable to apply them in organic catalysis, they still hold potential for their use as oxides.[24] They have been used in catalysis as pre-ligands, as well as for the extraction of cations as a mean of managing nuclear waste energy. The future of this project could lie in this useful application, which has not been explored in depth with phospholene oxides. If the basicity of our phospholene ligands transpose into a highly polar P=O bond, we could see interesting results in this field. Conversion of phosphole sulfides to phosphole oxides is known (Scheme 3.27) and it normal proceeds without any difficulties.



Scheme 3.27.

[24] Ackermann, L. *Synthesis* **2006**, *10*, 1557; Smythe, L. E.; Whateley, T. L.; Werner, R. L. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1553; Ionova, G.; Ionov, S.; Rabbe, C.; Hill, C.; Madic, C.; Gillaumont, R.; Krupa, J. C. *Solvent extraction and Ion Exchange* **2007**, *19*, 391

III Experimental

All reactions were performed under an inert atmosphere of nitrogen or argon by using standard Schlenk techniques. Toluene and dichloro methane were distilled over P_2O_5. Tetrahydrofuran and diethyl ether were distilled over sodium and benzophenone. Hexanes were distilled over sodium. Et_3N was dried over KOH. Columns were dry-packed, with the crude being mixed and dried with silica (or neutral alumina). Nuclear magnetic resonance spectra were obtained on a Bruker Avance 300 spectrometer operating at 300.1 MHz for ^1H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P or JEOL ECA400 spectrometer at 400 MHz for ^1H, 100.6 MHz for ^{13}C, and 161.9 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from external TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). All coupling constants (J values) are reported in hertz (Hz). All spectra were recorded at 298 K. HRMS spectra were recorded on a Waters Q-Tof MicroTM spectrometer or a Finnigan MAT95XP HRMS system by electrospray ionization (ESI). An X-ray crystallographic analysis was performed on a Bruker X8 APEX diffractometer. Infrared spectra were recorded with a Shimadzu IR Prestige- 21, either neat or in $CHCl_3$. Silica gel (230-400 mesh) was used for the chromatographic separations. For acid-sensitive reactions, neutral, activated aluminium oxide (58 Å, Brockmann Grade I) was used instead. $MgSO_4$ and celite were kept and dried in the oven (115 ^{0}C). 1-Phenyl-3,4-dimethylphosphole 1 was prepared according to the literature. All commercially available reagents were used as received from the suppliers, unless stated otherwise.

1-Phenylphospholene nickel complex (**1**).

0.5 g (2.27 mmol) of 1-phenylphospholene was dissolved in 10 mL THF. 0.56 g (3 mmol) of nickelocene was weighed quickly and added to the mixture as a solid. 1.0 mL (15 mmol) of methyl iodide was added and the mixture was refluxed for ~20h, until the color turned from green to deep pink. The reaction was also monitored by ^{31}P and TLC. The first column was done very quickly as a filtration with 50:50 petroleum ether/DCM mixture throughout. The second column was done slowly from 100 % P.E. -> 50:50 P.E./DCM to

afford 35 % yield of pure **1**. The eluent was left in test tubes for two days, which resulted in the formation of dark pink crystals that confirmed the structure of **1**. ^{31}P NMR ($CDCl_3$) δ 35.5; ^{1}H NMR ($CDCl_3$) δ 2.08 (s, Me), 2.97 (dd, 1H, J_{HH} = 17.4 Hz, J_{HP} = 10 Hz, CH_2P), 3.52 (d, 1H, J_{HH} = 17.4 Hz, J_{HP} = 0 Hz, CH_2P), 5.21 and 5.33 (2s, 2 x 1H, $=CH_2$), 5.40 (s, Cp), 6.14 (d, J_{HP} = 29.8 Hz, =CHP), 7.41 (s br, *m,p*-Ph), 7.91 (m, *o*-Ph); ^{13}C NMR ($CDCl_3$) δ 16.70 (d, J_{CP} = 11.5 Hz, Me), 38.61 (d, J_{CP} = 36.3 Hz, CH_2P), 93.35 (s, Cp), 111.56 (d, J_{CP} = 8.6 Hz, $=CH_2$), 128.64 (d, J_{CP} = 10.5 Hz, CH(Ph)), 129.43 (d, J_{CP} = 43.9 Hz, =CHP), 130.96 (s, *p*-CH(Ph)), 132.93 (d, J_{CP} = 12.4 Hz, CH(Ph)), 135.36 (d, J_{CP} = 40.1 Hz, ipso-C(Ph)), 148.89 (s, =C), 153.70 (d, J_{CP} = 4.8 Hz, =C).

1-Phenylphospholene (**2**).

0.78 g (1.8 mmol) of **1** was dissolved in 3 mL CH_2Cl_2 and 1 mL of diH_2O. Excess potassium cyanide was added as a solid, the solution was purged with argon for a minute and left to stir at 40 ^{0}C for one week in a closed thick ampoule. ^{31}P(crude in CH_2Cl_2) NMR δ -16.2; ^{1}H NMR ($CDCl_3$) δ 2.03 (s, Me), 2.65 (m, 1H, CH_2P), 3.10 (m, 1H, CH_2P), 5.05 (s br, 1H, $=CH_2$), 5.12 (s br, 1H, $=CH_2$), 6.24 (d, J_{HP} = 38.5 Hz, =CHP), 7.32 (m, 3H, *m,p*-Ph), 7.45 (m, 2H, *o*-Ph); ^{13}C NMR ($CDCl_3$) δ 16.71 (Me), 33.82 (d, J_{CP} = 7.6 Hz, CH_2P), 107.81 (d, J_{CP} = 3.8 Hz, $=CH_2$), 128.45 (d, J_{CP} = 7.6 Hz, CH(Ph)), 129.09 (s, *p*-CH(Ph)), 132.53 (d, J_{CP} = 20.0 Hz, CH(Ph)), 133.66 (d, J_{CP} = 13.3 Hz, =CHP), 140.61 (d, J_{CP} = 22.9 Hz, *ipso*-C(Ph)), 150.40 (s, β-C=), 152.55 (s, β-C=).

1-Phenylphospholene palladium complex (**3**).

The crude mixture of **2** was washed with brine a few times until the aqueous layer no longer contained KCN (no turning blue when mixed with the aqueous solution of Fe(II)SO_4). The crude was then dried with $MgSO_4$ and filtered into a new flask, all carefully done under the flow of argon. 0.16 g (0.9 mmol) of $PdCl_2$ was added as a solid and the mixture was allowed to stir overnight at room temperature. The mixture was purified by column chromatography (98:2 DCM/MeOH) to afford 28 % of the pure **3**. ^{31}P($CDCl_3$) NMR δ 32.6 and 33.1; ^{1}H NMR ($CDCl_3$) δ 1.81 (s, Me), 1.96 (s, Me), 3.04 (dd, 2H, J_{HH} = 28.8 Hz,

J_{HP} = 15.6 Hz, CH_2P), 3.78 (dd, 1H, J_{HH} = 18.1 Hz, J_{HP} = 6.7 Hz, CH_2P), 5.15 (s, 1H, $=CH_2$), 5.21 (s, 1H, $=CH_2$), 5.79 (d, J_{HP} = 29.8 Hz, =CHP), 6.04 (d, J_{HP} = 28.8 Hz, =CHP), 7.37 (m, 6H, *m,p*-Ph), 7.73 (m, 4H, *o*-Ph); ^{13}C NMR ($CDCl_3$) δ 16.79 (Me), 34.95 (d, J_{CP} = 23 Hz, CH_2P), 113.46 (t, J_{CP} = 10.4 Hz, $=CH_2$), 133.24 (t, J_{CP} = 10.4 Hz, *o*-CH(Ph)), 132.13 (s, *p*-CH_2(Ph)), 129.12 (d, J_{CP} = 11.51 Hz, *m*-CH(Ph)), 131.41 (dd, J_{CP} = 10.35 Hz, =CHP), 146.24 (dd, J_{CP} = 5.2 Hz, =C), 157.90 (dd, J_{CP} = 6.9 Hz, =C).

Procedure for cross-coupling reactions:

0.12 mL (1.0 mmol) of *p*-chlorotoluene and 0.007 g (0.01 mmol) of catalyst was dissolved in 2 mL of 1,4-dioxane, stirred for 10 min at 40 ^{0}C, to which the second flask of caesium carbonate (0.65 g, 2 mmol) and phenylboronic acid (0.135 g, 1.1 mmol) in 2 mL of dioxane were added. Finally, 0.22 mL (1.0 mmol) of n-dodecane was added as an internal standard. The schlenk was purged and filled with argon, and the mixture was heated at 90 ^{0}C in a closed schlenk tube for two days. After 48h, an aliquot was filtered through a silica gel (packed into a pipette) and washed with copious amounts of ethyl ether and dichloro methane. The eluent volume was reduced on rotavap and examined by GCMS.

1-*tert*-Butylphosphole sulfide (**4**).

5 mL (26.6 mmol) of 1-phenylphosphole was dissolved in 50 mL THF, to which ~10 x 2 cm long lithium wire was added, and stirred overnight. In the morning, the solution was transferred via a cannula into a new round bottom flask leaving lithium wires behind and 3.4 mL (31 mmol) of tBuCl was added. The reaction mixture was then heated at 55 ^{0}C for 2 h, or until the color turns orange. The mixture is then cooled to -80 ^{0}C and 3.2 g (30.2 mmol) of cyanogen bromide as a solid. The reaction is allowed to stir at -80 ^{0}C for 30 min and then slowly warmed to room temperature. $^{31}P_{(P\text{-}CN)}$ δ -51. The mixture is once again cooled to -80 ^{0}C and 16 mL (33 mmol) of 2M *tert*-butylmagnesium chloride in THF is added. The mixture is slowly warmed to room temperature. $^{31}P_{(P\text{-}tBu)}$ δ 27.1. Excess elemental sulfur is added as a solid at room temperature and stirred for 30 min. The compound is purified on

silica gel with 50:50 petroleum ether/dichloromethane to afford 50 % yield of pure **4**. ^{31}P NMR ($CDCl_3$) δ 72.1; ^{1}H NMR ($CDCl_3$) δ 1.18 (d, J_{HH} = 17.4 Hz, J_{HP} = 2.28 Hz, tBu), 2.02 (s, Me), 5.91 (d, J_{HP} = 30.2 Hz, P=CH).

1-*tert*-Butylphospholene sulfide (**5**).

2 g (10 mmol) of **4** was dissolved in 5 mL of acetic acid and 5 mL of trifluoroacetic acid and refluxed at 130 ^{0}C for 2.5 h. The mixture was cooled to 0 ^{0}C and KOH was added (9g in 10 mL diH_2O), dropwise. The color turns from clear pale yellow to cloudy white. This mixture was allowed to stir overnight and then extracted four times with 15 mL DCM followed by brine washings until pH ~ 6. The target was purified via column chromatography (50:50 petroleum ether/dichloromethane) to give 60 % of pure **5**. ^{31}P NMR ($CDCl_3$) δ 73.8; ^{1}H NMR ($CDCl_3$) δ 1.20 (d, J_{HP} = 17 Hz, tBu), 2.03 (s, Me), 2.81 (pseudo t, 1H, $J_{HH} \approx J_{HP} \approx$ 17 Hz, CH_2P), 3.15 (dd, 1H, J_{HH} = 17.9 Hz, J_{HP} = 5.5 Hz, CH_2P), 5.16 (s br, 1H, $=CH_2$), 5.25 (s br, 1H, $=CH_2$), 5.94 (d, J_{HP} = 24.3 Hz, =CHP); ^{13}C NMR ($CDCl_3$) δ 16.48 (d, J_{CP} =16.2 Hz, Me), 24.69 (s, Me (tBu)), 33.90 (d, J_{CP} = 51.5 Hz, CH_2P), 34.99 (d, J_{CP} = 50.6 Hz, C(tBu)), 112.02 (d, J_{CP} = 12.4 Hz, $=CH_2$), 124.70 (d, J_{CP} = 69.6 Hz, =CHP), 145.92 (d, J_{CP} = 7.6 Hz, C=), 156.42 (d, J_{CP} = 10.5 Hz, =C). Exact mass: calculated for $C_{10}H_{17}PS$, 200.0789; found, 201.00.

1-*tert*-butylphospholene nickel complex (**6**).

1.76 g (8.8 mmol) of **5** was dissolved in 30 mL THF. 2.1 g (19.3 mmol) of nickelocene and 3.2 mL (50 mmol) of methyl iodide were added. The mixture was refluxed at 80 ^{0}C until ^{31}P NMR crude showed a single peak at 60.2 ppm (~12 h). The color changes from green to deep purple. Due to the sensitive nature of the crude, two columns had to be run, first one being done very quickly more as a filtration. After the second column (70:30 petroleum ether/DCM), 56 % of the pure **6** was obtained. ^{31}P NMR ($CDCl_3$) δ 57.2; ^{1}H NMR ($CDCl_3$) δ 1.16 (d, J_{HP} = 15 Hz, tBu), 1.97 (s, Me), 2.80 (dd, 1H, J_{HH} = 17.4 Hz, J_{HP} = 7.3 Hz, CH_2P), 3.19 (d br, 1H, J_{HH} = 17.4 Hz, J_{HP} = 0 Hz, CH_2P), 5.14 and 5.20 (2s, 2 1H, $=CH_2$), 5.34 (s, Cp), 5.97 (d, J_{HP} = 28.8 Hz, =CHP); ^{13}C NMR

($CDCl_3$) δ 16.57 (d, J_{CP} = 10.5 Hz, Me), 27.41 (d, J_{CP} = 3.8 Hz, Me(tBu)), 32.94 (d, J_{CP} = 31.6 Hz, CH_2P), 34.58 (d, J_{CP} = 22 Hz, C(tBu)), 93.27 (s, Cp), 110.43 (d, J_{CP} = 7.7 Hz, $=CH_2$), 128.14 (d, J_{CP}= 38.3 Hz, =CHP), 149.50 (s, =C), 153.16 (s, =C).

1-*tert*-butylphospholene palladium complex (**9**).

0.83 g (2 mmol) of **6** was dissolved in 5 mL DCM, and excess KCN was added as a solid. 1.5 mL of diH_2O was added, and the mixture was stirred for 14 days at 40 ^{0}C, until ^{31}P NMR (crude) had only one signal, which appears at δ 7.1, indicating the trivalent species. The crude mixture was then extracted with 3x 10 mL of DCM, and washed with brine until no more KCN was present (no turning blue when brine washings were mixed with the aqueous solution of Fe(II)SO_4). The crude was then dried with $MgSO_4$ and filtered into a new flask, all carefully done under the flow of argon. 0.19 g (1.07 mmol) of $PdCl_2$ was added as a solid and the mixture was allowed to stir overnight at room temperature. The mixture was purified by column chromatography (95:5 DCM/MeOH) to afford 10 % of the pure **9**.

^{31}P NMR ($CDCl_3$) δ 66.9; ^{1}H NMR ($CDCl_3$) δ 1.28 (d, J_{HP} = 17.8 Hz, tBu), 1.99 (s, Me), 2.84 (1H, J_{HH} = 19.2 Hz, J_{HP} = 9.2 Hz, CH_2P), 3.36 (1H, J_{HH} = 18.8 Hz, J_{HP} = 10.5 Hz, CH_2P), 5.29 and 5.37 (2s, $=CH_2$), 6.37 (d, J_{HP} = 26.5, =CHP); ^{13}C NMR ($CDCl_3$) δ 17.01 (d, J_{CP} = 13.4 Hz, Me), 26.72 (d, J_{CP} = 37.4 Hz, CH_2P), 27.29 (d, J_{CP} = 2.7 Hz, Me(tBu)), 36.86 (d, J_{CP} = 25.4 Hz, C(tBu)), 112.60 (d, J_{CP} = 9.4 Hz, $=CH_2$), 121.25 (d, J_{CP}= 48.1 Hz, =CHP), 146.42 (d, J_{CP} = 5.4 Hz, =C), 153.16 (d, J_{CP} = 5.4 Hz, =C). Exact mass: calculated for $C_{20}H_{34}P_2Cl_3{}^{106}Pd_2$, $Pd_2L_2Cl_3$, 652.9271; found, 652.9274.

1-Isopropyl-2-phenylphosphole sulfide (**10**):

This experiment can be done on a large scale, up to 10 g of starting 3,4-dimethyl-1-phenylphosphole, therefore, only the molar ratios of reagents will be used to describe the procedure. 3,4-Dimethyl-1-phenylphosphole was dissolved in THF (usually for every 1 g, 15 mL of THF is used), and freeze-thaw-degassed twice. A 1.5 equivalents of vacuum-dried potassium tert-butoxide was added and the system was sealed and heated at 150 ^{0}C for 3-4

days or, until ^{31}P signal showed a signal at 72 ppm, indicating the 2-phenyl phospholide anion intermediate. At -40 ^{0}C, 1.2 equivalents of cyanogen bromide was added as a solid, and the reaction was stirred at room temperature for 2h, until ^{31}P δ -42, indicating the P-CN bond formation. The resulting trivalent compound is then purified by column chromatography (50:50 petroleum ether/dichloromethane), redissolved in THF, cooled to -78 ^{0}C, and 1.1 equivalents of 2M iPrMgCl in THF was added, and stirred for 3h, until ^{31}P δ 33, proving the formation of P-iPr bond. At this point, 1.2 equivalents of S_8 was added as a solid and the reaction can either be left to stir overnight or purified by column chromatography right away. ^{31}P of **10** is 67 ppm and the yield is 75 % or higher.

^{31}P NMR ($CDCl_3$) δ 66.4; ^{1}H NMR ($CDCl_3$) δ 1.02 (dd, J_{HH} = 15.2 Hz, J_{HP} = 5.6 Hz, Me (iPr)), 1.10 (dd, J_{HP} = 15.0 Hz, J_{HH} = 5.7 Hz, Me (iPr)), 1.98 (m, 1H, $PCHMe_2$), 1.99 and 2.15 (s, Me), 6.00 (d, 1H, J_{HP} = 24.3 Hz, PCH_2), 7.37 (m, 3H, *m,p*-Ph), 7.60 (m, *o*-Ph).

1-Isopropyl-2-phenylphospholene sulfide (**11**):

10 is dissolved in THF, cooled to -80 ^{0}C and 1.7 equivalents of 2M $NaN(SiMe_3)_2$ was added via syringe, resulting in immediate change of color, from green to deep red. After 10 min at -80 ^{0}C, 2.8 equivalents of 3M HCl is added via syringe, and the mixture is allowed to warm to room temperature. The isomerization can also be done by protonation using acetic acid/trifluoro acidic acid reflux, followed by deprotonation with $KOH_{(aq)}$, as described previously for the synthesis of **5**. After extractions with DCM, and washings with brine, the target **11** is purified by column chromatography (50:50 petroleum ether/dichloromethane), yielding 88 % of pure solid.

^{31}P NMR ($CDCl_3$) δ 71.9; ^{1}H NMR ($CDCl_3$) δ 0.45 (dd, J_{HP} = 18.8 Hz, J_{HH} = 6.9 Hz, Me), 1.07 (dd, J_{HH} = 18.3 Hz, J_{HP} = 7.3 Hz, Me), 1.86 (m, 1H, $PCHMe_2$), 2.13 (s, Me), 5.14 and 5.52 (2s, 2 1H, $=CH_2$), 4.43 (d, 1H, J_{HP} = 21.1 Hz, PCH_2), 6.06 (d, 1H, J_{HP} = 23.8 Hz, PCH_2), 7.33 (m, Ph).

1-Isopropyl-2-phenylphospholene nickel complex (**12**):

1.3 g (4.97 mmol) of **11** was dissolved in 25 mL THF and 1.22 g (6.46 mmol) of $NiCp_2$ was added, followed by 0.93 mL (14.9 mmol) of MeI. The mixture was left refluxing overnight but since the reaction was incomplete, additional 0.3 mL of MeI were added and the mixture was refluxed for another 24 h. The target was firstly filtered through a silica gel, very quickly, then ran through a column starting from 100 % petroleum ether and slowly increasing to 80:20 P.E./DCM. The pink layer was collected to afford 29 % yield of pure **12**.

^{31}P NMR ($CDCl_3$) δ 58.2; ^{1}H NMR ($CDCl_3$) δ 1.05 (q, J_{HH} = 5.2 Hz, Me(iPr)), 1.26 (q, J_{HH} = 5.4 Hz, Me(iPr)), 1.84 (s, 1H, Me), 2.05 (m, $PCHMe_2$), 2.91 (dd, 1H, J_{HP} = 5.9 Hz, J_{HH} = 13.1 Hz, PCH_2), 3.48 (d, 1H, J_{HH} = 13.5, PCH_2), 5.10 (s, Cp), 5.19 and 5.28 (s, 2x 1H, $=CH_2$), 7.41 (m, Ph); ^{13}C (CD_2Cl_2) δ 14.09 (d, J_{CP} = 7 Hz, Me), 18.03 and 18.92 (s, 2x Me (iPr)), 30.34 (d, J_{CP} = 17 Hz, PCH_2), 93.49 (s, Cp), 110.52 (s, $=CH_2$), 129.97 and 128.93 and 128.35 (s, 3x =C, *o, m, p* –Ph), 148.38 and 150.60 (s, 2x =C).

1-Isopropyl-2-phenylphospholene palladium complex (**14**):

0.6 g (1.26 mmol) of **12** was dissolved in minimum amount of DCM. Excess KCN was added, along with 10 % of the PTA (nBu_4NBr). The mixture was sealed in a pressure tube and stirred at 35 ^{0}C until the free phosphine ligand was observed by ^{31}P NMR, δ 11.5. The crude was washed with aqueous solution of brine several times, carefully under a constant flow of argon. After drying the mixture with $MgSO_4$, the solvent was reduced to ~15 mL and 0.25 g (1.38 mmol) of $PdCl_2$ were added. Reaction was stirred overnight at room temperature and purified on column (50:50 P.E./DCM -> 100 % DCM -> 95:5 DCM/MeOH) with 99:1 DCM:MeOH.

^{31}P NMR ($CDCl_3$) δ 59.5; ^{1}H NMR ($CDCl_3$) δ 0.91 (m, 2x Me (iPr)), 1.92 (s, Me), 2.68 (m, 2H, PCH_2), 5.38 and 5.47 (s, 2x 1H, $=CH_2$), 7.74 (d, J_{HH} = 5.6 Hz, *o*-Ph), 7.49 (t, J_{HH} = 5.6 Hz, *m*-Ph), 7.41 (d, J_{HH} = 5.4 Hz, *p*-Ph).

3,4-Dimethyl-1-*tert*butylphosphole-BH_3 (**15**):

The synthesis of **15** was parallel with the synthesis of **4**, with an exception of the last step: instead of elemental sulfur, 2M solution of $BH_3{\cdot}SMe_2$ (1.2

equivalents compared to the starting 1-phenyl phosphole) was added at -40 ^{0}C, and stirred for 1 h at room temperature. Target was purified on column (80:20 P.E./DCM) to afford 41 % of pure **15**.
^{31}P NMR ($CDCl_3$) δ 60.4; ^{1}H NMR ($CDCl_3$) δ 1.15 (d, 9H, J_{HP} = 14.2 Hz, tBu), 2.07 (s, 6H, 2x Me), 6.06 (d, 2H, J_{HP} = 31.6 Hz, =CH).

2,4-Dimethyl-1-*tert*butylphospholene-BH_3 (**16**):
1.67 g (9.3 mmol) of **15** was dissolved in 25 mL THF, and cooled to -80 ^{0}C. 13.2 mL (18.5 mmol) of *sec*-BuLi was added slowly, and the color turned dark brown. After stirring at -80 ^{0}C for ∼10 min, 1.7 mL of MeI was added dropwise. The mixture was allowed to stir at -80 ^{0}C for 1 h and then warmed to room temperature. The solvent was removed, and the target was purified on column with 85:15 P.E./DCM to afford 60 % yield of the pure **16**.
^{31}P NMR ($CDCl_3$) δ 55.23; ^{1}H NMR ($CDCl_3$) δ 1.10 (d, 9H, J_{HP} = 13.7 Hz, tBu), 1.35 (q, 3H, J_{HH} = 7.3 Hz, 2-Me), 1.99 (s, 3H, 4-Me), 2.85 (m, 1H, P-CH), 5.31 and 5.15 (s, 2x 1H, =CH_2), 5.85 (d, 1H, J_{HP} = 26.6 Hz, =CH) (note: $CDCl_3$ references to 7.2400).

2,4-Dimethyl-1-*tert*butylphospholene (**17**):
16 was refluxed in THF with 1.5 equivalents of Et_2NH for 2 h and the crude was ran through a neutral alumina column (100 % P.E.) under nitrogen flow.
^{31}P NMR (crude) δ 33.2.

1-Phenylphosphole heptacarbonyl diiron complex (**18**):
4 mL (21.3 mmol) of 3,4-dimethyl-1-phenylphosphole was added to the 60 mL THF solution containing 23.4 g (43 mmol) of $Fe_3(CO)_{12}$. The mixture was refluxed for 2.5 h. The solvent was removed and the target was purified with 90:10 hexane/toluene, yielding 55% of pure **18**. ^{31}P NMR ($CDCl_3$) δ 92.9; ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 6H, 2x Me), 2.98 (d, J_{Hp} = 24.7, =CHP), 7.19 (m, Ph). Exact mass: calculated for $C_{19}H_{13}PFe_2O_7$, 495.9098; found, 496.5173.

1-Phenyl-3-methyl-4-((methylthio)methyl)phosphole heptacarbonyldiiron complex (**19**):

Flask 1. LDA was prepared on the day it was needed, by mixing 0.88 mL (6.23 mmol) of freshly distilled diisopropylamine and 1.19 mL (8 mmol) of TMEDA in 6 mL of THF. After cooling it to -78 ^{0}C, 5.78 mL (9.25 mmol) of 1.6 M nBuLi was added. The mixture was stirred for 15 min and then allowed to warm to room temperature (for ~1 h). Flask 2. 2 g (4 mmol) of **18** was dissolved in 30 mL THF, cooled to -78 ^{0}C, and Flask 1 was added slowly (color changed slightly from black to black with a tint of red). The mixture was kept stirring at this temperature for 40 min, and 3.6 mL (40 mmol) of dimethyl disulfide was added slowly. The mixture was kept at -78 ^{0}C for another 1 h, after which it was warmed to R.T. and stirred overnight. In the morning, the reaction was quenched with NH_4Cl. The solvent was removed and the remaining slurry was quickly filtered through a ~10cm silica gel with 50:50 petroleum ether/DCM mixture. The second column was done slowly, starting from 100 % petroleum ether and increasing the polarity with DCM. After the starting material, the pure target was eluted, yielding 48 % of dark orange crystalline **19**. ^{31}P NMR (CD_2Cl_2) δ 91.6; ^{1}H NMR (CD_2Cl_2) δ 1.63 (s, SMe), 2.34 (s, Me), 3.14 (m, 3H, =CHP + CCH_2S), 3.81 (d, J_{HP} = 13.8 Hz, =CHP), 7.27 (m, Ph). Exact mass: calculated for $C_{20}H_{15}PSFe_2O_7$, 541.8975; found, 542.5835.

1-Phenyl-3-methyl-4-((methylthio)methyl)phosphole sulfide tricarbonyliron complex (**20**):

1.7 g (3.12 mmol) of **19** was dissolved in 35 mL of toluene and 2 g (62 mmol) of S_8 was added. The mixture was refluxed for 3 h, until ^{31}P δ 69.6. Solvent was removed and the target was purified on column with 80:20 petroleum ether/DCM mixture (note: the excess elemental sulfur has to be eluted first with copious amounts of petroleum ether) to afford 76 % of pure **20**. ^{31}P NMR (CD_2Cl_2) δ 70.7; ^{1}H NMR (CD_2Cl_2) δ 1.74 (s, SMe), 2.42 (s, Me), 2.78 (t, 2H, CCH_2S), 3.16 (d, J_{HP} = 13.8 Hz, =CHP), 3.83 (d, J_{HP} = 13.7, =CHP), 7.39 (s, 3H, *m*,*p*-Ph), 7.72 (m, 2H, *o*-Ph). Exact mass: calculated for $C_{20}H_{15}PSFe_2O_7$, 405.96; found, 406.79.

1-Phenyl-3-methyl-4-((methylthio)methyl)phosphole sulfide complex (**21**): 0.9 g (2.21 mmol) of **20** was dissolved in 10 mL acetonitrile and 3 mL iPrOH. Reaction was cooled to 0 ^{0}C and 2.47 g (4.5 mmol) of CAN, previously dried on vacuum, was added. The mixture was stirred for 45 min. Target was purified with 50:50 hexane/dichloromethane on neutral alumina to afford 53 % of pure **21**. ^{31}P NMR (CD_2Cl_2) δ 46.6; ^{1}H NMR (CD_2Cl_2) δ 2.04 (s, SMe), 2.22 (s, Me), 3.42 (s, 2H, CCH_2S), 6.15 (d, 2H, J_{HP} = 30.2 Hz, =CHP), 7.47 (m, 3H, *m,p*-Ph), 7.82 (m, 2H, *o*-Ph). Exact mass: calculated for $C_{13}H_{15}PS_2$, 266.0353; found, 267.00.

1-Phenyl-3-methyl-4-((methylthio)methyl)phospholene sulfide complex (**22**): 0.31 g (1.17 mmol) of **21** was dissolved in 20 mL THF, cooled to -78 ^{0}C, and 2.5 mL of 2M $NaN(SiMe_3)_2$ was added via syringe, dropwise. Color immediately turned dark red. After 10 min at -78 ^{0}C, 3.1 mL of 3M $HCl_{(aq)}$ was added and the color turned bright yellow. Target was purified on column (50:50 hexane/dichloromethane) to yield 36 % of pure **22**. ^{31}P NMR (CD_2Cl_2) δ 50.63; ^{1}H NMR (CD_2Cl_2) δ 2.11 (s, SMe), 2.42 (s, Me), 2.99 (m, 2H, CH_2P), 5.87 (d, 1H, J_{HP} = 25.6 Hz, =CHP), 6.49 (s, 1H, C=CHS), 7.47 (m, 3H, *m,p*-Ph), 7.80 (m, 2H, *o*-Ph). Exact mass: calculated for $C_{13}H_{15}PS_2$, 266.0353; found, 267.09.

1-Phenyl-3-methyl-4-((methylthio)methyl)phospholene nickel complex (**23**): 0.111 g (0.417 mmol) of **22** was dissolved in 6 mL THF to which 0.1 g (0.5 mmol) of $NiCp_2$ was added, followed by 0.6 mL (22.8 mmol) of MeI. The mixture was refluxed for 5 h, and the solvent (along with excess MeI) was removed. Target was purified on column (2:3 petroleum ether/DCM) to afford 69 % yield of pure **23**. Note: unlike the other nickel complexes described above, the complec **23** seemed to be easily decomposed in solution, thus, no MS could be recorded. ^{31}P NMR (CD_2Cl_2) δ 37.9; ^{1}H NMR (CD_2Cl_2) δ 2.05 (s, SMe), 2.56 (s, Me), 2.88 (m, 1H, CH_2P), 3.32 (d, 1H, J_{HH} = 17.8 Hz, CH_2P), 5.39 (s, Cp), 5.96 (d, 1H, J_{HP} = 30.2 Hz, =CHP), 6.44 (s, 1H, C=CHS), 7.42 (s, 3H, *m,p*-Ph), 7.88 (s, 2H, *o*-Ph).

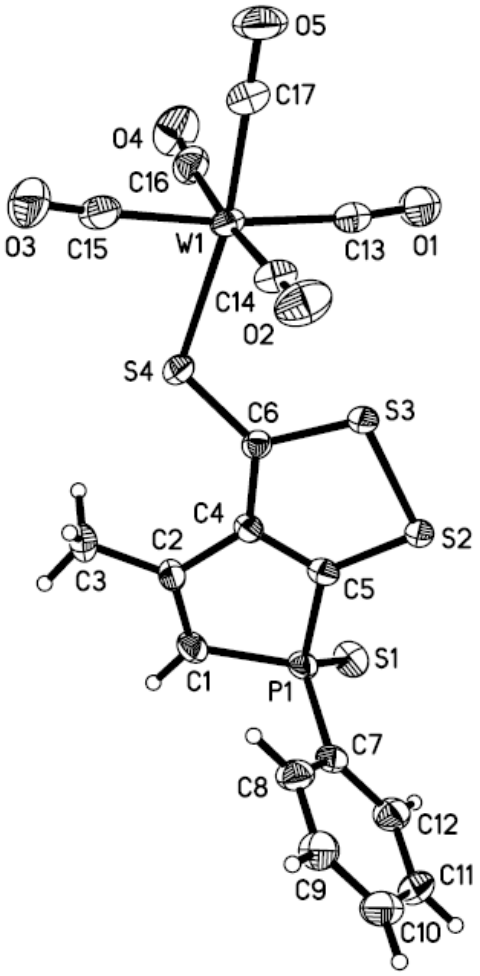
1-Phenyl-3-methyl-4-((methylthio)methyl)phospholene (**24**):

0.14 g (0.29 mmol) of **23** was dissolved in 5 mL DCM. 1.0 g (15.4 mmol) of KCN , 0.5 g (1.54 mmol) of $(nBu)_4NBr$, and 2 mL of diH_2O was added. The mixture was sealed in a pressure tube and stirred vigorously at 35 ^{0}C for 2 days, or until ^{31}P NMR) δ -13.2 ppm. Unfortunately, this compound was oxidized quickly upon attempted extractions/washings and unavailable for reaction with $PdCl_2$.

APPENDIX

X-Ray Structures and Tables, Chapter I

X-Ray structure and A1 table of angles and bond lengths for compound 2



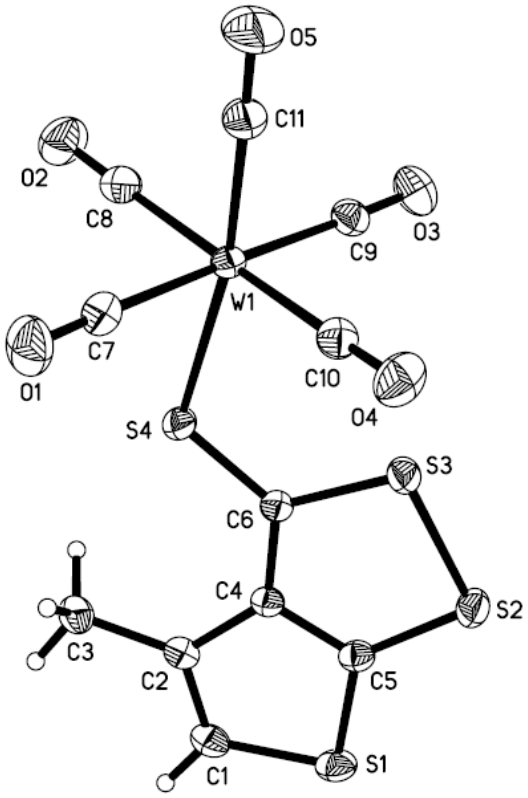
Formula	$C_{17}H_9O_5PS_4W$
Space Group	P 21/c
Cell Lengths	a 14.1649(5) b 11.2574(4) c 13.6364(5)
Cell Angles	α 90.00 β 107.435(2) γ 90.00
Cell Volume	2074.56
Z, Z'	Z: 4 Z': 0
R-Factor	3.4
Color	Brown

Atom1	Atom2	Atom3	*Angle*
C13	W1	C14	91.6(2)
C13	W1	C15	173.5(2)
C13	W1	C16	85.5(2)
C13	W1	C17	87.7(2)
C13	W1	S4	100.5(1)
C14	W1	C15	88.8(2)
C14	W1	C16	175.4(2)
C14	W1	C17	88.8(2)
C14	W1	S4	93.7(1)
C15	W1	C16	93.6(2)
C15	W1	C17	85.8(2)
C15	W1	S4	86.0(1)
C16	W1	C17	87.4(2)
C16	W1	S4	90.5(1)
C17	W1	S4	171.4(2)
H1	C1	C2	123.6(4)
H1	C1	P1	123.7(4)
C2	C1	P1	112.7(3)
C1	C2	C3	124.8(4)
C1	C2	C4	112.8(4)
C3	C2	C4	122.3(4)
C2	C3	H3A	109.5(5)
C2	C3	H3B	109.5(5)
C2	C3	H3C	109.5(5)
H3A	C3	H3B	109.4(5)
H3A	C3	H3C	109.5(5)
H3B	C3	H3C	109.5(5)
C2	C4	C5	113.2(3)
C2	C4	C6	130.9(3)
C5	C4	C6	115.9(3)
C4	C5	P1	110.4(3)
C4	C5	S2	120.5(3)
P1	C5	S2	129.1(2)
C4	C6	S3	113.3(3)
C4	C6	S4	127.3(3)
S3	C6	S4	119.3(2)
C8	C7	C12	120.6(4)
C8	C7	P1	119.1(3)
C12	C7	P1	120.3(3)
C7	C8	H8	120.0(4)
C7	C8	C9	120.0(4)
H8	C8	C9	120.0(4)
C8	C9	H9	119.9(4)
C8	C9	C10	120.2(4)
H9	C9	C10	119.9(4)
C9	C10	H10	120.3(5)
C9	C10	C11	119.5(4)

Atom1	Atom2	*Length*
W1	C13	2.042(5)
W1	C14	2.064(5)
W1	C15	2.048(5)
W1	C16	2.057(4)
W1	C17	1.982(5)
W1	S4	2.519(1)
C1	H1	0.930(4)
C1	C2	1.350(5)
C1	P1	1.788(5)
C2	C3	1.486(7)
C2	C4	1.501(6)
C3	H3A	0.961(6)
C3	H3B	0.960(5)
C3	H3C	0.960(5)
C4	C5	1.367(6)
C4	C6	1.430(4)
C5	P1	1.825(3)
C5	S2	1.697(4)
C6	S3	1.732(5)
C6	S4	1.668(4)
C7	C8	1.374(6)
C7	C12	1.393(6)
C7	P1	1.794(4)
C8	H8	0.929(4)
C8	C9	1.367(6)
C9	H9	0.929(4)
C9	C10	1.396(7)
C10	H10	0.931(5)
C10	C11	1.388(8)
C11	H11	0.930(4)
C11	C12	1.370(6)
C12	H12	0.929(4)
C13	O1	1.142(6)
C14	O2	1.122(6)
C15	O3	1.131(6)
C16	O4	1.132(6)
C17	O5	1.144(6)
P1	S1	1.943(2)
S2	S3	2.071(1)

A1 Table. Angles and bond lengths for compound 2

X-Ray structure and A2 table of angles and bond lengths for compound 3



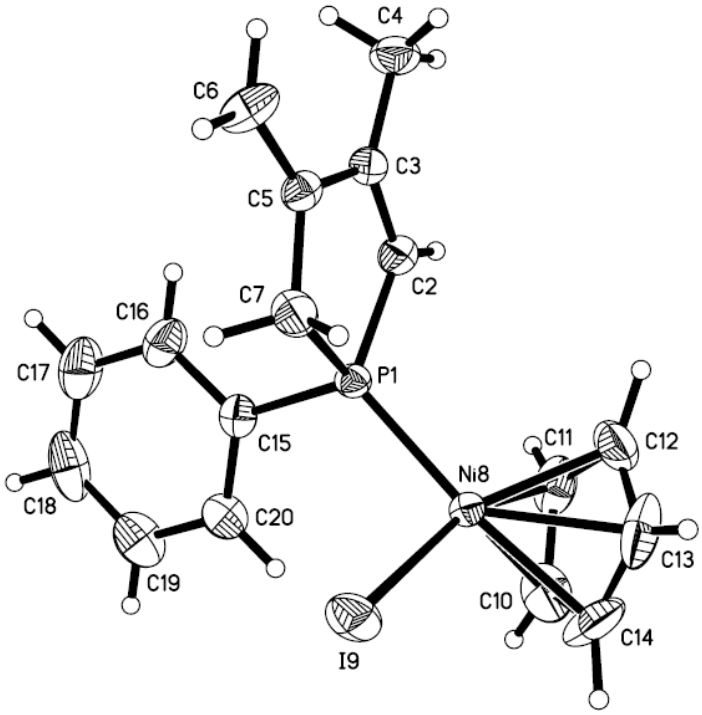
Formula	$C_{11}H_4O_5S_4W$
Space Group	P-1
Cell Lengths	a 7.6224(4) b 10.3544(6) c 10.5713(6)
Cell Angles	α 74.148(2) β 69.411(2) γ 75.033(2)
Cell Volume	739.06
Z, Z'	Z: 2 Z': 0
R-Factor	1.69
Color	Brown

Atom1	Atom2	Atom3	*Angle*
C7	W1	C8	91.4(1)
C7	W1	C9	177.4(1)
C7	W1	C10	85.4(1)
C7	W1	C11	89.5(1)
C7	W1	S4	84.81(8)
C8	W1	C9	91.2(1)
C8	W1	C10	175.2(1)
C8	W1	C11	88.1(1)
C8	W1	S4	85.28(9)
C9	W1	C10	91.94(9)
C9	W1	C11	90.4(1)
C9	W1	S4	95.59(7)
C10	W1	C11	88.3(1)
C10	W1	S4	97.99(6)
C11	W1	S4	171.17(9)
H1	C1	C2	123.0(2)
H1	C1	S1	123.0(2)
C2	C1	S1	114.0(2)
C1	C2	C3	123.9(2)
C1	C2	C4	110.5(2)
C3	C2	C4	125.6(2)
C2	C3	H3A	109.5(2)
C2	C3	H3B	109.5(2)
C2	C3	H3C	109.5(2)
H3A	C3	H3B	109.4(3)
H3A	C3	H3C	109.4(3)
H3B	C3	H3C	109.5(3)
C2	C4	C5	112.5(2)
C2	C4	C6	131.6(2)
C5	C4	C6	115.9(2)
C4	C5	S1	112.4(2)
C4	C5	S2	119.7(2)
S1	C5	S2	127.8(1)
C4	C6	S3	114.0(2)
C4	C6	S4	126.5(2)
S3	C6	S4	119.5(1)
W1	C7	O1	177.3(2)
W1	C8	O2	176.8(3)
W1	C9	O3	177.2(2)
W1	C10	O4	175.4(2)
W1	C11	O5	178.7(3)
C1	S1	C5	90.6(1)
C5	S2	S3	92.61(8)
C6	S3	S2	97.79(8)
W1	S4	C6	114.65(8)

Atom1	Atom2	*Length*
W1	C7	2.050(3)
W1	C8	2.054(3)
W1	C9	2.047(3)
W1	C10	2.039(2)
W1	C11	1.988(3)
W1	S4	2.5274(7)
C1	H1	0.949(2)
C1	C2	1.359(3)
C1	S1	1.733(2)
C2	C3	1.496(3)
C2	C4	1.440(3)
C3	H3A	0.981(2)
C3	H3B	0.979(3)
C3	H3C	0.980(4)
C4	C5	1.387(3)
C4	C6	1.426(3)
C5	S1	1.709(2)
C5	S2	1.723(2)
C6	S3	1.729(2)
C6	S4	1.669(2)
C7	O1	1.137(3)
C8	O2	1.135(4)
C9	O3	1.137(3)
C10	O4	1.141(3)
C11	O5	1.149(4)
S2	S3	2.0711(8)

A2 Table. Angles and bond lengths for compound 3

X-Ray structure and A1 table of angles and bond lengths for compound 1



Formula	$C_{17}H_{18}INiP$
Space Group	P b c a
Cell Lengths	a 7.3132(2) b 26.5460(6) c 34.4737(10)
Cell Angles	α 90.00 β 90.00 γ 90.00
Cell Volume	6692.59
Z, Z'	Z: 16 Z': 0
R-Factor (%)	4.18

Atom1	Atom2	Atom3	*Angle*
C10	Ni8	C11	38.7(2)
C10	Ni8	C12	65.6(2)
C10	Ni8	C13	64.4(2)
C10	Ni8	C14	38.5(2)
C10	Ni8	I9	119.5(1)
C10	Ni8	P1	131.0(1)
C11	Ni8	C12	40.8(2)
C11	Ni8	C13	65.2(2)
C11	Ni8	C14	64.7(2)
C11	Ni8	I9	158.0(1)
C11	Ni8	P1	102.8(1)
C12	Ni8	C13	37.4(2)
C12	Ni8	C14	63.9(2)
C12	Ni8	I9	147.1(1)
C12	Ni8	P1	107.1(1)
C13	Ni8	C14	37.9(2)
C13	Ni8	I9	112.1(1)
C13	Ni8	P1	138.7(1)
C14	Ni8	I9	99.2(1)
C14	Ni8	P1	167.5(1)
I9	Ni8	P1	92.89(3)
H2	C2	C3	123.8(4)
H2	C2	P1	123.8(3)
C3	C2	P1	112.4(3)
C2	C3	C4	124.8(3)
C2	C3	C5	113.7(3)
C4	C3	C5	121.5(3)
C3	C4	H4A	109.4(4)
C3	C4	H4B	109.5(4)
C3	C4	H4C	109.5(4)
H4A	C4	H4B	109.4(4)
H4A	C4	H4C	109.6(4)
H4B	C4	H4C	109.5(4)
C3	C5	C6	123.7(3)
C3	C5	C7	113.3(3)
C6	C5	C7	123.1(3)
C5	C6	H6A	120.0(4)
C5	C6	H6B	120.1(4)
H6A	C6	H6B	119.9(4)
C5	C7	H7A	110.1(3)
C5	C7	H7B	110.1(3)
C5	C7	P1	108.1(3)
H7A	C7	H7B	108.4(4)
H7A	C7	P1	110.1(3)
H7B	C7	P1	110.1(3)
Ni8	C10	H10	127.2(4)
Ni8	C10	C11	67.2(3)
Ni8	C10	C14	69.1(3)
H10	C10	C11	127.3(5)
H10	C10	C14	127.1(5)

Atom1	Atom2	*Length*
Ni8	C10	2.144(5)
Ni8	C11	2.053(5)
Ni8	C12	2.081(5)
Ni8	C13	2.125(5)
Ni8	C14	2.101(5)
Ni8	I9	2.4803(5)
Ni8	P1	2.1291(8)
C2	H2	0.949(4)
C2	C3	1.386(5)
C2	P1	1.809(4)
C3	C4	1.457(6)
C3	C5	1.473(5)
C4	H4A	0.980(4)
C4	H4B	0.980(4)
C4	H4C	0.980(4)
C5	C6	1.370(5)
C5	C7	1.469(5)
C6	H6A	0.949(4)
C6	H6B	0.949(4)
C7	H7A	0.990(4)
C7	H7B	0.991(4)
C7	P1	1.838(4)
C10	H10	1.001(5)
C10	C11	1.392(7)
C10	C14	1.400(7)
C11	H11	1.001(4)
C11	C12	1.442(7)
C12	H12	1.001(5)
C12	C13	1.349(7)
C13	H13	1.000(5)
C13	C14	1.373(7)
C14	H14	0.999(5)
C15	C16	1.377(5)
C15	C20	1.389(5)
C15	P1	1.827(4)
C16	H16	0.950(4)
C16	C17	1.394(7)
C17	H17	0.949(5)
C17	C18	1.383(7)
C18	H18	0.950(5)
C18	C19	1.382(7)
C19	H19	0.950(5)
C19	C20	1.402(6)
C20	H20	0.951(4)
Ni28	C30	2.095(6)
Ni28	C31	2.126(7)
Ni28	C32	2.101(6)
Ni28	C33	2.155(5)
Ni28	C34	2.028(7)
Ni28	I29	2.5010(5)

C11	C10	C14	105.6(4)
Ni8	C11	C10	74.2(3)
Ni8	C11	H11	125.9(4)
Ni8	C11	C12	70.6(3)
C10	C11	H11	125.9(5)
C10	C11	C12	107.8(4)
H11	C11	C12	126.0(5)
Ni8	C12	C11	68.6(3)
Ni8	C12	H12	126.2(4)
Ni8	C12	C13	73.1(3)
C11	C12	H12	126.2(5)
C11	C12	C13	107.5(4)
H12	C12	C13	126.2(5)
Ni8	C13	C12	69.5(3)
Ni8	C13	H13	125.7(4)
Ni8	C13	C14	70.1(3)
C12	C13	H13	125.6(5)
C12	C13	C14	108.7(5)
H13	C13	C14	125.7(5)
Ni8	C14	C10	72.4(3)
Ni8	C14	C13	72.0(3)
Ni8	C14	H14	124.9(4)
C10	C14	C13	110.2(4)
C10	C14	H14	124.9(5)
C13	C14	H14	124.9(5)
C16	C15	C20	119.4(4)
C16	C15	P1	119.8(3)
C20	C15	P1	120.7(3)
C15	C16	H16	119.3(4)
C15	C16	C17	121.2(4)
H16	C16	C17	119.5(4)
C16	C17	H17	120.5(5)
C16	C17	C18	119.0(4)
H17	C17	C18	120.5(5)
C17	C18	H18	119.6(5)
C17	C18	C19	120.7(5)
H18	C18	C19	119.6(5)
C18	C19	H19	120.2(5)
C18	C19	C20	119.6(4)
H19	C19	C20	120.2(5)
C15	C20	C19	120.0(4)
C15	C20	H20	119.9(4)
C19	C20	H20	120.1(4)
Ni8	P1	C2	118.9(1)
Ni8	P1	C7	118.5(1)
Ni8	P1	C15	114.0(1)
C2	P1	C7	91.7(2)
C2	P1	C15	106.3(2)
C7	P1	C15	104.5(2)
C30	Ni28	C31	36.4(2)
C30	Ni28	C32	63.0(2)

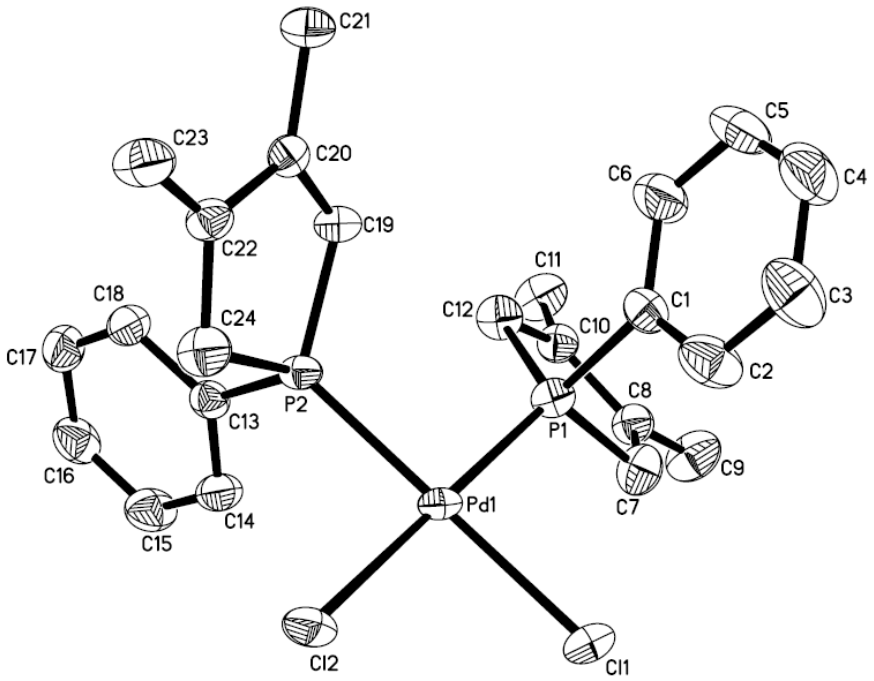
Ni28	P21	2.138(1)
C22	H22A	0.991(4)
C22	H22B	0.991(4)
C22	C23	1.456(6)
C22	P21	1.824(4)
C23	C24	1.384(6)
C23	C25	1.468(5)
C24	H24A	0.950(5)
C24	H24B	0.949(5)
C25	C26	1.433(6)
C25	C27	1.391(6)
C26	H26A	0.981(4)
C26	H26B	0.980(4)
C26	H26C	0.980(5)
C27	H27	0.949(4)
C27	P21	1.804(5)
C30	H30	1.002(6)
C30	C31	1.32(1)
C30	C34	1.385(9)
C31	H31	1.000(6)
C31	C32	1.378(9)
C32	H32	1.001(5)
C32	C33	1.365(8)
C33	H33	1.001(5)
C33	C34	1.409(9)
C34	H34	1.001(6)
C35	C36	1.387(5)
C35	C40	1.401(5)
C35	P21	1.832(4)
C36	H36	0.949(4)
C36	C37	1.398(6)
C37	H37	0.949(4)
C37	C38	1.377(6)
C38	H38	0.950(5)
C38	C39	1.389(7)
C39	H39	0.950(4)
C39	C40	1.382(7)
C40	H40	0.950(4)

C30	Ni28	C33	64.4(2)
C30	Ni28	C34	39.2(3)
C30	Ni28	I29	142.5(2)
C30	Ni28	P21	110.8(2)
C31	Ni28	C32	38.0(2)
C31	Ni28	C33	63.3(2)
C31	Ni28	C34	63.6(3)
C31	Ni28	I29	109.7(2)
C31	Ni28	P21	145.1(2)
C32	Ni28	C33	37.4(2)
C32	Ni28	C34	64.1(2)
C32	Ni28	I29	100.5(2)
C32	Ni28	P21	159.6(2)
C33	Ni28	C34	39.2(2)
C33	Ni28	I29	123.6(1)
C33	Ni28	P21	122.3(1)
C34	Ni28	I29	162.7(2)
C34	Ni28	P21	98.4(2)
I29	Ni28	P21	95.03(3)
H22A	C22	H22B	108.3(4)
H22A	C22	C23	110.1(4)
H22A	C22	P21	110.0(3)
H22B	C22	C23	110.1(4)
H22B	C22	P21	110.0(3)
C23	C22	P21	108.2(3)
C22	C23	C24	123.3(4)
C22	C23	C25	113.8(3)
C24	C23	C25	122.9(4)
C23	C24	H24A	120.0(5)
C23	C24	H24B	120.0(5)
H24A	C24	H24B	119.9(5)
C23	C25	C26	121.4(3)
C23	C25	C27	113.5(3)
C26	C25	C27	125.1(4)
C25	C26	H26A	109.5(4)
C25	C26	H26B	109.5(4)
C25	C26	H26C	109.5(4)
H26A	C26	H26B	109.4(4)
H26A	C26	H26C	109.4(4)
H26B	C26	H26C	109.4(4)
C25	C27	H27	124.3(4)
C25	C27	P21	111.5(3)
H27	C27	P21	124.2(4)
Ni28	C30	H30	125.9(5)
Ni28	C30	C31	73.1(4)
Ni28	C30	C34	67.8(4)
H30	C30	C31	126.0(6)
H30	C30	C34	125.8(6)
C31	C30	C34	108.1(6)
Ni28	C31	C30	70.5(4)
Ni28	C31	H31	125.7(5)

Ni28	C31	C32	70.0(4)
C30	C31	H31	125.7(7)
C30	C31	C32	108.7(6)
H31	C31	C32	125.7(6)
Ni28	C32	C31	72.0(4)
Ni28	C32	H32	125.0(4)
Ni28	C32	C33	73.4(3)
C31	C32	H32	124.9(6)
C31	C32	C33	109.9(5)
H32	C32	C33	125.0(5)
Ni28	C33	C32	69.2(3)
Ni28	C33	H33	127.8(4)
Ni28	C33	C34	65.5(3)
C32	C33	H33	127.7(5)
C32	C33	C34	104.4(5)
H33	C33	C34	127.9(5)
Ni28	C34	C30	73.0(4)
Ni28	C34	C33	75.3(4)
Ni28	C34	H34	125.5(5)
C30	C34	C33	108.4(6)
C30	C34	H34	125.3(7)
C33	C34	H34	125.6(6)
C36	C35	C40	119.5(3)
C36	C35	P21	118.8(3)
C40	C35	P21	121.6(3)
C35	C36	H36	119.9(4)
C35	C36	C37	120.2(4)
H36	C36	C37	119.9(4)
C36	C37	H37	119.9(4)
C36	C37	C38	120.1(4)
H37	C37	C38	120.0(4)
C37	C38	H38	120.0(5)
C37	C38	C39	119.8(4)
H38	C38	C39	120.2(5)
C38	C39	H39	119.7(5)
C38	C39	C40	120.7(4)
H39	C39	C40	119.6(5)
C35	C40	C39	119.7(4)
C35	C40	H40	120.2(4)
C39	C40	H40	120.1(4)
Ni28	P21	C22	119.9(1)
Ni28	P21	C27	118.1(2)
Ni28	P21	C35	112.2(1)
C22	P21	C27	92.0(2)
C22	P21	C35	106.1(2)
C27	P21	C35	106.1(2)

A1 Table. Angles and bond lengths for compound 1

X-Ray structure and A2 table of angles and bond lengths for compound 3



Formula	$C_{24}H_{26}Cl_2P_2Pd$
Space Group	P-1
Cell Lengths	a 10.7613(5) Å b 13.5506(6) Å c 17.8451(9) Å
Cell Angles	α 76.583(2) β 80.536(2) γ 70.512(2)
Cell Volume	2375.41(19) $Å^3$
Z	4
Goodness-of-fit on F2	1.155

P(1)-Pd(1)-P(2)	93.51(3)
P(1)-Pd(1)-Cl(2)	178.93(3)
P(2)-Pd(1)-Cl(2)	86.70(3)
P(1)-Pd(1)-Cl(1)	88.61(3)
P(2)-Pd(1)-Cl(1)	175.88(3)
Cl(2)-Pd(1)-Cl(1)	91.25(3)
P(4)-Pd(2)-P(3)	95.10(3)
P(4)-Pd(2)-Cl(3)	85.19(3)
P(3)-Pd(2)-Cl(3)	175.59(4)
P(4)-Pd(2)-Cl(4)	175.33(3)
P(3)-Pd(2)-Cl(4)	88.62(3)
Cl(3)-Pd(2)-Cl(4)	91.32(3)
C(6)-C(1)-C(2)	119.4(4)
C(6)-C(1)-P(1)	122.6(3)
C(2)-C(1)-P(1)	118.0(3)
C(3)-C(2)-C(1)	120.4(4)
C(3)-C(2)-H(2)	119.8
C(1)-C(2)-H(2)	119.8
C(4)-C(3)-C(2)	120.0(4)
C(4)-C(3)-H(3)	120
C(2)-C(3)-H(3)	120
C(3)-C(4)-C(5)	119.8(4)
C(3)-C(4)-H(4)	120.1
C(5)-C(4)-H(4)	120.1
C(4)-C(5)-C(6)	121.2(4)
C(4)-C(5)-H(5)	119.4
C(6)-C(5)-H(5)	119.4
C(1)-C(6)-C(5)	119.2(4)
C(1)-C(6)-H(6)	120.4
C(5)-C(6)-H(6)	120.4
C(8)-C(7)-P(1)	110.6(3)
C(8)-C(7)-H(7)	124.7
P(1)-C(7)-H(7)	124.7
C(7)-C(8)-C(9)	123.2(3)
C(7)-C(8)-C(10)	114.5(3)
C(9)-C(8)-C(10)	122.3(3)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(12)	122.4(3)
C(11)-C(10)-C(8)	124.0(3)
C(12)-C(10)-C(8)	113.6(3)
C(10)-C(11)-H(11A)	118(2)
C(10)-C(11)-H(11B)	123(3)
H(11A)-C(11)-H(11B)	119(4)
C(10)-C(12)-P(1)	108.1(2)
C(10)-C(12)-H(12A)	110.1
P(1)-C(12)-H(12A)	110.1
C(10)-C(12)-H(12B)	110.1

Pd(1)-P(1)	2.2389(9)
Pd(1)-P(2)	2.2389(8)
Pd(1)-Cl(2)	2.3396(9)
Pd(1)-Cl(1)	2.3615(8)
Pd(2)-P(4)	2.2400(9)
Pd(2)-P(3)	2.2488(9)
Pd(2)-Cl(3)	2.3523(9)
Pd(2)-Cl(4)	2.3618(8)
C(1)-C(6)	1.372(5)
C(1)-C(2)	1.392(5)
C(1)-P(1)	1.811(4)
C(2)-C(3)	1.389(6)
C(2)-H(2)	0.95
C(3)-C(4)	1.364(7)
C(3)-H(3)	0.95
C(4)-C(5)	1.367(7)
C(4)-H(4)	0.95
C(5)-C(6)	1.397(7)
C(5)-H(5)	0.95
C(6)-H(6)	0.95
C(7)-C(8)	1.398(5)
C(7)-P(1)	1.806(4)
C(7)-H(7)	0.95
C(8)-C(9)	1.446(5)
C(8)-C(10)	1.463(5)
C(9)-H(9A)	0.98
C(9)-H(9B)	0.98
C(9)-H(9C)	0.98
C(10)-C(11)	1.384(5)
C(10)-C(12)	1.460(5)
C(11)-H(11A)	1.07(5)
C(11)-H(11B)	0.89(5)
C(12)-P(1)	1.824(3)
C(12)-H(12A)	0.99
C(12)-H(12B)	0.99
C(13)-C(14)	1.374(5)
C(13)-C(18)	1.402(5)
C(13)-P(2)	1.813(3)
C(14)-C(15)	1.396(5)
C(14)-H(14)	0.95
C(15)-C(16)	1.359(6)
C(15)-H(15)	0.95
C(16)-C(17)	1.386(6)
C(16)-H(16)	0.95
C(17)-C(18)	1.383(5)
C(17)-H(17)	0.95
C(18)-H(18)	0.95
C(19)-C(20)	1.361(5)
C(19)-P(2)	1.798(3)
C(19)-H(19)	0.95
C(20)-C(21)	1.460(4)
C(20)-C(22)	1.470(4)

P(1)-C(12)-H(12B)	110.1
H(12A)-C(12)-H(12B)	108.4
C(14)-C(13)-C(18)	119.3(3)
C(14)-C(13)-P(2)	121.1(3)
C(18)-C(13)-P(2)	119.6(3)
C(13)-C(14)-C(15)	120.2(3)
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-H(14)	119.9
C(16)-C(15)-C(14)	120.2(4)
C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9
C(15)-C(16)-C(17)	120.6(4)
C(15)-C(16)-H(16)	119.7
C(17)-C(16)-H(16)	119.7
C(18)-C(17)-C(16)	119.7(3)
C(18)-C(17)-H(17)	120.2
C(16)-C(17)-H(17)	120.2
C(17)-C(18)-C(13)	120.0(3)
C(17)-C(18)-H(18)	120
C(13)-C(18)-H(18)	120
C(20)-C(19)-P(2)	112.0(2)
C(20)-C(19)-H(19)	124
P(2)-C(19)-H(19)	124
C(19)-C(20)-C(21)	123.5(3)
C(19)-C(20)-C(22)	114.9(3)
C(21)-C(20)-C(22)	121.6(3)
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)-C(20)	123.4(3)
C(23)-C(22)-C(24)	123.5(3)
C(20)-C(22)-C(24)	113.1(3)
C(22)-C(23)-H(23A)	120
C(22)-C(23)-H(23B)	120
H(23A)-C(23)-H(23B)	120
C(22)-C(24)-P(2)	107.1(2)
C(22)-C(24)-H(24A)	110.3
P(2)-C(24)-H(24A)	110.3
C(22)-C(24)-H(24B)	110.3
P(2)-C(24)-H(24B)	110.3
H(24A)-C(24)-H(24B)	108.5
C(30)-C(25)-C(26)	119.2(3)
C(30)-C(25)-P(3)	123.5(3)
C(26)-C(25)-P(3)	117.2(3)
C(25)-C(26)-C(27)	119.9(3)
C(25)-C(26)-H(26)	120
C(27)-C(26)-H(26)	120
C(28)-C(27)-C(26)	119.7(4)
C(28)-C(27)-H(27)	120.1

C(21)-H(21A)	0.98
C(21)-H(21B)	0.98
C(21)-H(21C)	0.98
C(22)-C(23)	1.356(5)
C(22)-C(24)	1.483(5)
C(23)-H(23A)	0.95
C(23)-H(23B)	0.95
C(24)-P(2)	1.832(3)
C(24)-H(24A)	0.99
C(24)-H(24B)	0.99
C(25)-C(30)	1.381(5)
C(25)-C(26)	1.390(5)
C(25)-P(3)	1.806(4)
C(26)-C(27)	1.410(6)
C(26)-H(26)	0.95
C(27)-C(28)	1.372(6)
C(27)-H(27)	0.95
C(28)-C(29)	1.406(6)
C(28)-H(28)	0.95
C(29)-C(30)	1.376(6)
C(29)-H(29)	0.95
C(30)-H(30)	0.95
C(31)-C(32)	1.488(5)
C(31)-P(3)	1.832(3)
C(31)-H(31A)	0.99
C(31)-H(31B)	0.99
C(32)-C(33)	1.356(5)
C(32)-C(34)	1.463(5)
C(33)-H(33A)	0.95
C(33)-H(33B)	0.95
C(34)-C(36)	1.364(5)
C(34)-C(35)	1.452(5)
C(35)-H(35A)	0.98
C(35)-H(35B)	0.98
C(35)-H(35C)	0.98
C(36)-P(3)	1.808(4)
C(36)-H(36)	0.95
C(37)-C(42)	1.384(6)
C(37)-C(38)	1.400(6)
C(37)-P(4)	1.820(4)
C(38)-C(39)	1.383(6)
C(38)-H(38)	0.95
C(39)-C(40)	1.376(7)
C(39)-H(39)	0.95
C(40)-C(41)	1.376(8)
C(40)-H(40)	0.95
C(41)-C(42)	1.395(7)
C(41)-H(41)	0.95
C(42)-H(42)	0.95
C(43)-C(44)	1.496(6)
C(43)-P(4)	1.835(4)
C(43)-H(43A)	0.99

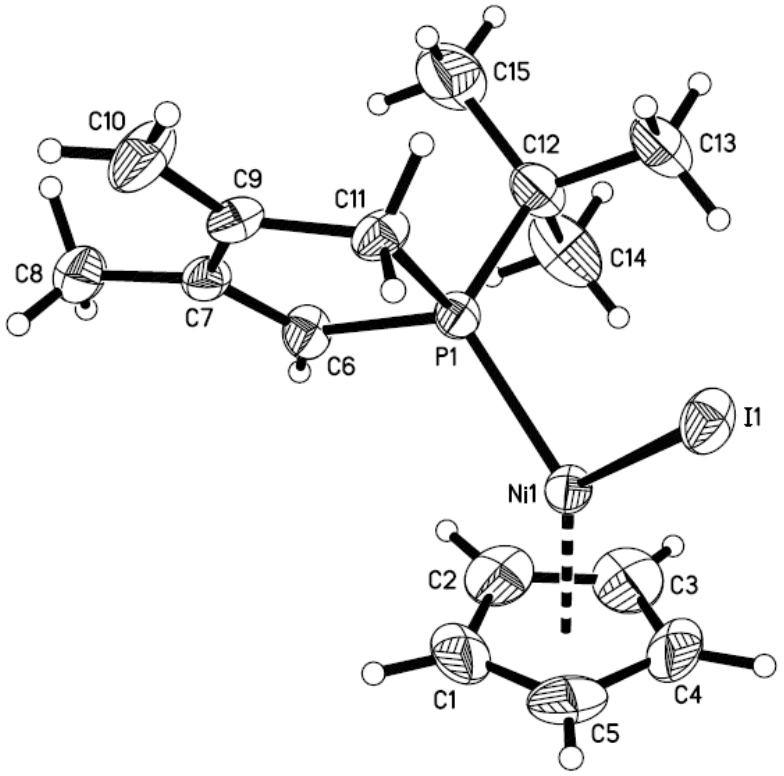
C(26)-C(27)-H(27)	120.1
C(27)-C(28)-C(29)	120.4(4)
C(27)-C(28)-H(28)	119.8
C(29)-C(28)-H(28)	119.8
C(30)-C(29)-C(28)	119.0(4)
C(30)-C(29)-H(29)	120.5
C(28)-C(29)-H(29)	120.5
C(29)-C(30)-C(25)	121.8(4)
C(29)-C(30)-H(30)	119.1
C(25)-C(30)-H(30)	119.1
C(32)-C(31)-P(3)	107.4(2)
C(32)-C(31)-H(31A)	110.2
P(3)-C(31)-H(31A)	110.2
C(32)-C(31)-H(31B)	110.2
P(3)-C(31)-H(31B)	110.2
H(31A)-C(31)-H(31B)	108.5
C(33)-C(32)-C(34)	124.0(3)
C(33)-C(32)-C(31)	122.7(3)
C(34)-C(32)-C(31)	113.3(3)
C(32)-C(33)-H(33A)	120
C(32)-C(33)-H(33B)	120
H(33A)-C(33)-H(33B)	120
C(36)-C(34)-C(35)	124.2(4)
C(36)-C(34)-C(32)	114.7(3)
C(35)-C(34)-C(32)	121.1(3)
C(34)-C(35)-H(35A)	109.5
C(34)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(34)-C(36)-P(3)	112.2(3)
C(34)-C(36)-H(36)	123.9
P(3)-C(36)-H(36)	123.9
C(42)-C(37)-C(38)	119.4(4)
C(42)-C(37)-P(4)	120.3(4)
C(38)-C(37)-P(4)	120.3(3)
C(39)-C(38)-C(37)	120.4(4)
C(39)-C(38)-H(38)	119.8
C(37)-C(38)-H(38)	119.8
C(40)-C(39)-C(38)	120.0(5)
C(40)-C(39)-H(39)	120
C(38)-C(39)-H(39)	120
C(41)-C(40)-C(39)	120.0(5)
C(41)-C(40)-H(40)	120
C(39)-C(40)-H(40)	120
C(40)-C(41)-C(42)	120.9(5)
C(40)-C(41)-H(41)	119.6
C(42)-C(41)-H(41)	119.6
C(37)-C(42)-C(41)	119.4(5)
C(37)-C(42)-H(42)	120.3
C(41)-C(42)-H(42)	120.3

C(43)-H(43B)	0.99
C(44)-C(45)	1.361(6)
C(44)-C(46)	1.472(5)
C(45)-H(45A)	0.95
C(45)-H(45B)	0.95
C(46)-C(48)	1.367(5)
C(46)-C(47)	1.463(5)
C(47)-H(47A)	0.98
C(47)-H(47B)	0.98
C(47)-H(47C)	0.98
C(48)-P(4)	1.795(4)
C(48)-H(48)	0.95

C(44)-C(43)-P(4)	107.2(3)
C(44)-C(43)-H(43A)	110.3
P(4)-C(43)-H(43A)	110.3
C(44)-C(43)-H(43B)	110.3
P(4)-C(43)-H(43B)	110.3
H(43A)-C(43)-H(43B)	108.5
C(45)-C(44)-C(46)	123.5(4)
C(45)-C(44)-C(43)	124.7(4)
C(46)-C(44)-C(43)	111.8(3)
C(44)-C(45)-H(45A)	120
C(44)-C(45)-H(45B)	120
H(45A)-C(45)-H(45B)	120
C(48)-C(46)-C(47)	123.9(3)
C(48)-C(46)-C(44)	114.9(3)
C(47)-C(46)-C(44)	121.2(3)
C(46)-C(47)-H(47A)	109.5
C(46)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(46)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(46)-C(48)-P(4)	112.3(3)
C(46)-C(48)-H(48)	123.9
P(4)-C(48)-H(48)	123.9
C(7)-P(1)-C(1)	105.74(17)
C(7)-P(1)-C(12)	92.73(17)
C(1)-P(1)-C(12)	108.76(17)
C(7)-P(1)-Pd(1)	116.39(13)
C(1)-P(1)-Pd(1)	109.55(11)
C(12)-P(1)-Pd(1)	121.80(12)
C(19)-P(2)-C(13)	107.30(15)
C(19)-P(2)-C(24)	92.81(16)
C(13)-P(2)-C(24)	106.73(16)
C(19)-P(2)-Pd(1)	119.29(12)
C(13)-P(2)-Pd(1)	111.65(11)
C(24)-P(2)-Pd(1)	117.07(12)
C(25)-P(3)-C(36)	107.07(17)
C(25)-P(3)-C(31)	109.12(17)
C(36)-P(3)-C(31)	92.31(17)
C(25)-P(3)-Pd(2)	110.21(12)
C(36)-P(3)-Pd(2)	115.38(13)
C(31)-P(3)-Pd(2)	120.99(12)
C(48)-P(4)-C(37)	106.17(17)
C(48)-P(4)-C(43)	92.07(18)
C(37)-P(4)-C(43)	109.7(2)
C(48)-P(4)-Pd(2)	121.04(12)
C(37)-P(4)-Pd(2)	111.05(14)
C(43)-P(4)-Pd(2)	115.11(14)

A2 Table. Angles and bond lengths for compound 3

X-Ray structure and A3 table of angles and bond lengths for compound 6



Formula	$C_{15}H_{22}INiP$
Space Group	P2(1)/c
Cell Lengths	a 7.9994(5) Å b 18.2951(11) Å c 13.7800(7) Å
Cell Angles	α 90° β 122.572(3)° γ 90°
Cell Volume	1699.50(17)$Å_3$
Z	4
Goodness-of-fit on F2	1.03

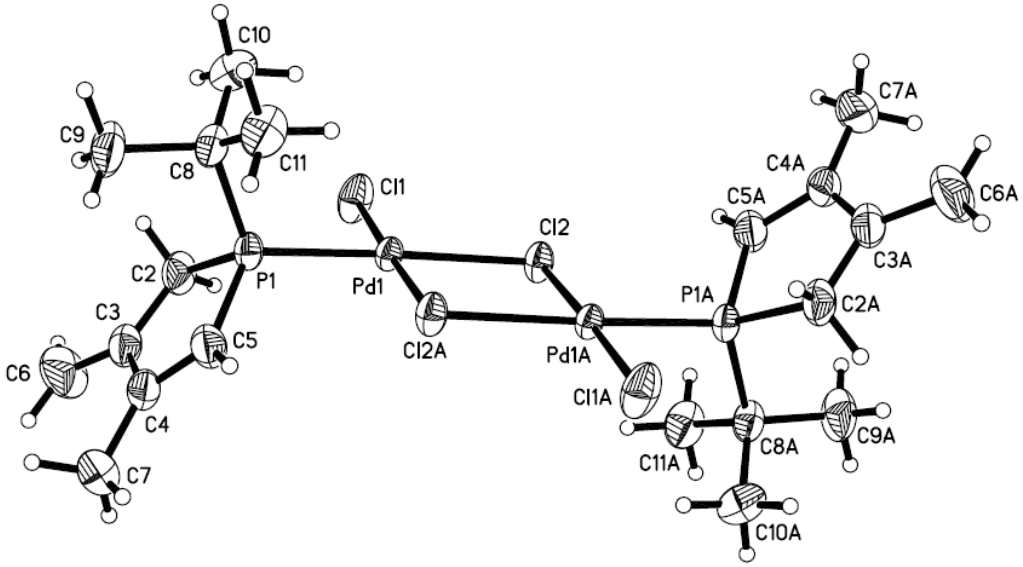
C(2)-Ni(1)-C(4)	64.6(3)
C(2)-Ni(1)-C(1)	39.6(3)
C(4)-Ni(1)-C(1)	63.7(2)
C(2)-Ni(1)-C(3)	39.0(3)
C(4)-Ni(1)-C(3)	38.0(3)
C(1)-Ni(1)-C(3)	64.9(3)
C(2)-Ni(1)-C(5)	64.9(3)
C(4)-Ni(1)-C(5)	39.5(3)
C(1)-Ni(1)-C(5)	36.9(2)
C(3)-Ni(1)-C(5)	65.2(3)
C(2)-Ni(1)-P(1)	96.64(19)
C(4)-Ni(1)-P(1)	156.2(3)
C(1)-Ni(1)-P(1)	111.9(2)
C(3)-Ni(1)-P(1)	118.2(2)
C(5)-Ni(1)-P(1)	147.1(2)
C(2)-Ni(1)-I(1)	165.33(18)
C(4)-Ni(1)-I(1)	100.9(2)
C(1)-Ni(1)-I(1)	133.8(2)
C(3)-Ni(1)-I(1)	129.7(2)
C(5)-Ni(1)-I(1)	102.95(19)
P(1)-Ni(1)-I(1)	97.90(3)
C(6)-P(1)-C(11)	91.4(2)
C(6)-P(1)-C(12)	104.4(2)
C(11)-P(1)-C(12)	107.6(2)
C(6)-P(1)-Ni(1)	117.57(15)
C(11)-P(1)-Ni(1)	116.76(15)
C(12)-P(1)-Ni(1)	115.89(18)
C(5)-C(1)-C(2)	109.0(6)
C(5)-C(1)-Ni(1)	72.5(3)
C(2)-C(1)-Ni(1)	67.1(3)
C(5)-C(1)-H(1)	125.5
C(2)-C(1)-H(1)	125.5
Ni(1)-C(1)-H(1)	126.5
C(3)-C(2)-C(1)	108.8(6)
C(3)-C(2)-Ni(1)	74.3(3)
C(1)-C(2)-Ni(1)	73.3(3)
C(3)-C(2)-H(2)	125.6
C(1)-C(2)-H(2)	125.6
Ni(1)-C(2)-H(2)	118.6
C(4)-C(3)-C(2)	105.8(6)
C(4)-C(3)-Ni(1)	70.1(3)
C(2)-C(3)-Ni(1)	66.6(3)
C(4)-C(3)-H(3)	127.1
C(2)-C(3)-H(3)	127.1
Ni(1)-C(3)-H(3)	127.6
C(3)-C(4)-C(5)	109.4(6)
C(3)-C(4)-Ni(1)	71.8(3)
C(5)-C(4)-Ni(1)	71.2(3)
C(3)-C(4)-H(4)	125.3
C(5)-C(4)-H(4)	125.3
Ni(1)-C(4)-H(4)	123.2
C(1)-C(5)-C(4)	106.6(6)

I(1)-Ni(1)	2.5016(6)
Ni(1)-C(2)	2.039(5)
Ni(1)-C(4)	2.117(5)
Ni(1)-C(1)	2.120(5)
Ni(1)-C(3)	2.139(5)
Ni(1)-C(5)	2.142(5)
Ni(1)-P(1)	2.1465(12)
P(1)-C(6)	1.800(4)
P(1)-C(11)	1.818(4)
P(1)-C(12)	1.872(5)
C(1)-C(5)	1.348(9)
C(1)-C(2)	1.411(9)
C(1)-H(1)	0.95
C(2)-C(3)	1.399(9)
C(2)-H(2)	0.9499
C(3)-C(4)	1.386(10)
C(3)-H(3)	0.95
C(4)-C(5)	1.438(10)
C(4)-H(4)	0.9499
C(5)-H(5)	0.95
C(6)-C(7)	1.359(6)
C(6)-H(6)	0.94
C(7)-C(9)	1.461(6)
C(7)-C(8)	1.465(6)
C(8)-H(8A)	0.97
C(8)-H(8B)	0.97
C(8)-H(8C)	0.97
C(9)-C(10)	1.334(7)
C(9)-C(11)	1.479(6)
C(10)-H(10A)	0.94
C(10)-H(10B)	0.94
C(11)-H(11A)	0.98
C(11)-H(11B)	0.98
C(12)-C(13)	1.517(7)
C(12)-C(14)	1.527(8)
C(12)-C(15)	1.550(9)
C(13)-H(13A)	0.97
C(13)-H(13B)	0.97
C(13)-H(13C)	0.97
C(14)-H(14A)	0.97
C(14)-H(14B)	0.97
C(14)-H(14C)	0.97
C(15)-H(15A)	0.97
C(15)-H(15B)	0.97
C(15)-H(15C)	0.97

C(1)-C(5)-Ni(1)	70.7(3)
C(4)-C(5)-Ni(1)	69.3(3)
C(1)-C(5)-H(5)	126.7
C(4)-C(5)-H(5)	126.7
Ni(1)-C(5)-H(5)	124.9
C(7)-C(6)-P(1)	112.9(3)
C(7)-C(6)-H(6)	123.5
P(1)-C(6)-H(6)	123.5
C(6)-C(7)-C(9)	114.4(4)
C(6)-C(7)-C(8)	123.5(4)
C(9)-C(7)-C(8)	122.1(4)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(10)-C(9)-C(7)	124.4(5)
C(10)-C(9)-C(11)	123.2(4)
C(7)-C(9)-C(11)	112.5(4)
C(9)-C(10)-H(10A)	120
C(9)-C(10)-H(10B)	120
H(10A)-C(10)-H(10B)	120
C(9)-C(11)-P(1)	108.6(3)
C(9)-C(11)-H(11A)	110
P(1)-C(11)-H(11A)	110
C(9)-C(11)-H(11B)	110
P(1)-C(11)-H(11B)	110
H(11A)-C(11)-H(11B)	108.4
C(13)-C(12)-C(14)	109.8(5)
C(13)-C(12)-C(15)	109.0(5)
C(14)-C(12)-C(15)	111.0(5)
C(13)-C(12)-P(1)	109.6(3)
C(14)-C(12)-P(1)	107.0(4)
C(15)-C(12)-P(1)	110.4(4)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(12)-C(15)-H(15A)	109.5
C(12)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5

A3 Table. Angles and bond lengths for compound 6

X-Ray structure and A4 table of angles and bond lengths for compound 9



Formula	$C_{20}H_{34}Cl_4P_2Pd_2$
Space Group	P2(1)/c
Cell Lengths	a 11.5787(4) Å b 10.0940(4) Å c 14.1606(5) Å
Cell Angles	α 90° β 126.416(2)° γ 90°
Cell Volume	1331.84(8) Å^3
Z	2
Goodness-of-fit on F2	1.095

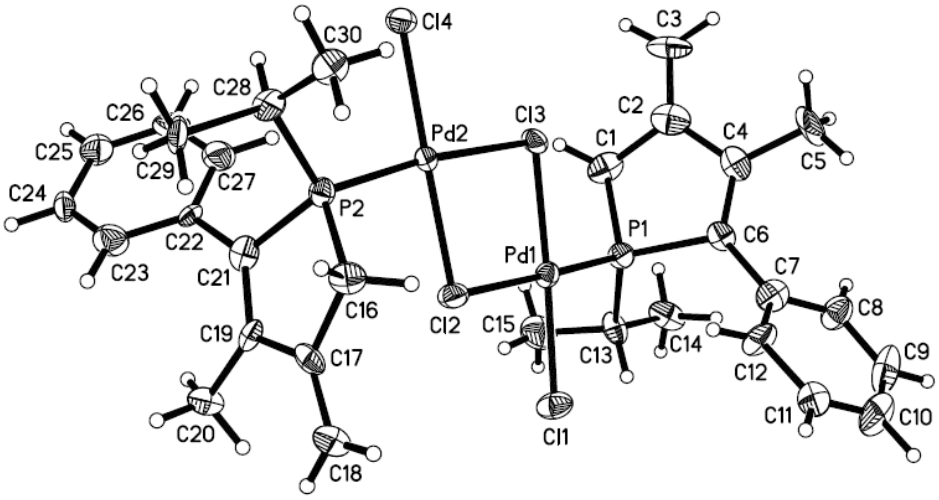
P(1)-Pd(1)-Cl(1)	88.99(2)
P(1)-Pd(1)-Cl(2)#1	92.330(19)
Cl(1)-Pd(1)-Cl(2)#1	178.15(2)
P(1)-Pd(1)-Cl(2)	177.95(2)
Cl(1)-Pd(1)-Cl(2)	92.102(19)
Cl(2)#1-Pd(1)-Cl(2)	86.615(18)
C(3)-C(2)-P(1)	107.93(18)
C(3)-C(2)-H(2A)	110.1
P(1)-C(2)-H(2A)	110.1
C(3)-C(2)-H(2B)	110.1
P(1)-C(2)-H(2B)	110.1
H(2A)-C(2)-H(2B)	108.4
C(6)-C(3)-C(2)	121.7(3)
C(6)-C(3)-C(4)	124.2(3)
C(2)-C(3)-C(4)	114.0(2)
C(5)-C(4)-C(7)	123.5(3)
C(5)-C(4)-C(3)	114.4(2)
C(7)-C(4)-C(3)	122.1(2)
C(4)-C(5)-P(1)	109.82(19)
C(4)-C(5)-H(5)	125.1
P(1)-C(5)-H(5)	125.1
C(3)-C(6)-H(6A)	120
C(3)-C(6)-H(6B)	120
H(6A)-C(6)-H(6B)	120
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(10)-C(8)-C(11)	109.7(2)
C(10)-C(8)-C(9)	109.6(2)
C(11)-C(8)-C(9)	110.6(2)
C(10)-C(8)-P(1)	109.45(16)
C(11)-C(8)-P(1)	108.72(16)
C(9)-C(8)-P(1)	108.76(17)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5

Pd(1)-P(1)	2.2094(5)
Pd(1)-Cl(1)	2.2775(6)
Pd(1)-Cl(2)#1	2.3277(5)
Pd(1)-Cl(2)	2.4491(5)
C(2)-C(3)	1.445(4)
C(2)-P(1)	1.808(2)
C(2)-H(2A)	0.99
C(2)-H(2B)	0.99
C(3)-C(6)	1.396(3)
C(3)-C(4)	1.459(4)
C(4)-C(5)	1.400(3)
C(4)-C(7)	1.443(4)
C(5)-P(1)	1.800(2)
C(5)-H(5)	0.95
C(6)-H(6A)	0.95
C(6)-H(6B)	0.95
C(7)-H(7A)	0.98
C(7)-H(7B)	0.98
C(7)-H(7C)	0.98
C(8)-C(10)	1.526(4)
C(8)-C(11)	1.529(3)
C(8)-C(9)	1.533(3)
C(8)-P(1)	1.854(2)
C(9)-H(9A)	0.98
C(9)-H(9B)	0.98
C(9)-H(9C)	0.98
C(10)-H(10A)	0.98
C(10)-H(10B)	0.98
C(10)-H(10C)	0.98
C(11)-H(11A)	0.98
C(11)-H(11B)	0.98
C(11)-H(11C)	0.98
Cl(2)-Pd(1)#1	2.3277(5)

H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
Pd(1)#1-Cl(2)-Pd(1)	93.384(18)
C(5)-P(1)-C(2)	93.54(12)
C(5)-P(1)-C(8)	109.25(12)
C(2)-P(1)-C(8)	109.37(11)
C(5)-P(1)-Pd(1)	114.10(8)
C(2)-P(1)-Pd(1)	116.14(9)
C(8)-P(1)-Pd(1)	112.82(7)

A4 Table. Angles and bond lengths for compound 9

X-Ray structure and A5 table of angles and bond lengths for compound 14



Formula	$C_{30}H_{38}Cl_4P_2Pd_2$
Space Group	C c
Cell Lengths	a 7.3331(4) Å b 18.4222(8) Å c 24.1357(11) Å
Cell Angles	α 90° β 96.141(3)° γ 90°
Cell Volume	3241.83
Z, Z'	Z: 4 Z': 0
R-Factor (%)	5.84

Atom1	Atom2	Atom3	*Angle*
Cl1	Pd1	Cl2	88.5(2)
Cl1	Pd1	Cl3	173.8(2)
Cl1	Pd1	P1	92.0(2)
Cl2	Pd1	Cl3	85.7(1)
Cl2	Pd1	P1	176.3(2)
Cl3	Pd1	P1	93.9(1)
Cl2	Pd2	Cl3	85.1(1)
Cl2	Pd2	Cl4	176.9(2)
Cl2	Pd2	P2	88.2(1)
Cl3	Pd2	Cl4	92.3(2)
Cl3	Pd2	P2	173.3(1)
Cl4	Pd2	P2	94.3(2)
H1A	C1	H1B	108(2)
H1A	C1	C2	110(2)
H1A	C1	P1	110(1)
H1B	C1	C2	110(2)
H1B	C1	P1	110(2)
C2	C1	P1	107(1)
C1	C2	C3	123(2)
C1	C2	C4	111(2)
C3	C2	C4	126(2)
C2	C3	H3A	120(2)
C2	C3	H3B	120(2)
H3A	C3	H3B	120(2)
C2	C4	C5	119(2)
C2	C4	C6	116(2)
C5	C4	C6	125(2)
C4	C5	H5A	109(2)
C4	C5	H5B	110(2)
C4	C5	H5C	109(2)
H5A	C5	H5B	110(2)
H5A	C5	H5C	109(2)
H5B	C5	H5C	109(2)
C4	C6	C7	130(2)
C4	C6	P1	109(1)
C7	C6	P1	121(1)
C6	C7	C8	121(2)
C6	C7	C12	121(2)
C8	C7	C12	117(2)
C7	C8	H8	120(2)
C7	C8	C9	121(2)
H8	C8	C9	120(2)
C8	C9	H9	119(2)
C8	C9	C10	121(2)
H9	C9	C10	119(2)
C9	C10	H10	121(2)
C9	C10	C11	119(2)
H10	C10	C11	120(2)
C10	C11	H11	120(2)
C10	C11	C12	120(2)
H11	C11	C12	120(2)
C7	C12	C11	121(2)

Atom1	Atom2	*Length*
Pd1	Cl1	2.280(5)
Pd1	Cl2	2.408(4)
Pd1	Cl3	2.342(4)
Pd1	P1	2.230(4)
Pd2	Cl2	2.316(4)
Pd2	Cl3	2.460(4)
Pd2	Cl4	2.295(5)
Pd2	P2	2.233(4)
C1	H1A	0.99(2)
C1	H1B	0.99(2)
C1	C2	1.50(3)
C1	P1	1.80(2)
C2	C3	1.31(3)
C2	C4	1.50(3)
C3	H3A	0.95(2)
C3	H3B	0.95(2)
C4	C5	1.48(2)
C4	C6	1.36(3)
C5	H5A	0.98(2)
C5	H5B	0.98(2)
C5	H5C	0.98(2)
C6	C7	1.44(3)
C6	P1	1.85(2)
C7	C8	1.39(3)
C7	C12	1.41(3)
C8	H8	0.95(2)
C8	C9	1.37(3)
C9	H9	0.95(2)
C9	C10	1.41(4)
C10	H10	0.95(2)
C10	C11	1.34(3)
C11	H11	0.95(2)
C11	C12	1.42(3)
C12	H12	0.95(2)
C13	H13	1.00(2)
C13	C14	1.48(2)
C13	C15	1.52(2)
C13	P1	1.85(2)
C14	H14A	0.98(2)
C14	H14B	0.98(2)
C14	H14C	0.98(2)
C15	H15A	0.98(2)
C15	H15B	0.98(2)
C15	H15C	0.98(2)
C16	H16A	0.99(2)
C16	H16B	0.99(1)
C16	C17	1.54(2)
C16	P2	1.80(2)
C17	C18	1.35(2)
C17	C19	1.45(2)
C18	H18A	0.95(2)
C18	H18B	0.95(2)

C7	C12	H12	120(2)
C11	C12	H12	119(2)
H13	C13	C14	108(2)
H13	C13	C15	108(2)
H13	C13	P1	108(1)
C14	C13	C15	112(2)
C14	C13	P1	111(1)
C15	C13	P1	110(1)
C13	C14	H14A	109(2)
C13	C14	H14B	110(2)
C13	C14	H14C	109(2)
H14A	C14	H14B	109(2)
H14A	C14	H14C	109(2)
H14B	C14	H14C	109(2)
C13	C15	H15A	110(2)
C13	C15	H15B	109(2)
C13	C15	H15C	109(2)
H15A	C15	H15B	110(2)
H15A	C15	H15C	110(2)
H15B	C15	H15C	109(2)
H16A	C16	H16B	108(2)
H16A	C16	C17	111(1)
H16A	C16	P2	111(1)
H16B	C16	C17	110(1)
H16B	C16	P2	110(1)
C17	C16	P2	106(1)
C16	C17	C18	125(1)
C16	C17	C19	111(1)
C18	C17	C19	125(1)
C17	C18	H18A	120(2)
C17	C18	H18B	120(2)
H18A	C18	H18B	120(2)
C17	C19	C20	119(1)
C17	C19	C21	117(1)
C20	C19	C21	124(1)
C19	C20	H20A	110(1)
C19	C20	H20B	109(1)
C19	C20	H20C	109(1)
H20A	C20	H20B	109(2)
H20A	C20	H20C	110(2)
H20B	C20	H20C	109(2)
C19	C21	C22	128(1)
C19	C21	P2	110(1)
C22	C21	P2	122(1)
C21	C22	C23	120(1)
C21	C22	C27	122(1)
C23	C22	C27	118(2)
C22	C23	H23	120(2)
C22	C23	C24	120(2)
H23	C23	C24	120(2)
C23	C24	H24	120(2)
C23	C24	C25	120(2)
H24	C24	C25	120(2)

C19	C20	1.48(2)
C19	C21	1.36(2)
C20	H20A	0.98(1)
C20	H20B	0.98(1)
C20	H20C	0.98(2)
C21	C22	1.50(2)
C21	P2	1.82(2)
C22	C23	1.38(2)
C22	C27	1.40(3)
C23	H23	0.95(2)
C23	C24	1.42(3)
C24	H24	0.95(2)
C24	C25	1.39(2)
C25	H25	0.95(2)
C25	C26	1.37(3)
C26	H26	0.95(2)
C26	C27	1.37(3)
C27	H27	0.95(2)
C28	H28	1.00(2)
C28	C29	1.58(2)
C28	C30	1.56(2)
C28	P2	1.82(1)
C29	H29A	0.98(2)
C29	H29B	0.98(1)
C29	H29C	0.98(2)
C30	H30A	0.98(2)
C30	H30B	0.98(2)
C30	H30C	0.98(2)

C24	C25	H25	121(2)
C24	C25	C26	119(2)
H25	C25	C26	121(2)
C25	C26	H26	119(2)
C25	C26	C27	121(2)
H26	C26	C27	119(2)
C22	C27	C26	121(2)
C22	C27	H27	120(2)
C26	C27	H27	119(2)
H28	C28	C29	108(1)
H28	C28	C30	108(1)
H28	C28	P2	108(1)
C29	C28	C30	111(1)
C29	C28	P2	111(1)
C30	C28	P2	110(1)
C28	C29	H29A	109(1)
C28	C29	H29B	110(1)
C28	C29	H29C	110(1)
H29A	C29	H29B	109(1)
H29A	C29	H29C	109(1)
H29B	C29	H29C	110(1)
C28	C30	H30A	109(1)
C28	C30	H30B	110(1)
C28	C30	H30C	110(1)
H30A	C30	H30B	109(2)
H30A	C30	H30C	109(2)
H30B	C30	H30C	110(2)
Pd1	Cl2	Pd2	95.3(1)
Pd1	Cl3	Pd2	93.2(1)
Pd1	P1	C1	112.4(7)
Pd1	P1	C6	114.1(5)
Pd1	P1	C13	114.4(6)
C1	P1	C6	94.2(8)
C1	P1	C13	110.2(9)
C6	P1	C13	109.8(8)
Pd2	P2	C16	113.2(6)
Pd2	P2	C21	112.3(5)
Pd2	P2	C28	117.3(6)
C16	P2	C21	93.1(7)
C16	P2	C28	109.1(8)
C21	P2	C28	109.2(8)

A5 Table. Angles and bond lengths for compound 14

POSTLUDE

I can see clearly now the rain is gone
I can see all obstacles [out of] my way
Gone are the dark clouds that had me down
It's gonna be a bright sun shiny day
It's gonna be a bright sun shiny day

Oh yes I can make it now the pain is gone
All of the bad feelings have disappeared
Here is that rainbow I've been praying for
It's gonna be a bright sun shiny day
Look all around there's nothing but blue skies
Look straight ahead there's nothing but blue skies

I can see clearly now the rain is gone
I can see all obstacles [out of] my way
Here is that rainbow I've been praying for
It's gonna be a bright sun shiny day
It's gonna be a bright sun shiny day
Bright sun shiny day.

~ Jimmy Cliff