A STUDY OF THE COORDINATION CHEMISTRY OF PHOSPHININES AND PHOSPHABARRELENES

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DECLARATION

This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

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Contents Page

Abstract

The syntheses of a series of 2,6-(2′-haloaryl)-4-tolylphosphinines, ranging from the fluoro, chloro, bromo and iodo derivatives, as well as the 2,6-dixylyl-4-phenylphosphinine ligand are reported. The coordination chemistry of these ligands has been evaluated by coordinating them to pentacarbonyltungsten(0), to form the complex $W(CO)_5(L)$, where L = fluoro, choloro, bromo, iodo or dixylyl derivatives of the phosphinine; secondly to $[Rh(COD)Cl]_2$, to form the complex Rh(COD)Cl(L), where COD = 1,5-cyclooctadiene, and L= fluoro, chloro, bromo or dixylyl derivatives of the phosphinine; and thirdly to $[Rh(CO)_2Cl]_2$ to form $[Rh(CO)Cl(L)]_2$, where L = 2,6,-dixylyl-4-phenylphosphinine only. These complexes were fully characterised by spectroscopic means, their coordination chemistry studied and the metal-phosphorus bond in these complexes is elucidated by comparison to analogous complexes of phosphines, and phosphites.

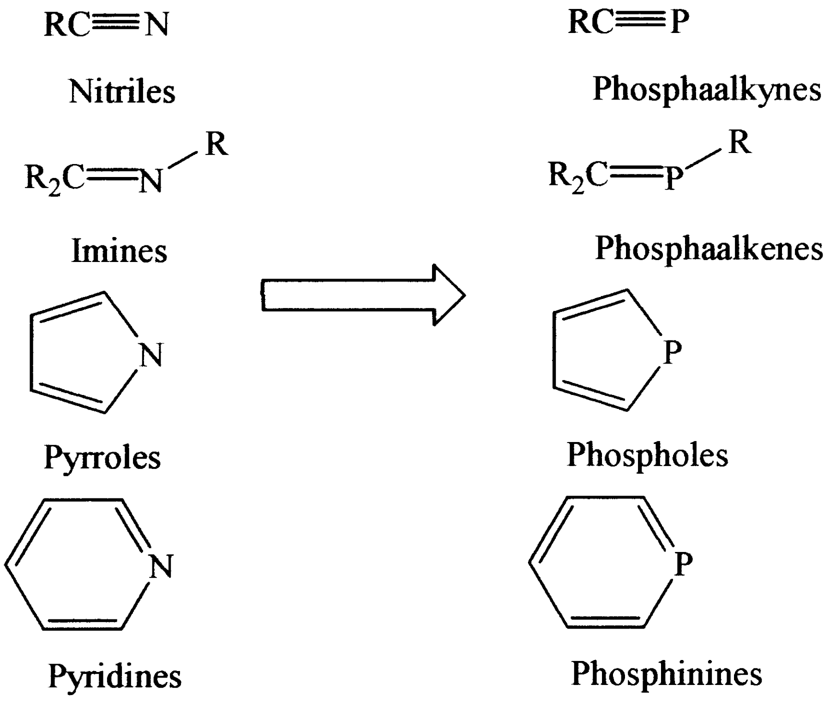
Finally the 2,6-dixylyl-4-phenylphosphabarrelene is synthesised from its parent phosphinine, and applied in a survey of transition metal complexes to evaluate its properties as a ligand. The complexes made were $W(CO)_5(L)$, $Re(CO)_4Cl(L)$, $Ru(cymene)(L)Cl_2$, $[Fe(\eta^5\text{-}C_5H_4SiMe_3)(CO)_2L]^+ PF_6^-$, $Rh(CO)Cl(L)_2$, Rh(COD)Cl(L), Ir(COD)Cl(L), $PtCl_2(L)_2$, $[Ag(L)_2]^+ Tf^-$, Cu(L)Cl, and $Pd(L)_n$. Where L = 2,6-dixylyl-4-phenylphosphabarrelene, cymene = 4-isopropyltoluene, Cp = cyclopentadienyl and COD = 1,5-cyclooctadiene are described. The coordination chemistry of the phosphabarrelene was established and the nature of the phosphorus-metal bond in each complex was elucidated by comparison to analogous complexes of triarylphosphines and triarylphosphites. In addition the phosphabarrelene was tested in the rhodium catalysed hydroformylation of 4-octene, in comparison with the commonly used (2,4-di-t-butylphenyl)phosphite.

CHAPTER 1

INTRODUCTION

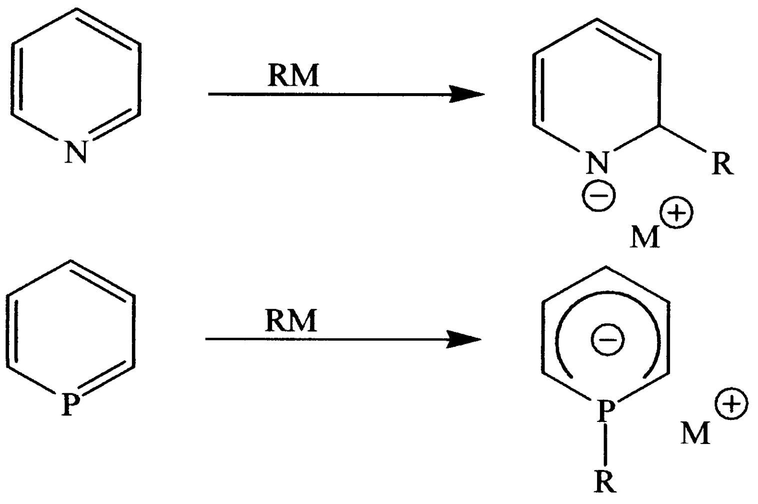
1.1 Introduction

The chemistry of nitrogen based heteroaromatic systems is one of the most widely known and established areas of chemistry. In particular the coordination chemistry of sp^2 nitrogen based ligands, such as imines, pyrroles and pyridines, has been extensively studied and the ligands feature prominently in the fields of bioinorganic chemistry and homogeneous catalysis. This is partly due to the fact that the nitrogen can coordinate to a wide array of transition metals in a variety of oxidation states; as well as being robustly versatile enough to undergo complex organic reactions in the synthesis of supramolecular organic structures. But until the 1960s it was believed that heavier analogues of the sp^2 nitrogen systems were not possible, as the heavier elements were unable to undergo the same sp^2 hybridisation as the nitrogen atom. However, with the discovery of phoshaalkynes, phosphaalkenes, and phosphinines in the 1960s, this belief was dismissed, and a new field of chemistry was born (scheme 1.1). The phosphinines in particular represented a major break through as they illustrated that the P=C bond could exist within a stable aromatic system, and hence the concept of aromaticity could be expanded to the heavier elements such as arsenic, antimony and bismuth.



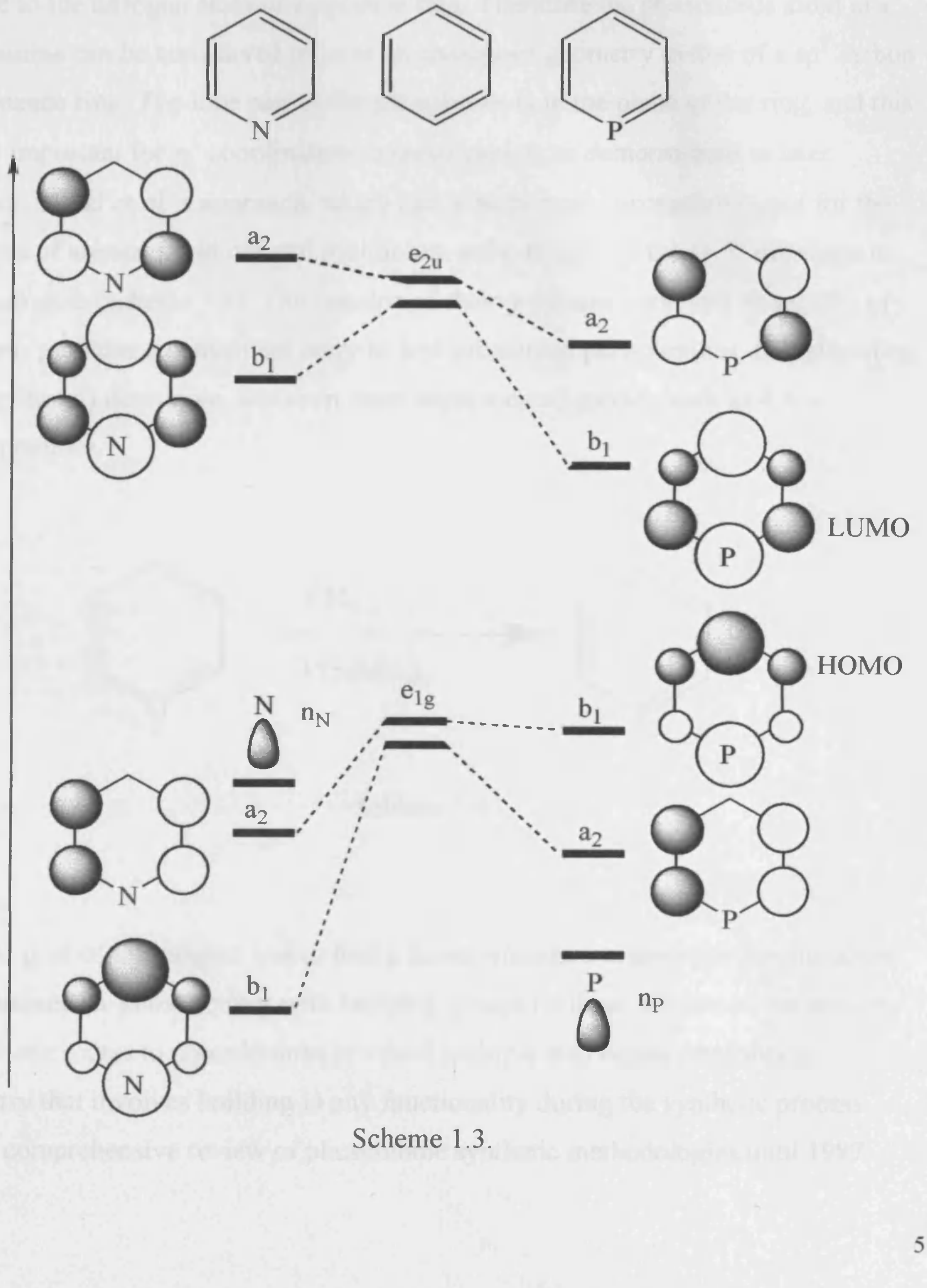
Scheme 1.1.

Phosphinines are 6 membered heteroaromatic systems that are planar in geometry, and contain a delocalised π electron conjugated ring system. They are remarkable systems as they are a direct analogue of pyridines, a recognised and well established ligand system. However, even though there are many similarities in terms of geometry (they are both planar), and structure (both are 6 membered, conjugated heteroaromatic ring systems), there are vital differences. The most important of these is the difference in their electronic structure. These differences stem from the fact that phosphorus is a less electronegative atom than nitrogen, and hence this affects the reactivity of the phosphinines compared to pyridines. Hence the phosphorus atom is considered to bear more of a positive charge, and the 2 and 6 carbons a more negative charge in a phosphinine ring, whereas the opposite is true in a pyridine. Therefore upon reaction with nucleophiles, the phosphinine will generally react at the phosphorus atom, whereas the pyridine generally reacts at the 2 or 6 carbon positions (scheme 1.2).



Scheme 1.2.

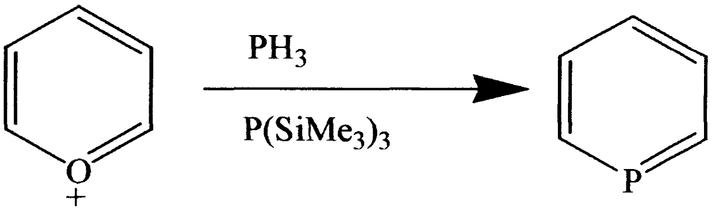
In terms of coordination chemistry the comparison of the MO diagrams of phosphinines and pyridines relative to benzene helps to explain the observations of phosphinines as a ligand to transition metals (scheme 1.3). The MO diagram illustrates that in the pyridine the nitrogen lone pair is the HOMO, whereas in the phosphinine ring the phosphorus lone pair is the $HOMO^{2-}$. This explains the increased σ-donor abilities of the pyridine compared to the phosphinine, as the orbital it uses to coordinate is at a higher energy, relative to the phosphinine, and hence can be more freely donated to generate the metal-nitrogen bond. The lower energy of the phosphorus lone pair also helps to explain the weaker basicity of the phosphinines as well. However, the LUMO of the phosphinine is at a much lower energy relative to the LUMO of the pyridine. Hence phosphinines show much better π-acceptor abilities than pyridines, as the orbital used is at a lower energy than the pyridine and is at a more appropriate energy level for back donation from filled d-orbitals on the metal centre.



Scheme 1.3.

1.2 Synthesis of Phosphinines

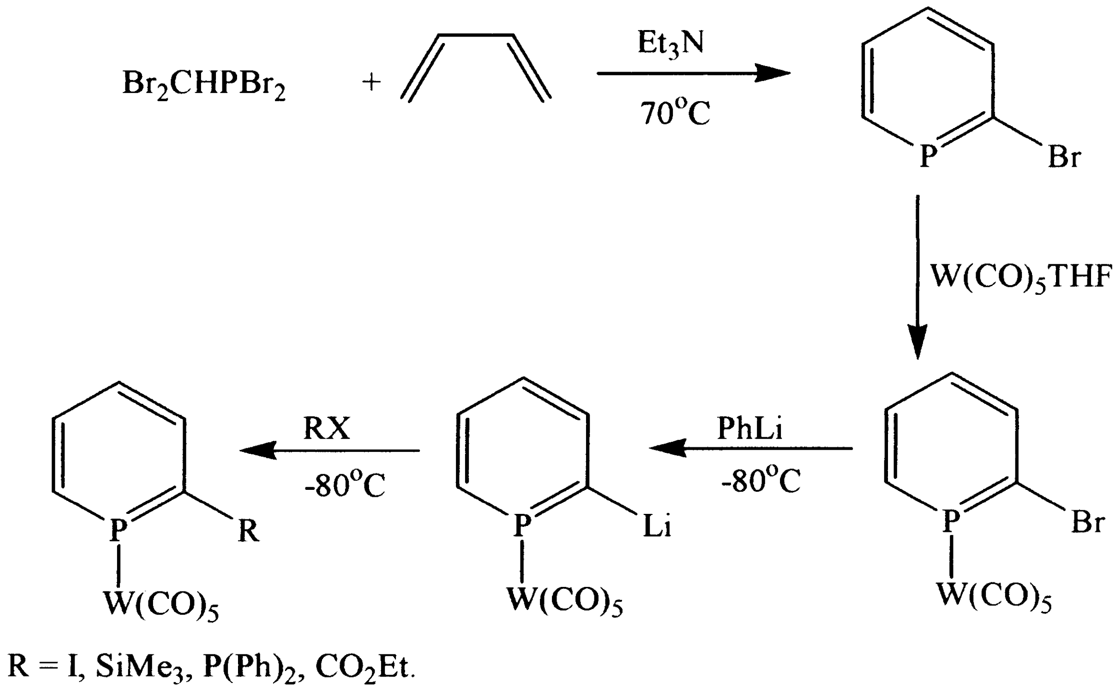
The first known phosphinine was reported by Markl, who synthesised 2,4,6-tiphenylphosphinine in 1966.[1] His discovery was a major event in organophosphorus chemistry as it demonstrated that phosphorus can form stable derivatives containing a P=C bond and that it can be part of a stable heteroaromatic system. The structure of a phosphinine ring is planar and is often compared to that of pyridine. However, phosphorus is less electronegative than nitrogen with the consequence that the phosphorus atom in a phosphinine ring is substantially more electrophilic in nature relative to the nitrogen atom in a pyridine ring. Therefore the phosphorus atom in a phosphinine can be considered to be in an analogous geometry to that of a sp^2 carbon in a benzene ring. The lone pair of the phosphorus is in the plane of the ring, and this will be important for η^1 coordination to metal centres as demonstrated in later chapters. Markl *et al.*'s approach, which had already been successfully used for the synthesis of arenes, pyridines and pyridinium salts, hinges on the O^+/P exchange in pyrylium salts (scheme 1.4). The reaction of their pyrylium salts with either PH_3 or $P(SiMe)_3$ provides a convenient entry to aryl substituted phosphinines, the interesting tris-(*tert*-butyl) derivative, and even more sophisticated species such as 4,4' – biphosphinines.



Scheme 1.4.

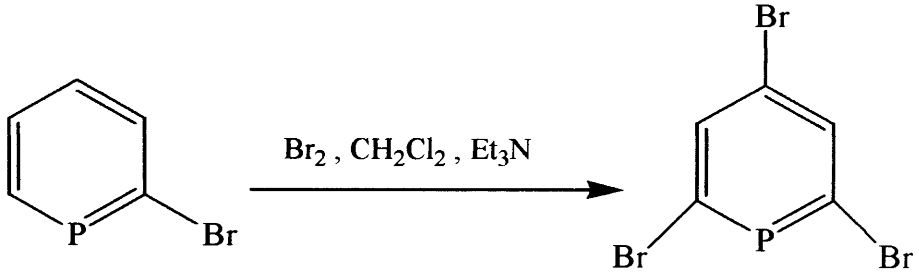
A major goal of this project was to find a facile procedure to generate functionalised phosphinines, or phosphinines with lablising groups on them. However, the majority of synthetic routes to phosphinines involved multiple step organophosphorus chemistry that involves building in any functionality during the synthetic process. Thus a comprehensive review of phosphinine synthetic methodologies until 1987 written by Markl is cited.[2] However, for the past two decades the field of phosphinine chemistry has been dominated by Francois Mathey and Pascal Le Floch. Their work has expanded the field and application of phosphinine chemistry significantly, including new synthetic methodologies, functionalisation, novel coordination chemistry, and catalysis. Consequently Mathey *et al.* have produced many reviews of this area themselves.[3] But even to this day, phosphinine chemistry remains a poorly studied and difficult area of science. Thus considering our aims, this introduction will focus mainly on the chemistry of phosphinines conducted in the last two decades.

In most phosphinine synthetic methodologies incorporation of any functional group has to be built into the synthetic procedure to the phosphinine. Mathey *et al.* however, developed a procedure that allows the functional group to be grafted onto the preformed phosphinine ring. Thus the 2-functionalised phosphinines can be prepared from 2-bromophosphinines *via* the 2-lithiophosphinine intermediates. 2-bromophosphinines however, cannot be lithiated directly as the phosphorus centre is susceptible to nucleophilic attack.[4] Thus, coordination of the 2-bromophosphinine to a metal centre provides protection for the phosphorus centre, while the bromo-lithium exchange occurs. This can then be reacted with the specific electrophilic "R" group to produce the desired 2-functionalised phosphinine. (Scheme 1.5). The pentacarbonyltungsten group can be removed using diphos to liberate the free 2-functionalised phosphinine in relatively good yield. Mathey also reported that the procedure can be performed using a wide range of electrophiles, which should allow for the facile synthesis of a range of possible donor functionalised phosphinines.



Scheme 1.5.

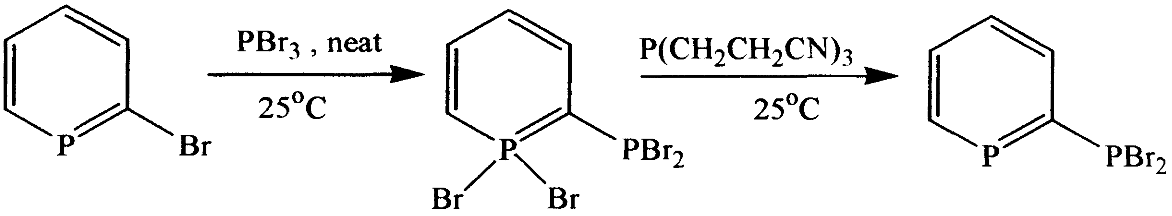
An interesting feature of the 2-bromophosphinines is their reaction with bromine which, providing the 4 and 6 positions are unsubstituted leads to the 2,4,6 – tribromophosphinine.[5] (Scheme 1.6).



Scheme 1.6.

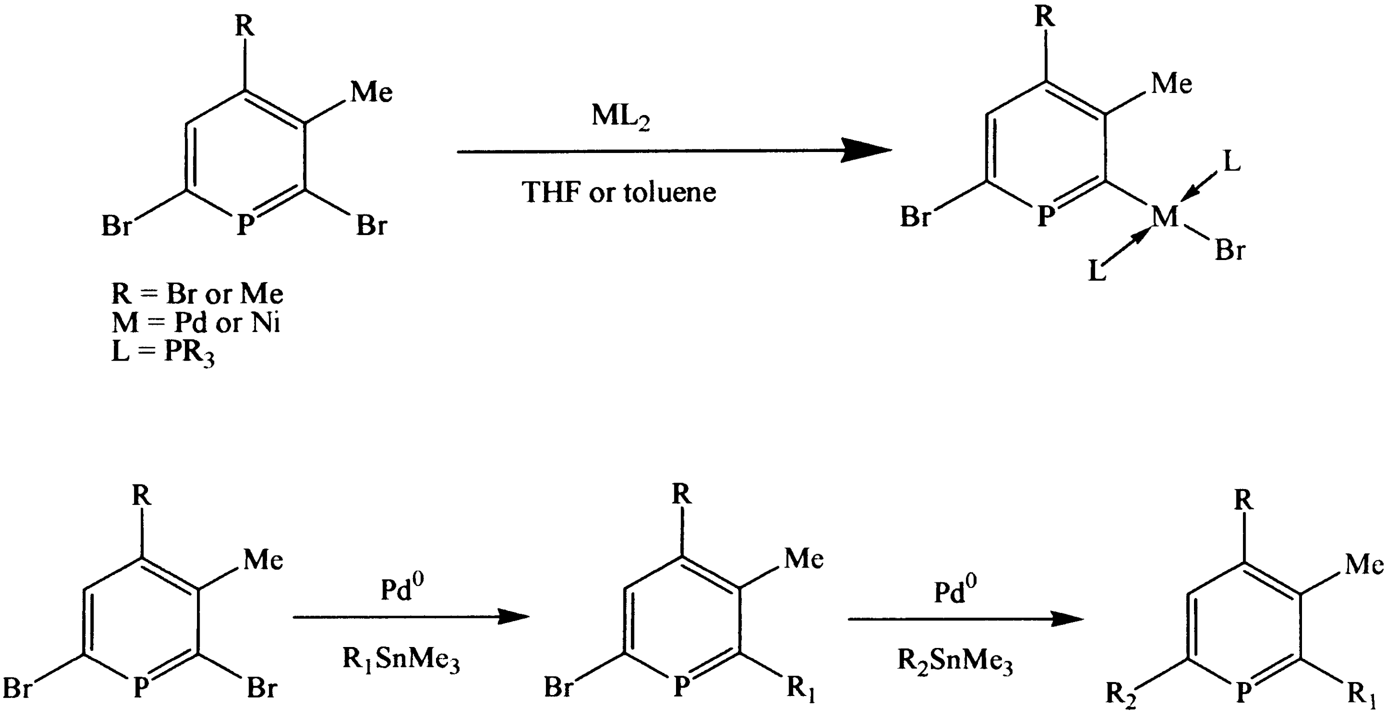
As described before most electrophiles and nucleophiles tend to attack the phosphorus core of phosphinines, hence the need for the tungsten pentacarbonyl protecting group in the lithiation procedure. But here the phosphorus core remains intact and the mechanism appears to go *via* a 1,2 or 1,4-addition of bromine, followed by the re-aromatisation of the ring by loss of HBr. In a similar manner, the direct phosphorylation of phosphinines can be achieved by reaction of a 2-

bromophosphinine with neat phosphorus tribromide. The reaction occurs *via* a 2-dibromophosphino-1,1-dibromo-λ^5-phosphinine which is reduced to give the λ^3-phosphino-phosphinine.[6] (Scheme 1.7.) The coordination chemistry of these ligands has already been investigated and will be discussed later.



Scheme 1.7.

Another procedure that utilises the 2-bromophosphinine has also been designed and exploited by Mathey *et al.* This involves the insertion of palladium(0) into the carbon-bromine bond, after initial coordination to the phosphorus atom. From this, palladium cross-coupling reactions can be carried out with arylzinc, heteroaryltin, alkynyltin and silylphosphine derivatives to give the corresponding functionalised phosphinines.[7] What makes this chemistry so striking is the regioselective control that can be employed. At 30°C the palladium will insert into the C2-Br bond exclusively, whereas at 100°C a competition reaction between the C2 and C6 position occurs. This allows the selective synthesis of either bidentate or tridentate functionalised phosphinines and has lead to the synthesis of functionalised phosphinines. It is also worth noting that the reaction occurs very efficiently with the 2,6-dibromophosphinines, and with the 2,4,6-tribromophosphinines, but proceeds very poorly with the 2-monobromophosphinines. This chemistry has also been achieved successfully with nickel(0). (Scheme 1.8).

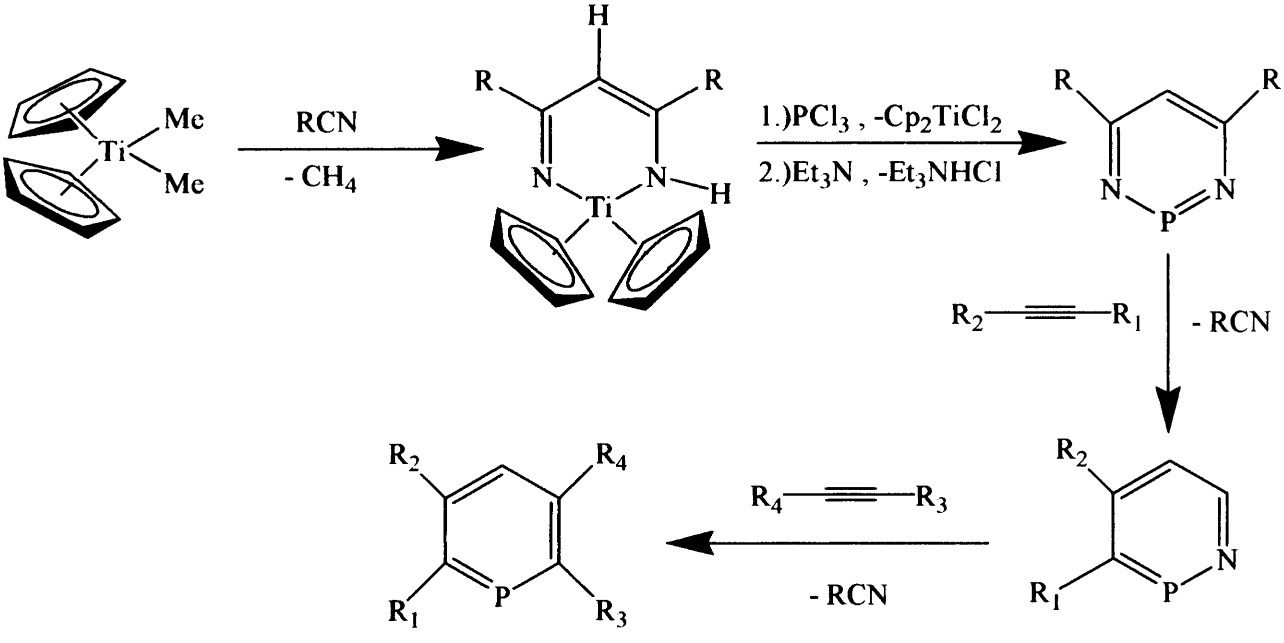


R = Br or Me
M = Pd or Ni
L = PR$_3$

R = Br or Me
R$_1$ and/or R$_2$ = furane, thiophene, N-methylpyrrole, alkyne, SR, P(Ph)$_2$

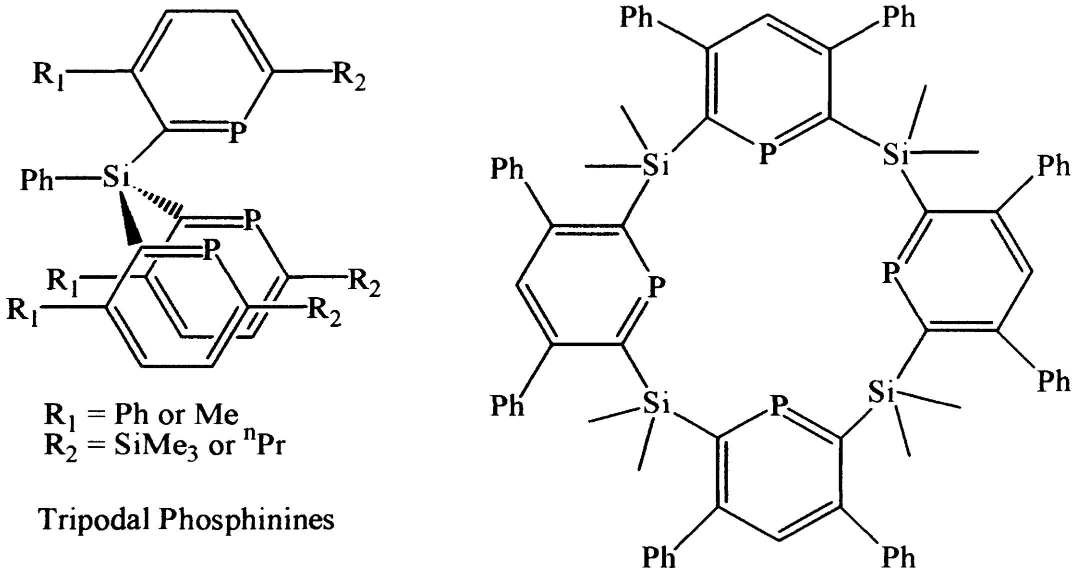
Scheme 1.8.

A completely different route to phosphinines uses 1,3,2 –diazatitanacyclohexadienes as efficient precursors producing 1,3,2 –diazaphosphinines, *via* an N-Ti, N-P bond metathesis. These were found to react further with alkynes to produce both symmetric and asymmetric tetrafunctional phosphinines *via* a (4 + 2) cycloaddition-cycloreversion reaction (scheme 1.9).[8] These (4 + 2) cycloaddition reactions proceed with a great degree of regioselectivity and under mild conditions. Indeed Mathey reports that, in general, addition of the alkyne to the diazaphosphinine adds the most electronegative of the sp carbons next to the phosphorus atom. It is also worth noting that this methodology has been expanded to include the arsine derivatives, to which Mathey reports the synthesis of a series of functionalised arsinines, with the same degree of regioselectivity as the phosphinines.



Scheme 1.9.

Mathey *et al.* have used this method of synthesis to develop complex phosphinine ligands, including tripodal[9] and the macrocyclic phosphinines (scheme 1.10).[10] The tripodal ligands can be built sequentially to include different alkyl or aryl groups, as well as the possibility to include different donor groups. Coordination and full characterisation of two different tungsten tricarbonyl complexes of these ligands established their potential as a new class of tripodal ligand for transition metals. The macrocyclic phosphinines are significant as they not only represent a very rare class of sp^2 based phosphorus macrocycle, but also they have been shown to stabilise metals in unusually low oxidation states. Hence both gold and rhodium complexes[11] were synthesised and their reduction potentials studied by EPR spectroscopy and DFT calculations. It was found that in the case of the gold phosphinine macrocycles, the macrocycles could be considered to be phosphorus equivalents of CO matrices, and in the case of the rhodium, were found to stabilise the reversible reduction of Rh(I) to Rh(0) to Rh(-I).



R_1 = Ph or Me
R_2 = $SiMe_3$ or ^nPr

Tripodal Phosphinines

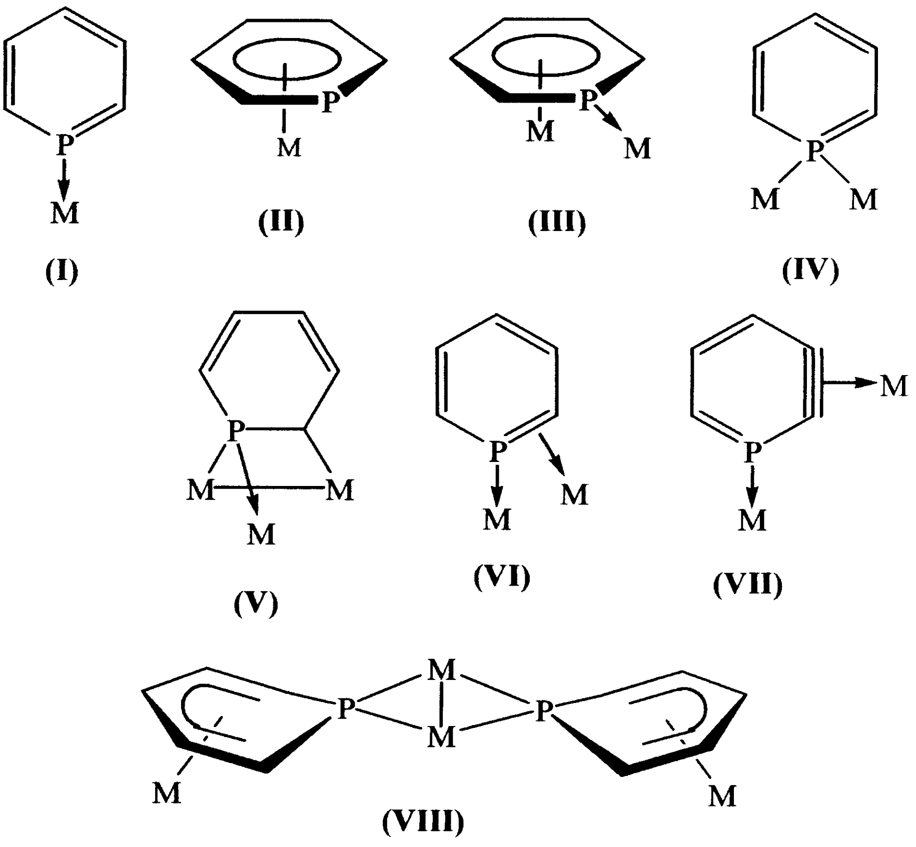
An example of a tetraphosphinine macrocycle

Scheme 1.10.

Finally, phosphinines have also been used in the field of metallic nanoparticle chemistry, with the first sp^2 phosphorus based gold nanoparticles being synthesised using phosphinines.[12] This was possible due to the ability of the phosphinines to stabilise highly electron rich metal centres because of their remarkable π-acceptor properties. In addition to this, and contrary to phosphines, the nanoparticles were formed using a substoichiometric amount of phosphinine ligand to gold ratio. The nanoparticles were also immobilised on both silica and titania hosts, and their properties and structure elucidated by both infra-red and transmission electron microscopy.

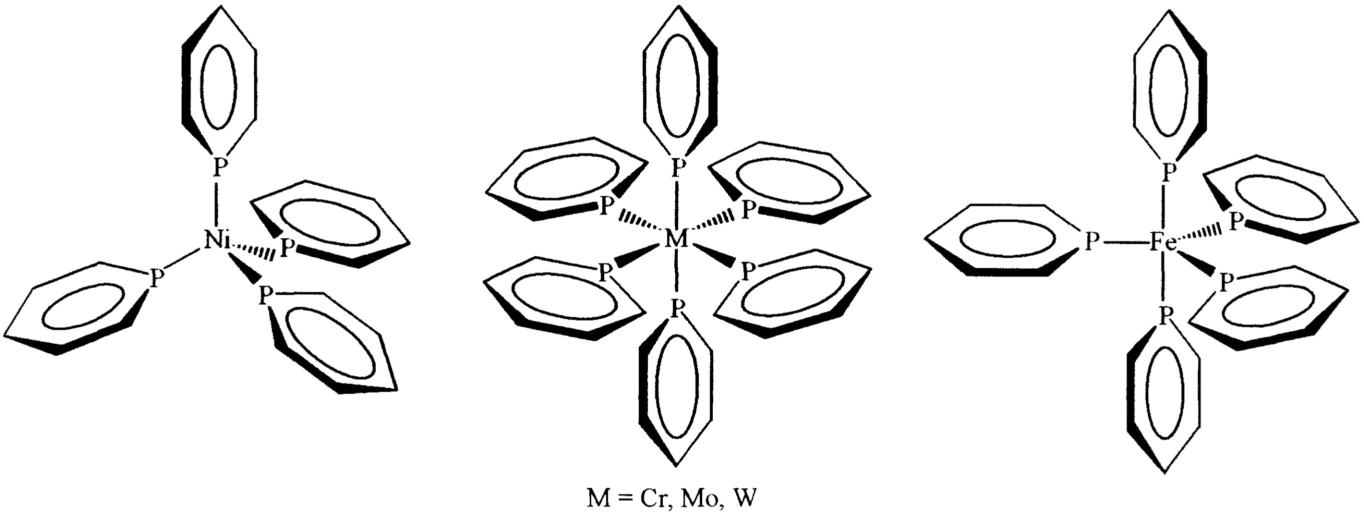
1.3 Coordination Chemistry of Phosphinines

Phosphinines have several modes of coordination to metal centres (scheme 1.11), ranging from the most common, η^1 where coordination occurs through the lone pair of the phosphorus (type I), to the η^6 coordination mode (type II) *via* the delocalised electrons of the phosphinine ring. A combination of these two modes to two metal centres is also known (type III). Rarer coordination modes include complexes where the phosphorus lone pair binds two metal centres (types IV and V), and a mode where the P=C bond acts as a binding site to one metal and the phosphorus binds to another metal centre (type VI). The mode of coordination (type VII) is *via* a 2,3-phosphabenzyne and the phosphorus lone pair, along with the final mode (type VIII) of coordination published by Elschenbroich in 2006 with manganese,[13] where the phosphinines bridge two metal centres whilst η^5 coordinated to another two metal fragments. Our review will mainly cover the η^1 mode of coordination, as this is the most relevant to our aims, and is the most useful for application in homogeneous catalysis.



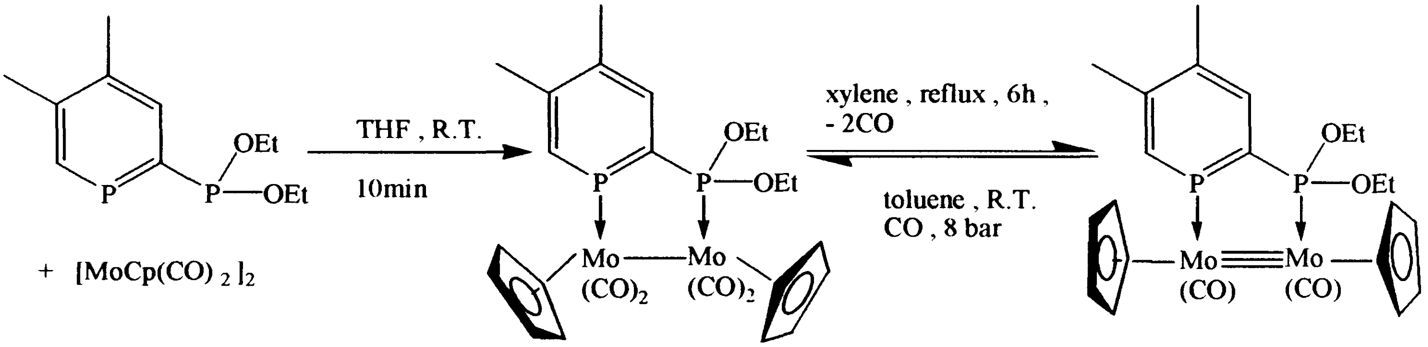
Scheme 1.11.

The 2,4,6-triphenylphosphinine derivative (L) remained the most commonly used phosphinine for complexation for a long time as it was the most readily accessible. Thus the complexes $LM(CO)_5$ (M = Cr, Mo, W) are known,[14] as are the functionalised phosphinine complexes of $W(CO)_5$ previously described,[4] as well as the pyridyl-phosphinine complexes of Group VI tetracarbonyls[15]along with rhodium(I) and iridium(I) dimers.[16] Complexes of the type $LNi(PR_3)_2$,[17] L_3RhCl, L_2RuCl_2[18] and LAuI[19] are known. More recently complexes of palladium(II) and platinum(II) and copper(I) have been reported.[20] However, the existence of these complexes does not highlight the exceptional π-acceptor ability of phosphinines, and thus their ability to stabilise metals in low oxidation states. Elschenbroich *et al.* exploited this property to produce a series of homoleptic complexes of the phosphinine C_5H_5P with zerovalent nickel,[21] chromium[22] and iron[23] (scheme 1.12).



Scheme 1.12.

As previously described the discovery of a "one-pot" synthesis of 2-phosphino-phosphinines by Mathey *et al.*[6] led to their study as bridging ligands in bimetallic complexes.[24] Their investigations found that the phosphino-phosphinine's bite angle can accommodate a variety of metal centre separations. This is demonstrated by the formation of a phosphonite-phosphinine biscyclopentadienyl dicarbonyl molybdenum complex that, upon heating, undergoes thermolysis to produce a triple bonded bis-molybdenum complex (scheme 1.13). They also found that the phosphino-phosphinines display very different coordination chemistry to their isostructural phosphino-pyridine analogues.

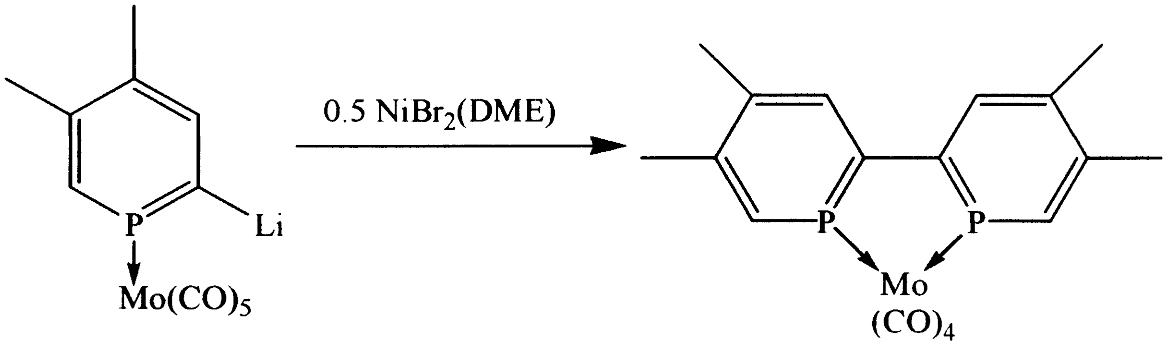


Scheme 1.13.

Studies have also been conducted to produce binuclear nickel carbonyl complexes as well as a tetranuclear, octahedral copper complex comprising two bridging phosphino-phosphinines and two bridging iodides.[25]

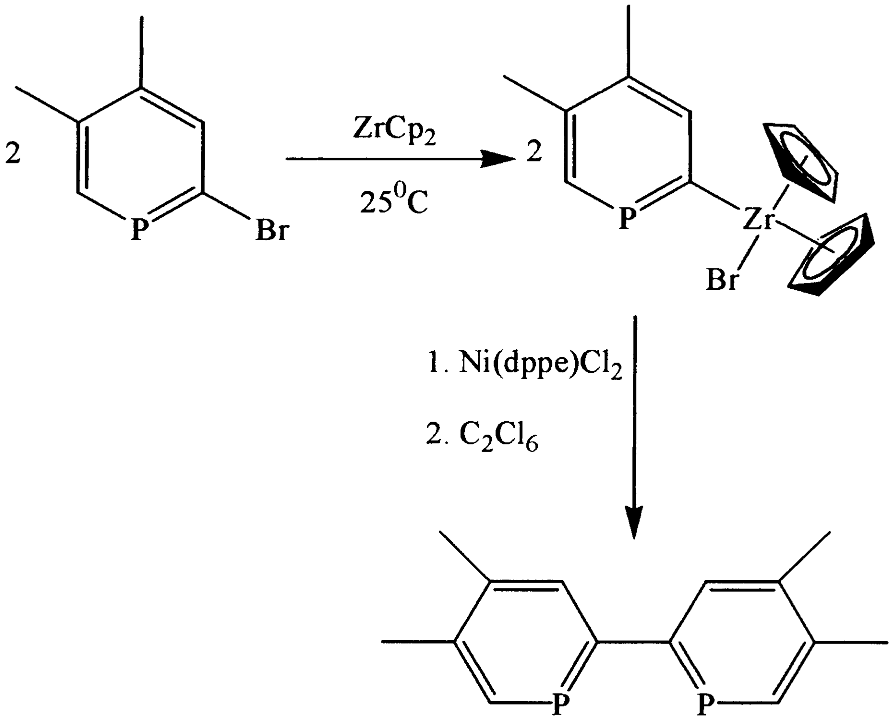
2,2′-biphosphinines have also been used extensively in coordination chemistry. This is mainly because they represent a direct phosphorus analogue of the widely known and established bipyridines. Bis phosphinines show the same electronic properties as the monophosphinines, i.e. they are very good π-acceptor ligands and hence are excellent at stabilising low valent metal centres. The most commonly used derivative in coordination chemistry is the 4,4′,5,5′-tetramethylbiphosphinine (tmbp), mainly due to its established and convenient synthesis.

One of the synthetic methodologies employed to tmbp was *via* the lithiation chemistry previously discussed (scheme 1.14). This method involved the homocoupling of 2-lithiophosphinines, complexed to molybdenum pentacarbonyl, with $NiBr_2$.DME.[26] Unfortunately the method had no real synthetic value as the free tmbp could not be released from the molybdenum metal.



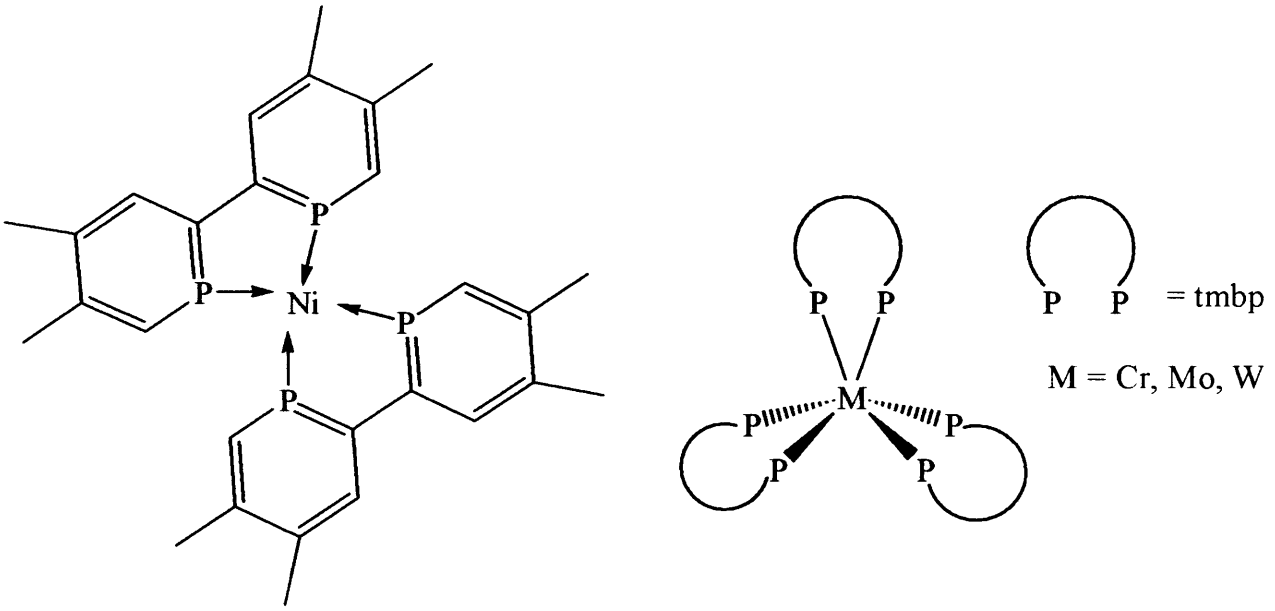
Scheme 1.14.

The most successful strategy employed is *via* 2-coordinated zirconium complexes of phosphinines. It has been reported that reaction of Ni(dppe)Cl_2 with 2 equivalents of $ZrCp_2$(2-phosphininyl)X generates the Ni(0)tmbp(dppe) complex in good yields.[27] The homocoupling reaction here is presumed to be a C-Zr>C-Ni bond metathesis, and is the best synthetic route to biphosphinines as the free ligand can be liberated by oxidation of the Ni(0) with hexachloroethane (scheme 1.15).



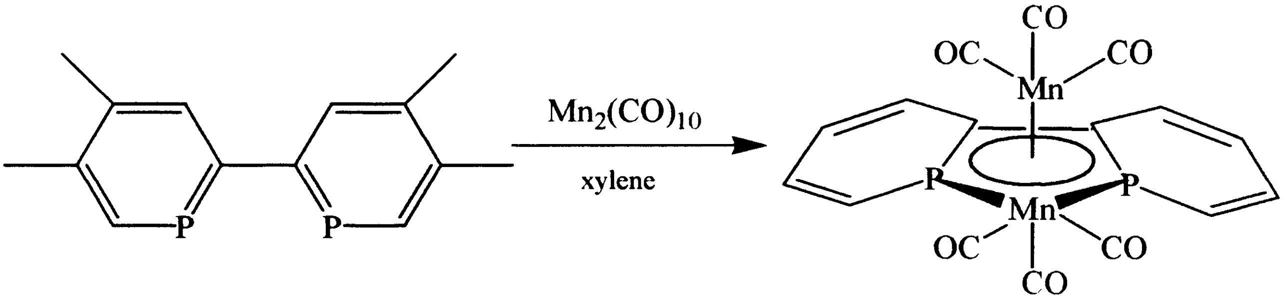
Scheme 1.15.

As with the monophosphinines the biphosphinines have shown exceptional ability in stabilising low valent metal centres. This is illustrated by the metal(0) complexes of biphosphinines, particularly $[Ni(tmbp)_2]$ (scheme 16).[28] Electrochemical experiments on $Ni(tmbp)_2$ showed that the complex could be reduced to a stable 19 electron anion, and was further reduced to the stable 20 electron dianionic species. This is in direct contrast with the analogous bipyridine nickel(0) $[Ni(bpy)_2]$ complex that decomposes upon reduction. This again reinforces the exceptional ability of phosphinines as π-acceptor ligands for transition metal complexes. In addition to this, and analogous to the monophosphinines, the group VI metal(0) complexes have been synthesised by reduction of the metal chloride salts with either zinc or magnesium, and 3 equivalents of tmbp.[29] Interestingly the crystal structure of the tungsten complex revealed that the complex is not octahedral in geometry, as would be expected, but is trigonal prismatic. (Geometry shown in scheme 1.16).



Scheme 1.16.

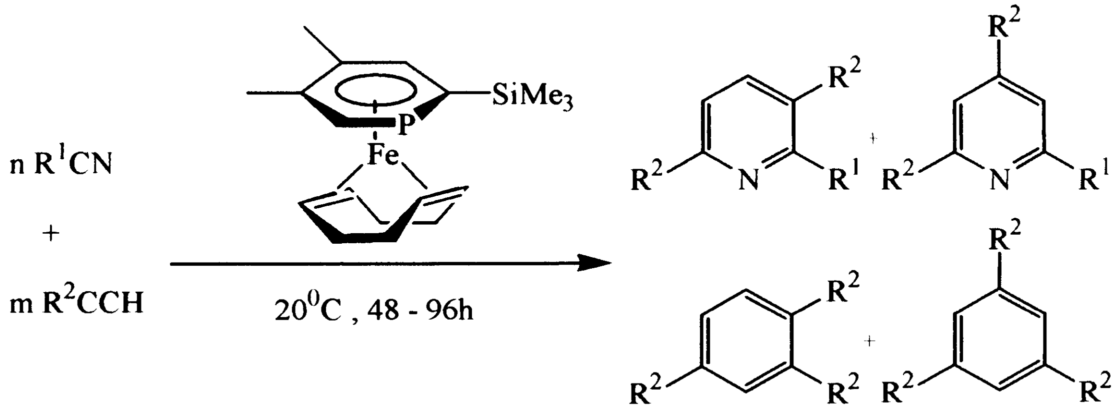
Finally upon reacting tmbp with $Mn_2(CO)_{10}$ a completely unexpected compound was synthesised, (scheme 1.17).[30] The crystal structure of this dimetallic complex showed that the tmbp was acting as an 8 electron donor to the two manganese centres. One of the Mn centres is bound by the 2 lone pairs of the phosphorus atoms, and the other in an η^2 fashion by the 2 P=C bonds of the biphosphinine rings, in doing so however, the aromaticity of the rings is destroyed.



Scheme 1.17.

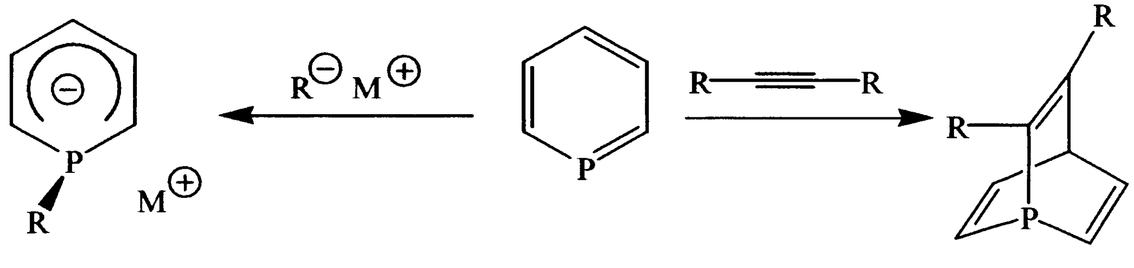
1.4 Phosphinines in Homogeneous Catalysis

One of the first uses of phosphinines in catalysis was reported by Zennick *et al.* who employed an η^6 coordinated phosphinine in the catalysis of pyridine formation.[31] They coordinated the phosphinine to an (η^4-1,5-cyclooctadiene)iron(0) metal fragment, and tested the complex under a series of different reaction conditions in the formation of pyridine (scheme 1.18). However, they report that this system is not good enough to rival industrial processes. They finally note that the system is far from optimised and different conditions and reagents still need to be tried to elucidate the full potential of the ligand as a catalyst for pyridine formation.



Scheme 1.18.

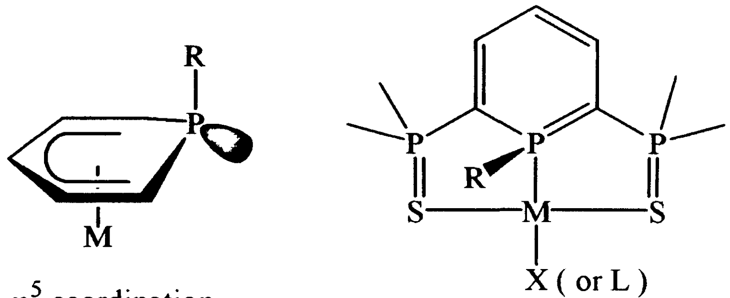
Phosphinines exhibit two interesting reactions which are brought about by their unusual electronic properties. The first is their reaction with nucleophiles due to the electrophilic nature of the phosphorus atom, to form phosphacyclohexadienyl anions; and the second is their ability to undergo Diels-Alder type reactions with alkynes, due to the diene character of the unsaturated ring, to form phosphabarrelenes (scheme 1.19). This ability has led to the discovery of new synthetic methodologies and coordination chemistry, however, the scope of this introduction will focus on the reactions that have led to species with interesting reactivity in homogeneous catalysis.



Scheme 1.19.

Mathey *et al.* found that reaction of their phosphinesulphide functionalised phosphinines with metal alkyls gave a phosphacyclohexadienyl ligand, that upon complexation to either palladium or rhodium, gave surprisingly good activity in catalysis. The 2-, or the 2,6-bisphosphinophosphininedisulphide (SP or SPS) can be synthesised either by the direct phosphorylation of the 2-bromophosphinine, or by palladium catalysed cross coupling reactions on the 2,6-dibromophosphinine with 2 equivalents of diphenyl(trimethylsilyl)phosphine, chemistry that has already been discussed. The interesting feature of this phosphinine is its reaction with a metal alkyl fragment. For example, the reaction of unsubstituted phosphinine with lithium gives the η^5 phosphacyclohexadienyl-lithium complex exclusively, even though η^1 coordination through the phosphorus lone pair is theoretically possible. This chemistry of the η^5 coordinated lithium complex has already been established and studied by DFT calculations.[32]

If however, periphery ligands are present, such as they are in the SPS phosphinines, then this promotes η^1 coordination exclusively (scheme 1.20).

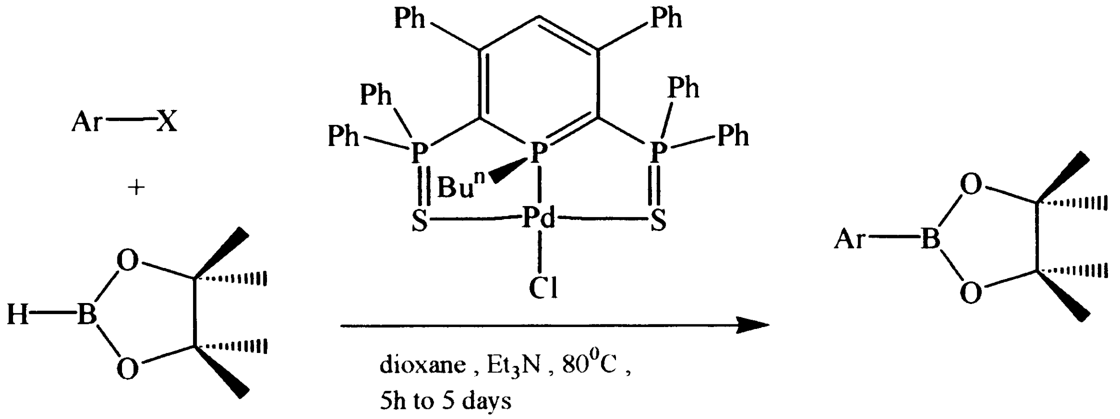


η^5 coordination

η^1 coordination

Scheme 1.20.

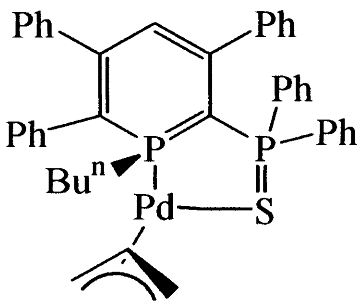
This has led to the formation of group 10 σ^4, λ^5-phosphinine complexes[33], which show interesting catalytic activity in the palladium catalysed formation of arylboronic esters (scheme 1.21).[34] Turnover numbers (TON's) of up to 10,000 were found for the palladium complex in the coupling reaction of iodobenzene and 4-iodotoluene. Le Floch *et al.* go on to postulate that the high activity of the systems is due to the rigidity provided by the sulphide pincer ligands and the conjugated ring structure of the phosphinine that helps to stabilise the ylide form. They also note that the strong σ-bond between the metal and the phosphorus, combined with the two pendant sulphide acceptor ligands is almost certainly essential to the reactivity of the complex.



Ar = p-MeC$_6$H$_4$, o-MeC$_6$H$_4$, 2-thienyl , 2-naphthyl , p-BrC$_6$H$_4$, p-MeOC$_6$H$_4$

Scheme 1.21.

In addition to this, bidentate (SP) systems have also shown good activity in catalysis (scheme 1.22). In fact, just recently the palladium derivative of the 2-phosphinsulphide-σ^4', λ^5-phosphinine complex (**1**) has proved to be a remarkably successful complex for catalysis.[35] In the Suzuki-Miyaura cross coupling reactions of bromoarenes with phenylboronic acid, TON's of up to 799,000 were obtained for the 4-bromoacetophenone. The interesting feature here is that sulphides are usually considered poisons for most catalytic processes, and yet here the phosphine sulphide ligand clearly plays an important role in the catalytic reactivity of the complex. In the same paper, Le Floch also reports on the use of the same ligand with a ruthenium-cymene complex (**2**) for the transfer hydrogenation of ketones, but states that the reactivity is modest compared to the efficient Noyori ruthenium based catalysts.



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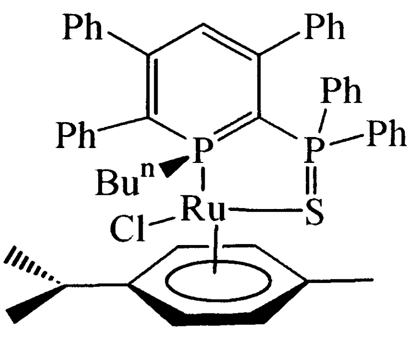

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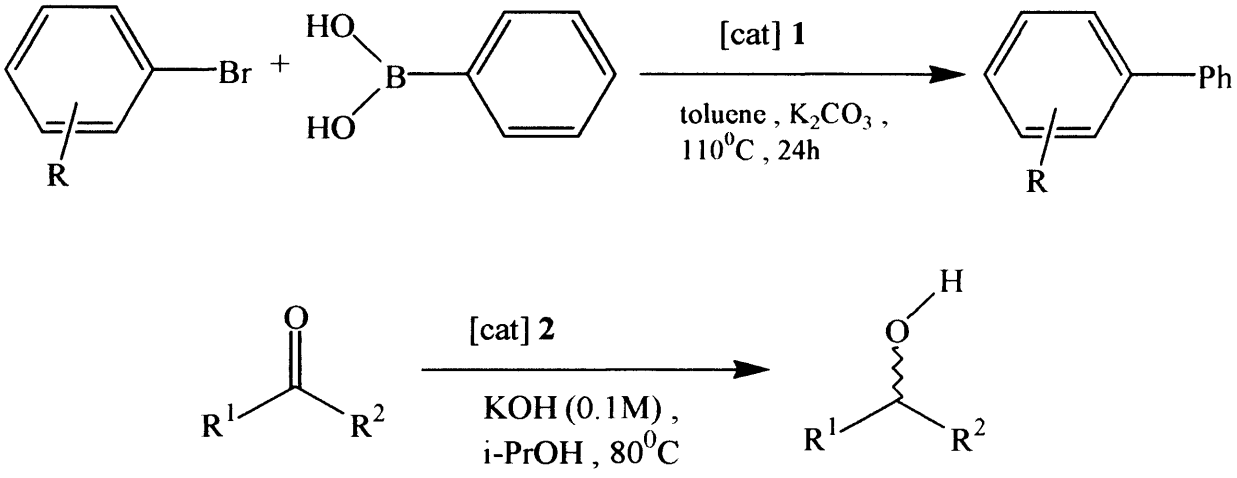
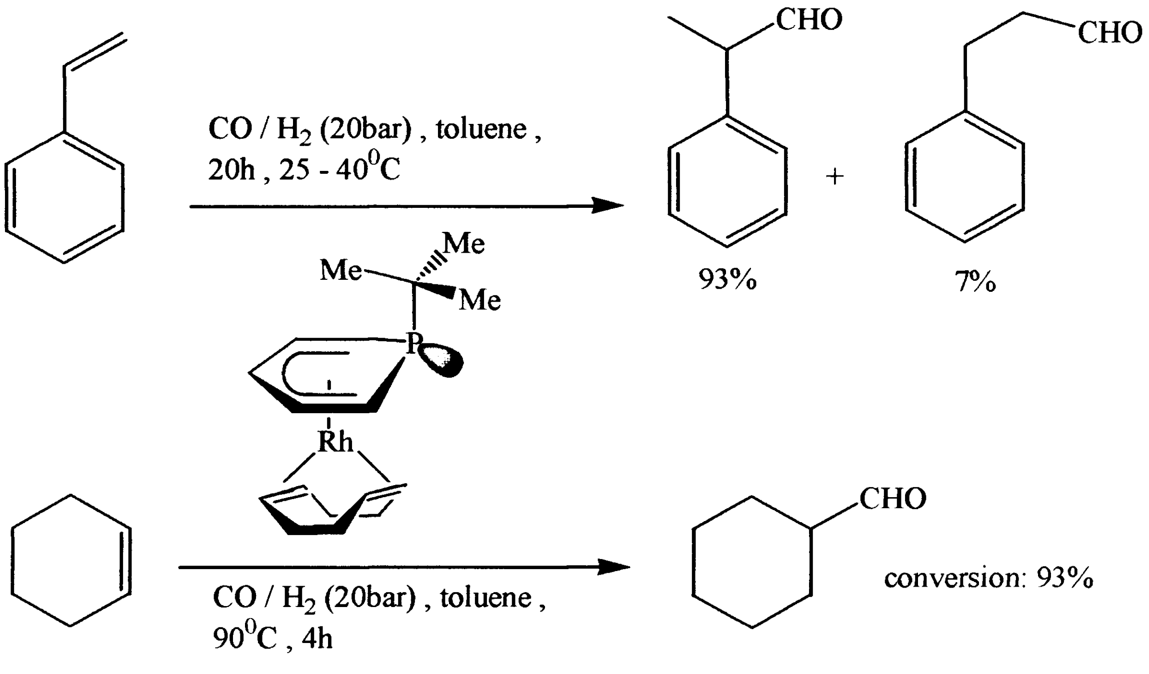


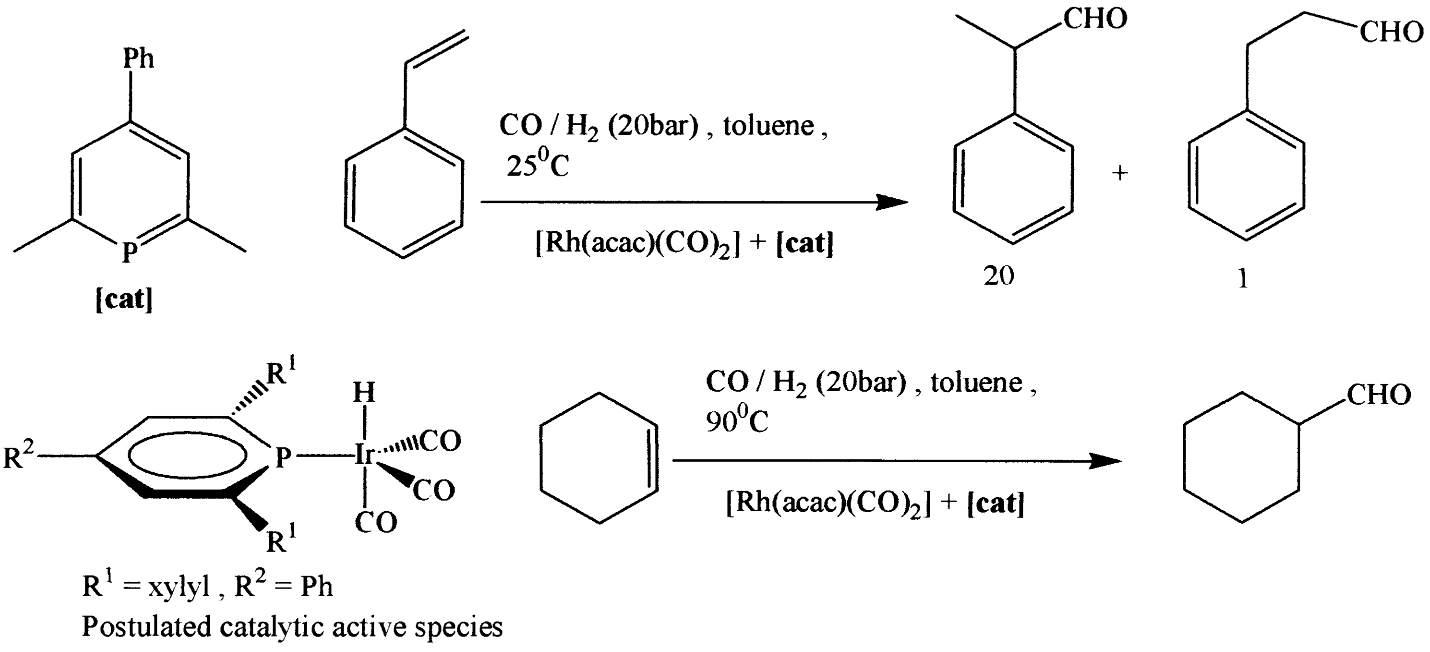
Scheme 1.22.

The η^5 mode of coordination has also been employed in catalysis, although very few examples of this are known. One example is the rhodium(I) complex of the phosphacyclohexadienyl anion, which shows remarkably good activity in the hydroformylation of olefins.[36] Good conversion rates and TON's were obtained under mild conditions for the hydroformylation of styrene and cyclohexene (scheme 1.23).



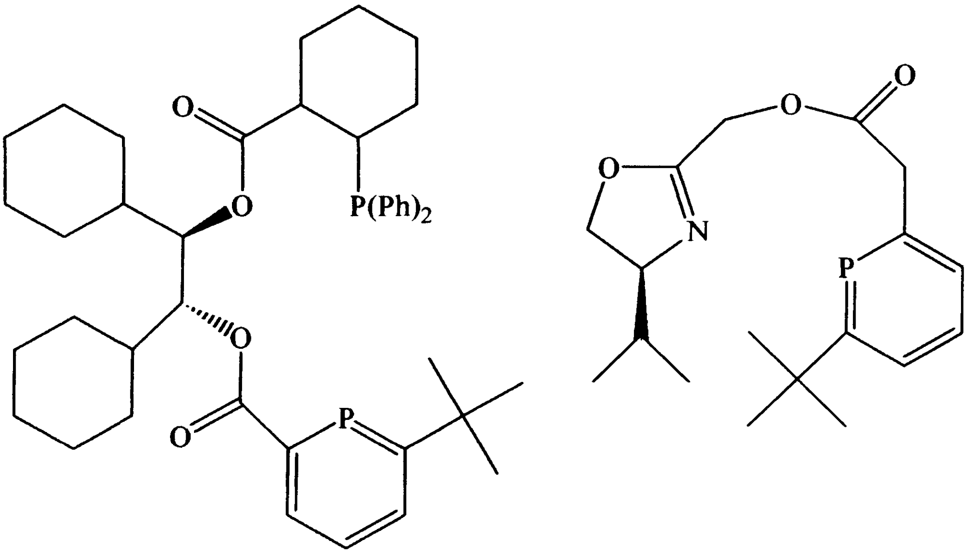
Scheme 1.23.

The phosphinine catalysis that is of most relevance to our aims is that of the η^1 coordinated monophosphinines. This work has been dominated by Breit *et al.* who have published several papers on the use of phosphinines in different types of hydroformylation.[37] The first focused on the hydroformylation of styrene which states that the 2,6-dimethyl-4-phenylphosphinine shows a regioselectivity that is twice as high as the industrially used Rh/PPh_3 system.[37a, b, c] In addition the selectivity of branched to linear aldehydes is also reported to be very good, (22.6:1) (scheme 1.24). This has been extended to the hydroformylation of 1-octene where, because the catalytic performance of the ligand is governed by steric factors, a five fold increase in activity is observed on going from the 2,6-dimethyl derivative to the 2,6-dixylyl-4-phenylphosphinine.[37d] The catalytically active species for the iridium based catalysis was elucidated to be the trigonal-bipyramidal 2,6-dixylyl-4-phenylphosphinine(tricarbonyl)hydridoiridium(I) complex.



Scheme 1.24.

The hydroformylation of internal aldehydes however, is known to proceed far better with good π-acceptor ligands such as triphenylphosphite. In addition, to this bulky phosphites show even better catalytic activity. Therefore, with the phosphinines being good π-acceptor ligands and with their tuneable 2,6 substituents, they can also be very bulky ligands, thus they were prime targets for the hydroformylation of internal aldehydes. Initially the conversion of cyclohexene was shown to proceed with good conversion rates. Breit *et al.* then expanded their work to include di-, tri-, and tetra-substituted olefins, all showing good regioselectivity and good conversion rates relative to the industrially recognised Rh/PPh_3 system.[37d] Finally Breit *et al.* demonstrated that potentially bidentate chelating phosphinine ligands can be employed in the hydroformylation of styrene as well.[37c] He noted that significant improvement in conversions is achieved on going from the 2,6-dimethylphosphinine to the potentially bidentate phosphinine ligands shown below (scheme 1.25).



Scheme 1.25.

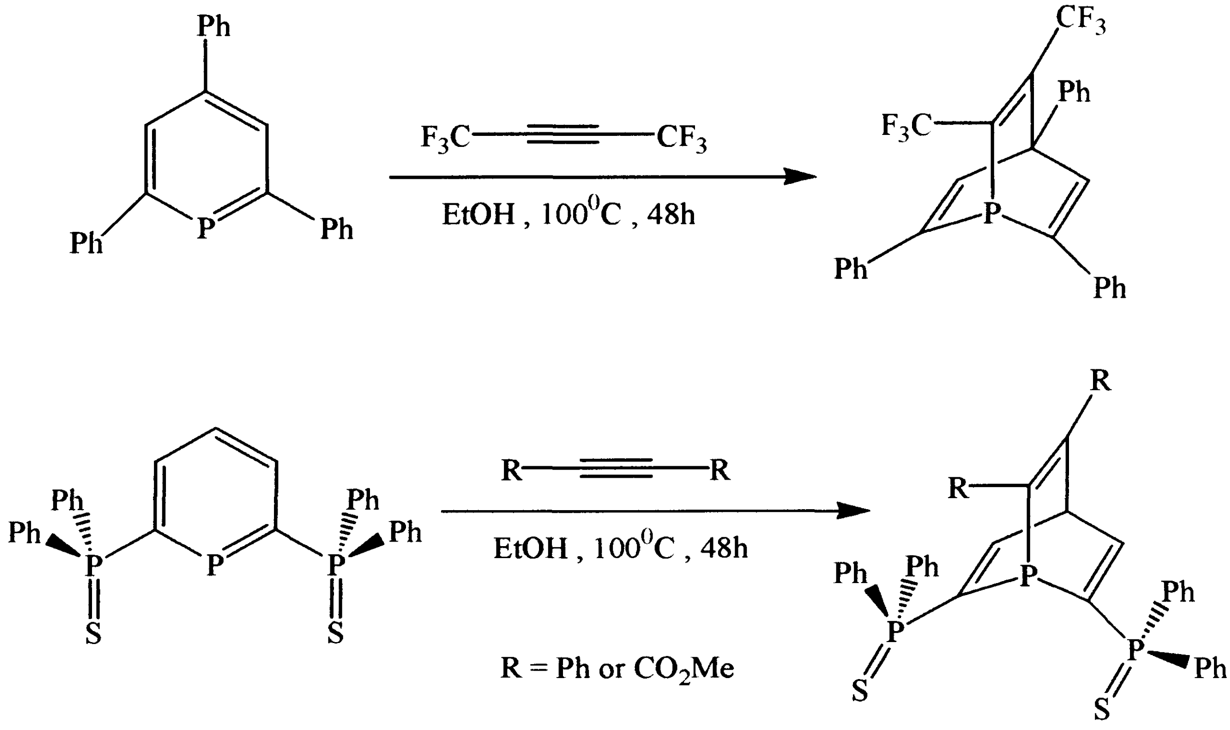
Similarly, Muller *et al.* have very recently published work using chiral, bidentate phosphinines in the rhodium catalysed asymmetric hydrogenation of olefins.[38] Their ligand system consists of a triarylphosphinine where one of the aryl groups on the 2 or 6 position of the phosphinine ring has a chiral phosphite attached. The phosphite used was the (S)-binol-phosphite enantiomer, and complexes of the type $[Rh(COD)(L_2)]^+$ BF_4^- were synthesised and tested in the asymmetric hydrogenation of methyl 2-(N-acetylamino)cinnamate and dimethyl itaconate. However, even though the catalysis of the methyl 2-(N-acetylamino)cinnamate was poor (TOF = 1030h^{-1} with 20%

conversion, and a selectivity of 62% *ee* of *R*-product; the dimethyl itaconate was hydrogenated with complete conversion and a high TOF of 5300h^{-1}, as well as a selectivity of 68% *ee* of the *S*-product.

Finally it is also noteworthy that phosphinines of the same type as Briet's have successfully been employed in nickel (0) catalysed carbocyclisation.[39] The reaction rates of these [4 + 2] cycloaddition reactions is influenced by the electronic properties of the coordinating ligand (i.e. a good π-acceptor) and steric bulk. Thus it was of little surprise to see that the most interesting reaction rates and conversions were obtained with the 2,4,6-triphenylphosphinine. However, disappointingly, a large nickel precursor [Ni(COD)$_2$] and phosphinine loading was required to achieve complete conversion.

1.5 Phosphabarralenes

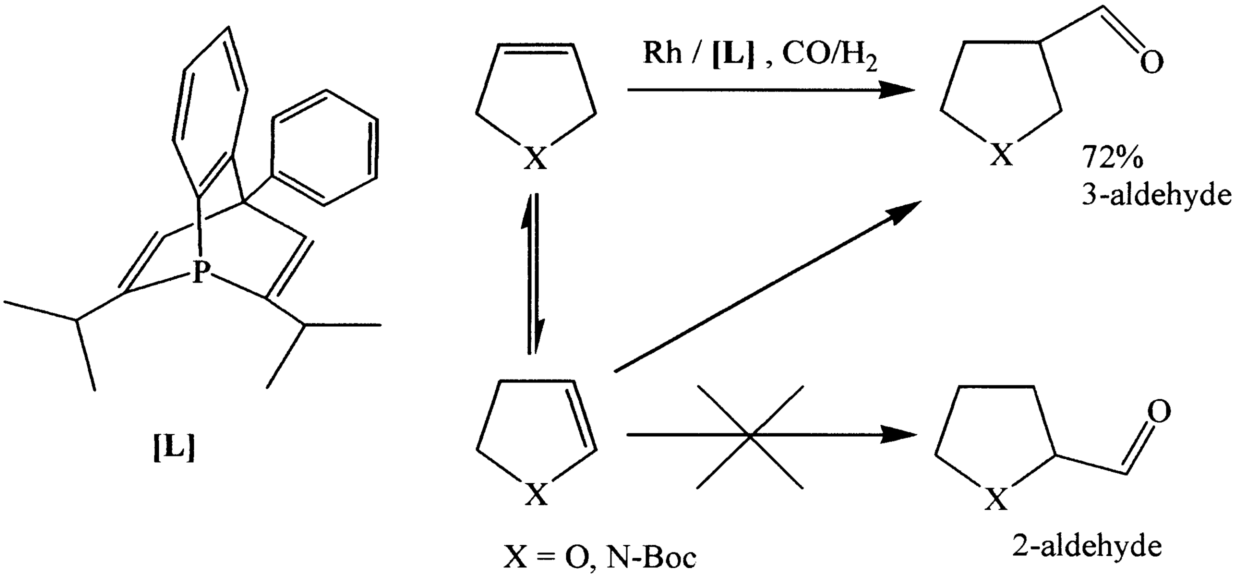
Due to the conjugated ring structure and the electrophilicity of the phosphorus atom in a phosphinine ring, interesting products have been observed upon reacting different reagents with phosphinines. One of these is the reaction with metal alkyls to produce the phosphacyclohexadienyl anions (see previous section). Another is their reaction with activated alkynes. It is generally noted that phosphinines do not react with alkynes, however, Markl showed that phosphinines will undergo [4 +2] Diels-Alder reactions with activated alkynes such as hexafluorobutyne[40] to produce the corresponding phosphabarrelenes. Much more recently Breit *et al.* showed that the same chemistry was possible by forming benzyne *in situ* and reacting it with the parent phosphinine to produce the corresponding phosphabarrelene.[41] To date, for alkyl or aryl substituted phosphinines, there appears to be only two methods for the preparation of phosphabarrelenes as an alkyne with two strong electron withdrawing groups is needed to induce the reaction. However, Le Floch *et al.* recently showed that phosphabarrelene analogues of their SPS phosphinine ligands were possible using less activated alkynes.[42] This is due to the phosphine sulphide ligands on the phosphinine ring, "activating the ring", and allowing the Diels-Alder type addition to occur with alkynes containing less electron withdrawing groups (scheme 1.26). Thus the reactions led to the formation of either the mono-substituted phosphine sulphide phosphabarrelene, or the di-substituted phosphine sulphide phosphabarrelene. (See previous section for the formation of SPS anions).



Scheme 1.26.

However, despite their obvious potential as excellent ligands for transition metals very little coordination chemistry has been conducted on phosphabarrelenes, and this is one of the features of phosphabarrelenes we will explore in this thesis. The only known complexes are those that have been prepared for use in catalysis, although in some cases the individual complexes are only postulated and not fully characterised.

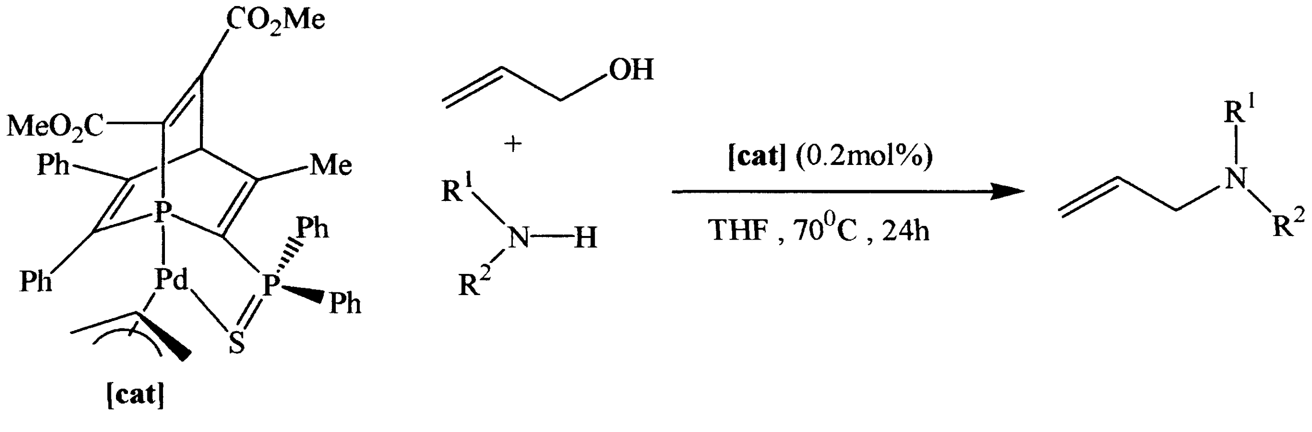
An example of this is by Breit *et al.* who have used the phosphabarrelenes in the rhodium hydroformylation of olefins.[41] They report an even better conversion rate and selectivity for the equivalent phosphabarrelene when compared to its parent phosphinine. In fact the phosphabarrelene system was reported to be 1000 times faster than the industrially used Rh/PPh_3 system. The most important discovery however, was the fact that the phosphabarrelene system promoted the hydroformylation of internal alkenes such as oct-2-ene, without provoking isomerisation to the corresponding terminal alkene. (These results are discussed in full in chapter 3.) Similar results were observed with the heterocyclic alkenes which are known to isomerise easily (scheme 1.27). Both 2,5-dihydrofuran and N-boc-pyrroline were hydroformylated in good yields under mild conditions, and with no alkene isomerisation.



Scheme 1.27.

Recently Breit *et al.* also reported the synthesis and catalysis of chiral bidentate phosphabarrelene-phosphite ligands in the rhodium catalysed asymmetric hydrogenation.[43] His ligand systems are very similar to that of the chiral bidentate phosphinine-phosphite ligand systems already reported by Muller *et al.* in the use of rhodium catalysed asymmetric hydrogenation.[38] The data is difficult to compare as the reaction conditions used were different, but despite this for the asymmetric hydrogenation of acetamidoacrylates Breit reports that the catalysis occurrs with a selectivity of up to 90% *ee*, far higher than any selectivity reported by Muller.

Mathey *et al.* showed that their bidentate and tridentate phosphine sulphide phosphabarrelenes could be coordinated to palladium and used in palladium cross coupling reactions with some success.[42] The tridentate analogues of the SPS phosphinine systems showed good activity in Suzuki-Miyaura cross coupling reactions, although their performance was only modest in terms of conversion rates, reaction conditions and TON's. The most significant catalytic activity they found was with the phosphabarrelene analogue of the phosphinophosphininesulphide (SP) ligand, in the allylation of secondary amines with allylic alcohols (scheme 1.28). Unlike known systems, the reaction did not stop after monoallylation and continued on to produce diallylamines in large quantities. Also, unlike in the nickel based systems, no additives such as Lewis acids were needed to complete the transformations. Although the mechanism of this transformation has not been elucidated, it is reasonable to suggest that the unique electronic and structural properties of the phosphabarrelene ligand must play an important role in the transformation. This is highlighted by the fact that bidentate tertiary phosphines with pendant phosphine sulphide arms show no activity in these transformations at all.



Scheme 1.28.

Thus following this introduction to phosphinine and phosphabarrelene chemistry, this thesis will present our efforts in this field of chemistry. We will report on the synthesis of novel 2-(halide substituted)aryl phosphinines, and our efforts to functionalise these systems further by the introduction of a potentially donating functional group. In addition to this the phosphinines will be coordinated to a variety of transition metals in an attempt to further understand the nature of the phosphorus-metal bond, by studying the infra red and NMR spectroscopic data of their complexes. Further we will present a survey of the coordination chemistry of phosphabarrelenes, including complexes of transition metals previously unreported. In addition to this we will further elucidate the nature of the phosphorus-metal bond in these complexes by comparing the IR, NMR and crystallographic data with well established analogous complexes of phosphines and phosphites.

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CHAPTER 2

TUNGSTEN (0) AND RHODIUM (I) COMPLEXES OF A SERIES OF 2-(2′-HALO)-TRIARYL SUBSTITUTED PHOSPHININES

2.1 Introduction

Over the last few years the synthesis, coordination chemistry and catalytic properties of phosphinines has undergone several investigations by various groups.[1] These have ranged from the development of new synthetic routes,[2] to the preparation of functionalised phosphinines,[3] and the generation of phosphinine anions.[4] In addition, their properties as ligands have been established. Reported phosphinines include SPS pincer ligands,[5] phosphino-phosphinines,[6] tripodal phosphinines[7] and macrocycles.[8] Almost all of these studies have highlighted that phosphinines can behave as good π–acceptors, and yet relatively poor σ donors. This however, has not hindered efforts to produce a wide variety of phosphinine-metal complexes.

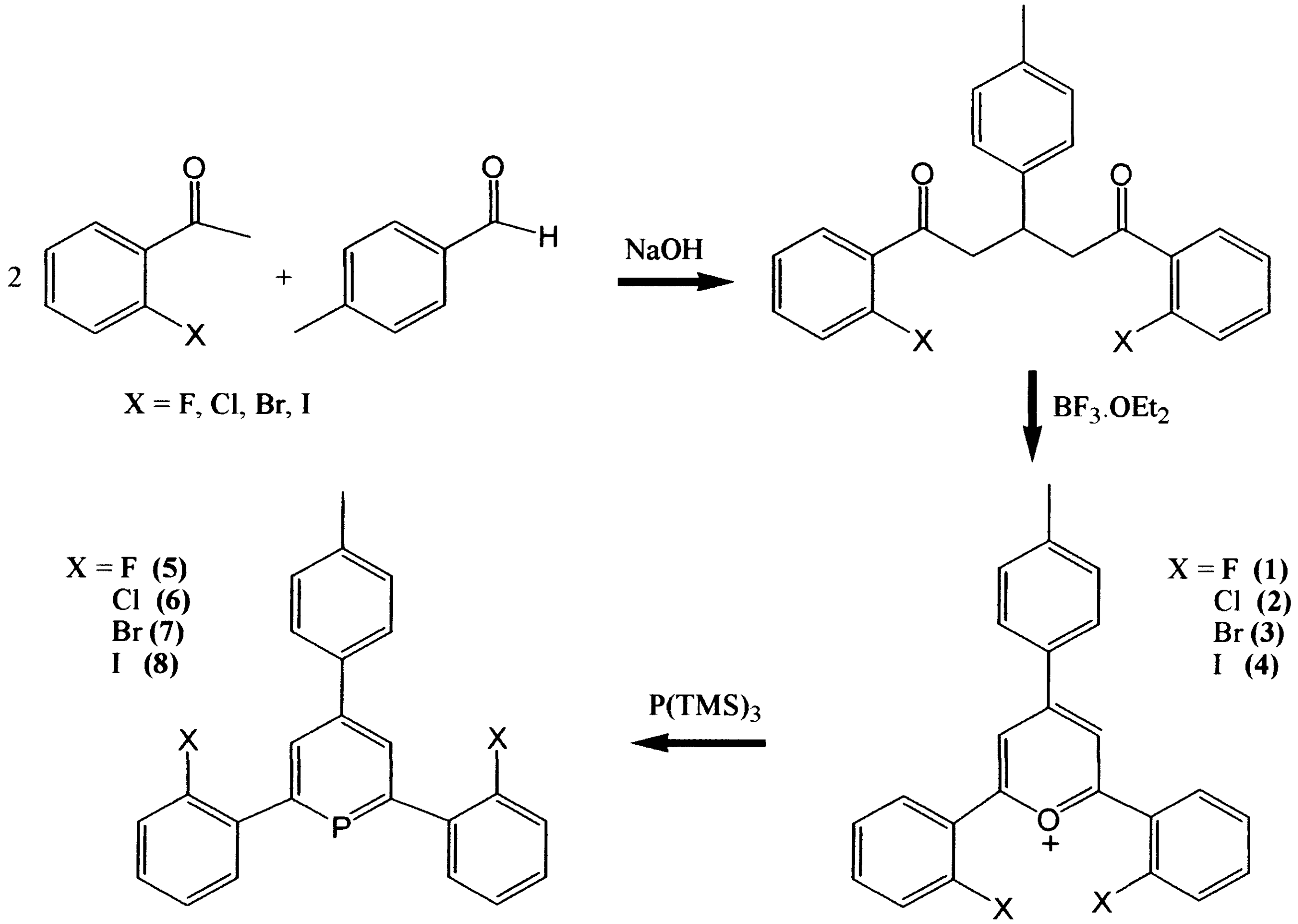
More recently the catalytic properties of phosphinines has come under closer scrutiny. This has focused again on the strong π-acceptor abilities of the phosphinines in order to exploit this in specific catalytic processes. For example in hydroformylation, π-acceptor ligands such as phosphites are known to be good for stabilizing the low oxidation states of the metal during the catalytic cycle. However, phosphites and other ligands containing one or more P-O bond are susceptible to decomposition under catalytic conditions and other more robust P-donors with similar properties to the phosphites have been exploited. Hence, studies have been published testing a wide variety of phosphinines in rhodium catalysed hydroformylation, principally based on their presumed strong π–acceptors property.[9]

Even though triaryl phosphinines are relatively common, (2,4,6-triphenyl phosphinine being the most widely used) as yet none have been made including a potentially labile group (such as halogen), that may allow incorporation of further functionality. Thus, our efforts here are two-fold: one is to produce a new class of "dihalo substituted" phosphinines; and secondly to elucidate their properties as ligands in coordination chemistry. This will include further investigation of the bonding in complexes of these ligands.

2.2 Results and Discussion

Compounds **(1-4)** were synthesised *via* a variation of a literature procedure. Unlike the published procedure,[10] we did not find it necessary to perform radial chromatography in order to obtain pure pyrylium salts. We have extended the synthesis to produce a series of halo substituted pyrylium salts (scheme 2.1). The fluoro-, chloro- and iodo- derivatives being reported here for the first time. The salts themselves are bright yellow solids, that are stable to both air and moisture, and are characterised by NMR spectroscopy.

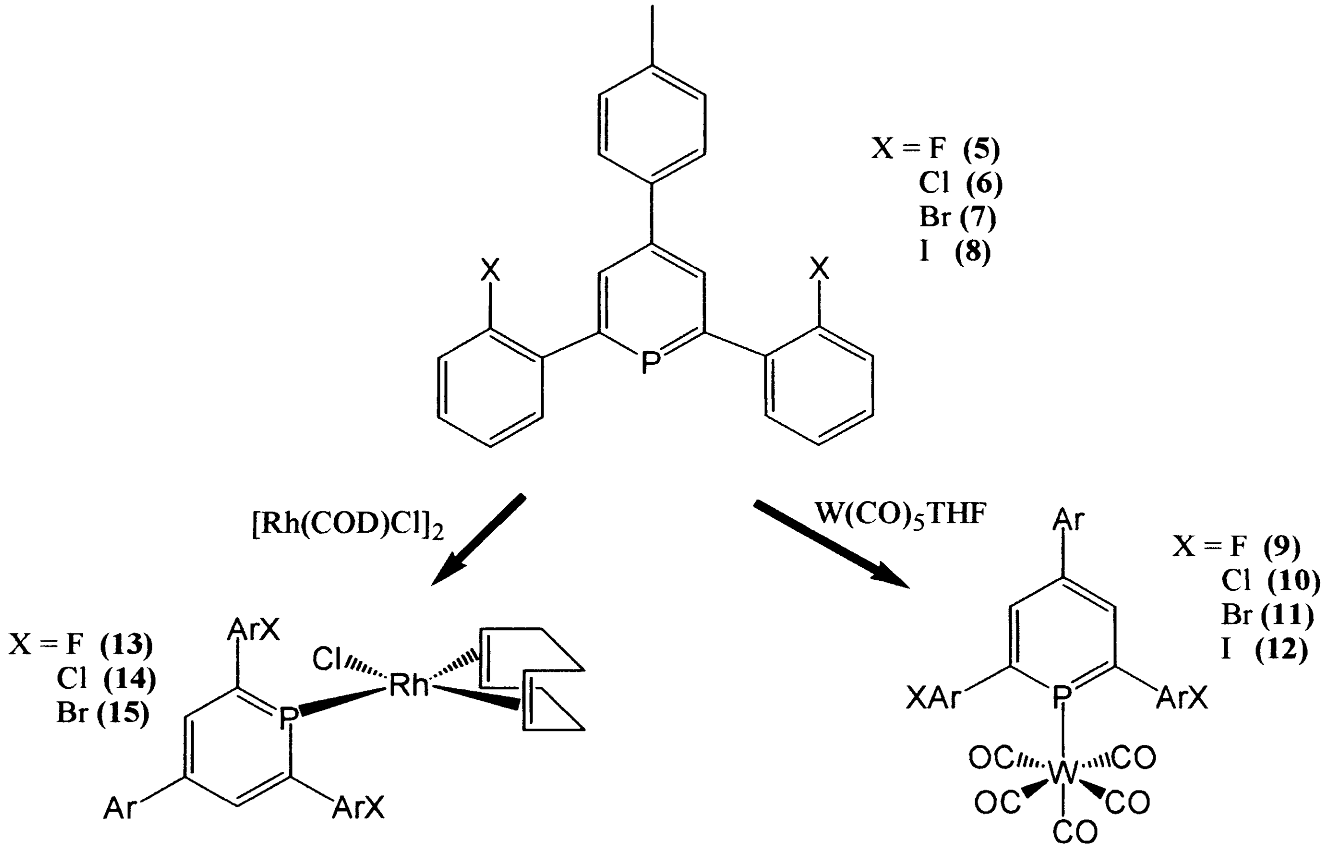
Compounds **(5-8)** were synthesised using a methodology introduced by Markl[11] and further developed by Briet to avoid the use of phosphine gas.[9] Thus compounds **(5-8)** were synthesised from their relevant pyrylium salt by reaction with 2 equivalents of $P(SiMe_3)_3$ in dimethoxyethane (scheme 2.1). The use of DME is preferred to acetonitrile; (used in Markl's original procedure for triphenyl phosphinines); as cleaner reactions result, with only the phosphinine and sometimes unreacted tris(trimethylsilyl)phosphine (PTMS) being observed in the ^{31}P NMR spectra. Excess PTMS can be removed as PH_3 by stirring the material in methanol at room temperature overnight. The phosphinines were all characterised by NMR spectroscopy and high resolution mass spectrometry, and are, to the best of our knowledge, the first reported phosphinines of their type. The compounds crystallised with feathery 'herring bone' morphologies, which made them unsuitable for X-ray crystallography. Also due to the large number of coincidental chemical shifts in the aromatic region of the ^{1}H NMR spectra, the majority of the peaks appear as multiplets, and precluded individual assignment of protons.



Scheme 2.1.

On comparing the ^{31}P, ^{1}H and ^{13}C spectroscopy data of the phosphinine series there seems to be very little difference in going from one halo phosphinine to the next. There are no significant differences in the ^{31}P chemical shifts, and the carbon atoms adjacent to the phosphorus atom in the phosphinine ring show little change in either shift or coupling constant across the halophosphinine series. The only notable difference is in compound **(5)** were the C-2′ carbon is clearly distinguished by its coupling to the fluorine atom.

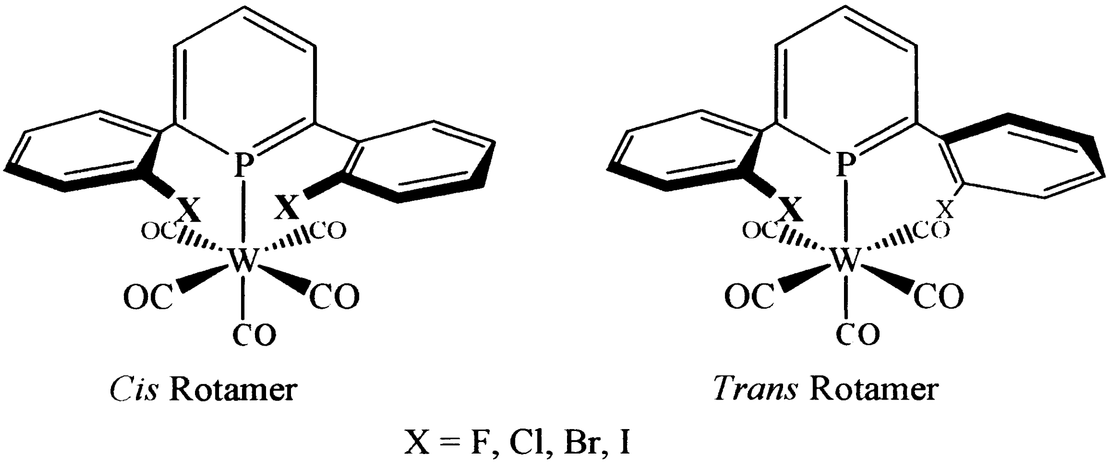
Compounds **(9-12)** were made by reacting the phosphinine with W(CO)$_5$THF, (made in situ by the photolysis of W(CO)$_6$ in THF), at room temperature (scheme 2.2). The resulting phosphinine – tungsten complexes, (phosphinine)W(CO)$_5$, were fully characterised by NMR spectroscopy and by their high resolution mass spectra. Unlike for most tertiary phosphines, the coordination induced shifts (ΔδP) are up-field for phosphinines, ascribed to the phosphorus atom in a phosphine being a sp^3 center, whereas the phosphorus atom in a phosphinine is a sp^2 centre).[1] The chemical shifts in the ^{31}P NMR spectra of our tungsten-phosphinine complexes **(9-12)** are similar to related complexes reported by Mathey and co-workers.[12] They also report up-field shifts from the free to the coordinated ligand, although their complexes give rise to resonances 20 ppm or further downfield. This is not surprising as the phosphinines of Mathey *et al.* are significantly different to ours.



Scheme 2.2.

On coordinating the phosphinines, the electronic difference at the phosphorus centre is evident by the changes, not in the chemical shifts, but in the coupling constants in the ^1H and ^{13}C NMR spectra. In particular, the protons of the C-3 and C-5 positions on the phosphinine ring, experience a change in the coupling constant from around 6 Hz to 17 Hz. A greater change is seen in the coupling constants of the C-2 and C-6 carbons adjacent to the phosphorus atom, as their coupling decreases from around 52 Hz to 15 Hz upon coordination. This change, although significant, is not uncommon as similar changes are seen in the carbon atoms α to the coordinated phosphorus atoms in phosphine complexes.

An interesting feature of these complexes arises in the ^{31}P NMR spectra where for the chloro-, bromo- and iodo- derivatives, two peaks of unequal intensity are observed. We propose that this is due to the bulk of the two aryl-halide substituted aromatic rings resulting in restricted P-C bond rotation which becomes greater on increasing the size of the halogen atoms. The two rotamers are due to *cis* and *trans* configurations of the halo-aryl group (scheme 2.3). This is confirmed by variable temperature ^{31}P NMR spectroscopic studies conducted with the fluoro-derivative, which gives a singlet at room temperature and which when cooled to 258 K gives rise to two resonances.



Scheme 2.3.

The variable temperature study allows estimation of the activation energy of the rotation which was calculated to be 50.8 kJ mol^{-1}. The chloro-derivative gives rise to two peaks at room temperature, which coalesced at 388 K upon heating. The activation energy for this rotation barrier was estimated by the method of Crabtree[13] (see experimental), to be 72.5 kJmol^{-1}. For the bromo-, and iodo- derivatives however, coalescence was not observed upon heating to 110 °C, indicating higher rotation barriers. The equilibrium constant between rotamers did not appear to be temperature dependent as the ratios of the peaks in the ^{31}P spectra remained constant (approximately 1:2). It is also plausible to suggest that the major rotatmer is the *trans* isomer, as this would provide the greater steric relief to the complex. The presence of two rotatmers, leads to broadening in the ^{1}H NMR spectra in the aromatic region, and thus unequivocal assignment of the peaks could not be made in some cases. Similar problems were encountered in the ^{13}C NMR spectra.

The Infra-red spectra of the phosphinine–tungsten complexes gave insight into the nature of the W-P bond, as the carbonyl stretching frequencies are sensitive to π-acceptor properties of the phosphinine ligands. The table below compares our phosphinines with other phosphorus based ligand complexes of pentacarbonyltungsten(0):

Table 2.1: Carbonyl stretching frequencies for complexes **9-12**.

L	**υ(CO) cm^{-1}**			
	A_1^2	**A_1^1**	**E**	**Ref**
$P(NMe_2)_3$	2067.3	1942.0	1933.0	14
PMe_3	2069.0	1948.5	1939.0	14
PPh_3	2071.2	1942.0	1942.0	15
$P(OMe)_3$	2078.9	1962.2	1947.8	15
12	2076.4	1983.1	1954.2	
11	2076.4	1983.1	1954.2	
10	2076.4	1983.1	1954.2	
9	2077.0	1980.7	1958.8	
$P(OPh)_3$	2082.5	1967.5	1958.5	14
$P(CF_3)_3$	2101	2006	1998	15

As can be seen from Table 2.1, the phosphinines are most closely similar to alkyl and aryl phosphites on this basis and in agreement with the observations of Kozlowski et al.[16] Although there seems to be no difference between the iodo-, bromo-, and chloro-derivatives, there is a small increase in the stretching frequencies with the fluoro-derivative indicating increased π-acceptor behaviour as might be expected with the enhanced electronegativity of the halide. The major and minor rotatmers in compounds **(10-12)** appear indistinguishable in the IR spectra, as only the three carbonyl stretches expected for a $M(CO)_5(L)$ complex are observed. The tungsten – phosphorus coupling for all the derivatives made was 280 Hz. This compares favourably with $(Ph_3P)W(CO)_5$ ($J_{P\text{-}W}$ = 280 Hz),[17] but is significantly smaller than that observed in $(PhO)_3PW(CO)_5$ ($J_{P\text{-}W}$ = 404 Hz).[18] This may indicate that the electronic properties of our phosphinines are more closely similar to those of Ph_3P, than those of $(PhO)_3P$ in analogous complexes. Taking both NMR and IR spectroscopic data into account, it is reasonable to suggest that the π-acceptor properties of our phosphinines lie between those of Ph_3P and $(PhO)_3P$.

Complexes **(13-15)** were synthesised by stirring the relevant phosphinine with $[Rh(COD)Cl]_2$, (COD: 1,5-cyclooctadiene) in dichloromethane (scheme 2). The formation of a Rh complex was confirmed by ^{31}P NMR spectroscopy in which, in each case, a doublet and a coordination chemical shift of around 10 ppm was observed, as well as a characteristically large phosphorus-rhodium coupling, (*ca.* 185 Hz). This phosphorus-rhodium coupling of 185 Hz lies between the coupling for the analogous complex, $[(Ph_3P)Rh(COD)Cl]$ ($J_{P\text{-}Rh}$ = 152 Hz)[19], and the complex, $[((PhO)_3P)Rh(COD)Cl]$ ($J_{P\text{-}Rh}$ = 273 Hz).[20] This is consistent with the observation that our phosphinines have electronic, and π-acceptor properties that lie somewhere between aryl-phosphines and phosphites in analogous complexes. No evidence of a rotational barrier was observed by ^{31}P NMR spectroscopy, presumably due to the complexes being square planar with a correspondingly low steric restriction to P-C rotation. The complexes were fully characterised by NMR spectroscopy. Unfortunately we were unable to grow suitable crystals for X-ray crystallography. The ^{1}H NMR spectra show the characteristic reduction in coupling for the protons in the C-3 and C-5 positions, as was observed for the tungsten complexes. However, the ^{13}C NMR spectra were not sufficiently well resolved to allow unequivocal assignment of the C-2 and C-6 carbons; hence, the tentative assignments in Table 2.2.

An iodo– phosphinine derivative of the rhodium complex was not obtained as upon addition of the phosphinine to the yellow rhodium dimer solution, the solution immediately turned black. There was no evidence of related complexes in the ^{1}H NMR spectra and the ^{31}P NMR spectrum was silent. No identifiable products could be isolated. This suggests that the phosphinine underwent some sort of cyclometallation at the iodo- (C-2′) position to the rhodium centre itself. It is reasonable to propose that C-X oxidative addition might be more facile for the iodo-phosphinine and which may provide a decomposition pathway. Furthermore, similar behaviour was observed on attempting to coordinate phosphinines **(5-8)** to palladium (II) with all the phosphinines including the fluoro- derivative. No discreet complexes could be obtained and ^{31}P (^{1}H) NMR spectra of the reaction mixtures were silent. No decomposition products could be identified. Phosphinine-palladium (II) complexes are known,[21] although none have a carbon-halide bond in an accessible position to the metal.

Our inability to isolate simple phosphinine complexes for a range of metals in a variety of oxidation states would appear to highlight an unexpected and general difficulty in the formation of phosphinine complexes. This indicates an inherent instability (lability), especially in the presence of other coordinating ligands and solvents, and may reflect the relatively poor σ-donor characteristics of phosphinines. This view is supported by our only successful complexation studies being from metal precursors with intrinsically labile ligands, $(THF)W(CO)_5$ and $[(COD)RhCl]_2$. In addition phosphinine complexes appear to be more readily accessible with metals in low oxidation states (W^0, Rh^I): and the relatively good π-acceptor properties of the phosphinines are no doubt important in stabilising these complexes. This may be of more general significance in that to obtain reasonably robust mono-phosphinine complexes, we need to be able to take advantage of the π-component of the M-P bond.

In conclusion, we describe a new series of 2-(2^1-halo)-substituted phosphinine ligands, and their tungsten and rhodium complexes. We have established the relative σ–donation / π-acceptor abilities of our phosphinines based on comparison of carbonyl stretching frequencies in their complexes. Now the synthesis of the phosphinines has been established, work is on going to substitute the halide group in an attempt to produce donor functionalised tridentate phosphinines.

Table 2.2. Selected NMR data for comparison of Phosphinines **5-8**.

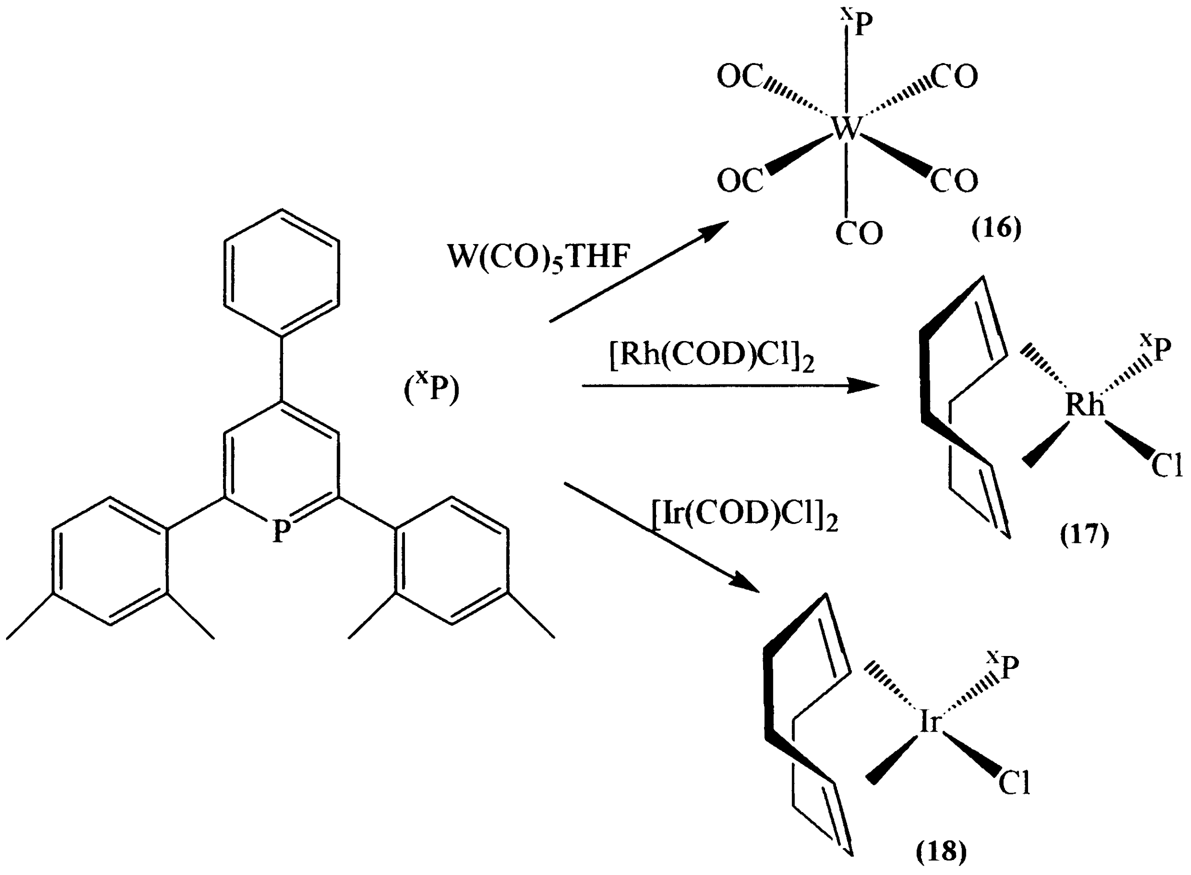
Phosphinine (L)	**NMR Data**	**L**	**LWCO5**	**LRh(COD)Cl**
5	^{31}P J$_{(P-Rh)}$	193.1	166.9	186.9 184.3Hz
CH3/5	^{1}H J$_{(H-P)}$	8.1 5.9Hz	8.1 17.4Hz	8.1 21.5Hz
C2/6	^{13}C J$_{(C-P)}$	165.3 52.8	160.9 15.1	(160.0)
	^{19}F	-117.2	-113.2	-116.2
6	^{31}P J$_{(P-Rh)}$	192.7	164.9	187.5 186.3Hz
CH3/5	^{1}H J$_{(H-P)}$	8.0 6Hz	7.9 17.6Hz	8.1 15.9Hz
C2/6	^{13}C J$_{(C-P)}$	168.9 52.8Hz	164.6 15.2Hz	(157.2)
7	^{31}P J$_{(P-Rh)}$	192.2	165.0	187.3 186.3Hz
CH3/5	^{1}H J$_{(H-P)}$	8.0 6.0Hz	7.9 17.6Hz	7.5 7.7Hz
C2/6	^{13}C J$_{(C-P)}$	168.9 52.7Hz	166.5 8.8Hz	(147.5)
8	^{31}P	192.2	164.9	N/A
CH3/5	^{1}H J$_{(H-P)}$	7.9 6.2Hz	7.9 17.6Hz	
C2/6	^{13}C J$_{(C-P)}$	173.7 52.8Hz	170.1 8.8Hz	

2.3 Transition Metal Complexes of 2,6-Dixylyl-4-phenylphosphinine - Introduction

Following our previous work on halo-substituted aryl phosphinines, our focus turned to the already established non-halo substituted aryl phosphinines. Breit had already explored their potential as ligands in homogeneous catalysis, but their coordination chemistry to transition metal centres has remained largely unexplored. Thus we synthesised the 2,6-dixylyl-4-phenyl phosphinine *via* the procedure of Breit[22] and surveyed the coordination chemistry of the ligand with a selected number of transition metals. The purpose of this was to establish the nature of the phosphorus-transition metal bond by comparison of relevant spectroscopic data with that of analogous complexes of triphenyl phosphine and triphenyl phosphite. We were also interested to see if some of the features we observed with the halo-substituted phosphinines, such as rotameric isomerisation in the phosphinine-pentacarbonyltungsten(0) complexes, were present in the dixylyl analogues. Complexes **(16-20)** below are reported here for the first time.

2.4 Results and Discussion

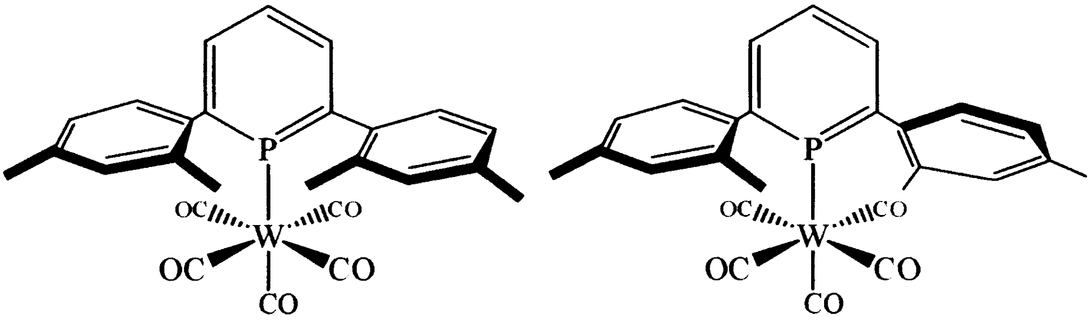
The dixylylphosphinine(pentacarbonyl)tungsten(0) **(16)** was made by reaction of the 2,6-dixylyl-4-phenylphosphinine with $W(CO)_5THF$ in dichloromethane at room temperature (scheme 2.4). **(16)** was isolated as a yellow solid and characterised by NMR and IR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum at room temperature showed two peaks in a ratio of 2:1, with upfield coordinated shifts, as is common for phosphinine coordination,[23] at 165.8 ppm and 165.7 ppm both with tungsten-183 satellites. This observation suggests the presence of two rotamers, a feature observed in this chapter, with the halo-substituted aryl phosphinines. In common with some of the halo-substituted aryl phosphinines, one of the rotamers predominated at room temperature by the greater intensity of one of the signals in the ^{31}P NMR spectrum. In this case the major rotamer gave the peak at 165.7 ppm, and due to the large difference in intensities, only the ^{1}H and ^{13}C NMR data for the major rotamer could be assigned.



Scheme 2.4.

Upon heating the sample to 90 ^{0}C (363 K) the two peaks coalesced to a single peak and from this data the free energy of activation for the rotation barrier was calculated to be 74.9 kJmol^{-1}. This value is very similar to that obtained for the chloro-substituted aryl phosphinine-pentacarbonyltungsten(0) complex which gave a $\Delta G^{\#}$ of 72.5 kJmol^{-1}. This is not surprising as it is generally accepted that chloride has a similar size to that of a methyl group, and that for the dixylylphosphinine, the rotation barrier is provided principally by the ortho methyl, as the para_methyl is in a position on the phosphinine ring that prevents it from causing any steric hindrance. This suggests that in these aryl substituted phosphinine systems a chloro-substituted aryl group and a dimethyl substituted aryl group have a similar $\Delta G^{\#}$ barrier for free rotation in these LW(CO)$_5$ systems. The difference in intensities in the peaks in the

^{31}P NMR spectrum suggests that one of the rotamers is more favoured over the other at room temperature. Thus the postulated theory of *cis* and *trans* isomerisation, used to explain the same observations in the halo-substituted aryl phosphines, again fits here in explaining the presence of a favoured rotamer (scheme 2.5). It is reasonable to assume that the larger signal in the ^{31}P NMR spectrum would correlate to the *trans* isomer of the complex. This would be due to greater steric relief provided by the xylyl groups being on opposite sides of the phosphinine ring. Thus making the *trans* isomer more likely to be the favoured species and gives the more intense peak in the ^{31}P NMR spectrum at room temperature.



Cis Rotamer

Trans Rotamer

Scheme 2.5.

The $^{1}J_{P\text{-}W}$ coupling constant of **(16)** also compares with that of the halo-substituted aryl phosphinine(pentacarbonyl)tungsten(0) complexes. The halo-substituted aryl phosphinines all gave a $^{1}J_{P\text{-}W}$ coupling constant of 280 Hz, and the dixylylphosphinine analogue also gives a $^{1}J_{P\text{-}W}$ coupling constant of 280 Hz. This suggests that there is little difference in the electronic nature of the coordinated phosphorus atom in the two tungsten complexes. On comparison with analogous systems of triphenyl phosphine and triphenyl phosphite, the same conclusions can be made as for the halo-substituted phosphinines. The dixylylphosphininepentacarbonyltungsten(0) complex exhibits a $^{1}J_{P\text{-}W}$ coupling constant (280 Hz) that is similar to triphenylphosphine (280 Hz),[24] but much lower than triphenylphosphite (404 Hz).[25] This suggests that in terms of electronic properties, the nature of the phosphorus-tungsten bond in **(16)** is similar to the phosphorus-tungsten bond in the analogous triphenylphosphine system.

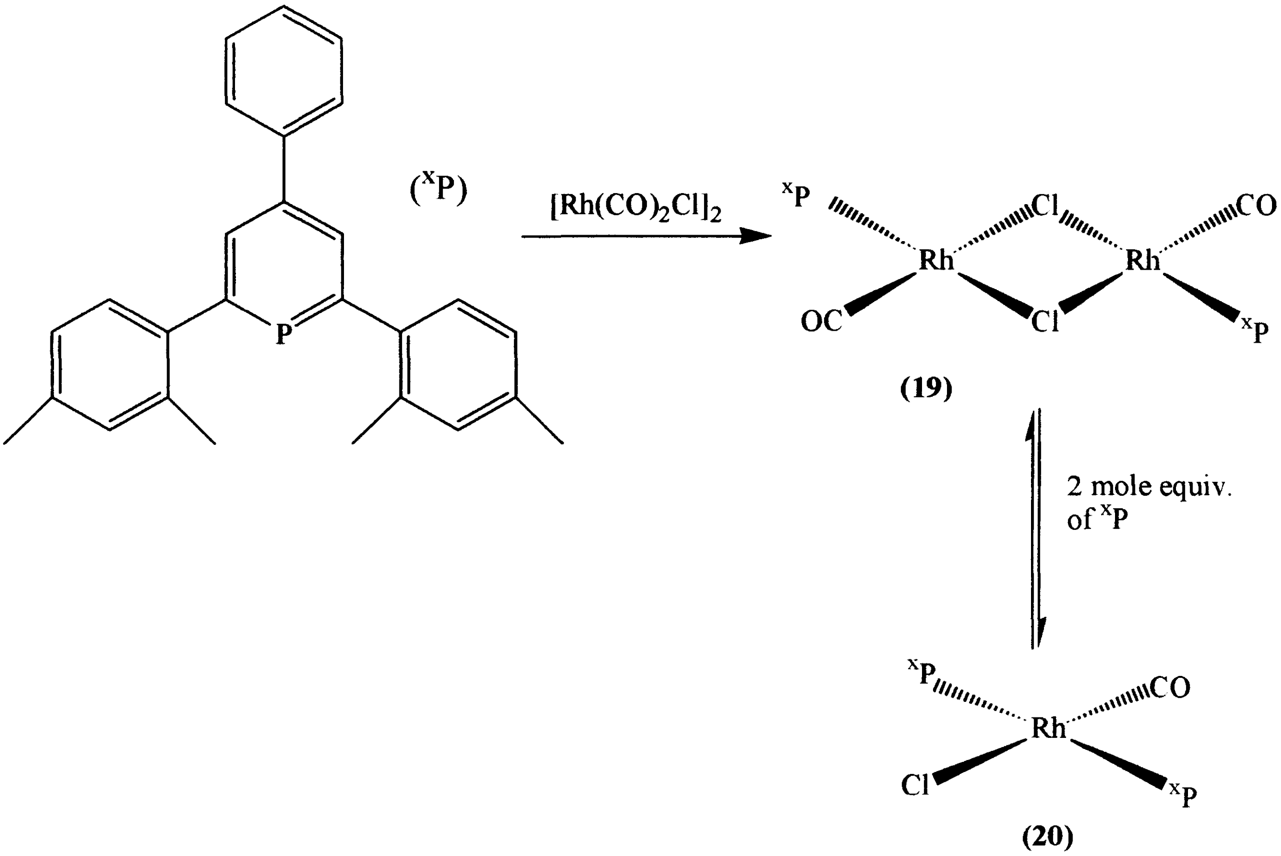
The ^{1}H NMR and ^{13}C NMR spectra both show the effects of phosphinine coordination, with the protons at the 3 and 5 positions on the phosphinine ring experiencing an increase in their J_{H-P} coupling constant from 6 Hz to 17 Hz, and the C-2 and C-6 carbons experiencing a decrease in their J_{C-P} coupling constant from 54 Hz to 10 Hz. The ^{13}C NMR also shows the two carbonyl peaks of **(16)** with the *cis* carbonyls being at 194 ppm and the *trans* carbonyl peak at 191 ppm. The *cis* carbonyl peak exhibits both the small $^{2}J_{C-P}$ coupling constant of 9 Hz, typical for complexes of this type, and the expected large $^{1}J_{C-W}$ coupling constant of 126 Hz. The *trans* carbonyl peak was too weak in intensity to discern any coupling constant data.

The infra-red data on **(16)** alludes to the nature of the phosphorus-tungsten bond, and also highlights the π-acceptor ability of the dixylylphosphinine ligand. The three carbonyl stretching frequencies are at 2074, 1982, and 1948 cm^{-1}. These are slightly lower compared with the carbonyl stretching frequencies of the halo-substituted aryl phosphinines (e.g. 2076, 1983, and 1954 cm^{-1}, see Table 2.1), but are slightly higher than in the triphenylphosphine(pentacarbonyl)tungsten(0) complex with $\nu_{(CO)}$ stretching frequencies at 2071, 1942, and 1942 cm^{-1}.[26] The slight increase in $\nu_{(CO)}$ in the halo-substituted aryl phosphinines complex compared to the dixylylphosphinine complex could be due to an affect of the presence of the electronegative halogen atoms on the aryl groups, compared to the dimethyl substituted aryl groups in the analogous phosphinine ligand systems. However, it is clear from the data that the dixylylphosphinine possesses greater π-acceptor properties than triphenyl phosphine in complexes of the type $LW(CO)_5$.

The chloro(COD)(dixylylphosphinine)rhodium(I) complex **(17)** was synthesised by addition of the phosphinine to a solution of the $[Rh(1,5\text{-}COD)Cl]_2$ dimer in dichloromethane (scheme 2.4). The desired compound was isolated as a yellow solid and was characterised by NMR and IR spectroscopy. The $^{31}P\{^{1}H\}$ NMR spectrum showed the characteristic upfield coordination shift of phosphinines to 187.9 ppm. The ^{1}H NMR spectrum of **(17)** also showed the characteristic signs of coordination with the protons in the 3 and 5 positions of the phosphinine ring showing a increase in their J_{H-P} coupling constant from 6 Hz, to 17 Hz. However, the C-2 and C-6 carbons gave such weak signals in the ^{13}C NMR spectrum of **(17)** that no coupling constant data could be calculated.

The $^{1}J_{P\text{-}Rh}$ coupling constant values provide us with an insight into the nature of the phosphorus-rhodium bond in these systems. The dixylylphosphinine-rhodium complex exhibits a $^{1}J_{P\text{-}Rh}$ coupling constant of 182 Hz, which is the same as the $^{1}J_{P\text{-}Rh}$ coupling constants observed for the halo-substituted aryl phosphinines. Therefore the nature of the phosphorus-rhodium bond in both types of complexes is believed to be similar. On comparison with the analogous triphenyl phosphine and triphenyl phosphite complexes, the data suggests that, as with the halo substituted aryl phosphinines, **(17)** lies between the analogous complexes of triphenyl phosphine ($J_{P\text{-}Rh}$ = 152 Hz),[27] and triphenyl phosphite ($J_{P\text{-}Rh}$ = 273 Hz).[28] This suggests that the dixylylphosphinine ligand has σ-donor / π-acceptor properties that lie between triphenyl phosphine and triphenyl phosphite in complexes of the type (L)Rh(COD)Cl.

The mono-phosphinine(chloro)(COD)iridium(I) complex **(18)** was made in an analogous way to that of **(17)**, with the addition of the phosphinine to chloro(COD)iridium(I) in dichloromethane at room temperature (scheme 2.4). **(18)** was isolated as a yellow solid and was characterised spectroscopically. The $^{31}P\{^{1}H\}$ NMR spectrum showed an upfield coordination shift at 176.4 ppm, characteristic of phosphinines upon coordination to transition metals. The ^{1}H NMR spectrum exhibited the expected increase in $J_{H\text{-}P}$ coupling constant of the protons at the 3 and 5 positions on the phosphinine ring from 6 Hz, to 20 Hz. While the ^{13}C NMR spectrum showed the expected reduction of the $J_{C\text{-}P}$ coupling constant of the C-2 and C-6 carbons from 52 Hz, to 19 Hz.



Scheme 2.6.

The *bis*-[chloro(carbonyl)(dixylylphosphinine)rhodium(I)] complex **(19)** was made by the reaction of the dicarbonyl(chloro)rhodium(I) dimer with 2 equivalents of the phosphinine ligand (scheme 2.6). The $^{31}P\{^1H\}$ NMR spectrum of the reaction solution shows a doublet at 178.8 ppm with a coupling constant of 223 Hz, suggesting the dimeric complex **(19)** had been formed. On addition of another two moles of phosphinine ligand to the solution, the ^{31}P NMR spectrum of the solution showed a doublet at 179.5 ppm, with a $J_{P\text{-}Rh}$ coupling constant of 172Hz, suggesting that the monomeric complex **(20)** was formed. Our evidence for the identity of compounds **(19)** and **(20)** is based upon two factors: the first is that Breit has reported a series of complexes that are analogous to **(20)** where the phosphinine ligand has very minor differences in its structure, (i.e. triphenylphosphinine or diisopropyl(phenyl)phosphinine).[22] He reported the $J_{P\text{-}Rh}$ coupling constants of these complexes to be in the region of 168 to 179 Hz, and our complex **(20)** has a $J_{P\text{-}Rh}$ coupling constant of 172 Hz. The second is that the analogous triphenyl phosphine complexes of **(19)** and **(20)** have a difference of around 50 Hz in their $J_{P\text{-}Rh}$ coupling constant, on going from the dimeric species[29] to the monmeric species.[30] Our complexes also show a difference of 50 Hz in their $J_{P\text{-}Rh}$ coupling constant, on going from the dimeric complex **(19)** to the monomeric complex **(20)**. Based on this evidence we therefore postulate that complex **(19)** is the *bis*-[chloro(carbonyl)(dixylylphosphinine)rhodium(I)], and complex **(20)** is the chloro(carbonyl)(*bis*-dixylylphosphinine)rhodium(I).

On concentration of this sample containing complex **(20)** and addition of $CDCl_3$, the ^{31}P NMR spectrum shows two doublets both of equal intensity: one at 178.7 ppm, and the other at 179.5 ppm, suggesting that now both the monomeric and dimeric complex are present. It is also worth noting that a small amount of what is presumed to be decomposition material is present around 30 ppm, however, the nature and decomposition pathway of this material remains unclear. Therefore upon addition of 2 mole equivalents of the phosphinine ligand to complex **(19)**, and concentration of the sample, we postulate that decomposition of the monomeric complex **(20)** occurs resulting in formation of the dimeric complex **(19)** and an unidentified decomposition material.

We were able to isolate and characterise complex **(19)** by spectroscopic means and it is, to the best of our knowledge, the first dimeric phosphinine-rhodium complex of its type. The ^1H NMR spectrum exhibits the classic increase from 6 Hz to 10 Hz, in the $J_{H\text{-}P}$ coupling constant of the protons on the 3 and 5 carbon positions of the phosphinine ring upon coordination. In addition there is a decrease from 52 Hz to 24 Hz in the $J_{C\text{-}P}$ coupling constants of the C-2 and C-6 carbons on the phosphinine core. The expected carbonyl resonance was too weak in the ^{13}C NMR spectrum to discern any coupling constants.

The infra red spectrum of complex **(19)** shows a single carbonyl stretching frequency at 1999 cm^{-1} which is in accordance with the literature.[29] The carbonyl stretching frequency is lower than that reported for the analogous triphenylphosphine complex (1983 cm^{-1})[29], which is not surprising as it is well established, by our work and others, that the phosphinine ligand is a better π-acceptor than triphenyl phosphine in analogous transition metal complexes.

Therefore in conclusion we report here, for the first time, a series of transition metal complexes of the dixylyl(phenyl)phosphinine ligand. Their structures have been elucidated by spectroscopic means, and the nature of their phosphorus-transition metal bonds established by comparison with analogous complexes of triphenyl phosphines and phosphites. In addition we have discovered and elucidated a surprising reactivity of a monomeric phosphinine-rhodium complex that, upon concentration in solution decomposes, *via* an unknown decomposition pathway, to the dimeric phosphinine-rhodium complex. This evidence, along with our experience of the halo-substituted aryl phosphinines, suggests that phosphinines as ligands to transition metals can, on occasions, be highly unpredictable.

2.5 Experimental

The compounds were synthesised under nitrogen using standard inert atmosphere (Schlenk) techniques. Compounds **(1-4)** were obtained and handled as air and moisture stable solids. Compounds **(5-12)** were handled and stored as air and moisture sensitive solids. Complexes **(13-19)** were handled as air and moisture sensitive compounds for manipulation, but were found to be air stable as solids. All solvents were freshly distilled from sodium or calcium hydride under nitrogen before use. The $^{31}P\{^{1}H\}$ NMR spectra were recorded on Jeol Eclipse 300 and Bruker DPX500 spectrometers operating at 121.7 and 202.5 Hz respectively, and referenced to 85% H_3PO_4 ($\delta = 0$ ppm). ^{1}H (400.8MHz) spectra were obtained on Bruker DPX400 spectrometer except in some cases where a BrukerDPX500 NMR spectrometer (field) was used as indicated. $^{13}C\{^{1}H\}$ (125.8 MHz) NMR spectra were obtained on a Bruker DPX500 spectrometer and are referenced to tetramethylsilane ($\delta = 0$ ppm). Infrared spectra were recorded either as a solution cell or as Nujol Mulls on a Nicolet 510 FT-IR spectrophotometer. Mass spectra were recorded on a Micromass Q-Toff mass spectrometer. All other chemicals were of reagent grade and used as supplied unless otherwise stated. Purity of the compounds was estimated by ^{1}H NMR, by comparison of peak intensities to a persistent impurity in the ligands which is carried through into the metal complexes. $\Delta G^{\#}$ were calculated by the method of Crabtree,[13] using the equation:- $\Delta G^{\#} = -RT[\ln(K/T_c) + \ln(h/k)]$. Where T_c is the temperature of coalescence in Kelvin. $K = (\pi/\sqrt{2})(\Delta v)\ s^{-1}$, where Δv is the difference in Hertz of the two peaks of the two rotamers at maximum separation. $R = 8.3143 JK^{-1}mol^{-1}$; $h = 6.6260x10^{-34}Js^{-1}$; $k = 1.38062x10^{-23}JK^{-1}$.

Synthesis of 2,6-Bis-(2′-fluorophenyl)-4-tolylpyrylium tetrafluoroborate (1):

Powdered NaOH (1.4 g 36 mmol), 2′-fluoroacetophenone (5.0g, 36 mmol) and p-tolylaldehyde (2.2 g, 18 mmol) were mixed together with a pestle and mortar for 25 min. The highly viscous yellow mixture was dissolved in ether (100 mL) and water, the organic phase was separated and washed with water (3 × 50 mL), brine (3 × 50 mL) and dried over $MgSO_4$, and the solvent was removed in *vacuo*. Without further purification the crude "diketone" was then converted to the pyrylium salt. Thus, under an argon atmosphere, a mixture of "diketone" (950 mg, 1.9 mmol), chalcone (395 mg, 1.9 mmol) and $BF_3.OEt_2$ (7 mL) was stirred at 100 °C for 2 h, then cooled to room temperature, and diluted with Et_2O (10 mL). After 12 h, the yellow precipitate was filtered off and washed thoroughly with Et_2O to yield 2,6-bis-(2′-fluorophenyl)-4-tolylpyrylium tetrafluoroborate **(1)** as a yellow solid (2.8 g, 34%). Purity 99%. ^{1}H-NMR ($(CD_3)_2CO$): δ = 2.5 (s, 3 H, CH_3); 7.3-7.4 (m, 2 H, Ar-H); 7.51 (t, 4 H, $J_{(H\text{-}H)}$= 7.5Hz, Ar-H); 7.7- 7.8 (m, 2 H, Ar-H); 8.2-8.3 (m, 2 H, Ar-H); 8.0 (d, 2 H, $J_{(H\text{-}H)}$=8.4Hz, Ar-H); 8.7 (s, 2 H, CH 3/5). ^{13}C-NMR (125.8 MHz; $(CD_3)_2CO$): δ = 21.9, 117.2, 117.7, 117.8, 117.9, 126.4, 129.4, 129.8, 130.7, 131.5, 137.6, 137.7, 149.2, 167.3. ^{19}F NMR (282.8 MHz, $(CD_3)_2CO$): δ = -153.1.

Synthesis of 2,6-Bis-(2′-chlorophenyl)-4-tolylpyrylium tetrafluoroborate ***(2)****:*

The synthesis of **(2)** was identical to that of **(1)** except that 2′-chloroacetophenone was used instead. The reaction yielded 2,6-bis-(2′-chlorophenyl)-4-tolypyrylium tetrafluoroborate **(2)** as a yellow solid (62%). Purity 99%. ^{1}H-NMR ($(CD_3)_2CO$): δ = 2.6 (s, 3 H, CH_3); 7.7-7.9 (m, 8 H, Ar-H); 8.3 (dt, 2 H, $^tJ_{(H\text{-}H)}$=6.5Hz, $^dJ_{(H\text{-}H)}$=1.2Hz Ar-H); 8.5 (d, 2 H, $J_{(H\text{-}H)}$=8.5Hz, Ar-H); 9.2 (s, 2 H, CH 3/5). ^{13}C-NMR (125.8 MHz; $(CD_3)_2CO$): δ = 21.9, 121.2, 129.3, 129.8, 130.6, 131.4, 132.1, 132.5, 134.0, 136.1, 149.6, 167.2, 171.7.

Synthesis of 2,6-Bis-(2′-bromophenyl)-4-tolylpyrylium tetrafluoroborate (3):

The synthesis of **(3)** was identical to that of **(1)** except that 2′-bromoacetophenone was used instead. The reaction yielded 2,6-bis-(2′-bromophenyl)-4-tolylpyrylium tetrafluoroborate **(3)** as a yellow solid (89%). Purity 99%. ^{1}H-NMR (CD_2Cl_2): δ = 2.6 (s, 3 H, CH_3); 7.6-7.7 (m, 6 H, Ar-H); 7.8- 7.9 (m, 2 H, Ar-H); 7.9-8.1 (m, 4 H, CH 3/5); 8.7 (s, 2 H, Ar-H). ^{13}C-NMR (125.8 MHz; CD_2Cl_2): δ = 22.3, 120.1, 122.3, 129.3, 129.5, 130.4, 130.5, 131.9, 133.3, 135.2, 135.4, 149.9, 166.4, 171.9.

*Synthesis of 2,6-Bis-(2′-iodophenyl)-4-tolylpyrylium tetrafluoroborate **(4)**:*

The synthesis of **(4)** was identical to that of **(1)** except that 2′-iodoacetophenone was used instead. The reaction yielded 2,6-bis-(2′-iodophenyl)-4-tolylpyrylium tetrafluoroborate **(4)** as a yellow solid (5%). Purity 95%. ^{1}H-NMR (CD_2Cl_2): $\delta = 2.5$ (s, 3 H, CH_3); 7.3-7.4 (m, 8 H, Ar-H); 7.5 (d, 2 H, $J_{(H-H)}$=8.2Hz, Ar-H); 7.6-7.7 (m, 2 H, Ar-H); 7.9 (dd, 2 H, $J_{(H-H)}$=1.5Hz, 7.8Hz, Ar-H); 8.0-8.1 (m, 2 H, Ar-H); 8.5 (s, 2 H, CH 3/5). ^{13}C-NMR (125.8 MHz; CD_2Cl_2): $\delta = 22.4$, 120.3, 129.7, 129.9, 130.6, 132.0, 133.0, 134.5, 135.1, 141.9, 150.1, 166.2, 173.9.

Synthesis of 2,6-Bis-(2′-fluorophenyl)-4-tolylphosphinine (5):

Tris-(trimethylsilyl) phosphine (0.84g, 1.2 equiv.) was added to a slurry of **(1)** (1.3g) in DME (40ml). The resulting mixture was refluxed for 16 h, in which time all the pyrylium salt dissolved. The DME was then removed in *vacuo* to yield a brown residue. The residue was dissolved in diethyl ether (20ml), and the resulting ether solution was passed through a pad of neutral aluminium, using ether (30ml) as eluant. The solution was pumped to dryness to yield an orange residue. The final product was recrystallised from petroleum ether to give 2,6-bis-(2′-fluorophenyl)-4-tolylphosphinine **(5)** as an orange solid. (0.7g, 56%.). Purity 95% . ^{31}P NMR (202.5 MHz, $CDCl_3$): $\delta = 193.1$. ^{1}H NMR ($CDCl_3$): $\delta = 2.3$ (s, 3 H, CH_3); 7.1-7.2 (m, 6 H); 7.23 (m, 2 H); 7.42-7.45 (m, 4 H); 8.1 (dd, 2 H, $J_{(H-F)}$= 1.5Hz, $J_{(H-P)}$= 5.9 Hz, CH 3/5). ^{13}C NMR ($CDCl_3$): $\delta = 21.3$ (s, CH_3); 116.3 (d, $J_{(C-P)}$= 22.6Hz, CH); 124.5 (s, CH); 127.8 (d, $J_{(C-P)}$= 18.9Hz, CH); 129.1 (s, CH); 129.8 (s, CH); 130.9 (dd, $J_{(C-P)}$= 0.1Hz, $J_{(C-F)}$= 0.2Hz, C); 131.7 (dd, $J_{(C-P)}$= 1.3Hz, $J_{(C-F)}$= 13.2Hz, CH); 134.0 (dd, $J_{(C-P)}$= 2.5Hz, $J_{(C-F)}$= 46.5Hz, CH); 138.1 (s, C); 138.9 (d, $J_{(C-P)}$= 2.5Hz, C); 143.1 (d, $J_{(C-P)}$= 13.8Hz, C); 159.1 (dd, $J_{(C-P)}$= 5.0Hz, $J_{(C-F)}$= 246.6Hz, C -2′); 165.3 (d, $J_{(C-P)}$= 52.8Hz, C 2/6). ^{19} F NMR (282.2 MHz, $CDCl_3$): $\delta = -117.3$ (d, J = 13.9 Hz). IR (Nujol) cm^{-1}: 1259.8; 1100.5; 1021.6; 802.6; 745.5. Mass Spec. (e/z): Obs. Mass 375.1119; Calc. Mass 375.1114: $M^+ = L^+$.

Synthesis of 2,6-Bis-(2′-chlorophenyl)-4-tolylphosphinine ***(6)****:*

Synthesis of **(6)** was the same as that of **(5)**, except that **(2)** was used as the pyrylium salt instead. The reaction gave 2,6-bis-(2′-chlorophenyl)-4-tolylphosphinine **(6)** as an orange solid (43%). Purity 98%. ^{31}P NMR (202.5 MHz, $CDCl_3$): $\delta = 192.7$. ^{1}H NMR ($CDCl_3$): $\delta = 2.3$ (s, 3 H, CH_3); 7.1-7.2 (m, 6 H); 7.4-7.5 (m, 6 H); 8.0 (d, 2 H, $J_{(H\text{-}P)}=$ 6.0 Hz, CH 3/5). ^{13}C NMR ($CDCl_3$): $\delta = 21.2$ (s, CH_3); 127.0 (s, CH); 128.1 (s, CH); 129.4 (s, CH); 129.8 (d, $J_{(C\text{-}P)}=$ 10.1Hz, CH); 130.2 (s, CH); 132.1 (d, $J_{(C\text{-}P)}=$ 10.1Hz, CH); 132.4 (d, $J_{(C\text{-}P)}=$ 6.3 Hz, C); 134.1 (d, $J_{(C\text{-}P)}=$ 11.3Hz, CH); 141.6 (s, C); 141.7 (d, $J_{(C\text{-}P)}=$ 23.9Hz, C); 142.1 (d, $J_{(C\text{-}P)}=$ 13.8Hz, C); 147.1 (s, C); 168.9 (d, $J_{(C\text{-}P)}=$ 52.8Hz, C 2/6). IR (Nujol) cm^{-1}: 1260.5; 1096.9; 1033.9; 801.9; 756.0. Mass Spec. (e/z): Obs Mass 407.0514; Calc. Mass 407.0523: $M^+ = L^+$.

Synthesis of 2,6-Bis-(2′-bromophenyl)-4-tolylphosphinine (7):

Synthesis of (7) was the same as that of (5), except that **(3)** was used as the pyrylium salt instead. The reaction gave 2,6-bis-(2′-bromophenyl)-4-tolylphosphinine (7) as an orange solid (27%). Purity 95%. ^{31}P NMR (202.5 MHz, $CDCl_3$): $\delta = 192.2$. ^{1}H NMR ($CDCl_3$): $\delta = 2.3$ (s, 3 H, CH_3); 7.1-7.2 (m, 2 H); 7.3 (dt, 2H, $^dJ_{(H\text{-}H)}=$ 0.8Hz, $^tJ_{(H\text{-}H)}=$ 7.5Hz); 7.4 (d, 2 H, $J_{(H\text{-}H)}=$ 7.6Hz); 7.5 (d, 2 H, $J_{(H\text{-}H)}=$ 8.1Hz); 7.7 (dd, 2 H, $J_{(H\text{-}H)}=$ 0.7Hz, $J_{(H\text{-}H)}=$ 8.0Hz); 8.0 (d, 2 H, $J_{(H\text{-}P)}=$ 6.0Hz, CH 3/5). ^{13}C NMR ($CDCl_3$): $\delta = 20.1$ (s, CH_3); 126.4 (s, CH); 126.5 (s, CH); 127.2 (s, CH); 128.1 (s, CH); 130.7 (d, $J_{(C\text{-}P)}=$ 10.1Hz, CH); 132.2 (s, CH); 132.9 (d, $J_{(C\text{-}P)}=$ 11.3Hz, CH); 136.9 (s, C); 137.6 (s, C); 140.8 (d, $J_{(C\text{-}P)}=$ 13.8Hz, C); 142.5 (d, $J_{(C\text{-}P)}=$ 22.6Hz, C); 147.3 (s, C); 168.9 (d, $J_{(C\text{-}P)}=$ 52.7Hz, C 2/6). IR (Nujol) cm^{-1}: 1260.3; 1094.2; 1020.7; 801.3. Mass Spec. (e/z): Obs. Mass 495.9125; Calc Mass 495.9119: $M^+ = L^+$.

*Synthesis of 2,6-Bis-(2′-iodophenyl)-4-tolylphosphinine (**8**):*

Synthesis of (**8**) was the same as that of (**5**), except that (**4**) was used as the pyrylium salt instead. The reaction gave 2,6-bis-(2′-iodophenyl)-4-tolylphosphinine (**8**) as an orange solid (63%). Purity 90%. ^{31}P NMR (202.5 MHz, CDCl$_3$): δ = 192.2. ^{1}H NMR (CDCl$_3$): δ = 2.3 (s, 3 H, CH$_3$); 6.9 t, 2 H, $J_{(H\text{-}H)}$= 7.6Hz); 7.1 (d, 2H, $J_{(H\text{-}H)}$= 7.9Hz); 7.3-7.4 (m, 4 H); 7.5 (d, 2 H, $J_{(H\text{-}H)}$= 8.1Hz); 7.9 (d, 2 H, $J_{(H\text{-}P)}$= 6.2Hz, CH 3/5). ^{13}C NMR (CDCl$_3$): δ = 20.1 (s, CH$_3$); 127.6 (s, CH); 128.0 (s, CH); 128.4 (d, $J_{(C\text{-}P)}$= 16.4Hz, CH); 129.3 (d, $J_{(C\text{-}P)}$= 12.6Hz, CH); 129.8 (s, CH); 130.4 (s, C); 134.0 (d, $J_{(C\text{-}P)}$= 11.3Hz, CH); 138.0 (s, C); 138.8 (s, C); 139.7 (d, $J_{(C\text{-}P)}$= 3.8Hz, CH); 140.5 (s, C); 147.5 (d, $J_{(C\text{-}P)}$= 22.6Hz, C); 173.7 (d, $J_{(C\text{-}P)}$= 52.8Hz, C 2/6). IR (Nujol) cm^{-1}: 1260.1; 1091.9; 1019.7; 800.9. Mass Spec. (e/z): 590.9257; Calc Mass 590.9236: M^{+} = L^{+}.

*Synthesis of [2,6-Bis-(2′-fluorophenyl)-4-tolylphosphinine]pentacarbonyltungsten(0) (**9**):*

A solution of (**5**) (0.1g, 0.27mmol) in THF was added at room temperature to a solution of W(CO)$_5$THF (90mg, 0.27mmol) in THF. The reaction mixture was stirred at room temperature for 18h, after which the solution was pumped to dryness. The crude material was washed with petrol and the resulting material was recrystallised from petrol, to give [2,6-bis-(2′-fluorophenyl)-4-tolylphosphinine]pentacarbonyl tungsten(0) (**9**) as an orange solid (0.12g, 67%). Purity 98%. ^{31}P NMR (202.5 MHz, CDCl$_3$): δ = 166.9 (s, $J_{(P\text{-}W)}$= 280.8Hz). ^{1}H NMR (CDCl$_3$): δ = 2.3 (s, 3 H, CH$_3$); 7.1-7.2 (m, 6 H); 7.3-7.4 (m, 6 H); 8.1 (d, 2 H, $J_{(H\text{-}P)}$= 17.4Hz, CH 3/5). ^{13}C NMR (CDCl$_3$): δ = 21.3 (s, CH$_3$); 116.3 (d, $J_{(C\text{-}P)}$= 21.4 Hz, CH); 124.4 (s, CH); 127.3 (s, CH); 129.0 (t, $J_{(C\text{-}P)}$= 15.1Hz, C); 129.9 (s, CH); 130.8 (d, $J_{(C\text{-}P)}$= 8.8 Hz, C); 132.6 (d, $J_{(C\text{-}P)}$= 7.5Hz, CH); 137.2 (d, $J_{(C\text{-}P)}$= 12.6Hz, CH); 137.6 (d, $J_{(C\text{-}P)}$=5.0Hz, C); 138.4 (s, C); 140.3 (d, $J_{(C\text{-}P)}$= 22.6Hz, C); 159.4 (dd, $J_{(C\text{-}P)}$= 7.5Hz, $J_{(C\text{-}F)}$= 240.3Hz, C –2′); 160.9 (d, $J_{(C\text{-}P)}$= 15.1Hz, C 2/6); 193.8 (d, $J_{(C\text{-}P)}$= 8.8Hz, CO); 197.8 (d, $J_{(C\text{-}P)}$= 32.7Hz, CO). ^{19}F NMR (282.2 MHz, CDCl$_3$): δ = -113.2. IR (Petrol) cm^{-1}: 2077.0 (w, CO); 1980.7 (sh, CO); 1958.8 (st, CO); 1260.9; 1101.9; 1016.5; 809.1; 737.8. Mass Spec.

(e/z): Obs. Mass 643.0149; Calc. Mass 643.0159: M^+ = (L)W(CO)$_3$; 614 (M^+– 3CO); 586 (M^+ – 4CO); 558 (M^+– 5CO); 375 (L^+).

*Synthesis of [2,6-Bis-(2′-chlorophenyl)-4-tolylphosphinine]pentacarbonyltungsten(0) (**10**):*

Compound (**10**) was made by the same procedure as that for complex (**9**) except phosphinine (**6**) was used instead. The reaction gave [2,6-bis-(2′-chlorophenyl)-4-tolylphosphinine]pentacarbonyltungsten(0) (**10**) as an orange solid that contains two rotamers (0.12g, 65%). Purity 95%. Not all the data for the minor rotamer could be obtained, what was collected is given below. Major rotamer: ^{31}P NMR (202.5 MHz, CDCl$_3$): δ = 164.9 (s, $J_{(P\text{-}W)}$= 280.9Hz). ^{1}H NMR (CDCl$_3$): δ = 2.28 (s, 3 H, CH$_3$); 7.13-7.16 (m, 4 H); 7.27-7.30 (m, 4 H); 7.38-7.44 (m, 4 H); 7.93 (d, 2 H, $J_{(H\text{-}P)}$= 17.6Hz, CH 3/5). ^{13}C NMR (CDCl$_3$): δ = 21.23 (s, CH$_3$); 126.90 (s, CH); 127.29 (s, CH); 129.91 (s, CH); 130.16 (d, $J_{(C\text{-}P)}$= 1.3Hz, CH); 130.37 (s, CH); 132.74 (d, $J_{(C\text{-}P)}$= 7.5Hz, CH); 133.67 (d, $J_{(C\text{-}P)}$= 8.8Hz, C); 137.08 (d, $J_{(C\text{-}P)}$= 11.3Hz, CH); 137.64 (t, $J_{(C\text{-}P)}$= 6.3Hz, C); 139.73 (d, $J_{(C\text{-}P)}$= 12.6Hz, C); 143.41 (s, C); 147.06 (s, C); 164.62 (d, $J_{(C\text{-}P)}$=15.1Hz, C 2/6); 193.79 (d, $J_{(C\text{-}P)}$= 8.8Hz, $J_{(P\text{-}W)}$= 125.5Hz, *cis*-CO); 197.74 (d, $J_{(C\text{-}P)}$= 32.7Hz, *trans*-CO). IR (Petrol) cm^{-1}: 2076.4 (w, CO); 1983.1 (sh, CO); 1954.2 (st, CO); 1261.8; 1171.2; 1147.9; 815.5; 739.7. Minor rotamer: ^{31}P NMR (202.5 MHz, CDCl$_3$): δ = 166.6 (s, $J_{(P\text{-}W)}$= 280.9Hz). ^{1}H NMR (CDCl$_3$): δ = 2.25 (s, 3 H, CH$_3$); 7.13-7.16 (m, 4 H); 7.27-7.30 (m, 4 H); 7.38-7.44 (m, 4 H); 7.90 (d, 2 H, $J_{(H\text{-}P)}$= 17.5Hz, CH 3/5). ^{13}C NMR (CDCl$_3$): δ = 21.13 (s, CH$_3$); 126.29 (s, CH); 127.03 (s, CH); 129.42 (s, CH); 129.69 (s, CH); 130.09 (s, CH); 132.29 (d, $J_{(C\text{-}P)}$= 7.5Hz, CH); 133.89 (d, $J_{(C\text{-}P)}$= 8.8Hz, C); 191.20 (s, CO). Mass Spec. (e/z): Obs Mass 674.9567; Calc Mass 674.9554: M^+ = (L)W(CO)$_3$; 619 (M^+ – 4CO); 590 (M^+ – 5CO).

Synthesis of [2,6- Bis-(2′-bromophenyl)-4-tolylphosphinine]pentacarbonyltungsten(0) (11):

Compound (**11**) was made by the same procedure as that for complex (**9**) except phosphinine (7) was used instead. The reaction gave [2,6-bis-(2′-bromophenyl)-4-

tolylphosphinine]pentacarbonyltungsten(0) (**11**) as an orange solid that contains two rotamers (0.1g, 63%). Purity 95%. Not all the data for the minor rotamer could be obtained, what was collected is given below. Major rotamer: ^{31}P NMR (121.7 MHz, $CDCl_3$): $\delta = 164.98$ (s, $J_{(P-W)}$= 280.8Hz). ^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 2.25$ (s, 3 H, CH_3); 7.03-7.07 (m, 2 H); 7.15 (t, 2 H, $J_{(H-H)}$= 7.4Hz); 7.21 (t, 2 H, $J_{(H-H)}$= 8.4Hz); 7.34 (t, 2 H, $J_{(H-H)}$= 7.3Hz); 7.41 (t, 2 H, $J_{(H-H)}$= 8.4Hz); 7.62 (t, 2 H, $J_{(H-H)}$= 8.2Hz); 7.92 (d, 2 H, $J_{(H-P)}$= 17.6Hz, CH 3/5). ^{13}C NMR ($CDCl_3$): $\delta = 21.44$ (s, CH_3); 127.26 (s, CH); 127.49 (s, CH); 128.25 (s, CH); 129.04 (s, CH); 129.89 (t, $J_{(C-P)}$= 5.0Hz, CH); 132.57 (d, $J_{(C-P)}$= 8.8Hz, CH); 137.13 (d, $J_{(C-P)}$= 12.5Hz, CH); 138.32 (s, C); 139.86 (s, C); 141.57 (d, $J_{(C-P)}$= 13.8Hz, C); 143.36 (s, C); 148.52 (s, C); 166.52 (d, $J_{(C-P)}$=8.8Hz, C 2/6); 193.76 (d, $J_{(C-P)}$= 8.8Hz, *cis*-CO); 197.74 (d, $J_{(C-P)}$= 32.7Hz, *trans*-CO). IR (Petrol) cm^{-1}: 2076.4 (w, CO); 1983.1 (sh, CO); 1954.2 (st, CO); 1261.8; 1171.2; 1147.9; 815.5; 739.7. Minor rotamer: ^{31}P NMR (121.7 MHz, $CDCl_3$): $\delta = 167.21$ (s, $J_{(P-W)}$= 2271.9Hz). ^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 2.28$ (s, 3 H, CH_3); 7.62 (t, 2 H, $J_{(H-H)}$= 8.1Hz); 7.88 (d, 2 H, $J_{(H-P)}$= 17.5Hz, CH 3/5). ^{13}C NMR ($CDCl_3$): $\delta = 21.13$ (s, CH_3); 127.08 (s, CH); 127.64 (s, CH); 128.18 (s, CH); 130.23 (s, CH); 131.91 (d, $J_{(C-P)}$= 7.5Hz, CH); 136.74 (d, $J_{(C-P)}$= 11.3Hz, CH); 141.80 (d, $J_{(C-P)}$= 12.6Hz, C). Mass Spec. (e/z) : Obs Mass 819.8140; Calc Mass 819.8159: $M^+ = (L)W(CO)_5$; 736 ($M^+ - 3CO$).

Synthesis of [2,6-Bis-(2′-iodophenyl)-4-tolylphosphinine]pentacarbonyltungsten(0) (12):

Compound (**12**) was made by the same procedure as that for complex (**9**) except phosphinine (**8**) was used instead. The reaction gave [2,6-bis-(2′-iodophenyl)-4-tolylphosphinine]pentacarbonyltungsten(0) (**12**) as an orange solid that contains two rotamers (79mg, 51%). Purity 95%. Only data for the major rotamer was isolated. ^{31}P NMR (202.5 MHz, $CDCl_3$): $\delta = 164.9$ (s, $J_{(P-W)}$= 280.9Hz). ^{1}H NMR ($CDCl_3$): $\delta =$ 2.28 (s, 3 H, CH_3); 7.13-7.16 (m, 4 H); 7.27-7.30 (m, 4 H); 7.38-7.44 (m, 4 H); 7.93 (d, 2 H, $J_{(H-P)}$= 17.6Hz, CH 3/5). ^{13}C NMR ($CDCl_3$): $\delta = 21.22$ (s, CH_3); 127.19 (d, $J_{(C-P)}$= 2.5Hz, CH); 128.36 (s, CH); 128.50 (s, CH); 129.88 (s, CH); 130.13 (s, CH); 130.50 (s, C); 131.33 (d, $J_{(C-P)}$= 7.5Hz, CH); 136.85 (s, C); 137.30 (d, $J_{(C-P)}$= 12.6Hz, C); 139.52 (s, CH); 139.76 (s, C); 145.32 (s, C); 170.12 (d, $J_{(C-P)}$= 8.8Hz, C 2/6); 193.69 (s, *cis*-CO). IR (Petrol) cm^{-1}: 2076.4 (w, CO); 1983.1 (sh, CO); 1954.2 (st, CO); 1261.8; 1171.2; 1147.9; 815.5; 739.7. Mass Spec. (e/z): Obs Mass 774.8265; Calc Mass 774.8276: M^+ = W(L).

Synthesis of [2,6-Bis-(2′-fluorophenyl)-4-tolylphosphinine]chloro(COD)rhodium(I) (13):

To a solution of chloro(COD)rhodium(I) dimer (66mg, 0.13mmol) in DCM (10ml) was added phosphinine (**5**) (0.1g, 0.27mmol) in DCM (10ml). The reaction mixture was allowed to stir at room temperature for 18h. After which time, the reaction was pumped to dryness and washed with petrol. The resulting yellow material was then recrystallised from petrol to yield a yellow solid of [2,6-bis-(*2′*-fluorophenyl)-4-tolylphosphinine]chloro(COD)rhodium(I) (**13**), (0.11g, 67%). Purity 90%. ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 186.9 (d, $J_{(P-Rh)}$= 184.3Hz). ^{1}H NMR ($CDCl_3$): δ 1.6 – 1.7 (m, 4H, COD-aliphatic); 2.0 (m, 4H, COD-aliphatic); 2.3 (s, 3H, CH_3); 3.3 (s, 2H, COD-olefin); 5.4 (s, 2H, COD-olefin); 6.96 – 7.11 (m, 4H, Ar-H); 7.36 (m, 2H, Ar-H); 7.42 (m, 4H, Ar-H); 8.07 (d, 2H, $J_{(H-P)}$= 21.5Hz, CH 3/5); 8.2 (m, 2H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 21.2 (s, CH_3); 28.7 (s, COD-aliphatic); 33.0 (s, COD-aliphatic); 71.3 (d, $J_{(C-Rh)}$= 12.6Hz, COD-olefin); 106.4 (s, COD-olefin); 115.7 (d, $J_{(C-P)}$= 22.6Hz, CH); 124.3 (s, CH); 127.3 (s, C); 127.5 (s, CH); 128.0 (s, C); 129.8 (s, CH); 130.3 (s, CH); 133.3 (s, CH); 137.2 (s, C); 138.0 (s, CH); 158.1 (s, C); 160.0 (s, C). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = -116.6. IR (Nujol) cm^{-1}: 1260.1, 1091.9, 1020.9, 801.5.

Synthesis of [2,6-Bis-(2′-chlorophenyl)-4-tolylphosphinine]chloro(COD)rhodium(I) (14):

Complex (**14**) was synthesised by the same procedure as (**13**) to yield [2,6,-bis-(*2′*-chlorophenyl)-4-tolylphosphinine]chloro(COD)rhodium(I) (**14**) as an orange-yellow solid (98mg, 61%). Purity 90%. ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 187.5 (d, $J_{(P-Rh)}$= 186.3Hz). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.71 – 1.73 (m, 4H, COD-aliphatic); 1.9

(m, 4H, COD-aliphatic); 2.3 (s, 3H, CH_3); 3.4 (s, 2H, COD-olefin); 5.3 (s, 2H, COD-olefin); 7.2 (d, 4H, $J_{(H-P)}$= 8.1Hz, Ar-H); 7.3 – 7.4 (m, 4H, Ar-H); 7.5 (d, 2H, $J_{(H-P)}$= 7.9Hz, Ar-H); 7.9 (m, 2H, Ar-H); 8.1 (d, 2H, $J_{(H-P)}$= 15.9Hz, CH3/5). ^{13}C NMR ($CDCl_3$): δ = 20.1 (s, CH_3); 28.7 (s, COD-aliphatic); 31.9 (s, COD-aliphatic); 70.4 (d, $J_{(C-Rh)}$= 12.6Hz, COD-olefin); 105.9 (s, COD-olefin); 125.8 (s, CH); 126.4 (s, CH); 127.7 (s, CH); 128.9 (s, CH); 128.7 (s, CH); 128.8 (s, CH)); 131.5 (d, $J_{(C-P)}$= 8.8Hz, C); 132.7 (s, C); 136.4 (s, C); 137.0 (s, CH); 137.2 (s, C); 146.0 (s, C); 157.2 (s, C). IR (Nujol) cm^{-1}: 1260.5, 1057.7, 1032.9, 816.6, 758.1.

Synthesis of [2,6-Bis-(2′-bromophenyl)-4-tolylphosphinine]chloro(COD)rhodium(I) (15):

Complex (**15**) was synthesised by the same procedure as (**13**) to yield [2,6-bis–(2′-bromophenyl)-4-tolylphosphinine]chloro(COD)rhodium(I) (**15**) as an orange-yellow solid (76mg, 51%). Purity 90%. ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 187.3 (d, $J_{(P-Rh)}$= 186.3Hz). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.7 (m, 4H, COD-aliphatic); 2.3 (s, 3H, CH_3); 2.4 (m, 4H, COD-aliphatic); 4.2 (s, 2H, COD-olefin); 5.1 (d, 2H, $J_{(H-P)}$= 3.7Hz, COD-olefin); 7.07 – 7.10 (m, 4H, Ar-H); 7.15 – 7.2 (m, 2H, Ar-H); 7.3 (d, 2H, $J_{(H-P)}$= 8.0Hz, Ar-H); 7.46 (dd, 2H, $^3J_{(H-P)}$= 7.7Hz, $^4J_{(H-Rh)}$= 1.6Hz, CH3/5); 7.49 (d, 2H, $J_{(H-P)}$= 7.3Hz, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 20.1 (s, CH_3); 29.9 (s, COD-aliphatic); 40.3 (s, COD-aliphatic); 77.7 (d, $J_{(C-Rh)}$= 15.1Hz, COD-olefin); 104.3 (s, COD-olefin); 125.3 (s, C); 126.2 (s, CH); 127.1 (s, CH); 128.0 (s, C); 128.1 (s, C); 128.3 (s, CH); 128.9 (s, CH); 130.0 (s, CH); 132.2 (s, CH); 135.3 (s, C); 135.5 (s, CH); 142.3 (s, C); 147.5 (s, C). IR (Nujol) cm^{-1}: 1260.0, 1097.6, 1021.6, 803.8.

Synthesis of [2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphinine]pentacarbonyltungsten(0) (16):

A solution of the phosphinine (0.1g, 0.26mmol) in THF was added at room temperature to a solution of $W(CO)_5THF$ (90mg, 0.26mmol) in THF. The reaction mixture was stirred at room temperature for 18h, after which the solution was pumped to dryness. The crude material was washed with petrol and the resulting material was recrystallised from petrol, to give [2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphinine]pentacarbonyltungsten(0) as a yellow solid, and two rotamers at room temperature (0.16g, 87%). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 165.65 (s, $J_{(P-W)}$= 280.8Hz, major rotamer); 165.79 (s, $J_{(P-W)}$= 275.4Hz, minor rotamer). ^{1}H NMR ($CDCl_3$): δ = 2.11 (s, 6H, CH_3); 2.28 (s, 6H, CH_3); 6.99-7.02 (m, 3H, Ar-H); 7.10 (t, 2H, $J_{(H-H)}$= 7.6Hz, Ar-H); 7.25 (d, 2H, $J_{(H-H)}$= 7.3Hz, Ar-H); 7.31 (t, 2H, $J_{(H-H)}$= 7.1Hz, Ar-H); 7.45 (d, 2H, $J_{(H-H)}$= 7.5Hz, Ar-H); 7.85 (dd, $J_{(H-H)}$= 3.2Hz, $J_{(H-P)}$= 17.8Hz, CH3/5). ^{13}C NMR ($CDCl_3$): δ = 20.76 (s, CH_3); 21.26 (s, CH_3); 126.55 (s, CH); 127.42 (s, CH); 128.20 (s, CH); 129.15 (s, CH); 131.20 (d, $J_{(C-P)}$= 7.5Hz, CH); 131.54 (s, CH); 135.79 (d, $J_{(C-P)}$= 7.5Hz, C); 136.16 (d, $J_{(C-P)}$= 10.1Hz, CH); 138.00 (s, C); 138.66 (s, C); 140.90 (s, C); 168.28 (d, $J_{(C-P)}$= 10.1Hz, C2/6); 191.20 (s, CO-*trans*); 194.09 (d, $^{2}J_{(C-P)}$= 8.8Hz, $^{1}J_{(C-W)}$= 125.8Hz, CO- *cis*). IR (petrol) cm^{-1}: 2074.1 (st, CO); 1982.5 (sh, CO); 1947.8 (b, CO); 1260.3; 1095.4; 1020.2; 802.2; 698.1.

Synthesis of [2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphinine]chloro(COD)rhodium(I) (17):

To a solution of chloro(COD)rhodium(I) dimer (0.13g, 0.26mmol) in DCM (10ml) was added the phosphinine (0.2g, 0.52mmol) in DCM (10ml). The reaction mixture was allowed to stir at room temperature for 18h. After which time, the reaction was pumped to dryness and washed with petrol. The resulting yellow material was then recrystallised from petrol to yield a yellow solid of [2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphinine]chloro(COD)rhodium(I) (**17**), (60mg, 37%).^{31}P NMR (121.7 MHz, $CDCl_3$): δ = 187.94 (d, $J_{(P-Rh)}$= 181.7Hz). ^{1}H NMR ($CDCl_3$): δ = 1.62-1.70 (m, 4H, COD-aliphatic); 2.15-2.28 (m, 4H, COD-aliphatic); 2.27 (s, 6H, CH_3); 2.32 (s, 6H, CH_3); 3.35 (s, 2H, COC-olefin); 5.19 (s, 2H, COD-olefin); 7.08-7.10 (m, 6H, Ar-H); 7.26 (d, 2H, $J_{(H-H)}$= 6.8Hz, Ar-H); 7.33 (t, 2H, $J_{(H-H)}$= 7.2Hz, Ar-H); 7.44 (d, 2H, $J_{(H-H)}$= 7.6Hz, Ar-H); 7.51 (d, 2H, $J_{(H-H)}$= 7.6Hz, Ar-H); 7.85 (d, 2H, $J_{(H-P)}$= 16.8Hz, CH3/5). ^{13}C NMR ($CDCl_3$): δ = 21.13 (s, CH_3); 21.30 (s, CH_3); 28.09 (s, COD-aliphatic); 30.95 (s, COD-aliphatic); 70.82 (d, $J_{(C-Rh)}$= 12.6Hz, COD-olefin); 105.23 (dd, $J_{(C-P)}$= 7.5Hz, $J_{(C-Rh)}$= 12.6Hz, COD-olefin); 126.27 (s, CH); 127.52 (s, CH);

127.92 (s, CH); 128.71 (s, C); 129.07 (s, CH); 131.18 (s, CH); 131.61 (d, $J_{(C-P)}$= 11.3Hz, CH); 135.53 (d, $J_{(C-P)}$= 7.5Hz, C); 136.15 (d, $J_{(C-P)}$= 12.6Hz, CH); 137.52 (d, $J_{(C-P)}$= 13.8Hz, C); 138.09 (s, C); 141.42 (s, C); 162.09 (s, C). IR (Nujol) cm^{-1}: 1261.2; 1155.2; 1030.8; 815.7; 763.7; 698.1.

*Synthesis of [2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphinine]chloro(COD)iridium(I) (**18**):*

To a solution of chloro(COD)iridium(I) dimer (0.17g, 0.26mmol) in DCM (10ml) was added the phosphinine (0.2g, 0.52mmol) in DCM (10ml). The reaction mixture was allowed to stir at room temperature for 18h. After which time, the reaction was pumped to dryness and washed with petrol. The resulting yellow material was then recrystallised from petrol to yield a yellow solid of [2,6-bis-(2′,4′-dimethylphenylphosphinine)-4-phenyl]chloro(COD)iridium(I) (**18**), (70mg, 37%).^{31}P NMR (121.7 MHz, $CDCl_3$): δ = 176.41. ^{1}H NMR ($CDCl_3$): δ = 1.45 (m, 4H, COD-aliphatic); 2.17-2.23 (m, 4H, COD-aliphatic); 2.27 (s, 6H, CH_3); 2.29 (s, 6H, CH_3); 2.93 (s, 2H, COC-olefin); 4.89 (s, 2H, COD-olefin); 7.00-7.04 (m, 3H, Ar-H); 7.26 (d, 2H, $J_{(H-H)}$= 7.3Hz, Ar-H); 7.32 (t, 2H, $J_{(H-H)}$= 8.4Hz, Ar-H); 7.38 (d, 2H, $J_{(H-H)}$= 7.6Hz, Ar-H); 7.45 (d, 2H, $J_{(H-H)}$= 7.2Hz, Ar-H); 7.92 (d, 2H, $J_{(H-P)}$= 19.6Hz, CH3/5). ^{13}C NMR ($CDCl_3$): δ = 21.22 (s, CH_3); 21.31 (s, CH_3); 29.35 (s, COD-aliphatic); 33.98 (s, COD-aliphatic); 54.71 (s, COD-olefin); 95.33 (s, $J_{(C-P)}$= 15.1Hz, COD-olefin); 126.11 (s, CH); 127.40 (s, $J_{(C-P)}$= 2.5Hz, CH); 127.90 (s, CH); 128.72 (s, C); 129.11 (s, CH); 131.06 (s, CH); 131.61 (d, $J_{(C-P)}$= 10.1Hz, CH); 135.54 (d, $J_{(C-P)}$= 7.5Hz, C); 137.10 (d, $J_{(C-P)}$= 12.6Hz, CH); 137.19 (d, $J_{(C-P)}$= 5.0Hz, C); 138.05 (s, C); 141.37 (d, $J_{(C-P)}$= 5.0Hz, C); 158.95 (d, $J_{(C-P)}$= 18.9Hz, C2/6). IR (Nujol) cm^{-1}: 1262.2; 1156.1; 1032.7; 815.7; 764.6; 698.1.

*Synthesis of di-{[2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphinine]carbonyl(μ-chloro)rhodium(I)} (**19**):*

To a solution of dicarbonyl(chloro)rhodium(I) dimer (0.10g, 0.26mmol) in DCM (10ml) was added the phosphinine (0.2g, 0.52mmol) in DCM (10ml). The reaction mixture was allowed to stir at room temperature for 18h. After which time, the reaction was pumped to dryness and washed with petrol. The resulting crude yellow solid was recrystallised from petrol to yield di-{[bis-2,6-(2′,4′-dimethylphenyl)-4-phenylphosphinine]carbonyl(μ-chloro)rhodium(I)} (**19**) as a yellow solid, (0.18g, 74%).^{31}P NMR (121.7 MHz, $CDCl_3$): δ = 178.77 (d, $J_{(P\text{-}Rh)}$= 223.4Hz). ^{1}H NMR ($CDCl_3$): δ = 2.25 (s, 12H, CH_3); 2.30 (s, 12H, CH_3); 6.90-7.00 (m, 10H, Ar-H); 7.29 (d, 4H, $J_{(H\text{-}H)}$= 7.2Hz, Ar-H); 7.36 (t, 4H, $J_{(H\text{-}H)}$= 7.6Hz, Ar-H); 7.48 (d, 4H, $J_{(H\text{-}H)}$= 7.2Hz, Ar-H); 7.86 (d, 4H, $J_{(H\text{-}P)}$= 10.8Hz, CH 3/5). ^{13}C NMR ($CDCl_3$): δ = 21.18 (s, CH_3); 126.49 (s, CH); 127.35 (s, CH); 127.94 (s, CH); 128.55 (s, C); 129.08 (s, CH); 131.22 (s, CH); 131.57 (s, CH); 135.69 (s, C); 136.73 (s, C); 137.36 (d, $J_{(C\text{-}P)}$= 8.8Hz, CH); 138.24 (s, C); 141.15 (s, C); 161.66 (d, $J_{(C\text{-}P)}$= 23.9Hz, C2/6); 206.86 (s, CO). IR (petrol) cm^{-1}: 1999.8 (st, CO); 1261.2; 1095.4; 802.2; 698.1.

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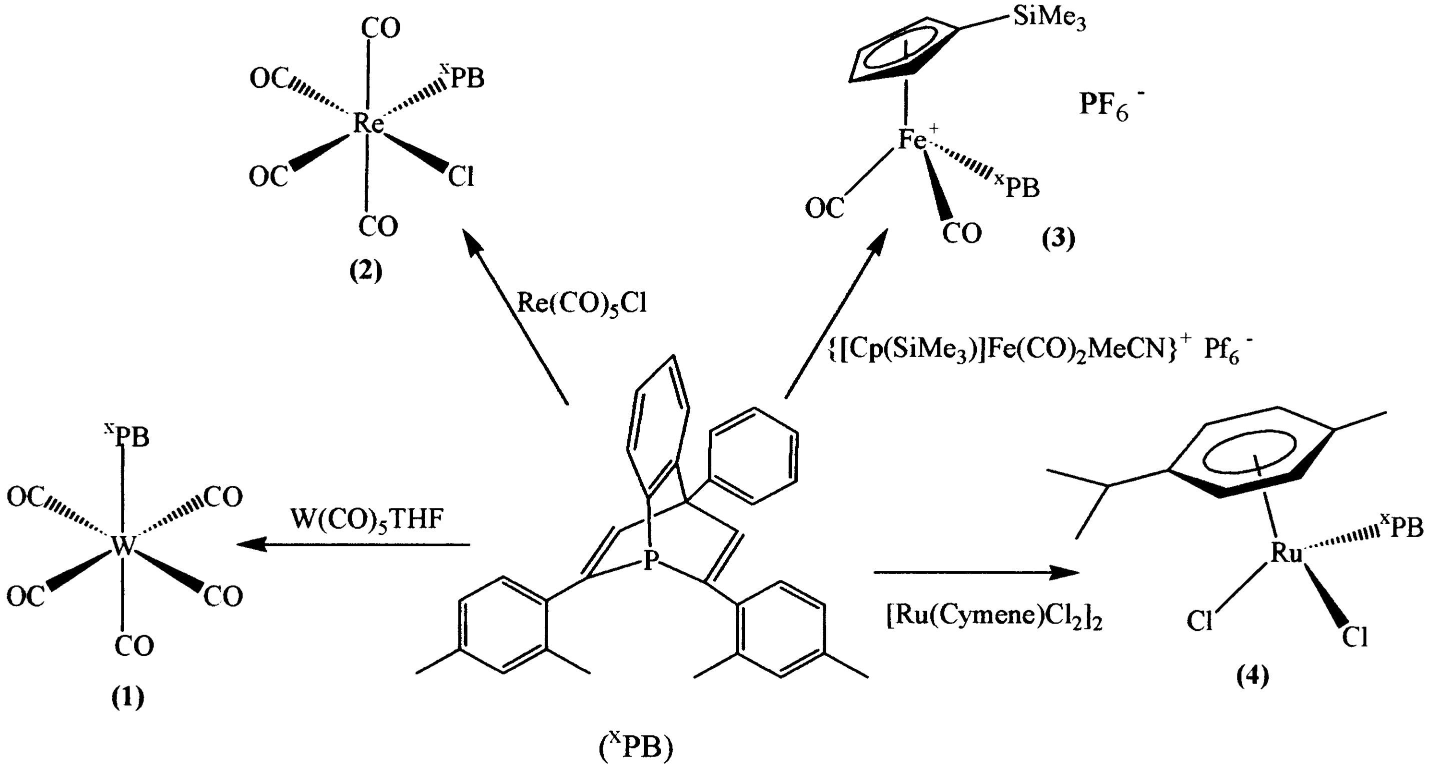
CHAPTER 3

A SYSTEMATIC SURVEY OF THE COORDINATION CHEMISTRY OF 2,6-DIXYLYL-4-PHENYLPHOSPHABARRELENE WITH TRANSITION METAL CENTRES

3.1 Introduction

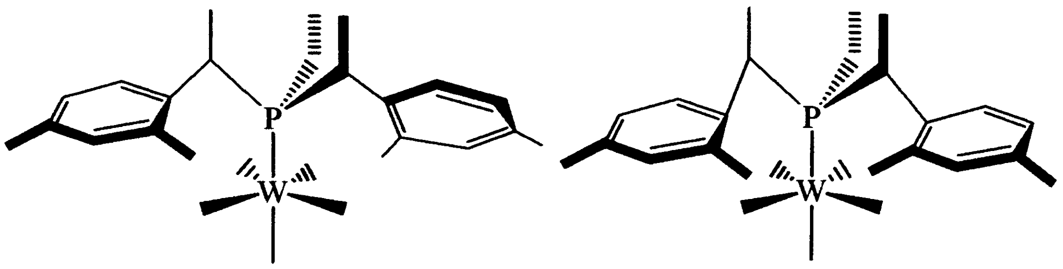
Following on from our work on the 2,6-dixylyl–4-phenylphosphinine, and our discovery of its unique coordination chemistry, we decided to use the phosphinine as a precursor to synthesise the 2,6-dixylyl-4-phenylphosphabarrelene *via* the procedure established by Breit *et. al.*[1] Therefore, considering there was very little literature on the coordination chemistry of phosphabarrelenes, this chapter presents our findings on a systematic survey of the coordination chemistry of the 2,6-dixylyl-4-phenylphosphabarrelene with a range of transition metal centres.

3.2 Transition metal complexes of Groups VI, VII and VIII – Results and Discussion



Scheme 3.1.

The mono-phosphabarrelenepentacarbonyltungsten(0) complex **(1)** was formed by the reaction of dixlylphosphabarrelene, with the precursor $W(CO)_5THF$ complex made *via* the photolysis of $W(CO)_6$ in THF, at room temperature. (Scheme 3.1.) **(1)** was isolated after recrystallisation from 40/60 petroleum spirit and was fully characterised by spectroscopic means. The presence of the complex was determined by a downfield shift in the ^{31}P NMR spectrum of the complex (-7.2 ppm), with tungsten satellites, compared to the singlet observed for the free ligand (-58 ppm). Interestingly and unlike the analogous complex of the parent phosphinine, only one single peak is seen in the ^{31}P NMR spectrum of the complex. However, upon cooling the sample this single peak splits at –34 ^{0}C, and upon further cooling two clear singlets are observed at 7.8 and 7.6 ppm, in a ratio of approximately 2:1. As with the analogous phosphinine complex, this observation can be explained by the presence of rotamer isomerisation (scheme 3.2). One, the *cis* isomer, would be where both xylyl groups are on the same side of the phosphabarrelene ring as each other, and the other, the *trans* isomer, is where the two xylyl groups are on opposite sides of the phosphabarrelene ring. It is also observed, in both the phosphinine and the phosphabarrelene complex that one peak is more dominate than the other. A possible explanation for this is that one of the rotamers is more thermodynamically favoured that the other. If our explanation of *cis* and *trans* isomers is true then it could be postulated that the *trans* isomer would be the more favoured and so constitute the more dominant peak seen in the ^{31}P NMR spectrum. This is because the configuration of the two xylyl groups on opposite sides of the phosphabarrelene ring would be the least sterically hindered, and hence the most thermodynamically favoured. $\Delta G^{\#}$ for this rotation barrier was calculated by the same method used in Chapter 2, and was estimated to be 48.2 $kjmol^{-1}$.



Trans Rotamer

Cis Rotamer

Scheme 3.2.

In addition to this, the fact that a single peak is observed for the phosphabarrelene species in the ^{31}P NMR spectrum at room temperature, compared to two peaks for the analogous phosphinine system suggests a steric difference between the two ligands. This was confirmed upon comparing the free activation energy ($\Delta G^{\#}$) for this rotation energy barrier. $\Delta G^{\#}$ for the parent dixylylphosphinine in the LW(CO)$_5$ complex was determined to be 74.9 kjmol^{-1}, whereas in the dixylylphosphabarrelene analogous complex it was determined to be 48.2 kjmol^{-1}. A possible explanation for this is that the structure of the phosphabarrelene is non-planar and the phosphorus atom is sp^3 hybridised, compared to the planar and sp^2 hybridised phosphorus atom of the phosphinine. This has the affect on the dixylyl groups of being "pulled back" further away from the metal centre, and this gives them a greater degree of free rotation as observed in the LW(CO)$_5$ complexes.

To understand further the nature of the tungsten-phosphorus bond in phosphabarrelenepentacarbonyltungsten complexes, the $^1J_{P\text{-}W}$ and the carbonyl stretching frequencies of **(1)** were compared with analogous complexes of phosphines and phosphites. There have been a series of papers published in an attempt to determine if there is a correlation between the σ-donor / π-acceptor abilities of a series of phosphorus ligands and their $^1J_{P\text{-}W}$, and/or their $\nu_{(CO)}$ stretching frequencies in phosphorus-pentacarbonyltungsten complexes.[2] Grim *et al.* showed that there was a linear correlation between the strongest carbonyl stretching frequency (the *E* mode) and the $^1J_{P\text{-}W}$ in phosphine and phosphite complexes of pentacarbonyltungsten[3] (Table 3.1.)

Table 3.1. *E* mode carbonyl stretching frequencices versus phosphorus-tungsten coupling constants in $LW(CO)_5$.

Ligand (L)	***E* (cm^{-1})**	**J$_{(P-W)}$ (Hz)**
$(PhO)_3P$	1959	411
$(MeO)_3P$	1953	398
$(EtO)_3P$	1949	391
$(Bu^nO)_3P$	1947	390
$(Pr^IO)_3P$	1944	378
$(MeO)_2PhP$	1950	323
$(Me_2N)_3P$	1950	297
$(Et_2N)_3P$	1948	296
$(MeO)Ph_2P$	1945	280
Ph_3P	1942	280
dixylylphosphabarrelene	**1942**	**265**
$MePh_2P$	1939	245
$EtPh_2P$	1938	240
Ph_2Pr^iP	1937	240
Ph_2Bu^nP	1938	250
Ph_2Bu^tP	1937	240
$PhBu^n_2P$	1937	235
Bu^n_3P	1934	200

The values of the J$_{P-W}$ coupling constant and the $\nu_{(CO)}$ (*E* mode) of 265Hz and 1942cm^{-1}for the phosphabarrelenepentacarbonyltungsten complex lies between those of triphenylphosphine and diphenyl(methyl)phosphine. Grim *et al.* suggest that better π-acceptor ligands give a higher *E* mode carbonyl stretching frequency and a larger ^{1}J$_{P-W}$ coupling constant. This was considered contradictory as $\nu_{(CO)}$ stretching frequencies were always considered to be a measure of π-acceptor ability, and phosphorus coupling constants to metal centres are known to increase with increasing *s* character at the phosphorus centre; i.e. a better σ-donor should create a shorter / stronger σ-bond to the metal and therefore the coupling constant would be higher.

However, Grim *et al.* suggest that the effects are synergetic, thus increasing the π backbonding ability of the metal to the phosphorus atom has the effect of shortening the metal-phosphorus bond which, in effect, strengthens the metal-phosphorus σ-bond and thus increases the size of the coupling constant. Therefore from the position of our phosphabarrelene ligand in this series, it can quite clearly be suggested that our ligand has π-acceptor abilities similar to that of triphenylphosphine. This is a reasonable assertion as in both ligand systems you have a coordinated sp^3 hybridised phosphorus atom bound to three sp^2 hybridised carbon atoms. Thus it is also reasonable to assume that the predominant differences between triphenylphosphine and our phosphabarrelene are due to sterics, as the phosphabarrelene is clearly a more sterically bulky ligand. This extra steric bulk is a result of the pendant xylyl groups on the phosphabarrelene core at the 2 and 6 positions, which may play a role in hindering the nature of the bond formed between the phosphorus and the tungsten centre. It is also well known that the angle of the carbons at the phosphorus has an effect on the coupling constants of phosphorus ligands. An opening of the angle causes an increase in the σ-donor ability of the phosphorus atom and thus increases its coupling constant to a metal centre. Due to the extra steric bulk of our phosphabarrelene ligand compared to triphenyl phosphine it is reasonable to assume that the angle at the phosphorus in triphenyl phosphine will be relative to our phosphabarrelene. Hence the relatively greater s character at the phosphorus atom causes a slight increase in the $^1J_{P\text{-}W}$ of the (triphenylphosphine)(pentacarbonyl)tungsten(0) complex compared to our analogous phosphabarrelene complex.

Grim has also examined the relationship between the effect of substituted aryl phosphines and their ^{31}P NMR chemical shifts and $\nu_{(CO)}$ stretching frequencies in $W(CO)_5(PR_3)$ complexes.[4] Grim found that there is a correlation between the basicity of the ligands and their ^{31}P NMR and IR spectra, such that the less basic triaryl phosphines (i.e. the better π-acceptor phosphine ligands) give a higher value for $^1J_{P\text{-}W}$ as well as a higher *E* mode carbonyl stretching frequency. He again explained this by the same synergtic effect argument as cited above, i.e. greater π-acceptor ability leads to greater metal back bonding which strengthens the metal-phosphorus σ-bond in phosphine-pentacarbonyltungsten complexes. Table 3.2 compares Grim's data of the

E mode of carbonyl stretching frequencies with their $J_{P\text{-}W}$ in the same manner as before.

Table 3.2. *E* mode of carbonyl stretching frequencies versus phosphorus-tungsten coupling constants for $LW(CO)_5$.

Ligand (L)	**$J_{(P\text{-}W)}$ (Hz)**	***E* mode (cm^{-1})**
$(3\text{-}CF_3C_6H_4)_3P$	266	1947
dixylylphosphabarrelene	**265**	**1942**
$(4\text{-}CF_3C_6H_4)_3P$	258	1948
$(4\text{-}ClC_6H_4)_3P$	254	1944
$(4\text{-}CH_3C_6H_4)_3P$	250	1941
$(4\text{-}CH_3SC_6H_4)_3P$	240	1940
$(4\text{-}^tBuC_6H_4)_3P$	236	1939

On comparison of our phosphabarrelene ligand with this data it can clearly be seen that our ligand fits with the aryl phosphines that have the higher *E* mode of carbonyl stretching frequencies and the higher $^1J_{P\text{-}W}$ values. Thus it is reasonable to suggest that the relative basicity of our phosphabarrelene ligand is weak compared with other triaryl phosphines. Thus again suggesting that our phosphabarrelene ligand shows a relative strong π-acceptor ability and a relatively weak σ-donor ability compared to triaryl phosphines. Hence it can be postulated that phosphabarrelenes can be considered to be a sterically bulky version of triphenylphosphine as ligands for transition metal coordination chemistry.

To the best of our knowledge there are no reported complexes of phosphabarrelenes with any of the transition metals of group VII. Therefore in the chloro(dixylyphosphabarrelene)(tetracarbonyl)rhenium(I) complex **(2)** we report the first phosphabarrelene complex of a group VII transition metal. **(2)** was made by refluxing the free phosphabarrelene with chloropentacarbonylrhenium(I) for 18h (scheme 3.1). The desired complex precipitated from petrol and was fully characterised by spectroscopic means. The ^{31}P NMR spectrum of the complex clearly exhibits the characteristic downfield shift from –58 ppm, to –23 ppm upon coordination of the phosphabarrelene ligand. In addition to this the ^{1}H NMR spectrum shows a downfield shift in the doubled doublet associated with the proton at the C-8 position. This again is a characteristic observation upon the coordination of phosphabarrelenes to most transition metal centres, although the extent of the shift upon coordination is dependant upon the complex (see later.) The three carbonyl resonances in the ^{13}C NMR spectrum are assigned to the three carbonyls *cis* to the phosphabarrelene, the carbonyl *trans* to the phosphabarrelene, and the carbonyl *trans* to the chloride. Thus the carbonyls *trans* to the phosphabarrelene exhibits a large $^{2}J_{(C-P)}$ coupling constant of 64 Hz, whereas the carbonyl *trans* to the phosphabarrelene exhibit a smaller coupling constant of 13 Hz. This observation is common for complexes of this type and was also observed for our phosphabarrelene(pentacarbonyl)tungsten(0) complex, where the *trans* carbonyls to the ligand had a large coupling constant (around 60 Hz), and those carbonyls *cis* had a small coupling constant of around 13 Hz. In addition, there relative intensity of the carbonyl peak assigned to the *cis* carbonyls is roughly three times the size of either of the peaks assigned to the *trans* carbonyls. The other *trans* carbonyl peak is too weak in intensity to discern any coupling.

The infra-red spectrum of **(2)** shows four carbonyl stretching frequencies which is in agreement with other complexes of this type.[5] On comparison of our complex with the analogous triphenyl phosphine complex, it can be seen that the infra red data for both complexes are very similar, reinforcing our hypothesis that the phosphabarrelene is a similar ligand in terms of electronic properties to that of triphenylphosphine. Thus the carbonyl stretching frequencies here seem to show that the phosphorus-rhenium bond in our complex and the analogous triphenyl phosphine are very similar in terms of their σ-donor and π-acceptor properties as show by the similar effect on the remaining carbonyl groups.

	Carbonyl Stretching Frequencies (cm^{-1})
$Re(CO)_4Cl(^{x}PB)$	2109 ; 2023 ; 2005 ; 1922.
$Re(CO)_4Cl(PPh_3)$	2106 ; 2018 ; 2002 ; 1945.[5]

The number and frequency of the carbonyl stretches also gives an indication of the conformation of our complex. In the same paper the authors suggest that the presence of four carbonyl stretching frequencies in the range 2150-1900 cm^{-1}, supports the *cis* configuration of the complex.[5] This is because $Re(CO)_4X(L)$ has C_3 symmetry which gives rise to four modes of stretching: 3A′ and A″. They go on to state that the A′(1) band could be assigned to the lowest stretching frequency and the highest stretching frequency to A′(3) band. Therefore it is reasonable to assume, based on the ^{13}C NMR and IR spectroscopic data, that our complex is the *cis*-chloro(dixylylphosphabarrelene)(tetracarbonyl)rhenium(I) complex.

The (η^5-$C_5H_4SiMe_3$)(dicarbonyl)(dixylyphosphabarrelene)iron(II) hexafluorophosphate complex **(3)** was synthesised *via* the addition of the phosphabarrelene to a solution of the (η^5-$C_5H_4SiMe_3$)(acetonitrile)(dicarbonyl)iron hexafluorophosphate precursor in dichloromethane (scheme 3.1). The desired complex, which to the best of our knowledge is the first phosphabarrelene-iron (II) complex was isolated and its structure elucidated by X-ray crystallography (figure 3.1). The ^{31}P NMR spectrum of the complex shows a characteristic upfield coordination shift to 10.6 ppm. The ^{1}H NMR was broad at room temperature but sharpened sufficiently upon cooling to –50 ^0C (223 K) allowing assignments to be made. This suggests there is some form of fluxional process occurring, but no broadening, or rotamers are seen in the ^{31}P NMR spectrum at room temperature. Thus whatever processes are occurring they do not affect the coordination of the ligands to the iron centre. In the ^{13}C NMR spectrum however, two of the quaternary carbons of the phosphabarrelene could not be assigned. This may be due to coalescence of the signals or is perhaps due to the inherent weakness of quaternary carbons in the NMR spectrum. This may also explain the absence of the carbon peaks of the carbonyl groups as well in our spectrum.

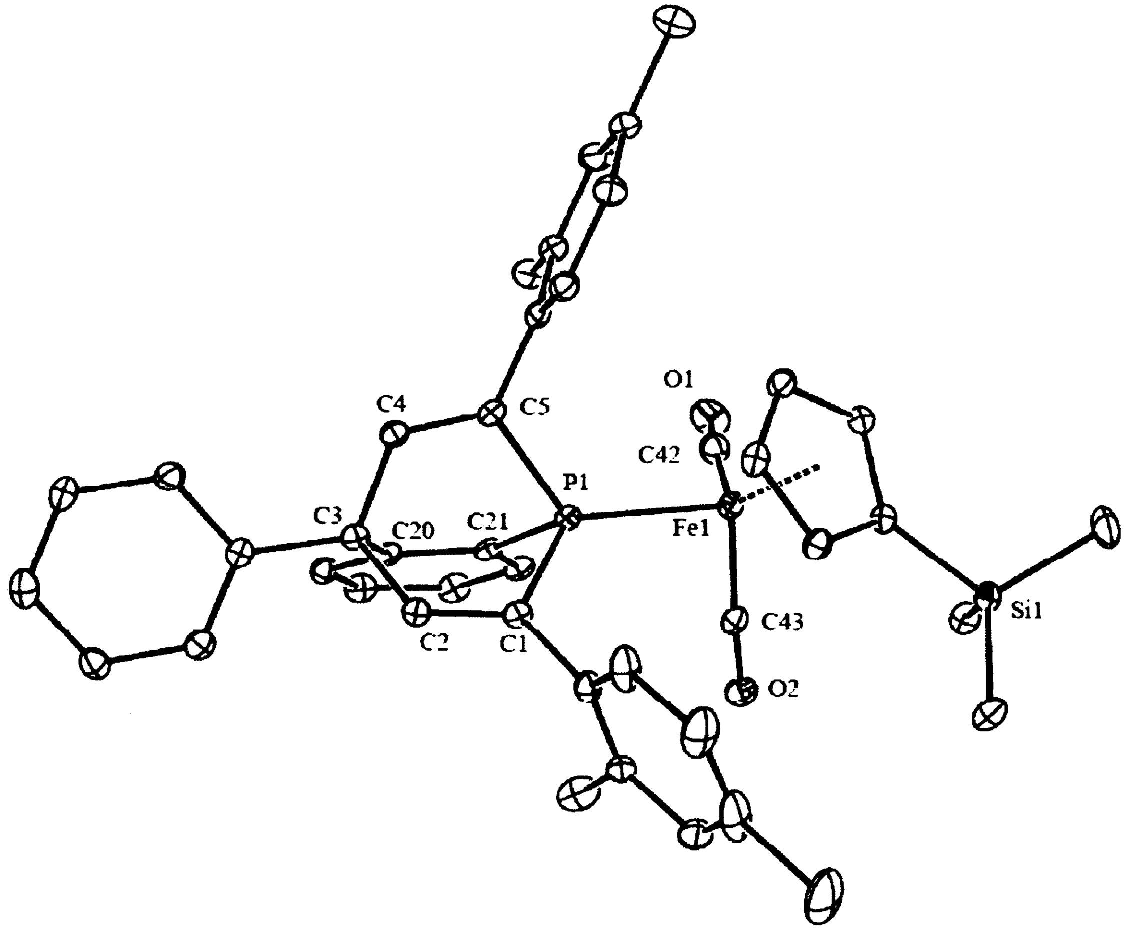


Figure 3.1. ORTEP representation of **(3)**. Hydrogens have been omitted for clarity. Selected bond lengths (Å): Fe(1)-P(1) 2.2177(13); P(1)-C(21) 1.824(5); P(1)-C(1) 1.850(5); P(1)-C(5) 1.851(5); Fe(1)-C(43) 1.775(5); Fe(1)-C(42) 1.787(5); O(1)-C(42) 1.132(6); O(2)-C(43) 1.137(6). Selected bond angles (deg): C(21)-P(1)-Fe(1) 118.93(15); C(1)-P(1)-Fe(1) 119.77(15); C(5)-P(1)-Fe(1) 121.52(16); C(43)-Fe(1)-P(1) 92.09(16); C(42)-Fe(1)-P(1) 94.90(17); O(1)-C(42)-Fe(1) 175.1(5); O(2)-C(43)-Fe(1) 176.6(5).

The infra-red data of **(3)** again compares to a similar complex of triphenylphosphine. The phosphine complex has an ethyl group on the Cp ring, instead of a trimethylsilyl group, but this is unlikely to have a great affect on the carbonyl groups.[6] Thus our complex exhibits two carbonyl stretching frequencies at 2055 and 2013 cm^{-1}, whereas the triphenylphosphine complex has two resonances at 2052 and 2008 cm^{-1} respectively. Therefore despite the minor structural differences it can clearly be seen that the phosphabarrelene is again showing similar electronic properties as a ligand to triphenylphosphine.

This similarity continues on comparison of the crystal structure of the two complexes. Again, there are minor structural difference but these appear to be insignificant (figure 3.1). Thus both crystal structures exhibit a three legged piano stool configuration, which is analogous to the parent $[CpFe(CO)_2PPh_3]^+ Cl^-$ species.[7] Comparison of the bond lengths and bond angles reveals very little difference between the two apart from the comparison of the iron-phosphorus bond length. **(3)** has an iron-phosphorus bond length of 2.2177(13) Å, whereas that on the triphenylphosphine derivative is 2.2380(15) Å. This shorter bond between the phosphabarrelene and the iron centre relative to triphenylphosphine could be due to a slight increase in the π-acceptor properties of the phosphabarrelene relative to triphenylphosphine. It is also worth noting that the analogous trimethyl phosphite complex[8] exhibits a phosphorus-iron bond length of 2.164(14) Å, which suggests that the increased π-acceptor ability of the phosphite, as well as its small steric bulk relative to the phosphabarrelene, allows it to form an even shorter bond to the iron centre. This also reinforces our own suggestion, that the electronic properties of the phosphabarrelenes seem to be comparable to triphenylphosphine.

Also in Group VIII we have synthesised the dichloro(cymene)(dixylyphosphabarrelene)ruthenium(II) complex **(4)** by reaction of the tetrachlorobis(4-cymene)ruthenium(II) dimer with the phosphabarrelene in dichloromethane at room temperature (scheme 3.1). **(4)** was isolated, including a single crystal suitable for X-ray crystallography, and was also fully characterised by spectroscopic means. The ^{31}P NMR spectrum at room temperature is very broad and seems to suggest two peaks around 2 ppm, but upon heating to 80 ^{0}C these two peaks combine and sharpen to a single peak at –5.4 ppm. Coalescence of the two peaks occurs at 60 ^{0}C (333 K), and upon cooling to –50 ^{0}C (223 K), the ^{31}P NMR spectrum of the complex shows two sharp peaks at 4.5 ppm and –7.7 ppm (ratio 10:1). These observations suggest rotamer isomerisation, as was observed with complex **(1)**. Thus the free energy to the activation barrier to rotation ($\Delta G^{\#}$) was calculated *via* our NMR experiments to be 59.8 $kJmol^{-1}$. Also at 223 K it is noteworthy to point out that the peak at 4 ppm is considerable stronger in intensity than the peak at –7 ppm. This would suggest that one of the rotamers is thermodynamically favoured over the other as was the case in the pentacarbonyl(phosphabarrelene)tungsten(0) complex. In the ruthenium case however, it is more difficult to explain the reason for rotameric isomerisation. Therefore it is postulated that the rotamers are due to restricted rotation around the phosphorus-ruthenium bond. Hence it can be assumed that if the benzene ring points "up" towards the cymene ring, this creates a different rotamer than if it points "down" away from the cymene group. Thus given the free rotation of the cymene group on the ruthenium metal, it is reasonable to suggest that if the benzene ring points away from the cymene group this provides a greater degree of steric relief for the complex as a whole and would thus be thermodynamically more favoured. The ORTEP representation of the crystal structure of **(4)**, (figure 3.2), clearly shows the benzene ring pointing away from the cymene group confirming our hypothesis.

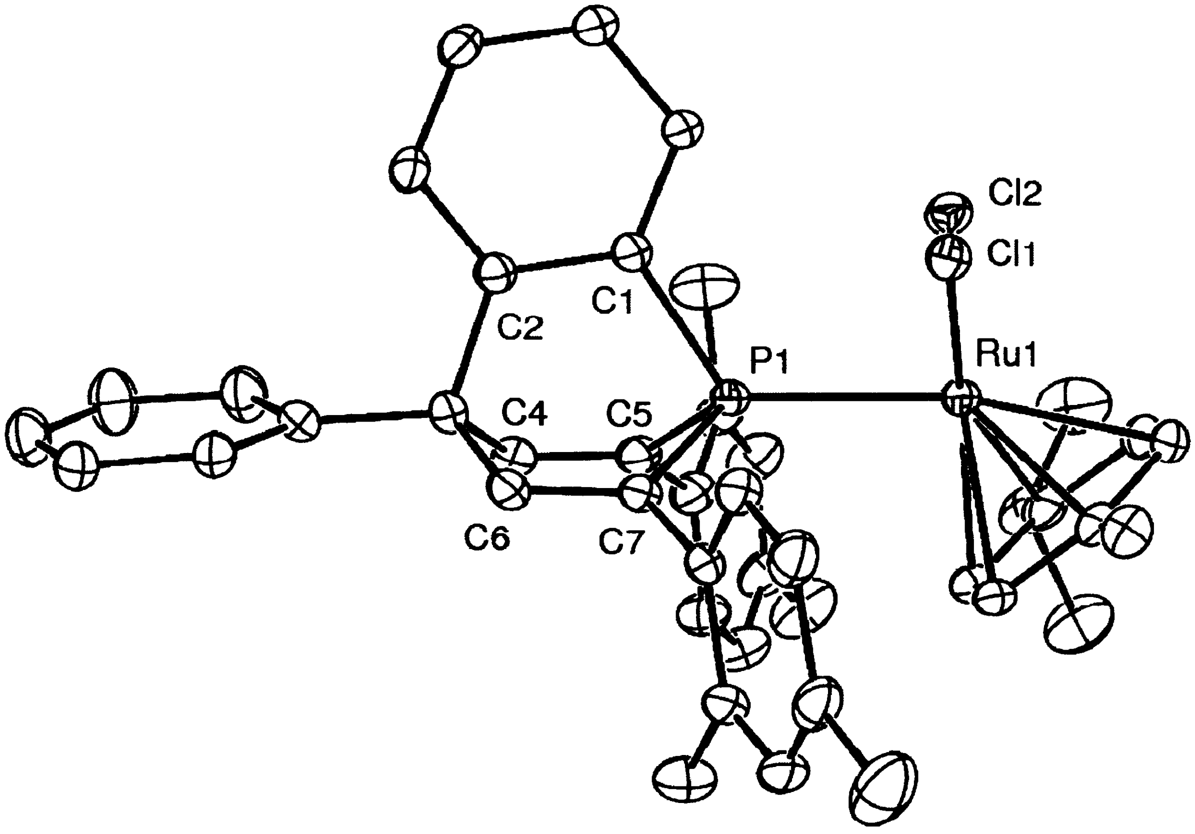


Figure 3.2. ORTEP representation of **(4)**. Hydrogens have been omitted for clarity. Selected bond lengths (Å): P(1)-Ru(1) 2.3619(12); Cl(1)-Ru(1) 2.4043(12); Cl(2)-Ru(1) 2.4044(12); P(1)-C(1) 1.846(4); P(1)-C(5) 1.825(5); P(1)-C(7) 1.862(4).

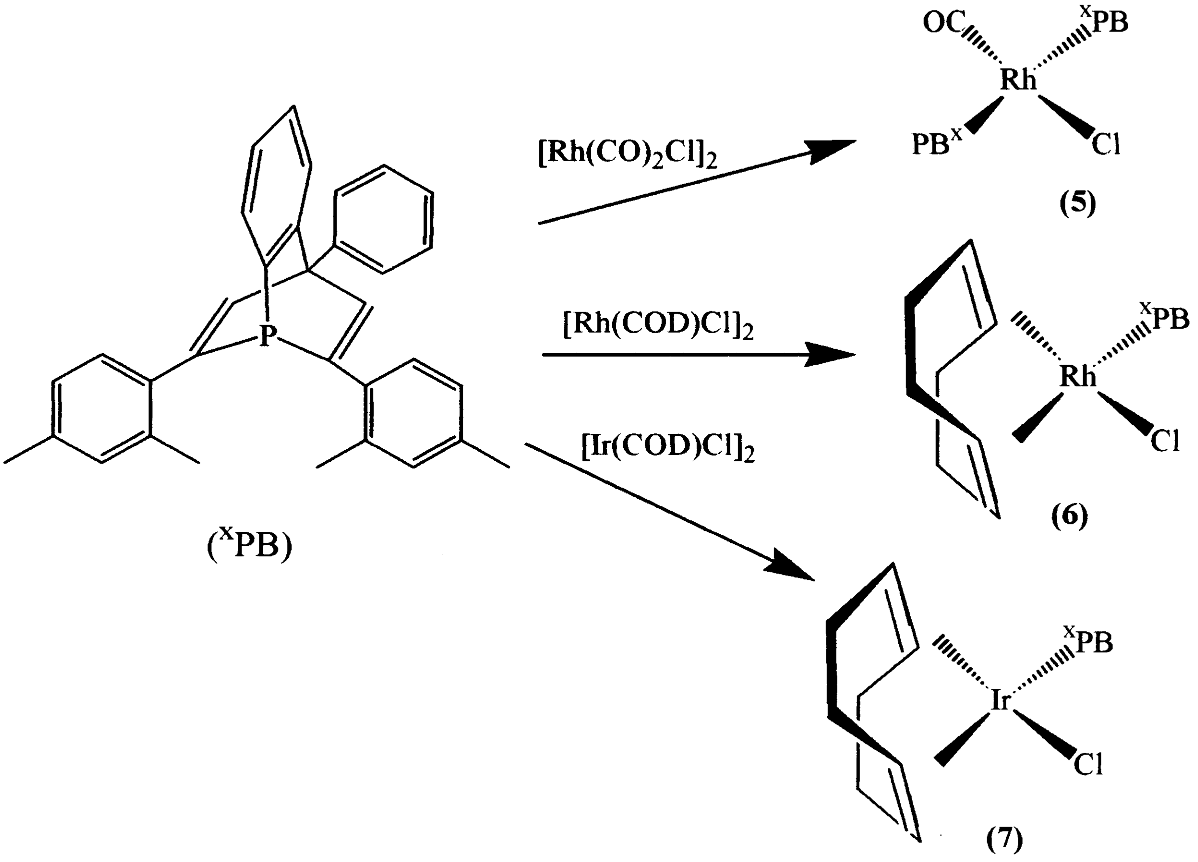
Selected bond angles (deg): P(1)-Ru(1)-Cl(1) 84.15(5); P(1)-Ru(1)-Cl(2) 88.78(5); C(1)-P(1)-Ru(1) 123.09(13); C(5)-P(1)-Ru(1) 121.56(14); C(7)-P(1)-Ru(1) 118.87(14).

On closer inspection of the crystal structure, the complex exhibits a three legged piano stool geometry that is consistent with complexes of this type. On comparison of the phosphorus-ruthenium bond lengths with analogous complexes of tri(*meta*-tolyl)phosphine[9] and triphenylphosphite[10] observations as to the nature of the metal-phosphorus bond can be made. Like with **(3)**, complex **(4)** shows similar phosphorus-ruthenium bond lengths to the phosphine: 2.3619(12) Å for the phosphabarrelene, and 2.379(13) Å for the phosphine. Again this suggests that the phosphabarrelene is showing similar bonding properties to that of triaryl phosphines. As with the iron species, the phosphite analogue exhibits a much shorter bond distance of 2.264(14) Å, clearly demonstrating again that the phosphites are able to form much stronger bonds to transition metal centres than the phosphabarrelenes can.

Finally, using the mathematical procedure established by Mingos,[11] we were also able to calculate the crystallographic cone angle for the phosphabarrelene complexes **3** and **4**, a property that, to the best of our knowledge, has yet too be established. The phosphabarrelene crystallographic cone angle was calculated to be 141.4^0 for complex **3**; and 145.3^0 for complex **4**. What is interesting, and perhaps surprising, about these values is that they are very similar to the Tolman cone angle for triphenyl phosphine of 145^0, and also fit in the range given for triphenyl phosphine complexes, 129.0-168.3^0. This suggests that phosphabarrelenes share very similar properties to triphenylphosphines in both steric and electronic parameters, thus providing an explanation for the remarkably similar phosphorus-metal bond lengths, phosphorus-metal coupling constants and carbonyl stretching frequency values we have obtained for all the phosphabarrelene complexes of Groups VI, VII and VIII transition metals presented here. However, despite this similarity the analogous triphenyl phosphine complexes do not exhibit properties such as rotameric isomerisation experienced with, say, the pentacarbonyl(phosphabarrelene)tungsten(0) complex seen here. This therefore suggests that although the overall cone angle of the phosphabarrelene upon complexation is similar to that of triphenylphosphine, the steric bulk of the two ligand systems still retain differences, due to the fact that the phosphabarrelene bearing the two pendant, and freely rotating dixylyl arms which result in properties such as rotameric isomerisation not observed with the analogous triphenylphosphine complexes.

The relative size of the cone angle of the phosphorus ligand also explains why the triphenylphosphite complexes have shown a greater phosphorus-metal coupling constant, shorter phosphorus-metal bond lengths and higher carbonyl stretching frequencies than either the phosphabarrelene or the triphenylphosphine analogous complexes. This is because triphenylphosphite exhibits much greater π-acceptor properties towards transition metals, but also it has a much smaller Tolman cone angle of 128^0,[12] compared to 145^0 for triphenylphosphine. This allows less steric interference upon coordination to the metal centre and therefore a much shorter phosphorus-metal bond can, and is, formed. This is reflected in the NMR, IR and crystallographic data in triphenylphosphite complexes of transition metals relative to the analogous complexes of triphenylphosphine or our dixylylphosphabarrelene.

3.3 Transition metal complexes of Groups IX, X and XI – Results and Discussion



Scheme 3.3.

The chloro(dicarbonyl)*bis*-(dixylylphosphabarrelene)rhodium(I) complex **(5)** was synthesised by the addition of four equivalents of the phosphabarrelene ligand to the $[Rh(CO)_2Cl]_2$ precursor in dichloromethane (scheme 3.3). **(5)** was isolated as a pale yellow solid and was characterised by spectroscopic means, as well as by X-ray crystallography. The $^{31}P\{^1H\}$ NMR spectrum exhibited the characteristic downfield coordination shift to –2.84 ppm, with a $^1J_{P\text{-}Rh}$ coupling constant of 143 Hz. The ^1H NMR spectrum of **(5)** is the only phosphabarrelene complex synthesised so far that does not exhibit the characteristic downfield doublet of the proton at the C-8 position of the phosphabarrelene ring. It is therefore assumed that this doublet is masked and becomes coincidental with other protons at similar shifts. The ^{13}C NMR spectrum of **(5)** gives an indication as to the geometry of complex **(5)**. It is common in phosphine complexes of this type that if they are in the *trans* geometry then the carbons α to the phosphorus atom, appear as a triplet in the ^{13}C NMR spectrum, whereas if the geometry is *cis* then a doublet is seen in the ^{13}C NMR spectrum for these α carbons. The ^{13}C NMR spectrum of **(5)** shows the two equivalent carbons at the C-2 and C-6 positions on the phosphabarrelene ring to be virtual triplets at 150.7 ppm, with a $J_{C\text{-}P}$ coupling constant value of 11 Hz. In addition to this the C-7 carbon of the phosphabarrelene can be seen as a virtual triplet at 135.9 ppm, with a $J_{C\text{-}P}$ coupling constant of 6 Hz. This evidence, along with the X-ray crystallography data, strongly supports the *trans* configuration of complex **(5)**.

The carbonyl stretching frequency of 1975 cm^{-1} in the IR spectrum of complex **(5)** compares with 1960 cm^{-1} for the analogous triphenylphosphine complex.[13] This is comparable with known complexes of this type[14] and correlates with the general trends observed. From this a correlation with Tolman's $Ni(CO)_3$(phosphine) systems can be made,[15] which again supports our findings that the electronic nature of the phosphabarrelene as a ligand to transition metals is comparable to triphenylphosphine. The $^1J_{P\text{-}Rh}$ coupling constant of 143 Hz for **(5)**, compares with the value of 125 Hz for the analogous triphenylphosphine complex.[13] For complexes of the type $Rh(CO)Cl(PR_nPh_{3\text{-}n})_2$, the $^1J_{P\text{-}Rh}$ coupling constant tends to decrease as *n* increases.[16] This correlates with the work of Grim *et al.*[17] on tertiary phosphine complexes of pentacarbonyltungsten(0), where aryl phosphines gave a higher value for their $^1J_{P\text{-}W}$ coupling constants as well as a higher *E* mode of carbonyl stretching frequency, than their analogous complexes of alkyl phosphine analogues. Therefore, as was seen previously in this chapter, complex **(5)** shows similar $^1J_{P\text{-}Rh}$ coupling constant data and a similar carbonyl stretching frequency to the related triphenylphosphine complex. This is not too surprising as both ligand systems are essentially an sp^3 hybridised phosphorus atom attached to three sp^2 hybridised carbon atoms. The slight increase in the values obtained for complex **(5)** compared to the triphenylphosphine equivalent is probably due to a slight increase in the π-acceptor abilities of the phosphabarrelene compared to the phosphine.

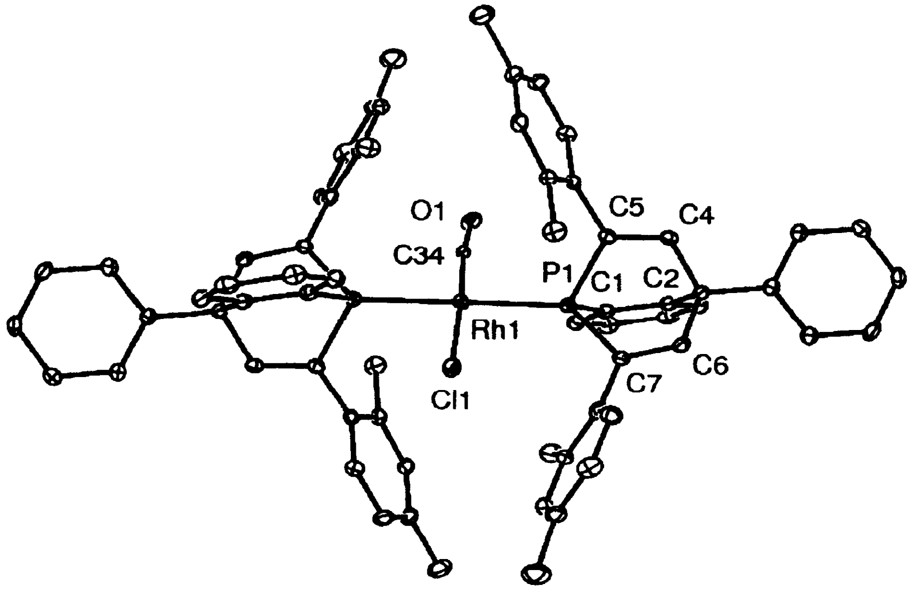


Figure 3.3. ORTEP representationof (**5**). Hydrogens have been omitted for clarity. Selected bond lengths (Å): Rh(1)-P(1) 2.3064(11); Rh(1)-C(34) 1.782(11); Rh(1)-Cl(1) 2.386(4); C(34)-O(1) 1.161(13); P(1)-C(1) 1.838(4); P(1)-C(5) 1.842(4); P(1)-C(7) 1.853(4). Selected bond angles (deg): P(1)-Rh(1)-P(1)′ 180.0 (7); C(34)-Rh(1)-Cl(1) 176.7(4); C(34)-Rh(1)-P(1) 86.9(4); C(34)-Rh(1)-P(1)′ 93.1(4); Cl(1)-Rh(1)-P(1) 84.3(10); Cl(1)-Rh(1)-P(1)′ 95.7(10); C(1)-P(1)-Rh(1) 121.82(12); C(5) -P(1)-Rh(1) 114.03(12); C(7) -P(1)-Rh(1) 125.99(12).

This postulation is reinforced by the X-ray crystallography data (figure 3.3), which shows that the phosphorus-rhodium bond in complex (**5**) is 2.3064(11) Å, compared to 2.326(11) Å for *trans*-Rh(CO)Cl(PPh_3)$_2$.[18] The structure also confirms that the two phosphabarrelene ligands sit perpendicular to each in order to allow the maximum amount of steric relief for the two pendant dixylyl arms. The crystallographic cone angle for the complex is 161.7^0, (using Mingos's method[19]), which lies towards the upper value in the range given for complexes of triphenylphosphine.[1] This confirms and fits with all data so far suggesting the similarity between the phosphabarrelene and triphenyl phosphine in this type of complex. However, even though the phosphabarrelene appears to exhibit a stronger π-acceptor ability than the phosphine, it is weaker than that exhibited by triphenylphosphite. The analogous complex of triphenylphosphite has a $^1J_{P\text{-}Rh}$ coupling constant of 273 Hz, and a carbonyl stretching frequency value of 1998 cm^{-1}.[18] In addition to this the *tri*(*ortho*-tolyl)phosphine (which has a large Tolman cone angle of 194^0),[20] exhibits a relatively short phosphorus–metal bond length of 2.291(12) Å.[21] This therefore suggests that the electronic properties of our phosphabarrelene, and the phosphorus-rhodium bond in this type of rhodium complex lie in between that of triaryl phosphines and triarylphosphites of the same complex.

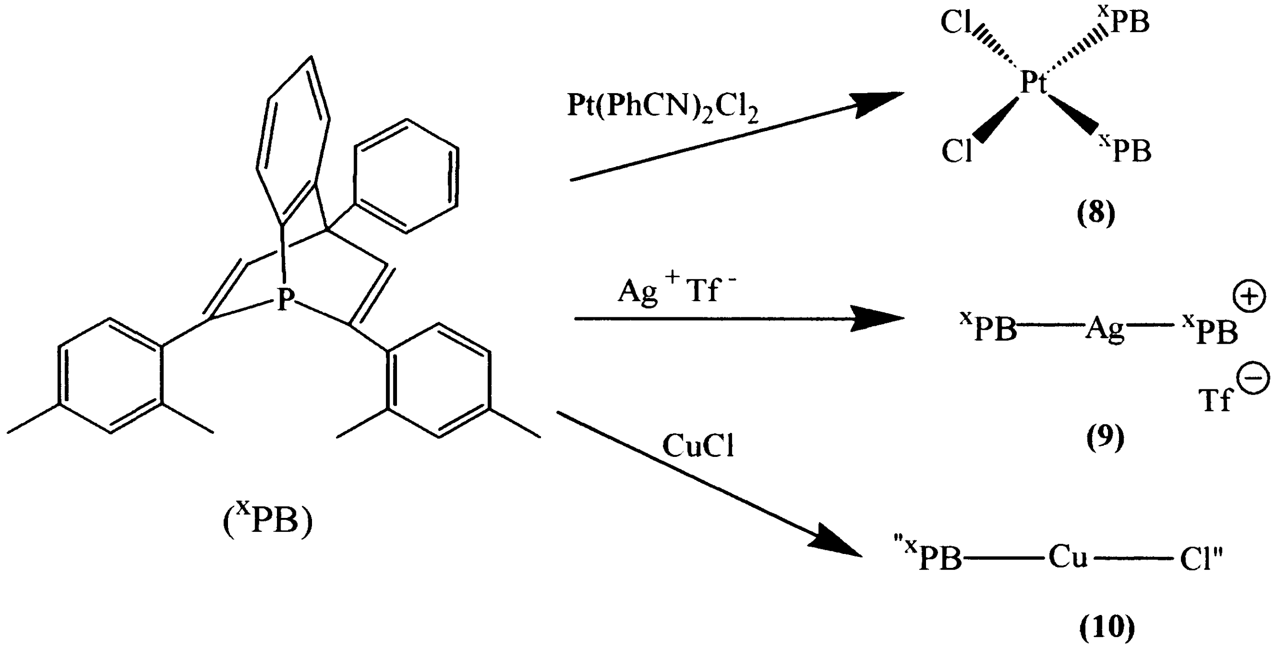
Subsequent to our work, Breit *et al.* published the synthesis and catalysis of a series of phosphabarrelene-rhodium complexes.[22] This included complex **(5)**, as well as the 2,6-diisopropyl derivative. Breit reported a similar coordinated shift in the ^{31}P NMR spectrum of –3.0 ppm, with a $J_{P\text{-}Rh}$ coupling constant of 144 Hz, compared to –2.84 ppm and 143 Hz we obtained for complex **(5)**. Breit also compared the carbonyl stretching frequency of the carbonyl group with the corresponding phosphinine, triphenylphosphine and triarylphosphite complexes. Like us, he places the phosphabarrelene ligand in between that of triphenylphosphine and the parent phosphinine, but much lower than the triarylphosphite complex. However, for the dixylylphosphabarrelene-rhodium complex, Breit reported a carbonyl stretching frequency of 1993 cm^{-1} whereas we report a value of 1975 cm^{-1}. Our data was reported as a solution cell in petrol, but we also ran the spectrum as a KBr disc and found the stretching frequency to be 1980 cm^{-1}. Both these values are lower than Breit's reported 1993 cm^{-1}, but Breit did not indicate in his publication what medium he obtained his IR spectroscopic data in. Similarly Breit also reported the crystallographic cone angle for complex **(5)** as well as the 2,6-diisopropyl derivative, he reported values of 181^0 and 161^0 respectively. This is surprising as we report a value of 161^0 for the dixylyl derivative not the isopropyl derivative; one may expect the diisopropyl derivative to have a greater cone angle than the dixylyl derivative.

Similarly the chloro(COD)(dixylylphosphabarrelene)rhodium(I) complex **(6)** was synthesised by addition of 2 equivalents of the phosphabarrelene ligand to the $[Rh(1,5\text{-}COD)Cl]_2$ dimer precursor in dichloromethane (scheme 3.3). Complex **(6)** was isolated as a yellow solid and characterised by spectroscopic means. The $^{31}P\{^1H\}$ NMR spectrum shows a downfield shifted doublet at –17.5 ppm, with a $^1J_{P\text{-}Rh}$

coupling constant of 160 Hz. The ^{1}H NMR spectrum shows the characteristic sign of coordination with the proton on the C-8 position of the phosphabarrelene shifting downfield from 7.8 ppm to 8.7 ppm. In addition the ^{13}C NMR spectrum shows the C-2 and C-6 carbon J_{C-P} coupling constants to have slightly decreased from 21 Hz to19 Hz, typical of coordinated phosphorus ligands.

The $^1J_{P-Rh}$ coupling constant of complex **(6)** follows the same trend as complex **(5)** upon comparison with the analogous complex of triphenylphosphine. Complex **(6)** exhibits a $^1J_{P-Rh}$ constant of 160 Hz, whereas the triphenylphosphine analogue has a value of 152 Hz.[23] This again suggests the similar electronic properties of phosphabarrelenes with triphenylphosphine in transition metal complexes.

The analogous chloro(COD)iridium(I) complex **(7)** was made in the same way as the rhodium complex **(6)**, with **(7)** being obtained as a yellow solid, and characterised by spectroscopic means (scheme 3.3). The $^{31}P\{^1H\}$ NMR spectrum exhibits the characteristic downfield coordination singlet at -24.1 ppm, and the ^{1}H NMR shows the coordinated downfield shifted doubled doublet of the proton on the C-8 position of the phosphabarrelene ring at 8.8 ppm. Interestingly, the C-2 and C-6 carbons of the phosphabarrelene show an increase in their J_{C-P} coupling constant values, from 21 Hz to 26 Hz. This is unlike the rhodium analogue that exhibits a decrease in the J_{C-P} coupling constants of the C-2 and C-6 carbons from 21 to 19 Hz. Also, and as was the case with complex **(6)**, the high resolution mass spectrum of complex Y is observed as $[Ir(COD)MeCN(phosphabarrelene)]^+$, through replacement of chloride by acetonitrile under the operating conditions of the mass spectrometer.



Scheme 3.4.

The dichloro(*bis*-dixylyphosphabarrelene)platinium(II) complex **(8)** was synthesised by reaction of 2 equivalents of the phosphabarrelene ligand with Pt(PhCN)$_2$Cl$_2$ precursor in dichloromethane (scheme 3.4). Complex **(8)** is, to the best of our knowledge, the first phosphabarrelene complex of its type to be characterised by spectroscopic means. The ^{31}P{^{1}H} NMR spectrum exhibits the coordinated downfield singlet at –27.8 ppm, with corresponding ^{195}Pt satellites, ($^1J_{P\text{-}Pt}$ coupling constant of 3860 Hz.) The ^{1}H NMR spectrum also shows the characteristic coordinated shift of the C-8 proton on the phosphabarrelene ring from 7.8 ppm to 8.6 ppm. The ^{13}C NMR spectrum is consistant with the *cis* configuration of the complex. This is indicated by the C-2 and C-6 carbons on the phosphabarrelene ring not only showing an increase in their $J_{C\text{-}P}$ coupling constant values from 21 Hz to 38 Hz, but also because these α carbons to the phosphorus atoms are doublets and not triplets, as would be expected if the complex had a *trans* configuration (as in complex **(5)**).

The evidence for the cis configuration of complex **(8)** also comes from comparison of the $^1J_{P\text{-}Pt}$ coupling constants for analogous phosphine complexes. It is reported that the $^1J_{P\text{-}Pt}$ coupling constant changes significantly on going from the *cis* isomer to the *trans* isomer of a phosphine complex of the type (L)$_2$PtCl$_2$. For example, *cis*-[(*p*-tolyl)$_3$P)$_2$PtCl$_2$ has a $^1J_{P\text{-}Pt}$ coupling constant of 3627 Hz, whereas *trans*-[(*p*-

tolyl)$_3$P)$_2$PtCl$_2$ has a $^1J_{P\text{-}Pt}$ coupling constant of 2650 Hz.[24] This appears to be the general trend for phosphine complexes of this type, i.e. the *trans* isomers exhibit a coupling constant that is around 1000 Hz lower than the *cis* isomers. The $^1J_{P\text{-}Pt}$ coupling constant of complex **(8)** (3860 Hz), and the analogous *cis*-tri(*p*-tolyl)phosphine complex (3627Hz), and the *cis*-triphenylphosphine analogue (3673 Hz),[25] suggesting the *cis* configuration for **(8)**.

In common with the rhodium complexes **(5)** and **(6)**, the phosphorus-metal coupling constant in complex **(8)** is slightly higher at 3860 Hz than the analogous triphenyl phosphine complex where a value of 3673 Hz is observed. Thus the higher π-acceptor ability of the phosphabarrelene can be assumed to be the major reason for the observed differences. This is reinforced by the work of Grim[26] who postulates that there is a trend in the $^1J_{P\text{-}Pt}$ coupling constants on going from alkyl to aryl phosphines. Thus he states that for PR_nPh_{3-n} as *n* decreases the $^1J_{P\text{-}Pt}$ coupling constant increase, that is the more phenyl groups on the phosphine, the better π-acceptor it is and thus the higher $^1J_{P\text{-}Pt}$ coupling constant is. Table 3.3 highlights this trend and places our phosphabarrelene accordingly.

Table 3.3. $^1J_{P\text{-}Pt}$ coupling constants for complexes of the type *cis*-(L)$_2$PtCl$_2$.

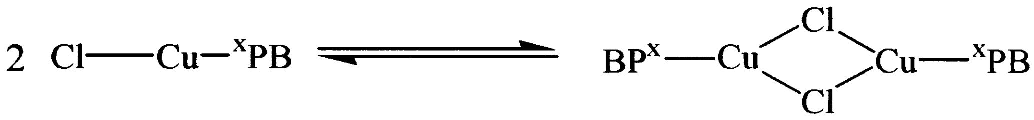
L	**$^1J_{P\text{-}Pt}$ coupling constant (Hz)**	**Reference**
(Me)$_3$P	3480	9
(Et)$_3$P	3517	9
(^{n}Pr)$_3$P	3530	11
Ph(Me)$_2$P	3549	11
Ph(Et)$_2$P	3530	11
Ph(^{n}Pr)$_2$P	3561	11
(Ph)$_2$MeP	3616	11
(Ph)$_2$EtP	3640	11
(Ph)$_2$^{n}PrP	3639	11
(*p*-tolyl)$_3$P	3627	9
(Ph)$_3$P	3673	10
dixylylphosphabarrelene	3860	

The *bis*-dixylylphosphabarrelenesilver(I) triflate complex **(9)** was synthesised by the reaction of two equivalents of the phosphabarrelene with silver(I) triflate in dichloromethane (scheme 3.4). (**(9)**) was isolated and characterised by spectroscopic means. In common with a number of other tertiary phosphine-silver complexes, the room temperature $^{31}P\{^1H\}$ NMR spectrum of (**(9)**) consists of a broad singlet around –20ppm.[27] Upon cooling the solutions to –50 ^0C the ^{31}P NMR spectrum became a doublet with a $^1J_{P\text{-}Ag(107/109)}$ coupling constant of 725 Hz. The system was not sufficiently resolved to observe the two individual coupling constants. The value of the $^1J_{P\text{-}Ag}$ coupling constant is surprisingly large, 725 Hz, far higher than that observed for $[(p\text{-tolyl})_3P]_2Ag^+ PF_6^-$ which exhibits a $^1J_{P\text{-}Ag}$ coupling constant of 496 Hz, or $(PhO_3P)_2Ag^+ BF_4^-$ which has a value of 667 Hz.[27] It is reported that in complexes of the type $(PR_3)_nAg^+X^-$, as *n* increases the value of the phosphorus-silver coupling constant tends to decrease,[28] for example, $[(p\text{-tolyl})_3P]_3Ag^+ PF_6^-$ exhibits a $^1J_{P\text{-}Ag}$ of 321 Hz, compared to 496 Hz for the corresponding *bis* species. It is also very important to recognise the role the counter anion plays in the geometry of the complex. It has been noted that smaller and less polarising anions (e.g. halides or CN^-) tend to form neutral complexes of the type L_nAgX; whereas more poorly coordinating anions such as PF_6^-, or ClO_4^- tend to form ionic complexes of the type $L_nAg^+ X^-$.[29] Thus the neutral L_2AgX complexes are reported to be trigonal in geometry and the ionic $L_2Ag^+ X^-$ complexes are considered to be linear. The effect of this is generally an increase in the phosphorus-silver coupling constants for the more ionic silver complexes compared to their analogous neutral counter-parts. The ^1H NMR spectrum also shows the characteristic downfield shift of the proton on the C-8 position of the phosphabarrelene ring from 7.8 to 8.2ppm. The high resolution mass spectrum confirms the identity of the complex as **(9)**, as the *bis*-(dixylylphosphabarrelene)silver (I) cation is detected. Considering this, it therefore seems reasonable to assume that due to the large phosphorus-silver coupling constant and the mass spectroscopic data, that the triflate complex **(9)** is of the more ionic, linear, $L_2Ag^+ X^-$ type.

The dixylylphosphabarrelenecopper(I) chloride complex **(10)**, was prepared by reacting copper(I) chloride with the phosphabarrelene ligand in DCM at room temperature (scheme 3.4). Complex **(10)** was isolated as a white solid that gave a broad singlet δ_p in the $^{31}P\{^1H\}$ NMR spectrum. Upon cooling the solution to 223 K (-

50 ^{0}C) the peak sharpened, but did not shift either downfield or upfield from the room temperature position of –39 ppm. The same was true of the ^{1}H NMR spectrum, which at room temperature was too broad to discern any fine coupling, but upon cooling to 223 K sharpened significantly to allow identification of specific protons in the ligand. The ^{13}C NMR spectrum was obtained at room temperature and the majority of carbon resonances were identified, but a couple of the quaternary carbons were not seen. These were not observed upon cooling to 223 K and so therefore are absent due to coalescence or the inherent weakness of quaternary carbons in ^{13}C NMR spectra.

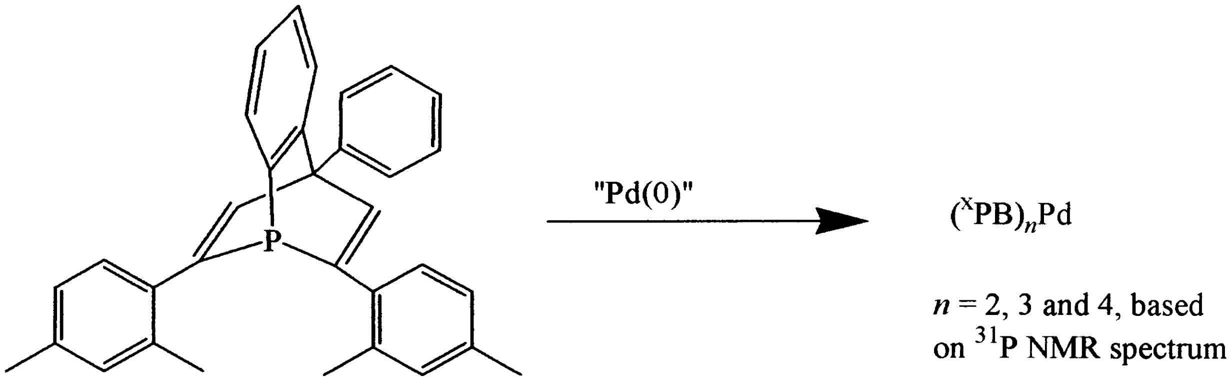
The broadening of the peaks in both the ^{31}P and ^{1}H NMR spectra of **(10)** is possibly due to the fluxional nature of the complex. Tertiary phosphine complexes of copper(I) halides of the type $L_mCu_nX_n$ (L = PR_3 (R= alkyl or aryl); X = Cl. Br, or I; $m{:}n$ = 3:1, 4:2, 3:2, 2:2, 4:4), have been elucidated in the solid state by X-ray crystallography, although the complete series is still not known.[30] In solution however, the complexes are known to be fluxional with the steric bulk of the phosphine ligand, the solvent, and the temperature all thought to play key roles in the equilibria observed. In general it is presumed that the larger the steric bulk of the phosphine ligand, the larger the degree of intramolecular steric repulsion between the ligand and the halide. This is thought to hinder the approach of the halide to the metal centre and effectively hinders the formation of a halide bridged di-metallic species.[30] It is therefore reasonable to assume that the broadening seen in the NMR spectra of complex **(10)** is due to the fluxional nature of the complex in solution. This may be due to an equilibrium between the monomeric species "LCuX" and the di-metallic species "$[LCuX]_2$ (figure 3.5).



Scheme 3.5.

Our assumption is supported by the work of Matsuda *et al.* who reports the synthesis and structure of the phosphinine-copper analogue.[31] These workers observe several different species in solution as determined by the ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of our complex appears to be temperature independent and the difference between the two complexes is probably due to the greater σ-donor ability of the phosphabarrelenes forming a stronger phosphorus-metal bond compared to the phosphinines, an observation we have noticed throughout our work.

Attempts to synthesise and isolate a palladium(0) complex of the dixylylphosphabarrelene were frustrated by the presence of several species. Complex **(11)** was synthesised by the reaction of the phosphabarrelene ligand with [(2-methylallyl)PdCl]$_2$ in methanol, *via* a literature procedure[32] at room temperature (scheme 3.6). The reaction mixture showed phosphorus containing species in the ^{31}P{^{1}H} NMR spectrum, and after extraction with petrol, and fractional recrystallisation, one of the species was isolated in approximately 90% purity. ^{1}H and ^{13}C NMR spectra of the complex were obtained, but upon standing the material was found to re-equilibrate in solution to give a multitude of phosphorus containing species, included oxidised phosphabarrelene, in the ^{31} P NMR spectrum. This therefore made identifying (**(11)**) very difficult and this explains why no proton integration is given in the experimental section as we were unable to discern the exact nature of the complex. Thus assignments that have been made are based on our experience with the systems and comparisons with other phosphabarrelene complexes.



(^{X}PB)

Scheme 3.6.

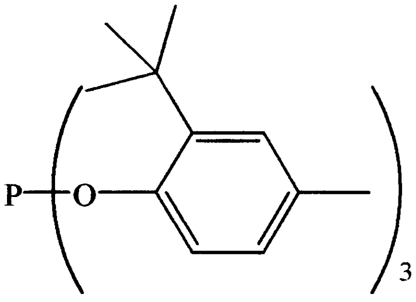
Phosphine-palladium(0) complexes are known to have dynamic solution equilibria with the phosphine ligand freely associating and disassociating at room temperature.[33]

The use of sterically bulky phosphine ligands, such as $P(^tBu)_3$, appears to stabilise low coordinate species such as $Pd(L)_2$.[34] Thus the more sterically bulky phosphines are generally reported as the two or three coordinate palladium complexes $Pd(L)_2$ or $Pd(L)_3$, whereas the less sterically bulky phosphines are generally isolated as the three or four coordinate species $Pd(L)_3$ or $Pd(L)_4$. The general trend of these complexes in their ^{31}P NMR spectra is that the higher the coordination number, the further upfield the chemical shift in the ^{31}P NMR spectra. Thus for $Pd(P^iPr_3)_n$, where n = 2 δ_P is 49ppm, but where n = 3 δ_P is 39ppm; and for $Pd(PPh_3)_n$, where n =3 δ_P is 23ppm, but where n = 3 δ_P is 18ppm.[35] With this trend in mind, it is reasonable to assume that the three peaks observed in the initial ^{31}P NMR spectra at –7ppm, -11ppm, and –14ppm could be the *bis-*, *tris-*, and *tetrakis-* phosphabarrelene palladium complexes respectively. Therefore the spectroscopic data obtained on the species at –11ppm, is likely to be that of the *tris*-[2,6-dixylyl-4-phenylphosphabarrelene]palladium(0) complex, but without further investigation this remains a tentative assignment.

Therefore, in conclusion we have surveyed the coordination chemistry of 2,6-dixylyl-4-phenylphosphabarreleme with transition metal complexes, and in doing so have expanded the range of known phosphabarrelene-transition metals complexes. We report here for the first time, to the best of our knowledge, a number of isolated phosphabarrelene complexes ranging from group 6 to group 11. In addition to this we have elucidated the unique coordination chemistry of the phosphabarrelene ligand with transition metal centres, including rotameric isomerisation and crystallographic cone angles. Also through a range of spectroscopic means, including NMR, IR and X-ray crystallography, we have also further elucidated the nature of the phosphorus metal bond in the phosphabarrelene-transition metal complexes, by comparison to well known and established phosphine and phosphite analogues.

3.4 Phosphabarrelenes as Ligands for Homogeneous Catalysis – Introduction

Since its discovery in 1938 by Roelen[36] hydroformylation has gone on to become one of the most important homogeneouly catalysed processes in industry, with around 7 million tonnes of product produced a year. However, even to this day the process remains far from being completely efficient and attempts are constantly being made to improve the selectivity and reactivity of the catalysts employed. The discovery of the rhodium/phosphine systems by Wilkinson *et al.*[37] was significant in establishing phosphorus based ligands as important, and industrially viable ligands for the commercial hydroformylation of olefins. Since then, several studies have established that good σ donor ligands severely hinder the process, whereas good π acceptor ligands cause an increase in both activity and selectivity.[38] Steric bulk has also been found to be a major factor in the process as it is believed that the active species during the catalysis is a monophosphite-rhodium complex.[39]

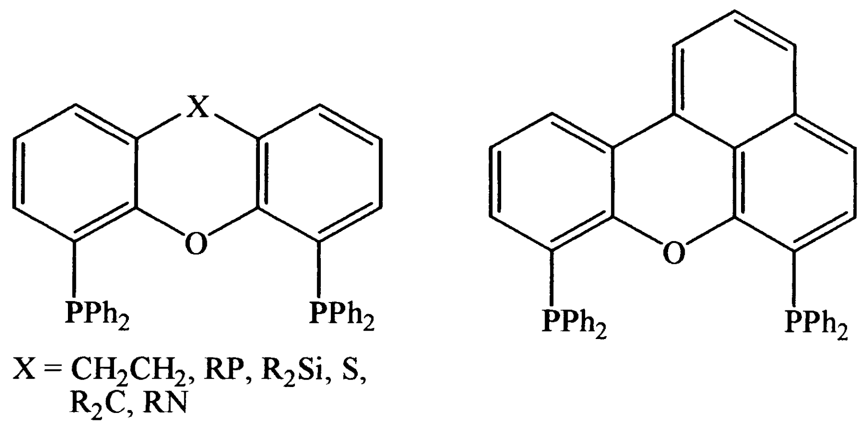


Scheme 3.7.

Subsequently van Leeuwen went on to study the use of the very bulky *tris*-(2-t-butyl-4-methylphenyl)phosphite (scheme 3.7), in the hydroformylation of oct-1-ene, cyclohexene and styrene.[40] He reports TOF's, of $39.8\times10^3 h^{-1}$ and $512h^{-1}$ for oct-1ene and cyclohexene respectively. He also elucidates that for oct-1-ene, the rate-determining step is the reaction of the hydrogen gas with the acylrhodium intermediate, as well as a negative order in the CO concentration being observed. For cyclohexene, the rate-limiting step was found to be the addition of the cyclohexene to the rhodium-hydride intermediate. For styrene however, the rate was found to be three times slower than the oct-1-ene, and the kinetics of the reaction were found to be far more complicated. In all cases however, the large steric bulk of the phosphite ligand played a vital role in the catalysis of the substrates.

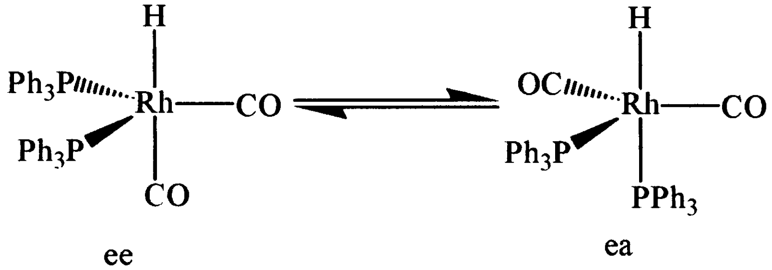
However, the major problem with the use of phosphites is their inherent lability towards hydrolysis and their tendency to undergo degradation reaction under industrial conditions.[41] The other problem is the regioselectivity, as in most cases the linear aldehyde is seen as more commercially valuable than the branched aldehyde. One of the solutions to this has been to use diphosphines or diphosphites, this has lead to a huge number of different ligands being tested, some of which have shown remarkably good activity and selectivity in producing terminal aldehydes from either terminal or internal olefins.[42]

In particular the xantphos family of ligands have shown very high activity in hydroformylating both terminal and internal olefins, with both high activities and good selectivity for the linear aldehyde (scheme 3.8).[43] In the case of oct-2-ene for example, the phenoxaphosphino-substituted xantphos ligand exhibited an unprecedented TOF of $112h^{-1}$, with a linear:branched (l:b) ratio of 9.2:1, and 90% of the linear aldehyde being produced. The reason for the activity was related to the bite angle of the bidentate xantphos ligands, which can be altered by modifications to the backbone of the ligand, as well as the lower bascicity of the phosphine groups.[44] In addition to this it has been established that the catalytically active species, the (diphosphine)Rh$(CO)_2$H complex, is an equilibrium mixture of *bis*-equatorial (ee) and equatorial-axial (ea) isomers. The effect of the xantphos ligand compared to other diphosphines, is that they adopt the *bis*-equatorial configuration in the trigonal bipyramidal complex exclusively. This is important as the ee configuration of the catalytically active species is thought to play a vital role in the regioselectivity of the hydroformylation of olefins, particularly in the selective production of linear aldehydes (scheme 3.9).



Xantphos family of ligands

Scheme 3.8.



Scheme 3.9.

As a result of this work, a whole series of phenoxaphosphino-modified xantphos ligands were synthesised with varying degrees of bite angles and tested in the hydroformylation of oct-2-ene.[45] An unprecedented TOF of $250h^{-1}$ and a regioselectivity of 96% toward the linear aldehyde was obtained for the hydroformylation of oct-2-ene. It was also found that regioselectivities are increased with an increase in the bite angle of the ligand, however, above 125^0C the selectivity drops off. The reasoning for the effect of the bite angle is still not fully understood, and work continues to provide a complete explanation for the remarkable activity of the xantphos family of ligands in the selective hydroformylation of both terminal and internal olefins to linear aldehydes.[46]

What has become apparent over the last few years is that there is a market, particularly in the fine chemicals and pharmaceutical industries, for branched aldehydes. So now research is starting to focus upon catalytically active species that will perform hydroformylation of internal alkenes, without isomerisation, and so produce the branched aldehyde products selectively. One of the first reported systems to achieve this was the afore-mentioned phosphinines in the rhodium catalysed hydroformylation of oct-2-ene, conducted by Breit and co-workers.[47] What was remarkable about these systems was that not only were they highly active but they also had an extraordinary selectivity for hydroformylating the internal olefin into the branched aldehyde with very little isomerisation occurring. Furthermore, Breit *et al.* found that the phosphabarrelenes exhibited an even higher activity for the selective rhodium catalysed hydroformylation of internal olefins to branched aldehydes.[48] His results are discussed in full and in comparison with the data we collected on the use of phosphabarrelenes in the rhodium catalysed hydroformylation of oct-4-ene.

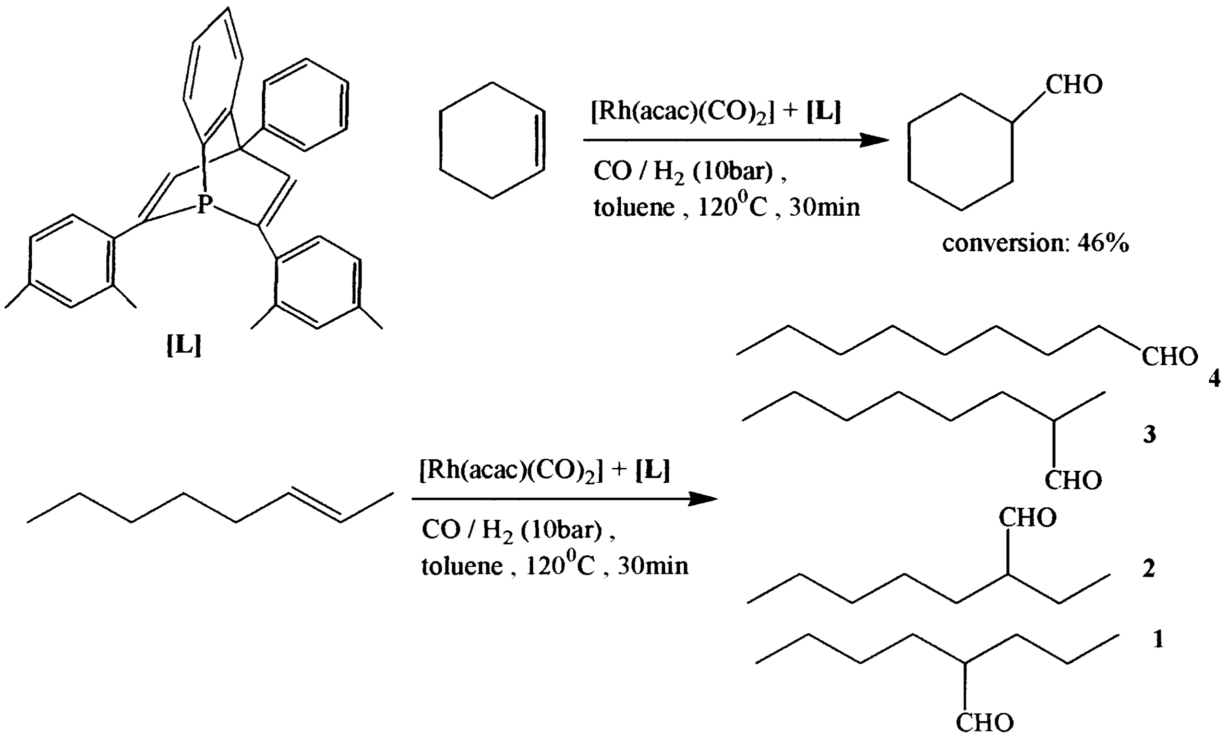
Finally, van Leeuwen *et al.* recently reported on the selective hydroformylation of internal olefins to the branched aldehydes, using an encapsulated rhodium catalyst.[49] Again, van Leeuwen's results will be discussed in full in comparison with Breit's and our data.

Therefore, after thoroughly studying the coordination chemistry of the 2,6-dixylyl-4-phenylphosphabarrelene, we decided to extend the application further by testing the phosphabarrelene in the rhodium catalysed hydroformylation of oct-4-ene. Thus if the ligand does promote the hydroformylation of the olefin rather than its isomerisation, then we should obtain similar results to that of Breit.

3.5 2,6-Dixyly-4-phenylphosphabarrelene as a Ligand for the Hydroformylation of Internal Olefins - Results and Discussion

Breit *et al.* first demonstrated the potential of phosphabarrelenes as ligands for the rhodium catalysed hydroformylation. They had already established that the phosphinines showed good activity in the selective hydroformylation of internal olefins to branched aldehydes. In fact, they found that the phosphabarrelenes were 1000 times faster than the industrially used Rh/PPh_3 system, with a TOF of 12000h^{-1}, in the hydroformylation of cyclohexene. Also they demonstrated the remarkable ability of the diisopropylphosphabarrelene to hydroformylate either dihydrofuran, or N-Boc-pyrroline, systems that are known to isomerise easily, selectively to the branched aldehyde with almost no isomerisation. (See Chapter 1.)

Most relevantly to this thesis they reported on the use of the 2,6-dixylyl-4-phenylphosphabarrelene in the rhodium catalysed hydroformylation of oct-2-ene (scheme 3.10). Not only did they find that the hydroformylation occurred with very little isomerisation, but also they found that compared to the parent 2,6-dixylyl-4-phenylphosphinine, the phosphabarrelene system actually showed a higher percentage of the branched aldehydes than either the phosphinine, or *tris*-(2,4-di-t-butylphenyl)phosphite ligand (Table 3.4).

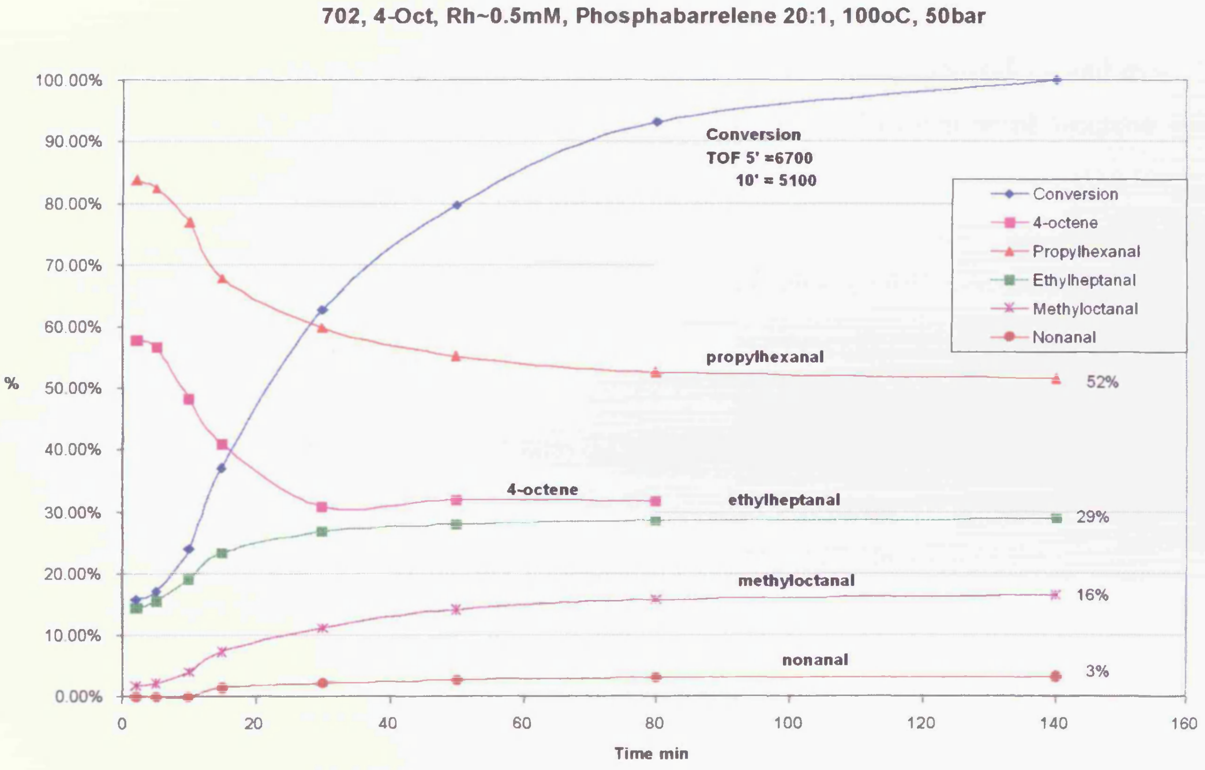


Scheme 3.10.

Table 3.4. Breit's results for the rhodium catalysed hydroformylation of oct-2-ene, with [Rh(CO)$_2$acac]/L at 70^{0}C, 10 bar(CO:H$_2$ 1:1) in toluene after 4h (oct-2-ene/L/Rh 7187:20:1).

L	**Oct-2-ene (mol%)**	**1 (mol%)**	**2 (mol%)**	**3 (mol%)**	**4 (mol%)**
***Tris*-(2,4-di-t-butlphenyl) Phosphite**	0.0	12.2	33.5	51.1	0.2
2,6-dixylyl-4-phenyl phosphinine	0.5	12.7	22.4	54.1	6.4
2,6-dixylyl-4-phenyl phosphabarrelene	4.5	0.2	35.7	57.6	0.0

Therefore we tested the 2,6-dixylyl-4-phenylphosphabarrelene in the rhodium catalysed hydroformylation of oct-4-ene under the standard protocols and conditions employed by Sasol UK Limited. The catalysis was performed at a syngas (CO:H_2 1:1) pressure of 50 bar, at 100 ^{0}C, with the rhodium catalysts being prepared *in situ* in the autoclave from the dixylylphosphabarrelene and for comparison the commonly used *tris*-(2,4-di-t-butylphenyl)phosphite. (Figure 3.4. Data and graphs are courtesy of Hendrik van Rensburg of Sasol UK Limited.)



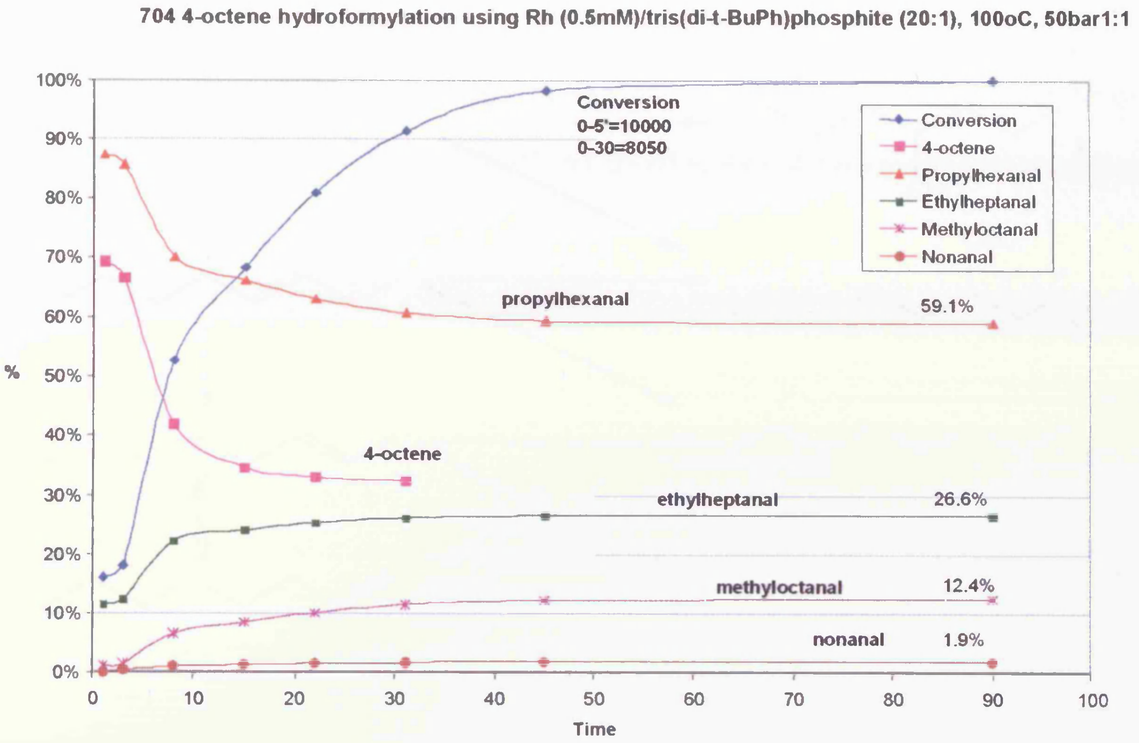
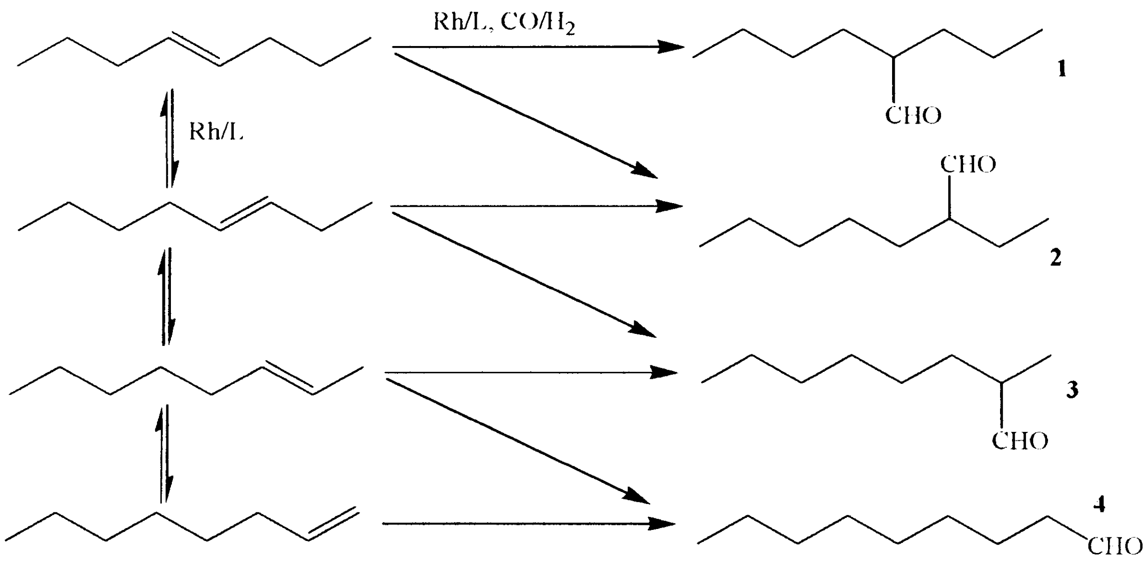


Figure 3.4. Graphs showing the performance of the dixylylphosphabarralene and *tris*-(2,4-di-t-butylphenyl)phosphite in rhodium catalysed hydroformylation of 4-octene.

As expected the phosphabarrelene performs well, and achieves full conversion of the olefin. After the initial reaction (5 min), the TOF of 5,100h^{-1} of the catalysis is modest, and is lower than the reported TOF of 39,800h^{-1} van Leeuwen achieved with this bulky tris-(2-t-butyl-4-methylphenyl)phosphite in the hydroformylation of oct-1-ene.[40] However, compared to the phosphite the results are not as encouraging. The phosphite achieves full conversion within approximately half the time of the phosphabarrelene and its TOF is higher still at 8,050h^{-1}.

The amount of isomerisation occurring during the catalytic run can be judged from the relative amounts of nonanal and methyloctanal produced. In order to form these products the catalyst must first isomerise the substrate and then perform the hydroformylation. Thus the less nonanal and methyloctanal is produced the less internal isomerisation is occurring (scheme 3.11).



Scheme 3.11

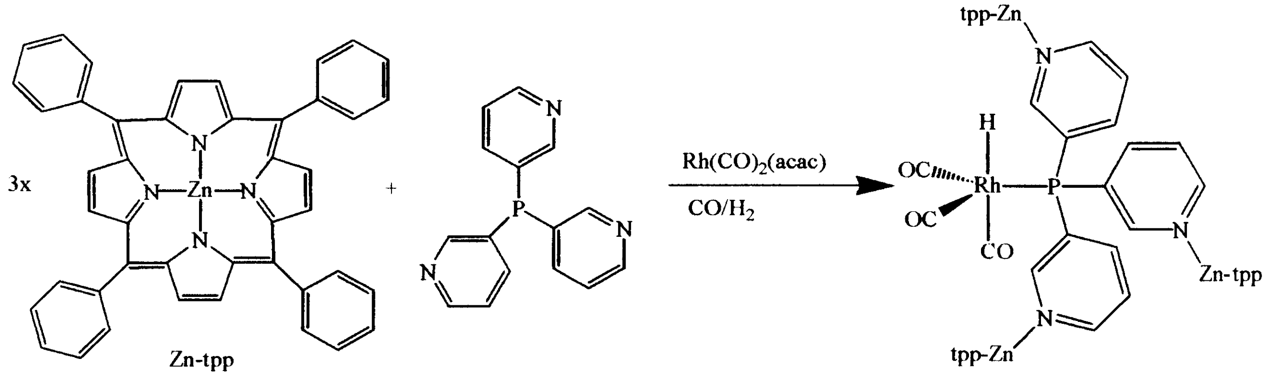
Table 3.5 Results from the hydroformylation of 4-octene at 50 bar pressure of CO/H_2, at 100^0C with a $Rh(acac)(CO)_2$:L ratio of 1:20, in toluene.

L	**Time to 100% conversion (min)**	**1 (%)**	**2 (%)**	**3 (%)**	**4 (%)**	**TOF (h^{-1})**
2,6-dixylyl-4-phenyl phosphabarrelene	140	52	29	16	3	6,700
(2,4-di-t-butylphenyl) phosphite	90	59.1	26.6	12.4	1.9	10,000

The data in Table 3.5 clearly shows that the amount of nonanal and methyloctanal are low. This therefore indicates that the amount of internal isomerisation is low with the phosphabarrelene and with the phosphite, suggesting that both ligand systems are selectively hydroformylating the internal C-C double bond, rather than isomerising the alkene. However, the selectivity between the propylhexanal (**1,** 52%), and ethylheptanal (**2**, 29%), is not as good as would be desired, although the phosphabarrelene does a slightly greater selectivity than the phosphite.

Our findings, in general, support those of Breit *et al.* who found that phosphabarrelenes appear to be highly active in the selective hydroformylation of internal alkenes.[1] They find that the phosphabarrelene gives good selectivity towards the branched aldehydes, (Table 3.4 vs Table 3.5). It is however worth noting that Breit's catalysis is performed under milder conditions than those employed by Sasol, 70 ^{0}C at 10 bar, compared to 100 ^{0}C at 50 bar, and as a result he observes a slightly different distribution of products. The propylhexanal remains the aldehyde with the highest product percentage with 57.6%, compared to 52% of propylhexanal we obtained by hydroformylating oct-4-ene under more forcing conditions. Unlike in the hydroformylation of oct-2-ene however, where Breit finds the dixylylphosphabarrelene to exhibit a relatively higher selectivity for the propylhexanal than the *tris*-(di-t-butylphenyl)phosphite, (57.6% compared to 51.1% respectively), our data seems to show that in the hydroformylation of oct-4-ene under slightly different reaction conditions the phosphabarrelene exhibits a slightly lower selectivity for propylhexanal than the phosphite, (52% compared to 59.1% respectively). Therefore perhaps the phosphabarrelene ligand is more selective under milder reaction conditions, or perhaps the nature of the substrate plays a vital role in the product distribution and hence the ligand used to hydroformylate it has to be considered in each case.

Finally, as mentioned before, very recently van Leeuwen has reported the use of an encapsulated rhodium complex in the selective hydroformylation of internal olefins to branched aldehydes.[49] His catalyst is synthesised by the reaction of Rh(CO)$_2$acac with *tris*-(meta-pyridyl)phosphine and zinc(II)tetraphenylporphin (Zn-tpp), under an atmosphere of CO and H$_2$ (1:1) (scheme 3.12). The complex he made was then tested, along with the unencapsulated rhodium species in the hydroformylation of 1-, 2- and 3-octene.



Scheme 3.12.

The most striking result he observes is the hydroformylation of oct-2-ene, to ethylheptanal and methyloctanal in a ratio of 87.8%:9.4%. This suggests that almost no isomerisation is occurring during the reaction, and this distribution of products is far superior to the product distribution achieved with either the phosphabarrelene or the phosphite system previously discussed. In addition the reaction conditions of 10 bar syngas ($CO:H_2$ 1:1), and a reaction temperature of 25 ^0C are also unprecedented. However, disappointingly the reaction takes 73 hours to achieve only a 32% conversion, although this conversion is still double that of the unencapsulated form. Van Leeuwen argues that the reason for the remarkable activity is due to the encapsulating ligand restricting free rotation of the coordinated alkene. Thus upon coordination, if the alkene can freely rotate prior to hydride migration both isomers are still possible. In the case of the encapsulated complex however, the steric restriction imposed by the ligand inhibits this rotation and so the regioselectivity of the product is predisposed for the branched aldehyde upon coordination of the alkene.

This restricted rotation proposed by van Leeuwen, may also provide an explanation for the selectivity of the dixylylphosphabarrelene in the hydroformylation of olefins. We have already demonstrated previously in this chapter that the coordination chemistry of the phosphabarrelene, seems to suggest that the two pendant xylyl arms can become restricted in their rotation upon coordination to transition metal centres. For example, we observed restricted rotation with the dixylylphosphabarrelene pentacarbonyltungsten(0) complex, where we believe that the restriction of the pendant xylyl arms with the pentacarbonyltungsten core, leads to the formation of *cis* and *trans* rotamers. Similar observations are noticed with the dixylylphosphabarrelene(cymene)dichlororuthenium(II) complex. Therefore, based upon our observations, and the work of van Leeuwen, it seems reasonable to suggest that the pendant xylyl arms of the dixylylphosphabarrelene ligand also restrict the free rotation of the alkene upon coordination to the rhodium centre. This would therefore cause a greater predominance for the regioselectivity to be determined upon coordination of the alkene, and hence favour the production of the branched aldehyde in the hydroformylation of the internal alkene.

One should recognise however, that another possible explanation for the phosphabarrelenes being selective for internal olefin hydroformylation is that they promote the migratory insertion of the CO into the M-alkyl bond. This would cause the equilibrium at this point in the catalytic cycle to be increased in favour of the product, and due to Le Chatelier's principle, this would effectively stifle alkene isomerisation occurring earlier on in the cycle, thus favouring hydroformylation of the internal olefin over isomerisation.

In conclusion, this thesis has highlighted the range of coordination chemistry possible by both phosphinines and phosphabarrelenes, and in doing so has elucidated unique properties of the ligands once bound to transition metal centres. The phosphorus-metal bonds in the complexes formed has been studied by spectroscopic means, and compared to known analogues of triarylphosphines and phosphites. Finally the catalytic potential of the 2,6-dixylylphosphabarrelene has been studied in the rhodium catalysed hydroformylation of 4-octene, and has shown to be modest, but comparable to (2,4-di-t-butylphenyl)phosphite.

3.6 Experimental

The compounds were synthesised under nitrogen using standard inert atmosphere (Schlenk) techniques. Complexes **1-11** were handled as air and moisture sensitive compounds for manipulation. All solvents were freshly distilled from sodium or calcium hydride under nitrogen before use. The $^{31}P\{^{1}H\}$ NMR spectra were recorded on Jeol Eclipse 300 and Bruker DPX500 spectrometers operating at 121.7 and 202.5 Hz respectively, and referenced to 85% H_3PO_4 ($\delta = 0$ ppm). ^{1}H (400.8 MHz) spectra were obtained on Bruker DPX400 spectrometer except in some cases where a BrukerDPX500 NMR spectrometer (field) was used as indicated. $^{13}C\{^{1}H\}$ (125.8 MHz) NMR spectra were obtained on a Bruker DPX500 spectrometer and are referenced to tetramethylsilane ($\delta = 0$ ppm). Infrared spectra were recorded either as a solution cell or as Nujol Mulls on a Nicolet 510 FT-IR spectrophotometer. Mass spectra were recorded on a Waters LCT Premier XE mass spectrometer. All other chemicals were of reagent grade and used as supplied unless otherwise stated. $\Delta G^{\#}$ was calculated as in Chapter 2.

Synthesis of [2,6-Bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]pentacarbonyltungsten(0) (1):

A solution of the phosphabarrelene (0.1g, 0.22mmol) in THF was added at room temperature to a solution of $W(CO)_5THF$ (70mg, 0.22mmol) in THF. The reaction mixture was stirred at room temperature for 18h, after which the solution was pumped to dryness. The crude material was washed with petrol and the resulting material was recrystallised from petrol, to give [2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]pentacarbonyltungsten(0) (**1**) as a yellow solid, (0.15g, 87%). ^{31}P NMR (202.5 MHz, $CDCl_3$): $\delta = -7.23$ (s, $J_{(P\text{-}W)}$= 265.3Hz). ^{1}H NMR ($CDCl_3$): $\delta = 2.21$ (s, 12H, CH_3); 6.52 (d, 1H, $J_{(H\text{-}H)}$= 7.7 Hz, Ar-H); 6.91 (m, 5H, Ar-H); 7.01 (t, 1H, $J_{(H\text{-}H)}$= 7.6Hz, Ar-H); 7.16 (m, 2H, Ar-H); 7.39 (t, 1H, $J_{(H\text{-}H)}$= 7.3Hz, Ar-H); 7.48 (t, 2H, $J_{(H\text{-}H)}$= 7.9Hz, Ar-H); 7.56 (d, 2H, $J_{(H\text{-}H)}$= 7.5 Hz, Ar-H); 7.73 (d, 2H, $J_{(H\text{-}P)}$= 17.3Hz, CH3/5); 7.97 (dd, 1H, $J_{(H\text{-}H)}$= 4.0Hz, $J_{(H\text{-}P)}$= 12.0Hz, CH-8). ^{13}C NMR ($CDCl_3$): $\delta = 21.13$ (s, CH_3); 61.79 (d, $J_{(C\text{-}P)}$= 8.8Hz, C); 124.66 (d, $J_{(C\text{-}P)}$=

12.6Hz, CH); 124.86 (d, $J_{(C-P)}$= 3.8Hz, CH); 126.30 (s, C); 126.44 (s, CH); 127.70 (s, CH); 127.97 (s, CH); 128.70 (s, CH); 128.86 (s, C); 129.02 (s, CH); 129.23 (s, CH); 131.02 (s, CH); 131.16 (s, CH); 131.53 (d, $J_{(C-P)}$= 18.9Hz, CH); 134.90 (d, $J_{(C-P)}$= 13.8Hz, C); 136.09 (s, C); 138.32 (s, C); 139.86 (s, C); 150.23 (s, C); 191.15 (d, $J_{(C-W)}$= 62.9Hz, CO-*trans*); 194.88 (d, $J_{(C-P)}$= 7.5Hz, CO-*cis*). IR (petrol) cm^{-1}: 2073.9 (w, CO); 1985.7 (w, CO); 1941.6 (st, CO); 1261.0; 1099.1; 1016.4; 858.0; 739.7.

Synthesis of [2,6-Bis-(2',4'-dimethylphenyl)-4-phenylphosphabarrelene](chloro)tetracarbonylrhenium(I) (2):

To a solution of chloropentacarbonylrhenium(I) (80mg, 0.22mmol) in DCM (10ml) was added the phosphabarrelene (0.1g, 0.22mmol) in DCM (10ml). The reaction mixture was refluxed for 18h. After which time, the reaction was allowed to cool, and then pumped to dryness. The desired compound was extracted into petrol (20ml) and filtered. The desired complex precipitated as a yellow solid from the petrol filtrate upon cooling. This was found to be [2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene](chloro)tetracarbonylrhenium(I) (**2**), (83mg, 48%).^{31}P NMR (121.7 MHz, $CDCl_3$): δ = -21.90 (s). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.21 (s, 6H, CH_3); 6.52 (d, 1H, $J_{(H-H)}$= 8.0Hz, Ar-H); 6.91 (m, 3H, Ar-H); 7.00 (t, 2H, $J_{(H-H)}$= 7.6Hz, Ar-H); 7.13 (m, 2H, Ar-H); 7.41 (d, 2H, $J_{(H-H)}$= 7.2Hz, Ar-H); 7.48 (t, 2H, $J_{(H-H)}$= 7.4Hz, Ar-H); 7.55 (d, 2H, $J_{(H-H)}$= 7.4Hz, Ar-H); 7.79 (d, 2H, $J_{(H-P)}$= 19.3Hz, CH3/5); 8.48 (b, dd, 1H, $J_{(H-P)}$= 9.25Hz, CH-8). ^{13}C NMR ($CDCl_3$): δ = 20.09 (s, CH_3); 60.75 (d, $J_{(C-P)}$= 10.1Hz, C); 123.47 (d, $J_{(C-P)}$= 12.6Hz, CH); 124.03 (s, CH); 126.86 (s, CH); 127.09 (s, CH); 127.44 (s, CH); 127.58 (s, CH); 128.01 (s, CH); 130.22 (s, CH); 132.02 (d, $J_{(C-P)}$= 12.6Hz, CH); 137.62 (s, CH); 138.32 (s, CH); 146.08 (s, C); 148.13 (s, C); 148.46 (s, C); 148.63 (s, C); 150.63 (s, C); 151.14 (s, C); 178.29 (s, *trans*-CO); 180.89 (d, $J_{(C-P)}$= 64.2Hz, *trans*-CO); 182.31 (d, $J_{(C-P)}$= 13.8Hz, *cis*-CO). IR (petrol) cm^{-1}: 2109.8 (m, CO); 2023.9 (st, CO); 2005.6 (st, CO); 1922.7 (st, b, CO); 1261.2; 1096.3; 1014.4; 734.8. Mass Spec. (e/z): Obs. Mass 755.1363; Calc. Mass 755.1361: M^+ = (L)$Re(CO)_4(CH_3CN)$.

Synthesis of [2,6-Bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]dicarbonyl-(trimethylsilyl)cyclopentadienyliron Hexafluorophosphate (3):

To a solution of (trimethylsilyl)cyclopentadienyl(dicarbonyl)acetonitrileiron hexafluorophosphate (96mg, 0.22mmol) in DCM (10ml) was added the phosphabarrelene (0.1g, 0.22mmol) in DCM (10ml). The reaction mixture was allowed to stir at room temperature for 18h. After which time, the reaction was pumped to dryness. The desired compound was isolated by crystalisation *via* vapour diffusion of ether into ethanol. The resulting yellow solid was found to be [2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]dicarbonyl-(trimethylsilyl)cyclopentadienyliron hexafluorophosphate (**3**), (40mg, 21%). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 10.59 (s, (barrelene)P-Fe); -144.17 (septet, $J_{(P-F)}$ = 712.8Hz, PF_6). ^{1}H NMR (500.1 MHz, $CDCl_3$, 223K): δ = 0.15 (s, 9H, $Si(CH_3)_3$); 2.16 (s, 3H, CH_3); 2.31 (s, 3H, CH_3); 4.07 (b, 2H, Cp-H); 4.37 (b, 2H, Cp-H); 6.62 (b, m, 1H, Ar-H); 6.89 (b, m, 1H, Ar-H); 7.10 (b, m, 8H, Ar-H); 7.60 (b, m, 6H, Ar-H); 8.00 (b, m, 1H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 1.04 (s, $Si(CH_3)_3$); 20.92 (s, CH_3); 21.02 (s, CH_3); 65.90 (s, ipso-C, Cp); 71.10 (s, Cp-CH); 72.80 (s, Cp-CH); 123.93 (s, CH); 124.07 (s, C); 126.46 (s, CH); 126.61 (s, CH); 127.46 (s, CH); 128.93 (s, CH); 129.01 (s, CH); 129.28 (s, CH); 131.01 (s, CH); 131.17 (s, CH); 135.25 (s, C); 136.38 (s, C); 136.98 (s, C); 138.17 (s, C); 149.68 (s, C); 150.91 (s, CH). IR (DCM) cm^{-1}: 2054.8 (CO); 2013.3 (CO); 1261.2; 1095.4; 1019.2; 734.8. Mass Spec. (e/z): Obs. Mass 705.2022; Calc. Mass 705.2041: $M^+ = (L)[Cp(SiMe_3)]Fe(CO)_2^+$.

Synthesis of [2,6-Bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]-η^6-cymene(dichloro)ruthenium(II) (4):

To a solution of tetrachlorobis(4-cymene)diruthenium(II) dimer (134mg, 0.22mmol) in DCM (10ml) was added the phosphabarrelene (0.2g, 0.44mmol) in DCM (10ml). The reaction mixture was allowed to stir at room temperature for 18h. After which time, the reaction was pumped to dryness and washed with petrol. The resulting yellow solid was found to be [2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]-η^6-cymene(dichloro)ruthenium(II) (**4**), (0.25g, 74%), and crystallised from dichloromethane / methanol .^{31}P NMR (121.7 MHz, $CDCl_3$, 353K): δ = -5.46 (s). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.01 (s, 3H, cymene-CH_3); 1.16 (d, 3H, $J_{(H-H)}$= 6.7Hz, $CH(C\mathit{H}_3)_2$); 1.21 (d, 3H, $J_{(H-H)}$= 6.8Hz, $CH(C\mathit{H}_3)_2$); 2.08 (s, 3H, CH_3); 2.24 (s, 3H, CH_3); 2.85 (septet, 1H, $J_{(H-H)}$= 6.9Hz, $C\mathit{H}(CH_3)_2$); 5.26 (d, 2H, $J_{(H-H)}$= 5.9Hz, cymene-CH_2); 5.40 (d, 2H, $J_{(H-H)}$= 6.0Hz, cymene-CH_2); 6.34 (d, 1H, $J_{(H-H)}$= 6.5Hz, Ar-H); 6.82 (t, 1H, $J_{(H-H)}$= 6.5Hz, Ar-H); 6.93 (m, 6H, Ar-H); 7.37 (t, 2H, $J_{(H-H)}$= 7.1Hz, Ar-H); 7.45 (t, 2H, $J_{(H-H)}$= 7.6Hz, Ar-H); 7.53 (d, 2H, $J_{(H-H)}$= Ar-H); 7.69 (d, 2H, $J_{(H-H)}$= 17.5Hz, CH3/5); 8.85 (s, 1H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 19.25 (s, CH_3); 21.27 (s, CH_3); 21.52 (s, $CH(\mathit{C}H_3)_2$); 22.30 (s, cymene-CH_3); 30.69 (s, $CH(\mathit{C}H_3)_2$); 60.64 (s, C); 80.77 (s, cymene-CH_2); 81.48 (s, cymene-CH_2); 96.82 (s, cymene-C); 101.25 (s, cymene-C); 123.35 (d, $J_{(C-P)}$= 10.1Hz, CH); 123.60 (s, CH); 126.13 (s, CH); 126.68 (s, CH); 127.81 (s, CH); 128.69 (s, CH); 129.12 (s, CH); 130.90 (s, CH); 135.82 (s, C); 136.88 (s, CH); 137.60 (s, C); 140.18 (s, C); 151.10 (s, C); 153.56 (s, CH). IR (Nujol) cm^{-1}: 1260.3; 1093.4; 1027.9; 806.1; 724.1. Mass Spec. (e/z): Obs. Mass 768.2087; Calc. Mass 768.2100: M^+ = (L)(Cymene)Ru(Cl)(CH_3CN).

Synthesis of di-[2,6-Bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]carbonyl(chloro)rhodium(I) (5):

To a solution of chloro(dicarbonyl)rhodium(I) dimer (86mg, 0.22mmol) in DCM (10ml) was added the phosphabarrelene (0.2g, 0.44mmol) in DCM (10ml). The reaction mixture was allowed to stir at room temperature for 18h. After which time, the reaction was pumped to dryness and washed with petrol. The resulting yellow solid was found to be di-[bis-2,6-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]carbonyl(chloro)-rhodium(I) (5), (0.2g, 84%), and crystallised from chloroform .^{31}P NMR (121.7 MHz, $CDCl_3$): δ = -2.84 (d, $J_{(P-Rh)}$= 143.0Hz). ^{1}H NMR ($CDCl_3$): δ = 1.99 (s, 12H, CH_3); 2.25 (s, 12H, CH_3); 6.35 (d, 2H, $J_{(H-H)}$= 7.1Hz, Ar-H); 6.87 (m, 14H, Ar-H); 7.35 (t, 2H, $J_{(H-H)}$= 7.2Hz, Ar-H); 7.44 (d, 4H, $J_{(H-H)}$= 7.5Hz, Ar-H); 7.58 (m, 12H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 21.22 (s, CH_3); 21.49 (s, CH_3); 61.23 (s, C); 123.62 (s, CH); 123.82 (t, $J_{(C-P)}$= 6.3Hz, CH);

125.96 (s, CH); 126.88 (s, CH); 127.63 (s, CH); 128.67 (s, CH); 129.02 (s, CH); 129.39 (s, CH); 130.52 (s, CH); 134.60 (s, CH); 135.97 (t, $J_{(C-P)}$= 6.3Hz, C); 136.11 (s, C); 137.57 (s, C); 140.44 (s, C); 150.71 (t, $J_{(C-P)}$= 11.3Hz, C); 150.93 (s, CH); 152.47 (s, CH); 206.80 (s, CO). IR (petrol) cm^{-1}: 1975 .7 (st, CO); 1261.2; 1038.5; 1015.3; 739.6. Mass Spec. (e/z): Obs. Mass 1084.3280; Calc. Mass 1084.3283: M$^+$ = $(L)_2Rh(Cl)(CH_3CN)$.

*Synthesis of [2,6-Bis-(2',4'-dimethylphenyl)-4-phenylphosphabarrelene]chloro(COD)rhodium(I) (**6**):*

To a solution of chloro(COD)rhodium(I) dimer (0.15mg, 0.22mmol) in DCM (10ml) was added the phosphabarrelene (0.2g, 0.44mmol) in DCM (10ml). The reaction mixture was allowed to stir at room temperature for 18h. After which time, the reaction was pumped to dryness and washed with petrol. The resulting yellow material was then recrystallised from petrol to yield a yellow solid of [2,6-bis-(2',4'-dimethylphenyl)-4-phenylphosphabarrelene]chloro(COD)rhodium(I) (**6**), (70mg, 40%).^{31}P NMR (202.5 MHz, $CDCl_3$): δ = -17.52 (d, $J_{(P-Rh)}$= 160.8Hz). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.66 (m, 4H, COD-aliphatic); 2.12 (s, 3H, CH_3); 2.23 (s, 3H, CH_3); 2.41 (m, 4H, COD-aliphatic); 3.27 (s, 2H, COD-olefin); 5.13 (s, 2H, COD-olefin); 6.39 (d, 1H, $J_{(H-H)}$= 7.8Hz, Ar-H); 6.95 (m, 3H, Ar-H); 7.06 (dt, 1H, $^dJ_{(H-H)}$= 2.1Hz, $^tJ_{(H-H)}$= 7.3Hz, Ar-H); 7.18 (m, 3H, Ar-H); 7.38 (m, 2H, Ar-H); 7.46 (t, 2H, $J_{(H-H)}$= 8.0Hz, Ar-H); 7.54 (d, 2H, $J_{(H-H)}$= 7.7Hz, Ar-H); 7.58 (d, 2H, $J_{(H-H)}$= 16.3Hz, CH3/5); 8.77 (dd, 1H, $J_{(H-H)}$= 7.8Hz, $J_{(H-P)}$= 9.7Hz, CH-8). ^{13}C NMR ($CDCl_3$): δ = 21.18 (s, CH_3); 21.40 (s, CH_3); 28.03 (s, COD-aliphatic); 32.67 (s, COD-aliphatic); 43.48 (s, COD-olefin); 69.24 (d, $J_{(C-P)}$= 12.6Hz, C); 103.99 (d, $J_{(C-P)}$= 12.6Hz, COD-olefin); 123.96 (s, CH); 124.03 (s, CH); 126.25 (s, CH); 127.06 (s, CH); 127.77 (s, CH); 128.69 (s, CH); 129.12 (s, CH); 129.62 (d, $J_{(C-P)}$= 5.0Hz, CH); 130.56 (s, CH); 131.21 (s, C); 134.32 (d, $J_{(C-P)}$= 18.9Hz, CH); 135.59 (s, C); 136.19 (d, $J_{(C-P)}$= 13.8Hz, C); 137.47 (s, C); 140.24 (s, C); 149.59 (d, $J_{(C-P)}$= 18.9Hz, C2/6); 151.81 (d, $J_{(C-P)}$= 3.8Hz, CH); 152.50 (s, C). IR (petrol) cm^{-1}: 1260.6; 1096.9; 1020.1; 801.8; 722.3. Mass Spec. (e/z): Obs. Mass 708.2251; Calc. Mass 708.2266: M$^+$ = $(L)Rh(COD)(CH_3CN)$.

Synthesis of [2,6-Bis-(2',4'-dimethylphenyl)-4-phenylphosphabarrelene]chloro(COD)iridium(I) (7):

To a solution of chloro(COD)iridium(I) dimer (0.15mg, 0.22mmol) in DCM (10ml) was added the phosphabarrelene (0.2g, 0.44mmol) in DCM (10ml). The reaction mixture was allowed to stir at room temperature for 18h. After which time, the reaction was pumped to dryness and washed with petrol. The resulting yellow material was then recrystallised from petrol to yield a yellow solid of [2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]chloro(COD)iridium(I) (7), (70mg, 40%).^{31}P NMR (202.5 MHz, $CDCl_3$): δ = -24.09 (s). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.21 (m, 4H, COD-aliphatic); 1.52 (m, 4H, COD-aliphatic); 2.09 (s, 6H, CH_3); 2.22 (s, 6H, CH_3); 2.93 (dd, 2H, $J_{(H-H)}$= 6.6Hz, $J_{(H-P)}$= 3.4Hz, COD-olefin); 4.73 (m, 2H, COD-olefin); 6.42 (d, 1H, $J_{(H-H)}$= 7.6Hz, Ar-H); 6.92 (m, 4H, Ar-H); 7.10 (d, 2H, $J_{(H-H)}$= 7.6Hz, Ar-H); 7.37 (t, 2H, $J_{(H-H)}$= 7.2Hz, Ar-H); 7.45 (t, 3H, $J_{(H-H)}$= 7.5Hz, Ar-H); 7.53 (d, 2H, $J_{(H-H)}$= 7.8Hz, Ar-H); 7.63 (d, 2H, $J_{(H-H)}$= 18.3Hz, CH3/5); 8.76 (dd, 1H, $J_{(H-H)}$= 7.3Hz, $J_{(H-P)}$= 10.5Hz, CH-8). ^{13}C NMR ($CDCl_3$): δ = 21.19 (s, CH_3); 21.44 (s, CH_3); 28.45 (s, COD-aliphatic); 33.58 (s, COD-aliphatic); 52.51 (s, COD-olefin); 60.98 (d, $J_{(C-P)}$= 11.3Hz, C); 93.60 (d, $J_{(C-P)}$= 15.1Hz, COD-olefin); 124.02 (d, $J_{(C-P)}$= 12.6Hz, CH); 124.85 (d, $J_{(C-P)}$= 1.3Hz, CH); 126.13 (s, CH); 127.14 (s, CH); 127.83 (s, CH); 128.68 (s, CH); 129.15 (s, CH); 129.60 (d, $J_{(C-P)}$= 5.0Hz, CH); 130.47 (s, CH); 132.71 (s, C); 133.85 (d, $J_{(C-P)}$= 16.4Hz, CH); 135.75 (d, $J_{(C-P)}$= 3.8Hz, C); 136.03 (d, $J_{(C-P)}$= 12.6Hz, C); 137.43 (t, $J_{(C-P)}$= 15.1Hz, C); 140.14 (s, C); 149.51 (d, $J_{(C-P)}$= 26.4Hz, C2/6); 152.28 (d, $J_{(C-P)}$= 2.5Hz, CH); 153.31 (d, $J_{(C-P)}$= 3.8Hz, C). IR (petrol) cm^{-1}: 1260.3; 1091.9; 1019.0; 803.3; 722.2. Mass Spec. (e/z): Obs. Mass 798.2815; Calc. Mass 798.2841: M^+ = (L)Ir(COD)(CH_3CN).

Synthesis of di-[2,6-Bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]dichloroplatinium(II) (8):

To a solution of bis-(benzonitrile)dichloroplatinium(II) (0.10g, 0.22mmol) in DCM (10ml) was added the phosphabarrelene (0.2g, 0.44mmol) in DCM (10ml). The reaction mixture was allowed to stir at room temperature for 18h. After which time, the reaction was pumped to dryness. The resulting yellow material was recrystallised from THF to yield a white solid of di-[2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]dichloroplatinium(II) (**8**), (0.13g, 57%).^{31}P NMR (121.7 MHz, $CDCl_3$): δ = -27.78 (s, $J_{(P\text{-}Pt)}$= 3860.0Hz). ^{1}H NMR ($CDCl_3$): δ = 1.97 (s, 12H, CH_3); 2.24 (s, 12H, CH_3); 6.46 (d, 2H, $J_{(H\text{-}H)}$= 7.2Hz, Ar-H); 6.73 (d, 4H, $J_{(H\text{-}H)}$= 7.4Hz, Ar-H); 6.82 (m, 4H, Ar-H); 6.97 (m, 8H, Ar-H); 7.29 (d, 4H, $J_{(H\text{-}H)}$= 7.3Hz, Ar-H); 7.40 (m, 10H, Ar-H); 8.60 (dd, 2H, $J_{(H\text{-}H)}$= 7.5Hz, $J_{(H\text{-}P)}$= 12.1Hz, CH-8). ^{13}C NMR ($CDCl_3$): δ = 20.99 (s, CH_3); 21.60 (s, CH_3); 60.95 (d, $J_{(C\text{-}P)}$= 16.4Hz, C); 124.26 (d, $J_{(C\text{-}P)}$= 5.0Hz, CH); 124.58 (d, $J_{(C\text{-}P)}$= 12.6Hz, CH); 126.80 (s, CH); 128.49 (s, CH); 128.83 (s, CH); 129.13 (s, C); 129.31 (s, CH); 131.05 (s, CH); 132.97 (s, CH); 134.38 (s, C); 134.47 (s, CH); 135.32 (s, CH); 135.93 (s, C); 138.30 (s, C); 139.16 (s, C); 147 .21 (d, $J_{(C\text{-}P)}$= 37.7 Hz, C2/6); 151.46 (s, C); 152.61 (s, CH). IR (Nujol) cm^{-1}: 1260.3; 1096.3; 1022.1; 806.1; 761.7; 701.0.

Synthesis of di-[2,6-Bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]silver(I) Triflate (9):

To a solution of silver(I) triflate (33mg, 0.22mmol) in DCM (10ml) was added the phosphabarrelene (0.1g, 0.22mmol) in DCM (10ml). The reaction mixture was allowed to stir at room temperature for 18h. After which time, the reaction was pumped to dryness and washed with diethyl ether. The resulting yellow material was recrystallised from diethyl ether to yield a greenish solid of di-[2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]silver(I) triflate (**9**), (0.2g, 85%).^{31}P

NMR (202.5 MHz, $CDCl_3$): δ = -24.2 (s, $J_{(P\text{-}Ag)}$= 725.0Hz, at 223K). ^{1}H NMR (*d*-toluene): δ = 1.93 (s, 12H, CH_3); 1.98 (s, 12H, CH_3); 6.28 (d, 2H, $J_{(H\text{-}H)}$= 7.8Hz, Ar-H); 6.49 (t, 2H, $J_{(H\text{-}H)}$= 7.6Hz, Ar-H); 6.77 (m, 12H, Ar-H); 7.01 (m, 12H, Ar-H); 7.34 (d, 4H, $J_{(H\text{-}P)}$= 15.8Hz, CH3/5); 8.20 (dd, 2H, $J_{(H\text{-}H)}$= 7.2Hz, $J_{(H\text{-}P)}$= 13.4Hz, CH-8). ^{13}C NMR (*d*-toluene):δ = 20.04 (septet, $J_{(C\text{-}F)}$= 18.9Hz, triflate); 20.69 (s, CH_3); 62.98 (d, $J_{(C\text{-}P)}$= 7.5Hz, C); 124.51 (d, $J_{(C\text{-}P)}$= 15.1Hz, CH); 125.27 (d, $J_{(C\text{-}P)}$= 15.1Hz, CH); 126.78 (s, CH); 127.69 (s, CH); 128.49 (d, $J_{(C\text{-}P)}$= 7.5Hz, CH); 128.59 (s, CH); 128.78 (s, CH); 129.03 (s, CH); 131.27 (s, CH); 132.39 (d, $J_{(C\text{-}P)}$= 27.8Hz, CH); 134.94 (s, C); 135.19 (s, C); 137.20 (s, C); 137 .97 (s, C); 139.63 (s, C); 149.55 (d, $J_{(C\text{-}P)}$= 13.8Hz, C); 150.74 (d, $J_{(C\text{-}P)}$= 3.7Hz, CH); 152.19 (d, $J_{(C\text{-}P)}$= 3.8Hz, C). ^{19}F NMR (282.9 MHz, *d*-toluene): δ -77.10. IR (Nujol) cm^{-1}: 1260.3; 1096.3; 1024.2; 806.1; 700.0; 636.4. Mass Spec. (e/z): Obs. Mass 1019.3028; Calc. Mass 1019.3065: $M^+ = (L)_2Ag^+$.

*Synthesis of [2,6-Bis-(2',4'-dimethylphenyl)-4-phenylphosphabarrelene]copper(I) Chloride (**10**):*

To a solution of copper(I) chloride (22mg, 0.22mmol) in DCM (10ml) was added the phosphabarrelene (0.1g, 0.22mmol) in DCM (10ml). The reaction mixture was stirred for 18h, after which time the reaction was pumped to dryness. The desired complex was precipitated as a white solid from DCM and petrol, to give [2,6-bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]copper(I) chloride (**10**), (65mg, 53%).^{31}P NMR (121.7 MHz, 223K, $CDCl_3$): δ = -39.15 (s). ^{1}H NMR (500.1 MHz, 223K, $CDCl_3$): δ = 2.17 (s, 6H, CH_3); 6.44 (m, 1H, Ar-H); 6.92 (m, 3H, Ar-H); 7.03 (m, 2H, Ar-H); 7.08 (m, 2H, Ar-H); 7.45 (m, 2H, Ar-H); 7.54 (m, 2H, Ar-H); 7.60 (m, 2H, Ar-H); 7.74 (d, 2H, $J_{(H\text{-}P)}$= 15.6Hz, CH3/5); 8.08 (m, 1H, CH-8). ^{13}C NMR ($CDCl_3$): δ = 21.12 (s, CH_3); 62.45 (s, C); 124.51 (s, CH); 124.94 (d, $J_{(C\text{-}P)}$= 13.8Hz, CH); 126.75 (s, CH); 126.75 (s, CH); 127.80 (s, CH); 128.00 (s, CH); 128.56 (d, $J_{(C\text{-}P)}$= 6.3Hz, CH); 128.68 (s, CH); 129.22 (s, CH); 131.32 (s, CH); 131.72 (s, CH); 135.32 (s, C); 137.82 (s, C); 140.21 (s, C); 150.44 (s, CH). Mass Spec. (e/z): Obs. Mass 560.1566; Calc. Mass 560.1568: $M^+ = (L)Cu(CH_3CN)^+$.

Synthesis of n-[2,6-Bis-(2',4'-dimethylphenyl)-4-phenylphosphabarrelene]palladium(0) (11):

To a suspension of [(2-methylallyl)PdCl]$_2$ (90mg, 0.22mmol) in methanol (4ml) was added the phosphabarrelene (0.5g, 0.22mmol) in methanol (10ml), and then NaOH (2ml, of 0.018M) at room temperature. The reaction mixture was stirred for 18h, after which time the reaction was pumped to dryness. The resulting material was washed with methanol and recrystallisation from this methanol filtrate gave n-[2,6-bis-(2',4'-dimethylphenyl)-4-phenylphosphabarrelene]palladium(0) (**11**), (65mg, 53%) in 90% purity. The purity of the complex meant that elemental analysis was not possible and mass spectroscopy failed to identify any specific palladium complex. ^{31}P NMR (121.7 MHz, CDCl$_3$): δ = -11.36 (s). ^{1}H NMR (500.1 MHz, CDCl$_3$): δ = 2.18 (s, CH$_3$); 2.22 (s, CH$_3$); 6.46 (d, $J_{(H\text{-}H)}$= 7.6Hz, Ar-H); 6.88 (m, Ar-H); 6.94 (d, $J_{(H\text{-}H)}$= 6.4Hz, Ar-H); 7.00 (t, $J_{(H\text{-}H)}$= 7.6Hz, Ar-H); 7.44 (d, $J_{(H\text{-}H)}$= 7.2Hz, Ar-H); 7.52 (t, $J_{(H\text{-}H)}$= 7.2Hz, Ar-H); 7.61 (d, $J_{(H\text{-}H)}$= 7.6Hz, Ar-H); 7.71 (d, $J_{(H\text{-}P)}$= 16.8Hz, Ar-H); 7.76 (d, $J_{(H\text{-}P)}$= 17.2Hz, Ar-H); 9.32 (dd, $J_{(H\text{-}P)}$= 10.1Hz, $J_{(H\text{-}H)}$= 7.2Hz, CH-8). ^{13}C NMR (CDCl$_3$): δ = 19.84 (s, CH$_3$); 20.12 (s, CH$_3$); 60.95 (d, $J_{(C\text{-}P)}$= 12.6Hz, C); 122.75 (s, CH); 123.91 (b, t, C); 125.02 (d, $J_{(C\text{-}P)}$= 16.4Hz, CH); 126.51 (d, $J_{(C\text{-}P)}$= 27.7Hz, CH); 127.50 (d, $J_{(C\text{-}P)}$= 28.9Hz, CH); 127.82 (s, CH); 128.06 (s, CH); 129.29 (s, CH); 129.65 (s, CH); 134.91 (s, CH); 135.23 (s, C); 135.54 (s, C); 135.87 (d, $J_{(C\text{-}P)}$= 7.5Hz, CH); 139.75 (s, C); 148.83 (d, $J_{(C\text{-}P)}$= 12.6Hz, C); 151.94 (s, CH); 152.25 (s, C).

Hydroformylation of 4-octene:

The hydroformylation of 4-octene was carried out using the following conditions:

Rh(acac)(CO)$_2$: 4.3mg = 0.016mmol, ~0.55mM
2,6-dixyly-4-phenylphosphabarrelene: 135mg = ~0.3mmol ~ 20:1
*tri*s-(2,4-di-^{t}butylphenyl)phosphite: 47mg = ~0.3mmol ~ 20:1
4-Octene: 5ml
Toluene: 25ml
Temp: 100°C

Syngas: (CO_2:H_2 1:1): 50bar

The rhodium precursor and phosphabarrelene ligand were added to degassed toluene in the autoclave and heated to 100°C under 20 bar syngas. At 100°C the olefin was injected to 50bar and syngas was fed from a ballast vessel on demand at 50bar. Small liquid samples were taken during the reaction. The reaction was stopped after 3h. The exact same procedure and conditions were used for the testing of the *tris*-(2,4–di-^{t}butylphenyl)phosphite ligand.

3.7 References

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Appendix

[2,6-Bis-(2′,4′-dimethylphenyl)-4-phenylphosphabarrelene]dicarbonyl-(trimethylsilyl)cyclopentadienyliron Hexafluorophosphate (3):

Table 1. Crystal data and structure refinement for cj501.

Identification code	cj501
Empirical formula	C43 H42 F6 Fe O2 P2 Si
Formula weight	850.65
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	orthorhombic, Pna2(1)
Unit cell dimensions	a = 17.285(4) A alpha = 90 deg.
	b = 18.104(4) A beta = 90 deg.
	c = 12.811(3) A gamma = 90 deg.
Volume	4008.8(14) A^3
Z, Calculated density	4, 1.409 Mg/m^3
Absorption coefficient	0.550 mm^-1
F(000)	1760
Crystal size	0.25 x 0.22 x 0.20 mm
Theta range for data collection	3.00 to 26.00 deg.
Limiting indices	-21<=h<=21, -21<=k<=22, -15<=l<=14
Reflections collected / unique	21070 / 7692 [R(int) = 0.0450]
Completeness to theta = 26.00	99.5 %
Max. and min. transmission	Sortav 0.897 and 0.851
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7692 / 13 / 498

Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0580, wR2 = 0.1459
R indices (all data)	R1 = 0.0708, wR2 = 0.1546
Absolute structure parameter	0.01(2)
Largest diff. peak and hole	0.954 and -0.471 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cj501. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	1297(1)	8291(1)	8566(1)	38(1)
P(1)	462(1)	7760(1)	9646(1)	33(1)
Si(1)	2247(1)	9894(1)	7395(1)	44(1)
F(1)	2321(6)	6587(6)	6962(8)	75(3)
O(1)	2571(2)	7268(3)	8941(4)	74(1)
C(1)	-344(3)	8307(2)	10198(4)	37(1)
P(2)	2786(1)	6524(1)	5929(1)	72(1)
F(2A)	2150(7)	7043(8)	5346(10)	121(4)
O(2)	1878(2)	9297(2)	10155(3)	59(1)
C(2)	-787(2)	7906(2)	10821(4)	36(1)
F(3)	2963(5)	7411(5)	5935(9)	85(3)
C(3)	-609(3)	7086(2)	11053(4)	36(1)
F(4)	3537(7)	6386(8)	6714(9)	123(4)
C(4)	-572(3)	6698(3)	9996(4)	37(1)
F(5)	2680(9)	5694(6)	5863(12)	132(5)
C(5)	-102(3)	6936(2)	9255(4)	37(1)
F(6)	3502(6)	6550(5)	5116(8)	87(3)

C(6)	-441(3)	9101(3)	9948(4)	44(1)
C(7)	-31(3)	9627(3)	10491(4)	49(1)
C(8)	-92(5)	10368(3)	10183(6)	82(2)
C(9)	-577(5)	10560(5)	9345(7)	101(3)
C(10)	-1000(4)	10035(4)	8828(8)	90(3)
C(11)	-941(3)	9321(4)	9126(5)	65(2)
C(12)	393(4)	9451(4)	11390(6)	81(2)
C(13)	-608(6)	11407(4)	9053(10)	145(5)
C(14)	-1189(2)	6768(3)	11833(4)	37(1)
C(15)	-1299(3)	7121(3)	12769(4)	44(1)
C(16)	-1781(3)	6839(3)	13533(5)	50(1)
C(17)	-2180(3)	6185(3)	13363(5)	56(1)
C(18)	-2077(3)	5822(3)	12411(5)	54(1)
C(19)	-1598(3)	6110(3)	11653(4)	46(1)
C(20)	226(2)	7072(2)	11495(3)	33(1)
C(21)	812(2)	7402(2)	10890(4)	35(1)
C(22)	1557(3)	7445(3)	11261(4)	40(1)
C(23)	1740(3)	7140(3)	12216(4)	47(1)
C(24)	1194(3)	6783(3)	12788(5)	49(1)
C(25)	431(3)	6738(2)	12434(4)	41(1)
C(26)	-37(3)	6598(3)	8199(4)	39(1)
C(27)	544(3)	6088(3)	7977(4)	45(1)
C(28)	572(3)	5788(3)	6975(4)	55(1)
C(29)	42(3)	5984(3)	6199(4)	55(1)
C(30)	-517(3)	6482(3)	6431(4)	52(1)
C(31)	-577(3)	6786(3)	7428(4)	45(1)
C(32)	1149(3)	5864(3)	8770(4)	54(1)
C(33)	113(5)	5644(4)	5117(5)	82(2)
C(34)	1546(3)	9083(3)	7402(4)	41(1)
C(35)	742(3)	9109(3)	7694(4)	44(1)

C(36)	393(3)	8417(3)	7467(4)	47(1)
C(37)	962(3)	7951(3)	7062(4)	50(1)
C(38)	1673(3)	8362(3)	7005(4)	47(1)
C(39)	1668(3)	10707(3)	7839(5)	60(2)
C(40)	2566(4)	10005(4)	6008(5)	78(2)
C(41)	3099(3)	9719(3)	8244(4)	54(1)
C(42)	2054(3)	7640(3)	8802(4)	53(1)
C(43)	1636(3)	8896(3)	9555(4)	45(1)
F(1A)	2108(6)	6583(6)	6736(9)	82(3)
F(3A)	3144(6)	7248(5)	6406(9)	95(3)
F(4A)	3283(9)	5905(9)	6493(11)	149(6)
F(5A)	2261(7)	5816(6)	5478(9)	107(4)
F(6A)	3131(13)	6468(11)	4783(13)	186(7)
F(2)	2215(10)	6666(12)	5089(14)	182(8)

Table 3. Bond lengths [A] and angles [deg] for cj501.

Fe(1)-C(43)	1.775(5)
Fe(1)-C(42)	1.787(5)
Fe(1)-C(35)	2.089(5)
Fe(1)-C(37)	2.103(5)
Fe(1)-C(38)	2.106(5)
Fe(1)-C(34)	2.113(5)
Fe(1)-C(36)	2.115(5)
Fe(1)-P(1)	2.2177(13)
P(1)-C(21)	1.824(5)
P(1)-C(1)	1.850(5)
P(1)-C(5)	1.851(5)
Si(1)-C(41)	1.859(5)
Si(1)-C(39)	1.868(6)
Si(1)-C(40)	1.871(6)
Si(1)-C(34)	1.903(5)
F(1)-P(2)	1.553(9)
O(1)-C(42)	1.132(6)
C(1)-C(2)	1.323(6)
C(1)-C(6)	1.483(6)
P(2)-F(2)	1.484(14)
P(2)-F(5)	1.516(11)
P(2)-F(1A)	1.567(9)
P(2)-F(3A)	1.573(9)
P(2)-F(4A)	1.585(12)
P(2)-F(6A)	1.588(15)

P(2)-F(6)	1.617(9)
P(2)-F(2A)	1.629(11)
P(2)-F(3)	1.634(9)
P(2)-F(4)	1.660(11)
P(2)-F(5A)	1.674(10)
O(2)-C(43)	1.137(6)
C(2)-C(3)	1.546(6)
C(3)-C(14)	1.527(7)
C(3)-C(4)	1.528(6)
C(3)-C(20)	1.551(6)
C(4)-C(5)	1.322(6)
C(5)-C(26)	1.488(7)
C(6)-C(7)	1.375(8)
C(6)-C(11)	1.419(8)
C(7)-C(12)	1.402(9)
C(7)-C(8)	1.404(8)
C(8)-C(9)	1.405(12)
C(9)-C(10)	1.369(13)
C(9)-C(13)	1.580(10)
C(10)-C(11)	1.351(9)
C(14)-C(15)	1.373(7)
C(14)-C(19)	1.404(7)
C(15)-C(16)	1.384(7)
C(16)-C(17)	1.387(7)
C(17)-C(18)	1.397(8)
C(18)-C(19)	1.378(7)
C(20)-C(25)	1.392(7)
C(20)-C(21)	1.408(6)
C(21)-C(22)	1.374(6)
C(22)-C(23)	1.379(7)
C(23)-C(24)	1.357(8)
C(24)-C(25)	1.398(7)
C(26)-C(27)	1.394(7)
C(26)-C(31)	1.401(7)
C(27)-C(28)	1.395(7)
C(27)-C(32)	1.513(7)
C(28)-C(29)	1.399(8)
C(29)-C(30)	1.354(8)
C(29)-C(33)	1.522(8)
C(30)-C(31)	1.395(7)
C(34)-C(38)	1.418(7)
C(34)-C(35)	1.440(7)
C(35)-C(36)	1.420(7)
C(36)-C(37)	1.397(8)
C(37)-C(38)	1.439(8)

C(43)-Fe(1)-C(42)	92.5(2)
C(43)-Fe(1)-C(35)	95.5(2)
C(42)-Fe(1)-C(35)	153.5(2)
C(43)-Fe(1)-C(37)	157.7(2)
C(42)-Fe(1)-C(37)	99.4(2)
C(35)-Fe(1)-C(37)	65.9(2)
C(43)-Fe(1)-C(38)	122.5(2)
C(42)-Fe(1)-C(38)	88.6(2)
C(35)-Fe(1)-C(38)	65.8(2)
C(37)-Fe(1)-C(38)	40.0(2)
C(43)-Fe(1)-C(34)	91.0(2)
C(42)-Fe(1)-C(34)	114.7(2)
C(35)-Fe(1)-C(34)	40.07(18)
C(37)-Fe(1)-C(34)	67.0(2)
C(38)-Fe(1)-C(34)	39.3(2)

C(43)-Fe(1)-C(36)	130.7(2)
C(42)-Fe(1)-C(36)	136.5(2)
C(35)-Fe(1)-C(36)	39.49(19)
C(37)-Fe(1)-C(36)	38.7(2)
C(38)-Fe(1)-C(36)	65.8(2)
C(34)-Fe(1)-C(36)	66.89(19)
C(43)-Fe(1)-P(1)	92.09(16)
C(42)-Fe(1)-P(1)	94.90(17)
C(35)-Fe(1)-P(1)	110.02(14)
C(37)-Fe(1)-P(1)	105.41(15)
C(38)-Fe(1)-P(1)	145.05(15)
C(34)-Fe(1)-P(1)	150.08(13)
C(36)-Fe(1)-P(1)	88.96(14)
C(21)-P(1)-C(1)	96.0(2)
C(21)-P(1)-C(5)	97.2(2)
C(1)-P(1)-C(5)	98.0(2)
C(21)-P(1)-Fe(1)	118.93(15)
C(1)-P(1)-Fe(1)	119.77(15)
C(5)-P(1)-Fe(1)	121.52(16)
C(41)-Si(1)-C(39)	112.3(3)
C(41)-Si(1)-C(40)	109.9(3)
C(39)-Si(1)-C(40)	111.2(3)
C(41)-Si(1)-C(34)	111.7(2)
C(39)-Si(1)-C(34)	105.4(2)
C(40)-Si(1)-C(34)	106.0(3)
C(2)-C(1)-C(6)	126.6(4)
C(2)-C(1)-P(1)	111.9(3)
C(6)-C(1)-P(1)	121.4(3)
F(2)-P(2)-F(5)	92.9(10)
F(2)-P(2)-F(1)	105.1(10)
F(5)-P(2)-F(1)	93.3(7)
F(2)-P(2)-F(1A)	88.1(10)
F(5)-P(2)-F(1A)	90.8(7)
F(1)-P(2)-F(1A)	17.3(5)
F(2)-P(2)-F(3A)	113.5(9)
F(5)-P(2)-F(3A)	153.6(8)
F(1)-P(2)-F(3A)	79.1(6)
F(1A)-P(2)-F(3A)	88.9(5)
F(2)-P(2)-F(4A)	144.4(10)
F(5)-P(2)-F(4A)	52.4(7)
F(1)-P(2)-F(4A)	86.8(7)
F(1A)-P(2)-F(4A)	98.8(7)
F(3A)-P(2)-F(4A)	101.5(8)
F(2)-P(2)-F(6A)	65.8(10)
F(5)-P(2)-F(6A)	86.0(9)
F(1)-P(2)-F(6A)	170.8(11)
F(1A)-P(2)-F(6A)	153.5(11)
F(3A)-P(2)-F(6A)	105.4(10)
F(4A)-P(2)-F(6A)	100.0(9)
F(2)-P(2)-F(6)	92.1(9)
F(5)-P(2)-F(6)	94.9(6)
F(1)-P(2)-F(6)	160.5(7)
F(1A)-P(2)-F(6)	174.3(6)
F(3A)-P(2)-F(6)	85.8(6)
F(4A)-P(2)-F(6)	84.3(6)
F(6A)-P(2)-F(6)	28.3(8)
F(2)-P(2)-F(2A)	28.0(8)
F(5)-P(2)-F(2A)	117.7(8)
F(1)-P(2)-F(2A)	89.9(7)
F(1A)-P(2)-F(2A)	76.0(7)
F(3A)-P(2)-F(2A)	87.8(6)

F(4A)-P(2)-F(2A)	169.3(8)
F(6A)-P(2)-F(2A)	82.3(9)
F(6)-P(2)-F(2A)	101.8(6)
F(2)-P(2)-F(3)	87.6(9)
F(5)-P(2)-F(3)	175.2(6)
F(1)-P(2)-F(3)	91.2(5)
F(1A)-P(2)-F(3)	94.0(5)
F(3A)-P(2)-F(3)	26.6(4)
F(4A)-P(2)-F(3)	126.3(7)
F(6A)-P(2)-F(3)	89.8(8)
F(6)-P(2)-F(3)	80.3(5)
F(2A)-P(2)-F(3)	64.0(6)
F(2)-P(2)-F(4)	170.4(9)
F(5)-P(2)-F(4)	88.8(7)
F(1)-P(2)-F(4)	84.3(6)
F(1A)-P(2)-F(4)	101.3(6)
F(3A)-P(2)-F(4)	65.4(6)
F(4A)-P(2)-F(4)	36.4(6)
F(6A)-P(2)-F(4)	104.9(10)
F(6)-P(2)-F(4)	78.3(6)
F(2A)-P(2)-F(4)	153.2(7)
F(3)-P(2)-F(4)	90.0(6)
F(2)-P(2)-F(5A)	61.4(8)
F(5)-P(2)-F(5A)	32.4(6)
F(1)-P(2)-F(5A)	94.0(6)
F(1A)-P(2)-F(5A)	82.7(6)
F(3A)-P(2)-F(5A)	170.3(5)
F(4A)-P(2)-F(5A)	84.8(7)
F(6A)-P(2)-F(5A)	80.5(9)
F(6)-P(2)-F(5A)	102.4(5)
F(2A)-P(2)-F(5A)	85.2(7)
F(3)-P(2)-F(5A)	148.8(6)
F(4)-P(2)-F(5A)	121.2(6)
C(1)-C(2)-C(3)	121.9(4)
C(14)-C(3)-C(4)	115.8(4)
C(14)-C(3)-C(2)	110.9(4)
C(4)-C(3)-C(2)	106.2(4)
C(14)-C(3)-C(20)	111.5(4)
C(4)-C(3)-C(20)	106.0(4)
C(2)-C(3)-C(20)	105.7(3)
C(5)-C(4)-C(3)	120.9(4)
C(4)-C(5)-C(26)	124.4(4)
C(4)-C(5)-P(1)	113.1(4)
C(26)-C(5)-P(1)	122.5(3)
C(7)-C(6)-C(11)	119.7(5)
C(7)-C(6)-C(1)	120.2(4)
C(11)-C(6)-C(1)	120.1(5)
C(6)-C(7)-C(12)	121.8(5)
C(6)-C(7)-C(8)	118.8(6)
C(12)-C(7)-C(8)	119.2(6)
C(7)-C(8)-C(9)	119.7(7)
C(10)-C(9)-C(8)	121.1(7)
C(10)-C(9)-C(13)	122.7(9)
C(8)-C(9)-C(13)	116.2(10)
C(11)-C(10)-C(9)	119.2(8)
C(10)-C(11)-C(6)	121.6(7)
C(15)-C(14)-C(19)	118.0(4)
C(15)-C(14)-C(3)	119.1(4)
C(19)-C(14)-C(3)	122.9(4)
C(14)-C(15)-C(16)	122.0(5)
C(15)-C(16)-C(17)	120.3(5)

C(16)-C(17)-C(18)	118.4(5)
C(19)-C(18)-C(17)	120.9(5)
C(18)-C(19)-C(14)	120.5(5)
C(25)-C(20)-C(21)	118.5(4)
C(25)-C(20)-C(3)	123.9(4)
C(21)-C(20)-C(3)	117.5(4)
C(22)-C(21)-C(20)	120.5(4)
C(22)-C(21)-P(1)	126.3(4)
C(20)-C(21)-P(1)	113.1(3)
C(21)-C(22)-C(23)	119.9(5)
C(24)-C(23)-C(22)	120.6(4)
C(23)-C(24)-C(25)	120.6(5)
C(20)-C(25)-C(24)	119.6(5)
C(27)-C(26)-C(31)	119.8(4)
C(27)-C(26)-C(5)	120.8(4)
C(31)-C(26)-C(5)	119.4(4)
C(26)-C(27)-C(28)	118.1(5)
C(26)-C(27)-C(32)	122.6(4)
C(28)-C(27)-C(32)	119.3(5)
C(27)-C(28)-C(29)	122.1(5)
C(30)-C(29)-C(28)	118.8(5)
C(30)-C(29)-C(33)	121.8(6)
C(28)-C(29)-C(33)	119.4(6)
C(29)-C(30)-C(31)	121.0(5)
C(30)-C(31)-C(26)	120.1(5)
C(38)-C(34)-C(35)	105.8(4)
C(38)-C(34)-Si(1)	127.5(4)
C(35)-C(34)-Si(1)	126.2(4)
C(38)-C(34)-Fe(1)	70.1(3)
C(35)-C(34)-Fe(1)	69.0(3)
Si(1)-C(34)-Fe(1)	131.0(3)
C(36)-C(35)-C(34)	109.1(4)
C(36)-C(35)-Fe(1)	71.3(3)
C(34)-C(35)-Fe(1)	70.9(3)
C(37)-C(36)-C(35)	108.1(4)
C(37)-C(36)-Fe(1)	70.2(3)
C(35)-C(36)-Fe(1)	69.3(3)
C(36)-C(37)-C(38)	107.9(5)
C(36)-C(37)-Fe(1)	71.1(3)
C(38)-C(37)-Fe(1)	70.1(3)
C(34)-C(38)-C(37)	109.1(5)
C(34)-C(38)-Fe(1)	70.6(3)
C(37)-C(38)-Fe(1)	69.9(3)
O(1)-C(42)-Fe(1)	175.1(5)
O(2)-C(43)-Fe(1)	176.6(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cj501.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Fe(1)	37(1)	34(1)	44(1)	2(1)	2(1)	-3(1)
P(1)	31(1)	30(1)	39(1)	1(1)	-2(1)	-1(1)
Si(1)	42(1)	44(1)	46(1)	5(1)	4(1)	-5(1)
O(1)	60(2)	88(3)	75(3)	6(2)	-1(2)	32(2)
C(1)	36(2)	35(2)	39(2)	2(2)	-5(2)	4(2)
P(2)	100(1)	62(1)	55(1)	-9(1)	14(1)	1(1)
O(2)	63(2)	55(2)	57(2)	-9(2)	-2(2)	-16(2)
C(2)	29(2)	37(2)	41(2)	4(2)	-2(2)	5(2)
C(3)	37(2)	34(2)	37(2)	0(2)	-4(2)	2(2)
C(4)	35(2)	36(2)	39(2)	-2(2)	-5(2)	-3(2)
C(5)	35(2)	30(2)	46(3)	2(2)	-6(2)	-1(2)
C(6)	42(2)	40(3)	49(3)	11(2)	10(2)	9(2)
C(7)	57(3)	36(3)	53(3)	0(2)	15(3)	5(2)
C(8)	102(5)	42(3)	103(5)	-4(4)	55(5)	10(3)
C(9)	111(6)	73(5)	120(7)	65(5)	63(6)	59(5)
C(10)	72(4)	66(4)	131(8)	47(5)	26(5)	28(4)
C(11)	47(3)	70(4)	76(4)	40(3)	13(3)	22(3)
C(12)	78(4)	62(4)	101(6)	-12(4)	-7(4)	1(4)
C(13)	161(9)	64(5)	209(12)	71(6)	92(9)	48(5)
C(14)	31(2)	38(3)	43(3)	8(2)	-5(2)	1(2)
C(15)	44(3)	40(3)	48(3)	4(2)	-4(2)	2(2)
C(16)	53(3)	54(3)	42(2)	5(3)	6(3)	5(2)
C(17)	46(3)	63(3)	61(4)	21(3)	6(3)	4(2)
C(18)	53(3)	48(3)	59(3)	12(3)	3(3)	-12(2)
C(19)	55(3)	38(3)	46(3)	0(2)	0(2)	-2(2)
C(20)	34(2)	29(2)	38(2)	-1(2)	-7(2)	-1(2)
C(21)	37(2)	23(2)	44(2)	-3(2)	-5(2)	3(2)

C(22)	34(2)	33(2)	53(3)	-3(2)	-7(2)	3(2)
C(23)	34(2)	45(3)	62(3)	0(2)	-14(2)	9(2)
C(24)	56(3)	44(3)	47(3)	4(2)	-13(2)	10(2)
C(25)	39(2)	35(2)	49(3)	3(2)	2(2)	3(2)
C(26)	38(2)	37(3)	42(2)	1(2)	1(2)	-12(2)
C(27)	55(3)	35(3)	44(3)	-2(2)	3(2)	-3(2)
C(28)	67(3)	44(3)	54(3)	-9(2)	-2(3)	3(3)
C(29)	70(3)	49(3)	47(3)	-7(2)	1(3)	-16(3)
C(30)	54(3)	60(3)	43(3)	-1(2)	-11(2)	-9(3)
C(31)	48(3)	40(3)	46(3)	-1(2)	-3(2)	-8(2)
C(32)	63(3)	51(3)	48(3)	0(2)	-6(2)	11(2)
C(33)	112(6)	82(5)	52(4)	-21(3)	2(4)	-11(4)
C(34)	43(2)	40(3)	38(2)	7(2)	1(2)	-2(2)
C(35)	44(2)	38(3)	50(3)	9(2)	-2(2)	3(2)
C(36)	44(2)	47(3)	51(3)	12(2)	-1(2)	-7(2)
C(37)	65(3)	43(3)	43(3)	0(2)	-3(2)	-17(3)
C(38)	55(3)	43(3)	44(3)	0(2)	11(2)	-3(2)
C(39)	58(3)	40(3)	82(4)	1(3)	-2(3)	-6(2)
C(40)	76(4)	106(6)	52(3)	9(4)	13(3)	-34(4)
C(41)	43(3)	52(3)	67(4)	8(3)	2(2)	2(2)
C(42)	50(3)	55(3)	53(3)	2(2)	5(2)	0(2)
C(43)	42(2)	40(3)	53(3)	4(2)	2(2)	-8(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cj501.

	x	y	z	U(eq)
H(2)	-1227	8129	11135	43

H(4)	-890	6280	9869	44
H(8)	194	10739	10539	99
H(10)	-1330	10171	8268	108
H(11)	-1242	8958	8778	77
H(12A)	47	9454	11997	121
H(12B)	804	9816	11491	121
H(12C)	622	8959	11312	121
H(13A)	-565	11464	8294	217
H(13B)	-179	11667	9393	217
H(13C)	-1101	11617	9290	217
H(15)	-1037	7574	12896	53
H(16)	-1838	7093	14177	59
H(17)	-2515	5989	13882	68
H(18)	-2341	5371	12284	64
H(19)	-1544	5861	11004	55
H(22)	1945	7685	10860	48
H(23)	2253	7179	12476	56
H(24)	1333	6563	13434	59
H(25)	53	6481	12833	49
H(28)	965	5438	6814	66
H(30)	-875	6626	5905	63
H(31)	-983	7122	7584	54
H(32A)	1072	5346	8964	81
H(32B)	1101	6176	9392	81
H(32C)	1665	5926	8467	81
H(33A)	-216	5917	4627	123
H(33B)	-52	5127	5142	123
H(33C)	653	5671	4885	123
H(35)	485	9523	7991	53
H(36)	-135	8293	7572	57
H(37)	893	7450	6860	60
H(38)	2150	8181	6743	57
H(39A)	1455	10608	8533	90
H(39B)	1245	10796	7346	90
H(39C)	2002	11144	7869	90
H(40A)	2873	10458	5941	117
H(40B)	2111	10036	5554	117
H(40C)	2882	9579	5804	117
H(41A)	3258	9201	8177	81
H(41B)	2962	9822	8972	81
H(41C)	3526	10041	8031	81

[2,6-Bis-(2',4'-dimethylphenyl)-4-phenylphosphabarrelene]-η^6-cymene(dichloro)ruthenium (II) (4):

Table 1. Crystal data and structure refinement for cj444.

Identification code	cj444

Empirical formula	C43.50 H44 Cl3 P Ru
Formula weight	805.18
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 10.238(2) A alpha = 107.20(3) deg. b = 13.693(3) A beta = 103.59(3) deg. c = 16.451(3) A gamma = 106.38(3) deg.
Volume	1982.2(7) A^3
Z, Calculated density	2, 1.349 Mg/m^3
Absorption coefficient	0.667 mm^-1
F(000)	830
Crystal size	0.35 x 0.25 x 0.15 mm
Theta range for data collection	2.92 to 25.90 deg.
Limiting indices	-12<=h<=12, -16<=k<=16, -20<=l<=20
Reflections collected / unique	13631 / 7520 [R(int) = 0.0352]
Completeness to theta = 25.90	97.5 %
Max. and min. transmission	Sortav 0.900 and 0.706
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7520 / 6 / 458
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0525, wR2 = 0.1409
R indices (all data)	R1 = 0.0675, wR2 = 0.1500
Largest diff. peak and hole	1.460 (near Cl3) and -0.637 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cj444. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

U(eq)		x	y	z
33(1)	Ru(1)	4906(1)	1380(1)	1632(1)
39(1)	Cl(1)	4596(1)	-471(1)	1509(1)
31(1)	P(1)	5422(1)	1765(1)	3195(1)
32(1)	C(1)	6639(4)	1264(3)	3831(3)
43(1)	Cl(2)	7430(1)	1729(1)	1866(1)
32(1)	C(2)	6758(4)	1541(3)	4747(3)
73(1)	Cl(3)	-801(3)	-3294(2)	-1244(2)
35(1)	C(3)	5888(4)	2236(3)	5099(3)
73(1)	Cl(4)	-1170(4)	-4210(2)	133(2)
39(1)	C(4)	6356(5)	3266(4)	4890(3)
37(1)	C(5)	6228(5)	3201(4)	4051(3)
35(1)	C(6)	4315(5)	1558(3)	4489(3)
33(1)	C(7)	3905(4)	1265(3)	3596(3)
37(1)	C(8)	7610(5)	1182(4)	5288(3)
39(1)	C(9)	8348(5)	561(4)	4919(3)
38(1)	C(10)	8240(5)	295(4)	4019(3)
34(1)	C(11)	7371(4)	642(3)	3469(3)
38(1)	C(12)	6160(5)	2520(4)	6111(3)
40(1)	C(13)	5222(5)	1906(4)	6425(3)
47(1)	C(14)	5473(5)	2203(4)	7349(3)
57(1)	C(15)	6709(6)	3089(4)	7975(3)
63(2)	C(16)	7664(6)	3676(5)	7670(3)
53(1)	C(17)	7399(6)	3406(4)	6750(3)
41(1)	C(18)	6727(5)	4227(4)	3871(3)
50(1)	C(19)	8102(5)	4652(4)	3829(4)
60(1)	C(20)	8526(6)	5674(4)	3741(4)

C(21)	7612(6)	6253(4)	3685(4)	60(1)
C(22)	6282(6)	5826(4)	3732(4)	57(1)
C(23)	5839(6)	4842(4)	3827(3)	49(1)
C(24)	9147(6)	4094(5)	3919(5)	72(2)
C(25)	8126(7)	7354(5)	3580(5)	80(2)
C(26)	2382(4)	514(4)	2994(3)	34(1)
C(27)	1252(5)	911(4)	2858(3)	42(1)
C(28)	-147(5)	156(5)	2333(3)	47(1)
C(29)	-481(5)	-978(5)	1973(3)	48(1)
C(30)	636(5)	-1348(4)	2123(3)	45(1)
C(31)	2052(5)	-615(4)	2616(3)	38(1)
C(32)	1553(6)	2127(5)	3298(4)	65(2)
C(33)	-2049(6)	-1789(6)	1422(4)	70(2)
C(34)	4935(5)	2793(4)	1203(3)	43(1)
C(35)	3921(5)	2598(4)	1633(3)	40(1)
C(36)	2781(5)	1543(4)	1332(3)	39(1)
C(37)	2682(5)	650(4)	592(3)	40(1)
C(38)	3743(5)	835(4)	157(3)	43(1)
C(39)	4829(5)	1878(4)	454(3)	43(1)
C(40)	6003(5)	3942(4)	1484(4)	54(1)
C(41)	5211(7)	4609(5)	1122(5)	80(2)
C(42)	7347(7)	4010(6)	1195(5)	84(2)
C(43)	1530(5)	-473(4)	261(3)	50(1)
C(44)	-59(14)	-3368(11)	-194(8)	72(3)

Table 3. Bond lengths [A] and angles [deg] for cj444.

Ru(1)-C(35)	2.177(4)
Ru(1)-C(36)	2.204(4)
Ru(1)-C(38)	2.221(4)
Ru(1)-C(39)	2.228(4)
Ru(1)-C(37)	2.232(4)

Ru(1)-C(34)	2.240(4)
Ru(1)-P(1)	2.3619(12)
Ru(1)-Cl(2)	2.4044(12)
Ru(1)-Cl(1)	2.4043(12)
P(1)-C(1)	1.846(4)
P(1)-C(5)	1.852(5)
P(1)-C(7)	1.862(4)
C(1)-C(11)	1.383(5)
C(1)-C(2)	1.407(6)
C(2)-C(8)	1.390(6)
C(2)-C(3)	1.559(5)
Cl(3)-C(44)	1.761(13)
C(3)-C(6)	1.520(6)
C(3)-C(4)	1.524(6)
C(3)-C(12)	1.529(6)
Cl(4)-C(44)	1.681(12)
C(4)-C(5)	1.329(6)
C(5)-C(18)	1.497(6)
C(6)-C(7)	1.326(6)
C(7)-C(26)	1.496(6)
C(8)-C(9)	1.391(6)
C(9)-C(10)	1.385(6)
C(10)-C(11)	1.396(5)
C(12)-C(13)	1.389(6)
C(12)-C(17)	1.391(7)
C(13)-C(14)	1.392(6)
C(14)-C(15)	1.384(7)
C(15)-C(16)	1.371(8)
C(16)-C(17)	1.386(7)
C(18)-C(19)	1.389(7)
C(18)-C(23)	1.407(6)
C(19)-C(20)	1.405(7)
C(19)-C(24)	1.485(7)
C(20)-C(21)	1.392(7)
C(21)-C(22)	1.353(8)
C(21)-C(25)	1.525(7)
C(22)-C(23)	1.363(7)
C(26)-C(31)	1.389(6)
C(26)-C(27)	1.411(6)
C(27)-C(28)	1.386(7)
C(27)-C(32)	1.511(7)
C(28)-C(29)	1.393(7)
C(29)-C(30)	1.376(6)
C(29)-C(33)	1.533(7)
C(30)-C(31)	1.383(6)
C(34)-C(35)	1.396(6)
C(34)-C(39)	1.431(7)
C(34)-C(40)	1.500(7)
C(35)-C(36)	1.431(7)
C(36)-C(37)	1.407(6)
C(37)-C(38)	1.440(6)
C(37)-C(43)	1.494(7)
C(38)-C(39)	1.397(7)
C(40)-C(41)	1.536(7)
C(40)-C(42)	1.546(8)
C(35)-Ru(1)-C(36)	38.12(17)
C(35)-Ru(1)-C(38)	79.05(17)
C(36)-Ru(1)-C(38)	67.04(16)
C(35)-Ru(1)-C(39)	66.48(17)
C(36)-Ru(1)-C(39)	79.09(16)

C(38)-Ru(1)-C(39)	36.60(18)
C(35)-Ru(1)-C(37)	67.65(17)
C(36)-Ru(1)-C(37)	36.97(16)
C(38)-Ru(1)-C(37)	37.74(16)
C(39)-Ru(1)-C(37)	67.18(17)
C(35)-Ru(1)-C(34)	36.82(16)
C(36)-Ru(1)-C(34)	67.77(17)
C(38)-Ru(1)-C(34)	67.10(18)
C(39)-Ru(1)-C(34)	37.36(17)
C(37)-Ru(1)-C(34)	80.15(17)
C(35)-Ru(1)-P(1)	94.54(12)
C(36)-Ru(1)-P(1)	98.05(12)
C(38)-Ru(1)-P(1)	162.77(13)
C(39)-Ru(1)-P(1)	152.95(14)
C(37)-Ru(1)-P(1)	125.04(12)
C(34)-Ru(1)-P(1)	116.53(13)
C(35)-Ru(1)-Cl(2)	124.79(13)
C(36)-Ru(1)-Cl(2)	161.74(12)
C(38)-Ru(1)-Cl(2)	108.05(13)
C(39)-Ru(1)-Cl(2)	87.12(12)
C(37)-Ru(1)-Cl(2)	144.77(12)
C(34)-Ru(1)-Cl(2)	94.03(12)
P(1)-Ru(1)-Cl(2)	88.78(5)
C(35)-Ru(1)-Cl(1)	147.70(13)
C(36)-Ru(1)-Cl(1)	109.95(13)
C(38)-Ru(1)-Cl(1)	92.76(13)
C(39)-Ru(1)-Cl(1)	122.32(13)
C(37)-Ru(1)-Cl(1)	86.70(13)
C(34)-Ru(1)-Cl(1)	159.27(13)
P(1)-Ru(1)-Cl(1)	84.15(5)
Cl(2)-Ru(1)-Cl(1)	87.50(5)
C(1)-P(1)-C(5)	95.32(19)
C(1)-P(1)-C(7)	95.03(18)
C(5)-P(1)-C(7)	96.50(19)
C(1)-P(1)-Ru(1)	123.09(13)
C(5)-P(1)-Ru(1)	121.56(14)
C(7)-P(1)-Ru(1)	118.87(14)
C(11)-C(1)-C(2)	120.3(4)
C(11)-C(1)-P(1)	125.3(3)
C(2)-C(1)-P(1)	114.5(3)
C(8)-C(2)-C(1)	119.8(4)
C(8)-C(2)-C(3)	123.1(4)
C(1)-C(2)-C(3)	117.1(3)
C(6)-C(3)-C(4)	106.6(3)
C(6)-C(3)-C(12)	114.5(3)
C(4)-C(3)-C(12)	112.0(4)
C(6)-C(3)-C(2)	105.1(3)
C(4)-C(3)-C(2)	106.1(3)
C(12)-C(3)-C(2)	111.8(3)
C(5)-C(4)-C(3)	121.6(4)
C(4)-C(5)-C(18)	120.3(4)
C(4)-C(5)-P(1)	113.6(3)
C(18)-C(5)-P(1)	126.1(3)
C(7)-C(6)-C(3)	121.6(4)
C(6)-C(7)-C(26)	121.1(4)
C(6)-C(7)-P(1)	113.6(3)
C(26)-C(7)-P(1)	125.1(3)
C(2)-C(8)-C(9)	119.5(4)
C(10)-C(9)-C(8)	120.8(4)
C(9)-C(10)-C(11)	119.9(4)
C(1)-C(11)-C(10)	119.7(4)

C(13)-C(12)-C(17)	118.0(4)
C(13)-C(12)-C(3)	122.2(4)
C(17)-C(12)-C(3)	119.8(4)
C(12)-C(13)-C(14)	121.0(4)
C(15)-C(14)-C(13)	120.1(5)
C(16)-C(15)-C(14)	119.1(5)
C(15)-C(16)-C(17)	121.0(5)
C(16)-C(17)-C(12)	120.6(5)
C(19)-C(18)-C(23)	118.5(4)
C(19)-C(18)-C(5)	122.0(4)
C(23)-C(18)-C(5)	119.2(4)
C(18)-C(19)-C(20)	118.0(4)
C(18)-C(19)-C(24)	122.5(5)
C(20)-C(19)-C(24)	119.5(5)
C(21)-C(20)-C(19)	122.1(5)
C(22)-C(21)-C(20)	118.8(5)
C(22)-C(21)-C(25)	121.4(5)
C(20)-C(21)-C(25)	119.8(5)
C(21)-C(22)-C(23)	120.7(5)
C(22)-C(23)-C(18)	121.8(5)
C(31)-C(26)-C(27)	119.1(4)
C(31)-C(26)-C(7)	119.0(4)
C(27)-C(26)-C(7)	121.7(4)
C(28)-C(27)-C(26)	118.4(4)
C(28)-C(27)-C(32)	120.8(4)
C(26)-C(27)-C(32)	120.7(4)
C(27)-C(28)-C(29)	122.3(4)
C(30)-C(29)-C(28)	118.2(4)
C(30)-C(29)-C(33)	121.0(5)
C(28)-C(29)-C(33)	120.8(5)
C(29)-C(30)-C(31)	120.9(5)
C(30)-C(31)-C(26)	120.9(4)
C(35)-C(34)-C(39)	117.3(4)
C(35)-C(34)-C(40)	120.0(4)
C(39)-C(34)-C(40)	122.5(4)
C(35)-C(34)-Ru(1)	69.1(2)
C(39)-C(34)-Ru(1)	70.8(2)
C(40)-C(34)-Ru(1)	135.2(3)
C(34)-C(35)-C(36)	122.4(4)
C(34)-C(35)-Ru(1)	74.1(2)
C(36)-C(35)-Ru(1)	72.0(2)
C(37)-C(36)-C(35)	119.8(4)
C(37)-C(36)-Ru(1)	72.6(2)
C(35)-C(36)-Ru(1)	69.9(2)
C(36)-C(37)-C(38)	118.2(4)
C(36)-C(37)-C(43)	121.9(4)
C(38)-C(37)-C(43)	119.8(4)
C(36)-C(37)-Ru(1)	70.4(2)
C(38)-C(37)-Ru(1)	70.7(2)
C(43)-C(37)-Ru(1)	129.7(3)
C(39)-C(38)-C(37)	120.8(4)
C(39)-C(38)-Ru(1)	72.0(3)
C(37)-C(38)-Ru(1)	71.6(2)
C(38)-C(39)-C(34)	121.3(4)
C(38)-C(39)-Ru(1)	71.4(2)
C(34)-C(39)-Ru(1)	71.8(2)
C(34)-C(40)-C(41)	109.0(4)
C(34)-C(40)-C(42)	114.8(5)
C(41)-C(40)-C(42)	110.6(5)
Cl(4)-C(44)-Cl(3)	117.5(7)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cj444.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Ru(1)	38(1)	46(1)	31(1)	23(1)	19(1)	25(1)
Cl(1)	48(1)	48(1)	37(1)	24(1)	20(1)	26(1)
P(1)	36(1)	40(1)	31(1)	20(1)	18(1)	23(1)
C(1)	35(2)	38(2)	31(2)	17(2)	16(2)	19(2)
Cl(2)	40(1)	58(1)	47(1)	30(1)	21(1)	26(1)
C(2)	34(2)	36(2)	34(2)	18(2)	16(2)	17(2)
Cl(3)	48(2)	47(1)	121(3)	43(2)	9(2)	21(1)
C(3)	41(2)	43(2)	30(2)	18(2)	18(2)	22(2)
Cl(4)	84(2)	46(2)	70(2)	15(1)	21(2)	11(1)
C(4)	43(2)	41(2)	37(2)	14(2)	16(2)	23(2)
C(5)	40(2)	40(2)	41(2)	21(2)	17(2)	23(2)
C(6)	39(2)	42(2)	34(2)	19(2)	20(2)	22(2)
C(7)	35(2)	42(2)	34(2)	20(2)	18(2)	23(2)
C(8)	40(2)	48(3)	31(2)	21(2)	14(2)	19(2)
C(9)	40(2)	48(3)	37(2)	25(2)	12(2)	23(2)
C(10)	41(2)	45(2)	39(2)	21(2)	16(2)	25(2)
C(11)	39(2)	45(2)	33(2)	21(2)	17(2)	26(2)
C(12)	46(3)	44(2)	32(2)	14(2)	18(2)	26(2)
C(13)	49(3)	45(2)	30(2)	15(2)	14(2)	25(2)
C(14)	59(3)	58(3)	42(3)	29(2)	26(2)	33(3)
C(15)	80(4)	61(3)	31(2)	12(2)	20(3)	32(3)
C(16)	71(4)	61(3)	36(3)	7(3)	11(3)	12(3)

C(17)	50(3)	62(3)	37(3)	15(2)	13(2)	15(2)
C(18)	42(3)	41(2)	42(2)	18(2)	12(2)	19(2)
C(19)	39(3)	62(3)	61(3)	37(3)	15(2)	22(2)
C(20)	42(3)	62(3)	74(4)	37(3)	13(3)	11(2)
C(21)	57(3)	51(3)	70(4)	33(3)	7(3)	18(3)
C(22)	48(3)	49(3)	75(4)	29(3)	12(3)	22(2)
C(23)	53(3)	42(3)	60(3)	25(2)	20(2)	25(2)
C(24)	51(3)	70(4)	100(5)	35(4)	25(3)	31(3)
C(25)	67(4)	61(4)	103(5)	47(4)	9(4)	10(3)
C(26)	36(2)	53(3)	30(2)	23(2)	20(2)	25(2)
C(27)	43(3)	66(3)	40(2)	30(2)	24(2)	36(2)
C(28)	36(2)	84(4)	45(3)	36(3)	22(2)	37(3)
C(29)	32(2)	81(4)	41(3)	36(3)	15(2)	22(2)
C(30)	45(3)	55(3)	38(2)	25(2)	14(2)	18(2)
C(31)	41(2)	50(3)	35(2)	22(2)	17(2)	24(2)
C(32)	72(4)	78(4)	70(4)	33(3)	31(3)	55(3)
C(33)	39(3)	102(5)	63(4)	46(3)	9(3)	13(3)
C(34)	50(3)	54(3)	43(3)	34(2)	18(2)	29(2)
C(35)	46(3)	49(3)	39(2)	23(2)	17(2)	31(2)
C(36)	36(2)	61(3)	36(2)	25(2)	17(2)	31(2)
C(37)	42(2)	56(3)	32(2)	25(2)	11(2)	27(2)
C(38)	57(3)	61(3)	28(2)	24(2)	19(2)	39(3)
C(39)	50(3)	67(3)	38(2)	38(2)	24(2)	35(2)
C(40)	55(3)	61(3)	63(3)	44(3)	21(3)	24(3)
C(41)	85(4)	66(4)	108(5)	60(4)	26(4)	32(3)
C(42)	72(4)	85(5)	129(6)	69(5)	52(4)	32(4)
C(43)	47(3)	60(3)	41(3)	18(2)	10(2)	22(2)
C(44)	74(5)	74(5)	63(5)	17(4)	36(4)	21(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cj444.

	x	y	z	U(eq)
H(4)	6749	3973	5372	46
H(6)	3609	1340	4752	41
H(8)	7688	1359	5906	45
H(9)	8933	317	5289	46
H(10)	8756	-124	3776	46
H(11)	7284	451	2849	41
H(13)	4397	1274	6001	48
H(14)	4796	1796	7552	56
H(15)	6893	3287	8607	69
H(16)	8522	4278	8096	76
H(17)	8068	3830	6553	63
H(20)	9468	5978	3719	72
H(22)	5650	6216	3698	68
H(23)	4904	4565	3866	58
H(24A)	9111	3807	4397	107
H(24B)	10130	4624	4078	107
H(24C)	8891	3482	3342	107
H(25A)	8406	7961	4164	121
H(25B)	7339	7387	3129	121
H(25C)	8964	7422	3379	121
H(28)	-906	422	2215	57
H(30)	431	-2119	1885	54
H(31)	2809	-888	2698	46
H(32A)	1713	2329	3947	97
H(32B)	721	2280	3014	97
H(32C)	2420	2560	3219	97
H(33A)	-2712	-1403	1502	104
H(33B)	-2273	-2394	1633	104
H(33C)	-2165	-2088	778	104
H(35)	3991	3187	2145	48
H(36)	2093	1447	1630	47
H(38)	3703	240	-339	51
H(39)	5511	1982	152	51
H(40)	6359	4292	2162	65
H(41A)	4932	4333	460	120
H(41B)	5856	5390	1387	120
H(41C)	4339	4531	1288	120
H(42A)	7857	3602	1449	127
H(42B)	8000	4785	1422	127
H(42C)	7036	3687	532	127
H(43A)	1050	-506	708	75
H(43B)	1970	-1028	177	75
H(43C)	813	-622	-318	75
H(44A)	767	-3603	-214	86
H(44B)	340	-2613	281	86

Di-[2,6-Bis-(2',4'-dimethylphenyl)-4-phenylphosphabarrelene]carbonyl(chloro)rhodium (I) (5):

Table 1. Crystal data and structure refinement for cj432.

Identification code	c:\bono\chris\p-1
Empirical formula	C71 H62 Cl13 O P2 Rh
Formula weight	1556.91
Temperature	150(2) K
Wavelength	0.71069 A
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 10.520(5) A alpha = 97.800(5) deg. b = 12.532(5) A beta = 101.563(5) deg. c = 14.300(5) A gamma = 108.390(5) deg.
Volume	1712.1(12) A^3
Z, Calculated density	1, 1.510 Mg/m^3
Absorption coefficient	0.848 mm^-1
F(000)	792
Crystal size	0.15 x 0.12 x 0.10 mm
Theta range for data collection	2.98 to 25.99 deg.
Limiting indices	-12<=h<=12, -15<=k<=15, -17<=l<=17
Reflections collected / unique	12266 / 6652 [R(int) = 0.0514]
Completeness to theta = 25.99	99.0 %
Max. and min. transmission	Sortav 0.945 and 0.753
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6652 / 6 / 416
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0515, wR2 = 0.1068
R indices (all data)	R1 = 0.0802, wR2 = 0.1180
Largest diff. peak and hole	0.850 and -0.656 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cj432. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Rh(1)	0	0	10000	19(1)
Cl(1)	-1187(4)	990(3)	10835(3)	27(1)
Cl(2)	2979(1)	1820(1)	5861(1)	61(1)
Cl(3)	1031(2)	2874(2)	6252(1)	86(1)
Cl(4)	3427(2)	4153(1)	5663(1)	79(1)
Cl(5)	-3504(1)	2640(1)	10154(1)	45(1)
Cl(6)	-1698(1)	4696(1)	11545(1)	58(1)
Cl(7)	-3972(1)	3125(1)	12062(1)	56(1)
P(1)	-1033(1)	528(1)	8647(1)	18(1)
C(1)	-2850(4)	443(3)	8401(3)	21(1)
C(2)	-3247(4)	959(3)	7642(3)	21(1)
C(3)	-2136(3)	1486(3)	7093(3)	19(1)
C(4)	-906(3)	2380(3)	7883(3)	19(1)
C(5)	-280(3)	2069(3)	8647(3)	18(1)
C(6)	-1642(3)	513(3)	6740(3)	20(1)
C(7)	-1133(4)	-45(3)	7359(3)	19(1)
C(8)	-3799(4)	-102(3)	8888(3)	24(1)
C(9)	-5141(4)	-105(3)	8633(3)	28(1)
C(10)	-5530(4)	435(3)	7904(3)	28(1)
C(11)	-4590(4)	965(3)	7406(3)	24(1)
C(12)	-2720(3)	1985(3)	6264(3)	20(1)
C(13)	-3462(4)	1289(3)	5349(3)	24(1)

C(14)	-4073(4)	1714(4)	4609(3)	29(1)
C(15)	-3958(4)	2855(3)	4759(3)	30(1)
C(16)	-3232(4)	3553(3)	5670(3)	35(1)
C(17)	-2630(4)	3133(3)	6410(3)	32(1)
C(18)	880(3)	2897(3)	9449(3)	18(1)
C(19)	2251(4)	2947(3)	9534(3)	22(1)
C(20)	3309(4)	3800(3)	10254(3)	24(1)
C(21)	3056(4)	4585(3)	10911(3)	26(1)
C(22)	1691(4)	4508(3)	10828(3)	27(1)
C(23)	621(4)	3674(3)	10110(3)	23(1)
C(24)	2586(4)	2133(3)	8828(3)	30(1)
C(25)	4239(4)	5497(4)	11689(3)	39(1)
C(26)	-685(4)	-1017(3)	7066(3)	22(1)
C(27)	-1377(4)	-2128(3)	7185(3)	22(1)
C(28)	-918(4)	-3006(3)	6879(3)	30(1)
C(29)	192(4)	-2840(3)	6459(3)	31(1)
C(30)	868(4)	-1731(4)	6354(3)	35(1)
C(31)	438(4)	-830(3)	6647(3)	28(1)
C(32)	-2601(4)	-2368(3)	7624(3)	34(1)
C(33)	589(5)	-3837(4)	6077(4)	51(1)
C(34)	-799(11)	770(11)	10683(10)	21(3)
C(35)	2179(4)	2805(4)	5546(3)	36(1)
C(36)	-2707(4)	3248(4)	11401(3)	37(1)
O(1)	-1361(14)	1306(10)	11045(9)	32(3)

Table 3. Bond lengths [A] and angles [deg] for cj432.

Rh(1)-C(34)#1	1.782(11)
Rh(1)-C(34)	1.782(11)
Rh(1)-P(1)	2.3064(11)
Rh(1)-P(1)#1	2.3064(11)
Rh(1)-Cl(1)#1	2.386(4)

Rh(1)-Cl(1)	2.386(4)
Cl(2)-C(35)	1.757(4)
Cl(3)-C(35)	1.737(4)
Cl(4)-C(35)	1.744(5)
Cl(5)-C(36)	1.758(5)
Cl(6)-C(36)	1.749(4)
Cl(7)-C(36)	1.761(4)
P(1)-C(1)	1.838(4)
P(1)-C(5)	1.842(4)
P(1)-C(7)	1.853(4)
C(1)-C(8)	1.389(5)
C(1)-C(2)	1.396(5)
C(2)-C(11)	1.388(5)
C(2)-C(3)	1.562(5)
C(3)-C(12)	1.525(5)
C(3)-C(6)	1.533(5)
C(3)-C(4)	1.537(5)
C(4)-C(5)	1.329(5)
C(5)-C(18)	1.483(5)
C(6)-C(7)	1.333(5)
C(7)-C(26)	1.478(5)
C(8)-C(9)	1.384(5)
C(9)-C(10)	1.381(6)
C(10)-C(11)	1.387(5)
C(12)-C(13)	1.391(5)
C(12)-C(17)	1.395(5)
C(13)-C(14)	1.382(5)
C(14)-C(15)	1.380(5)
C(15)-C(16)	1.384(6)
C(16)-C(17)	1.375(5)
C(18)-C(23)	1.391(5)
C(18)-C(19)	1.403(5)
C(19)-C(20)	1.390(5)
C(19)-C(24)	1.508(5)
C(20)-C(21)	1.391(5)
C(21)-C(22)	1.388(5)
C(21)-C(25)	1.515(5)
C(22)-C(23)	1.385(5)
C(26)-C(31)	1.398(5)
C(26)-C(27)	1.404(5)
C(27)-C(28)	1.387(5)
C(27)-C(32)	1.508(5)
C(28)-C(29)	1.390(6)
C(29)-C(30)	1.390(6)
C(29)-C(33)	1.506(6)
C(30)-C(31)	1.388(5)
C(34)-O(1)	1.161(13)

C(34)#1-Rh(1)-C(34)	180.0(7)
C(34)#1-Rh(1)-P(1)	93.1(4)
C(34)-Rh(1)-P(1)	86.9(4)
C(34)#1-Rh(1)-P(1)#1	86.9(4)
C(34)-Rh(1)-P(1)#1	93.1(4)
P(1)-Rh(1)-P(1)#1	180.0
C(34)#1-Rh(1)-Cl(1)#1	3.3(4)
C(34)-Rh(1)-Cl(1)#1	176.7(4)
P(1)-Rh(1)-Cl(1)#1	95.70(10)
P(1)#1-Rh(1)-Cl(1)#1	84.30(10)
C(34)#1-Rh(1)-Cl(1)	176.7(4)
C(34)-Rh(1)-Cl(1)	3.3(4)
P(1)-Rh(1)-Cl(1)	84.30(10)

P(1)#1-Rh(1)-Cl(1)	95.70(10)
Cl(1)#1-Rh(1)-Cl(1)	180.00(16)
C(1)-P(1)-C(5)	96.44(16)
C(1)-P(1)-C(7)	94.79(16)
C(5)-P(1)-C(7)	97.61(16)
C(1)-P(1)-Rh(1)	121.82(12)
C(5)-P(1)-Rh(1)	114.03(12)
C(7)-P(1)-Rh(1)	125.99(12)
C(8)-C(1)-C(2)	120.6(3)
C(8)-C(1)-P(1)	125.0(3)
C(2)-C(1)-P(1)	114.3(2)
C(11)-C(2)-C(1)	119.2(3)
C(11)-C(2)-C(3)	123.7(3)
C(1)-C(2)-C(3)	117.1(3)
C(12)-C(3)-C(6)	113.0(3)
C(12)-C(3)-C(4)	113.7(3)
C(6)-C(3)-C(4)	106.6(3)
C(12)-C(3)-C(2)	111.7(3)
C(6)-C(3)-C(2)	105.9(3)
C(4)-C(3)-C(2)	105.4(3)
C(5)-C(4)-C(3)	120.5(3)
C(4)-C(5)-C(18)	123.0(3)
C(4)-C(5)-P(1)	114.0(3)
C(18)-C(5)-P(1)	122.9(3)
C(7)-C(6)-C(3)	121.4(3)
C(6)-C(7)-C(26)	124.3(3)
C(6)-C(7)-P(1)	112.8(3)
C(26)-C(7)-P(1)	122.8(3)
C(9)-C(8)-C(1)	119.4(4)
C(10)-C(9)-C(8)	120.3(3)
C(9)-C(10)-C(11)	120.4(4)
C(10)-C(11)-C(2)	120.0(4)
C(13)-C(12)-C(17)	117.1(3)
C(13)-C(12)-C(3)	121.1(3)
C(17)-C(12)-C(3)	121.7(3)
C(14)-C(13)-C(12)	121.8(4)
C(15)-C(14)-C(13)	120.5(4)
C(14)-C(15)-C(16)	118.2(4)
C(17)-C(16)-C(15)	121.5(4)
C(16)-C(17)-C(12)	120.9(4)
C(23)-C(18)-C(19)	119.0(3)
C(23)-C(18)-C(5)	119.7(3)
C(19)-C(18)-C(5)	121.2(3)
C(20)-C(19)-C(18)	118.7(3)
C(20)-C(19)-C(24)	120.3(3)
C(18)-C(19)-C(24)	121.0(3)
C(19)-C(20)-C(21)	122.5(3)
C(22)-C(21)-C(20)	118.0(3)
C(22)-C(21)-C(25)	121.2(4)
C(20)-C(21)-C(25)	120.8(3)
C(23)-C(22)-C(21)	120.6(4)
C(22)-C(23)-C(18)	121.2(3)
C(31)-C(26)-C(27)	119.4(3)
C(31)-C(26)-C(7)	119.3(3)
C(27)-C(26)-C(7)	121.3(3)
C(28)-C(27)-C(26)	118.4(3)
C(28)-C(27)-C(32)	120.6(3)
C(26)-C(27)-C(32)	121.0(3)
C(27)-C(28)-C(29)	123.2(4)
C(28)-C(29)-C(30)	117.4(4)
C(28)-C(29)-C(33)	121.1(4)

C(30)-C(29)-C(33)	121.4(4)
C(31)-C(30)-C(29)	121.2(4)
C(30)-C(31)-C(26)	120.4(4)
O(1)-C(34)-Rh(1)	173.4(16)
Cl(3)-C(35)-Cl(4)	111.7(3)
Cl(3)-C(35)-Cl(2)	110.3(2)
Cl(4)-C(35)-Cl(2)	110.3(2)
Cl(6)-C(36)-Cl(5)	109.5(2)
Cl(6)-C(36)-Cl(7)	110.1(2)
Cl(5)-C(36)-Cl(7)	110.2(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+2

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cj432.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Rh(1)	20(1)	20(1)	19(1)	5(1)	4(1)	9(1)
Cl(1)	31(2)	32(3)	22(2)	1(2)	3(2)	23(2)
Cl(2)	57(1)	63(1)	81(1)	38(1)	18(1)	35(1)
Cl(3)	105(1)	119(2)	73(1)	30(1)	57(1)	68(1)
Cl(4)	79(1)	45(1)	84(1)	26(1)	-13(1)	0(1)
Cl(5)	48(1)	45(1)	38(1)	-1(1)	2(1)	20(1)
Cl(6)	68(1)	34(1)	53(1)	3(1)	21(1)	-8(1)
Cl(7)	52(1)	57(1)	55(1)	12(1)	27(1)	7(1)
P(1)	19(1)	17(1)	17(1)	3(1)	2(1)	6(1)
C(1)	19(2)	19(2)	21(2)	1(2)	3(2)	5(2)
C(2)	22(2)	17(2)	20(2)	1(2)	4(2)	5(2)
C(3)	19(2)	19(2)	16(2)	1(2)	2(2)	7(2)
C(4)	19(2)	14(2)	22(2)	3(2)	6(2)	4(2)
C(5)	15(2)	15(2)	22(2)	4(2)	6(2)	4(2)

C(6)	21(2)	20(2)	16(2)	1(2)	4(2)	5(2)
C(7)	22(2)	16(2)	19(2)	3(2)	7(2)	6(2)
C(8)	29(2)	24(2)	20(2)	4(2)	10(2)	9(2)
C(9)	25(2)	29(2)	29(2)	3(2)	12(2)	6(2)
C(10)	21(2)	27(2)	32(2)	-4(2)	7(2)	9(2)
C(11)	24(2)	23(2)	22(2)	1(2)	2(2)	10(2)
C(12)	19(2)	23(2)	19(2)	5(2)	5(2)	8(2)
C(13)	22(2)	25(2)	23(2)	5(2)	2(2)	10(2)
C(14)	30(2)	35(2)	16(2)	0(2)	-3(2)	10(2)
C(15)	34(2)	32(2)	24(2)	13(2)	-2(2)	13(2)
C(16)	47(3)	20(2)	33(3)	6(2)	-4(2)	12(2)
C(17)	41(2)	25(2)	24(2)	4(2)	-6(2)	14(2)
C(18)	19(2)	17(2)	19(2)	7(2)	5(2)	6(2)
C(19)	24(2)	21(2)	20(2)	5(2)	5(2)	7(2)
C(20)	16(2)	25(2)	26(2)	6(2)	0(2)	6(2)
C(21)	27(2)	22(2)	21(2)	3(2)	-1(2)	1(2)
C(22)	34(2)	22(2)	22(2)	-3(2)	6(2)	8(2)
C(23)	21(2)	22(2)	27(2)	5(2)	8(2)	8(2)
C(24)	25(2)	32(2)	33(2)	2(2)	7(2)	11(2)
C(25)	38(2)	32(2)	33(3)	-4(2)	2(2)	1(2)
C(26)	17(2)	26(2)	20(2)	2(2)	0(2)	8(2)
C(27)	27(2)	19(2)	20(2)	3(2)	3(2)	10(2)
C(28)	36(2)	23(2)	27(2)	3(2)	-4(2)	13(2)
C(29)	37(2)	28(2)	28(2)	-5(2)	-1(2)	20(2)
C(30)	26(2)	43(3)	36(3)	-2(2)	8(2)	17(2)
C(31)	23(2)	24(2)	33(2)	4(2)	5(2)	7(2)
C(32)	38(2)	27(2)	37(3)	5(2)	16(2)	9(2)
C(33)	59(3)	42(3)	51(3)	-8(2)	3(3)	32(3)
C(34)	25(5)	19(5)	19(5)	0(4)	-5(4)	17(4)
C(35)	42(2)	40(3)	32(3)	12(2)	8(2)	20(2)

C(36)	37(2)	33(2)	38(3)	6(2)	10(2)	10(2)
O(1)	35(5)	39(7)	26(6)	-9(4)	-1(4)	30(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cj432.

	x	y	z	U(eq)
H(4)	-590	3161	7825	23
H(6)	-1699	304	6065	24
H(8)	-3530	-469	9393	28
H(9)	-5798	-481	8960	34
H(10)	-6448	443	7743	33
H(11)	-4866	1332	6903	29
H(13)	-3553	501	5229	29
H(14)	-4574	1216	3992	35
H(15)	-4367	3153	4251	36
H(16)	-3147	4340	5786	42
H(17)	-2147	3632	7029	38
H(20)	4239	3849	10298	28
H(22)	1490	5032	11269	33
H(23)	-308	3632	10067	28
H(24A)	3590	2306	8990	45
H(24B)	2271	2224	8161	45
H(24C)	2115	1339	8875	45
H(25A)	4211	5315	12332	58
H(25B)	4147	6250	11682	58
H(25C)	5124	5515	11557	58
H(28)	-1386	-3757	6961	36
H(30)	1638	-1589	6077	42
H(31)	909	-81	6563	33
H(32A)	-2272	-2106	8336	51
H(32B)	-3130	-3197	7458	51
H(32C)	-3198	-1958	7363	51
H(33A)	282	-4031	5362	76
H(33B)	145	-4504	6335	76
H(33C)	1599	-3624	6286	76
H(45)	1638	2523	4846	43
H(43)	-2094	2827	11656	44

Abbreviations

s – singlet
d – doublet
dd – double-doublet
t – triplet
q – quartet
m – multiplet
b – broad
st – strong
md – medium
w – weak
sh- shoulder
4-cymene = 4-isopropyltoluene
Cp = cyclopentadienyl
COD = 1,5-cyclooctadiene
Tf^- = Triflate anion
TON = Turnover Number
TOF = Turnover Frequency
$\Delta G^{\#}$ = Gibb's Free Energy of Activation
^{X}P = 2,6-dixylyl-4-phenylphosphinine
^{X}PB = 2,6-dixylyl-4-phenylphosphabarrelene