SYNTHESIS AND REACTIVITY

OF

TERMINAL PHOSPHIDO COMPLEXES OF IRIDIUM(III)

by

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Date July 24th 1987
Abstract

The iridium(III) methyl diarylphosphido complexes, Ir(CH$_3$)(PR$_2$)[$N$(SiMe$_2$CH$_2$PPh$_2$)$_2$] (2a: R = phenyl, 2b: R = meta-tolyl), have been successfully prepared by transmetalation of the iridium(III) methyl iodide complex, Ir(CH$_3$)(I)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], with the corresponding lithium diarylphosphide. Based primarily on a nuclear Overhauser effect difference experiment, these complexes are assigned a stereochemistry intermediate between square pyramidal and trigonal bipyramidal forms. The pyramidal geometry at the phosphido ligand is evident from the $^{31}$P{$^{1}$H} NMR spectral data.

The complex 2a affords a mixture of at least three, as yet uncharacterized complexes when heated to 60°C for 5 hours in benzene solution; however, clean formation of the planar iridium(I) methyl-diphenylphosphine complex, Ir(PCH$_3$Ph$_2$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], 3a, takes place when 2a is exposed to light for 24 hours in benzene solution. A crossover experiment indicates that the latter reaction involves an intra-molecular mechanism.

The nucleophilicity of the phosphido ligand is evident from the reaction of 2a with CH$_3$I; the product afforded in this reaction is Ir(CH$_3$)(PCH$_3$Ph$_2$)(I)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], 4. A labelling experiment with CD$_3$I shows that the reaction is intermolecular as the product observed is Ir(CH$_3$)(PCD$_3$Ph$_2$)(I)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$].
Exposure of 2a at room temperature to one atmosphere of H₂ produces a mixture of the iridium(III) dihydride Ir(H)₂(PPh₂)[N(SiMe₂CH₂-PPh₂)₂], 5, and methyl hydride Ir(CH₃)(H)(PPh₂)[N(SiMe₂CH₂PPh₂)₂], 6, in 70 and 30% yields, respectively. The analogous reaction with one atmosphere of D₂ reveals that the formation of the methyl hydride complex involves an intramolecular proton abstraction by the phosphide ligand from the bound methyl group, as the minor product observed in this reaction is Ir(CH₂D)(D)(PPh₂)[N(SiMe₂CH₂PPh₂)₂]. A mechanism is proposed involving the formation of Ir(=CH₂)(PPh₂)[N(SiMe₂CH₂PPh₂)₂] followed by trapping with D₂ to give the methyl hydride product. The dihydride complex observed in these reactions is apparently produced by heterolytic cleavage of dihydrogen.

Under excess CO, complex 2a is converted to an octahedral carbonyl complex Ir(CH₃)(CO)(PPh₂)[N(SiMe₂CH₂PPh₂)₂], 9; the carbonyl and the phosphide ligands in this complex are in cis arrangement. Upon removing the excess CO from the reaction mixture, another stereoisomer, 10, is produced in which the carbonyl and the phosphide ligands are trans to one another. It is suggested that the carbonyl complex 9 observed under excess CO is the kinetically favoured isomer which rearranges to the more thermodynamically stable isomer, 10, upon removal of the excess CO. Both of the carbonyl isomers are unstable in solution at room temperature as they convert to the planar iridium(I) complex Ir(CO)[N(SiMe₂CH₂PPh₂)₂] and methyldiphenylphosphine.
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Glossary of Abbreviations

Å angstrom unit, 10⁻⁸ cm
atm atmosphere
br broad
n-Bu n-butyl
°C degree celsius
cm⁻¹ wavenumber
COE cyclooctene, η²-C₈H₁₄
Cp cyclopentadienyl, C₅H₅⁻
Cp* pentamethylcyclopentadienyl, (CH₃)₅C₅⁻
d doublet
decomposition
dt doublet of triplets
Et ethyl, C₂H₅
FAB fast atom bombardment
fac facial
gem geminal
g gram(s)
{¹H} proton decoupled (NMR)
Hz hertz, sec⁻¹
h hour(s)
IR infrared
i-pr isopropyl, (CH₃)₂CH
J coupling constant
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<th>Definition</th>
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<tr>
<td>$J_{\text{app}}$</td>
<td>apparent coupling constant (virtual coupling)</td>
</tr>
<tr>
<td>L</td>
<td>a neutral unidentate ligand</td>
</tr>
<tr>
<td>m</td>
<td>moderate intensity (IR)</td>
</tr>
<tr>
<td></td>
<td>multiplet (NMR)</td>
</tr>
<tr>
<td>M</td>
<td>the central metal atom in a complex</td>
</tr>
<tr>
<td>Me</td>
<td>methyl, CH$_3$</td>
</tr>
<tr>
<td>mer</td>
<td>meridional</td>
</tr>
<tr>
<td>min</td>
<td>minute(s)</td>
</tr>
<tr>
<td>mmol</td>
<td>millimole(s)</td>
</tr>
<tr>
<td>m.p.</td>
<td>melting point</td>
</tr>
<tr>
<td>m-tol</td>
<td>meta-tolyl, CH$_3$C$_6$H$_4$</td>
</tr>
<tr>
<td>mL</td>
<td>millilitre</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOEDIFF</td>
<td>nuclear Overhauser effect difference</td>
</tr>
<tr>
<td>o-tol</td>
<td>ortho-tolyl, CH$_3$C$_6$H$_4$</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl, C$_6$H$_5$</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million (chemical shift)</td>
</tr>
<tr>
<td>q</td>
<td>quartet</td>
</tr>
<tr>
<td>s</td>
<td>strong intensity (IR)</td>
</tr>
<tr>
<td></td>
<td>singlet (NMR)</td>
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<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>ultraviolet-visible</td>
</tr>
<tr>
<td>w</td>
<td>weak intensity</td>
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<td>W</td>
<td>watt</td>
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CHAPTER 1

INTRODUCTION

During the last two decades, interest in tertiary phosphine complexes of the transition metals \( \text{L}_n \text{M-PR}_3 \; (R = \text{alkyl, aryl and hydride}) \) has grown tremendously. This has been due, in part, to the observations that many of these derivatives are catalyst precursors for such industrially significant processes as hydrogenation, hydroformylation and polymerization.\(^1\) As a result, the examples of phosphine-derived complexes are numerous. In addition to the well known tertiary phosphines, ligands for other valences of phosphorus are known but less studied. These include metallated phosphoranes \((-\text{PR}_4)\), phosphides \((-\text{PR}_2)\) and phosphinidenes \((=\text{PR})\).\(^2\) Although phosphorane and phosphinidene complexes are still extremely rare, the chemistry of transition metal phosphide complexes has become a rapidly growing research area.

Structural data indicate that a terminal phosphido ligand \( \text{PR}_2^- \; (R = \text{alkyl, aryl, halide and hydride}) \) in the complex \( \text{L}_n \text{M-PR}_2 \) can have one of two possible geometries: it can either be pyramidal,\(^3-5\) or planar\(^6-14\) (Fig. 1.1). A simple bonding scheme distinguishes these two configurations,
Fig. 1.1 A transition metal complex incorporating (a) a pyramidal phosphido ligand, and (b) a planar phosphido ligand as shown by (a) and (b), according to the number of electrons donated to the metal by the phosphorus atom. In the case of pyramidal geometry, the PR$_2^-$ ligand is a 2 electron donor and possesses a σ-bond with the metal; in planar geometry, the ligand is a 4 electron donor and is capable of π-bonding with the metal because of the availability of the filled phosphorus 3p orbital.

An obvious distinguishable feature of the two configurations is the metal-phosphorus bond lengths: complexes containing planar phosphido group possess a shorter M-P bond length compared to that of complexes containing pyramidal phosphido group. Another distinction is found in metal-phosphorus-substituent bond angles; the respective ranges are reported to be 127-140° and 106-114° for planar and pyramidal phosphido complexes.

These two modes of bonding are best exemplified by the bis(cyclopentadienyl)bis(diethylphosphido)hafnium(IV) complex (Fig. 1.2). In this complex, the geometry about P(2) is pyramidal with a non-bonding
pair of electrons, while that at P(1) is planar with the lone pair being involved in \(\pi\)-bond formation with hafnium. This \(\pi\)-donor interaction is quite substantial as evidenced from the shorter Hf-P(1) bond length of 2.488 Å compared to the Hf-P(2) bond length of 2.682 Å.

In addition to the hafnium complex mentioned above, a wide variety of titanium, zirconium, molybdenum, tungsten, rhenium, iron, osmium, rhodium, iridium and nickel phosphido complexes have been reported in the last few years. The majority of these complexes possess pyramidal geometry at the phosphido ligand with very few examples of the complexes containing a planar phosphido group.

1.1 Synthesis

A limiting factor in the syntheses of transition metal complexes containing terminal phosphido groups is their strong tendency to undergo dimerization; only in a few sterically or electronically favourable
cases are they preparatively accessible in the terminal mode. Typical methods used in their preparation are summarized below.

1.1.1 Metal carbonylate nucleophilic attack

Nucleophilic attack of transition metal carbonylate anion species on halophosphines has been used most extensively in the formation of terminal phosphido complexes of group 6 metals (Eq. 1.1).\textsuperscript{16a}

\[
[Cp(CO)\textsubscript{3}M]\textsuperscript{Na} + PCl\textsubscript{3} \xrightarrow{-NaCl} \text{Cp(CO)\textsubscript{3}M(PCl\textsubscript{2})} \\
M = \text{Cr, Mo, W}
\] (1.1)

1.1.2 Transmetalation

A variety of hafnium and zirconium phosphide complexes, synthesized in the early eighties, involved transmetalation of the respective group 4 bis(cyclopentadienyl) dichloride complexes with lithium phosphides (Eq. 1.2).\textsuperscript{12}

\[
\text{Cp}_2\text{MCl}_2 + 2\text{LiPR}_2 \xrightarrow{} \text{Cp}_2\text{M(PR}_2)_2 + 2\text{LiCl} \\
M = \text{Zr, Hf} \\
R = \text{Me, Et, Ph, Cy, t-Bu}
\] (1.2)
1.1.3 Diphosphine cleavage

The iron complex \((\eta^5-C_5H_5)Fe(CO)_2(P(CF_3)_2)\) was prepared by the action of tetrakis(trifluoromethyl)-diphosphine on the bis(cyclopentadienyldicarbonyliron(II)) complex (Eq. 1.3).\(^{30}\)

\[
[(\eta^5-C_5H_5)Fe(CO)_2]_2 + (CF_3)_2P\cdot P(CF_3)_2 \longrightarrow 2 (\eta^5-C_5H_5)Fe(CO)_2\{P(CF_3)_2\}
\] (1.3)

This route is analogous to that reported for the preparation of the arsenido complex \((\eta^5-C_5H_5)Fe(CO)_2\{As(CF_3)_2\}\).\(^{31}\)

1.1.4 Oxidative addition

The first six-coordinate rhodium(III) and iridium(III) complexes containing \(PX_2\) \((X = F, Cl, H)\) ligands were prepared by a method which involved oxidative addition of a \(PX_2Y\) species to low valent Vaska-type rhodium(I) and iridium(I) substrates (Eq. 1.4).\(^{5,26-28}\)

\[
\text{trans-}[M(CO)C\ell(P\text{Et}_3)_2] + PX_2Y \longrightarrow \text{trans-}[M(CO)C\ell\text{A}Y(P\text{Et}_3)_2(PX_2)]
\] (1.4)

\[
\begin{align*}
M &= \text{Rh, Ir} \\
X &= F; \ Y = \text{Cl, Br, I, H} \\
X &= \text{Cl}; \ Y = \text{Cl} \\
X &= H; \ Y = H
\end{align*}
\]

1.1.5 Dehydrohalogenation

A general synthetic route used to prepare terminal phosphido complexes of ruthenium and osmium involves dehydrohalogenation of an ionic
halo-metal-alkyl(or aryl) phosphine species with a strong non-nucleophilic base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Eq. 1.5). \(^{24}\)

\[
\begin{align*}
\text{OC} & \quad \text{PPh}_3 \\
\text{P} & \quad \text{H} \\
\text{OC} & \quad \text{PPh}_3 \\
\text{Cl} & \quad \text{Ph}
\end{align*}
\begin{align*}
\text{OC} & \quad \text{PPh}_3 \\
\text{P} & \quad \text{Cl} \\
\text{OC} & \quad \text{PPh}_3
\end{align*}
\text{ClO}_4^- \\
\text{DBU} \\
\text{M} = \text{Ru}; \ R = \text{H} \\
\text{M} = \text{Os}; \ R = \text{H, Ph, I, OMe}
\]

This dehydrohalogenation route has also been used in the syntheses of tungsten phosphido complexes with planar phosphido groups (Eq. 1.6). \(^{32}\)

\[
\begin{align*}
\text{W} & \quad \text{Cl} \\
\text{OC} & \quad \text{H}
\end{align*}
\begin{align*}
\text{OC} & \quad \text{P} \\
\text{R} & \quad \text{R}
\end{align*}
\text{DBU} \\
\text{-DBU.HCl}
\]

1.2 Reactivity

The reactivity patterns observed for terminal phosphido complexes depend mainly on the geometry of the phosphido ligand. Nucleophilic properties of the phosphorus centre are normally associated with the pyramidal configuration due to the presence of a lone pair of electrons;
however, the formal charges present in planar phosphido derivatives suggest that the phosphorus centre should display electrophilic character.

1.2.1 Nucleophilicity

Molybdenum and tungsten complexes containing pyramidal phosphido ligands, trans-[Cp(CO)₂(PMe₃)M(PPh₂)], demonstrate the high nucleophilicity of the phosphido ligand by formation of [Cp(CO)₂(PMe₃)M(PPh₂R)]⁺X⁻ (R = H, Me, Br) upon reaction with the electrophiles MeI, HCl and Br₂ (Eqs. 1.7).¹⁷

\[
\begin{align*}
\text{trans-[Cp(CO)₂(PMe₃)M(PPh₂)]} & \xrightarrow{\text{MeI}} [\text{Cp(CO)₂(PMe₃)M(PPh₂Me)}]⁺I⁻ \\
& \xrightarrow{\text{HCl}} [\text{Cp(CO)₂(PMe₃)M(PPh₂H)}]⁺Cl⁻ \\
M & = \text{Mo, W}
\end{align*}
\]

The iridium(III) complex, trans-[Ir(CO)Cl₂(PEt₃)₂(PCl₂)], can easily be converted to trans-[Ir(CO)Cl₂(PEt₃)₂(PCl₂Y)] (Y = O, S or Se) as the nucleophilic phosphido ligand reacts with O₂, S₈ or Se₈ (Eqs. 1.8).⁵

\[
\begin{align*}
\text{trans-[Ir(CO)Cl₂(PEt₃)₂(PCl₂)]} & \xrightarrow{\text{S₈}} \text{trans-[Ir(CO)Cl₂(PEt₃)₂(PCl₂S)]} \\
& \xrightarrow{\text{O₂}} \text{trans-[Ir(CO)Cl₂(PEt₃)₂(PCl₂Se)]} \\
& \xrightarrow{\text{Se₈}} \text{trans-[Ir(CO)Cl₂(PEt₃)₂(PCl₂O)]}
\end{align*}
\]
1.2.2 Electrophilicity

Complexes containing planar phosphido groups are rare, hence little is known about their reactivity. Studies done on the complex $\text{Cp(CO)}_2 W\{\text{P}(\text{CMe}_3)_2\}$ suggest that the phosphorus center has electrophilic character (Eq. 1.9). This complex undergoes spontaneous reaction with ROH to form the derivative in which the alcohol has formally added across the tungsten-phosphorus double bond.

\[
\text{Cp(CO)}_2 W\{\text{P}(\text{CMe}_3)_2\} + \text{ROH} \rightarrow \text{Cp(CO)}_2 \text{H} \{\text{P}(\text{CMe}_3)_2\} \quad (1.9)
\]

1.2.3 Other reactions: Hydrogenolysis and Carbonylation

Hydrogenolysis and carbonylation studies attempted on planar hafnium phosphido complexes have produced interesting results. The reaction of a dialkyl(di-tert-butylphosphido)hafnium(IV) complex with $H_2$ induces clean loss of methane and formation of a dimeric phosphido-bridged complex (Eq. 1.10).

\[
2 \text{Cp}^*\text{HfMe}_2\{\text{P}(\text{CMe}_3)_2\} + 2 H_2 \rightarrow [\text{Cp}^*\text{Hf}(\text{H})\text{Me}\{\text{P}(\text{CMe}_3)_2\}]_2 + 2 \text{CH}_4 \quad (1.10)
\]

The phosphido ligand acts as an ancilliary ligand in this reaction. However, it is susceptible to hydrogenolysis as shown when the complexes
Cp*HfCl{P(CMe3)2}2 and Cp*HfCl2{P(CMe3)2} are exposed to H2 (Eqs. 1.11, 1.12). The bis(di-tert-butylphosphido)hafnium complex reacts very rapidly with H2 to generate both di-tert-butylphosphine, and a dimeric complex with hydride and phosphido bridges (Eq. 1.11). However, the reactivity

\[
\begin{align*}
\text{Cp*HfCl\{P(CMe_3)\}_2} + \text{H}_2 & \longrightarrow \left[\text{Cp*HfCl(μ-H}\{μ-P(CMe_3)\}_2}\right] + \text{HP(CMe}_3)\_2 \\
\text{Cp*HfCl}_2\{P(CMe_3)\}_2 + \text{H}_2 & \text{HP(CMe}_3)\_2 \longrightarrow \left[\text{Cp*HfCl}_2\text{H}\right] + \text{Cp*HfCl}_3 + (\text{Cp*HfH}_2\text{Cl}) \\
& + \ldots. 
\end{align*}
\]

(1.11)

(1.12)

of the mono(di-tert-butylphosphido)hafnium complex is much slower (Eq. 1.12); the reaction proceeds over days to produce di-tert-butylphosphine and disproportionation products, Cp*HfCl3 and (Cp*HfH2Cl)x, plus 40% decomposition.

Carbonylation studies done on the mono(di-tert-butylphosphido)hafnium complex, Cp*HfCl2{P(CMe3)2}, show that it reacts very rapidly with CO to afford a carboxyphosphide complex, Cp*HfCl2{η2-C(0)P(CMe3)2} (Eq. 1.13)

\[
\text{Cp*HfCl}_2\{P(CMe}_3\}_2 + \text{CO} \longrightarrow \text{Cp*HfCl}_2\{\eta^2-C(0)P(CMe}_3\}_2 
\]

(1.13)

The latter complex is the first carboxyphosphide derivative of a transition element to be reported. Three valence forms for this complex are possible
Fig. 1.3 Three valence forms of $\text{Cp}^*\text{HfCl}_2\{\eta^2-\text{C}(\text{O})\text{P(CMe}_3)\}_2\}$

(Fig. 1.3). Spectroscopic data suggest that form (c) is the preferred structure for this complex in which significant $\pi$-bonding between the carbonyl carbon and the phosphorus atom takes place. Diagnostic of this resonance form is the upfield $^{13}\text{C}^{}\{^{1}\text{H}\}$ NMR shift of the carbonyl carbon atom (3.03 ppm, $^1J_{PC} = 101$ Hz) when compared to the characteristic low field values for "carbene-like" or "carbenium-like" acyl complexes.\(^34\)

1.3 Applications of phosphido complexes

Terminal phosphido complexes have been utilized as precursors to phosphido-bridged complexes and terminal phosphinidene complexes.

1.3.1 Phosphido-bridged complexes

Binuclear transition metal complexes have been the subject of intense research since they find extensive use in the designed syntheses of metal clusters\(^35,39\) and in studies related to catalysis by adjacent metal sites.\(^35,40\) Phosphide ligands as bridging groups are of particular
interest in bimetallic systems since they enhance the stability of the binuclear systems with respect to dissociation to mononuclear fragments.\textsuperscript{35-39}

Phosphido bridged di-cobalt and di-manganese complexes have been known since the early sixties.\textsuperscript{38} The dimer $\text{Co}_2(\text{CO})_6(\mu-\text{PPh}_2)$ was synthesized via phosphorus-phosphorus bond cleavage of $\text{Ph}_2\text{P}^*\text{PPh}_2$ by $\text{Co}_2(\text{CO})_8$ (Eq. 1.14).

$$\text{Co}_2(\text{CO})_8 + \text{Ph}_2\text{P}^*\text{PPh}_2 \rightarrow (\text{CO})_3\text{Co}^*\text{PPh}_2\text{Co}(\text{CO})_3 + 2\text{CO} \quad (1.14)$$

More recently, Geoffroy\textsuperscript{35} has reported a number of heterodinuclear complexes which can be synthesized easily from their terminal phosphido counterparts. The direct reaction of the anionic monophosphido tungsten

$$\text{Li}[\text{W}(\text{CO})_4(\text{PHPh}_2)(\text{PPh}_2)] + \text{trans-RhCl}(\text{CO})(\text{PPh}_3)_2$$

$$\rightarrow \begin{array}{c}
\begin{array}{c}
\text{(CO)}_4\text{W} \\
\text{PPh}_2
\end{array} \\
\begin{array}{c}
\text{Rh} \\
\text{PPh}_2
\end{array} \\
\text{H} \\
\begin{array}{c}
\text{CO} \\
\text{PPh}_3
\end{array}
\end{array} + \text{LiCl}$$

reagent with rhodium halide affords the diphenylphosphide bridged tungsten-rhodium complex (Eq. 1.15).\textsuperscript{35a} The corresponding tungsten-iridium phosphido bridged complexes can also be prepared easily by a similar reaction.\textsuperscript{35b}
1.3.2 Phosphinidene complexes

The understanding of transition metal–main group element multiple bonding has made continuous progress, gaining a strong impetus especially from the findings in carbene, carbyne, and nitrene and nitride coordination chemistry. Transition metal double bonding to the phosphorus homologues of carbenes (CR₂), namely PR, is a new field of research. The ligand PR, in a complex LₙM=PR, is named a phosphinidene. Terminal phosphinidene complexes have been implicated as intermediates in reactions involving terminal phosphido complexes, but a stable example is yet to be isolated.

Terminal monohalophosphido complexes, LₙMPXR, are of particular interest since they are, through halide loss, potential precursors for terminal phosphinidene complexes, (LₙM=PR)⁺. Roper has reported an osmium(II) complex with a pyramidal iodophenylphosphido ligand; its reaction with silver salt leads to a product indicative of a cationic phosphinidene intermediate (Eq. 1.16).

![Chemical diagram](attachment:chemical_diagram.png)

\[ [\text{Os}] = \text{OsCl(PPh}_3\text{)}_2\text{(CO)}_2 \]
The osmium phosphido complex (f) upon coordination with silver(I) produces intermediate (g). Intramolecular elimination of AgI from the latter would produce the cationic phosphinidene intermediate (h); insertion of such a species into the O-H bond of methanol affords (i). All attempts to trap (h) were unsuccessful.

Bridging phosphinidene complexes, $[L_n M]_2 PR$, have been well characterized. The first bridging phosphinidene complex to be reported, $[\text{Cp(CO)}_2 \text{Mn}]_2 \text{PPh}$, was prepared by a sequence of metalation and demetalation reactions as shown below (Eq. 1.17).

![Diagram](image)

The treatment of $\text{Na}_2 \text{M}_2 (\text{CO})_{10}$ with $\text{RPCl}_2$ is a general synthetic route for the syntheses of bridging phosphinidene complexes.$^{43}$

1.4. Hybrid ligand strategy

A subtle variation in ligand design can dramatically influence the reactivity of transition metal complexes. For this reason, considerable effort has been directed towards the syntheses of new ligands.
The chelating hybrid ligand shown below (Fig. 1.4) was first synthesized in our laboratory.\textsuperscript{45} The impetus for the design of this ligand was the fact that soft tertiary phosphines form relatively few derivatives of the hard early transition metals,\textsuperscript{46,47} while the hard amide donors provide very few stable, late metal derivatives.\textsuperscript{48} Thus, it was thought that incorporation of the amido donor NR$_2$ into a chelating array of phosphines might allow ligand coordination to a wide range of transition metals. This indeed was the case as a variety of amido phosphine complexes of Ni(II), Pd(II), Pt(II),\textsuperscript{49,50} Zr(IV), Hf(IV),\textsuperscript{51} Ir(I) and Rh(I)\textsuperscript{52,53} have been synthesized.

1.5 Dihydrogen activation

Activation of dihydrogen may involve a) homolytic cleavage, b) oxidative addition or c) overall heterolytic splitting; these can be represented by general equations 1.18 - 1.20.\textsuperscript{54a}
These different processes of hydrogen activation have been discussed in detail in a number of review articles on hydrogenation. Of particular relevance to the hydrogenation reaction described in this thesis is the heterolytic splitting of dihydrogen, which will be considered briefly in the following section.

1.5.1 **Heterolytic activation of dihydrogen**

Heterolytic activation of dihydrogen involves the cleavage of the hydrogen molecule into a hydride (coordinated to the metal) and a proton (usually stabilized by a base) (Eq. 1.20). Heterolytic \( \text{H}_2 \) cleavage is difficult to distinguish from oxidative addition of \( \text{H}_2 \) (step a, Eq. 1.21), followed by deprotonation of a hydride with a base (step b, Eq. 1.21).
Hydrogenation of the complex Ir(CH$_3$)(I)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (containing the basic amido ligand) generates a mixture of the iridium(III) amine monohydride complex and the corresponding amine dihydride derivative (Eq. 1.22). This reaction proceeds via an apparent heterolytic cleavage of dihydrogen; however, the mechanism involved in this transformation is not clearly understood.

![Chemical diagram](image)

### 1.6 Objectives

Iridium phosphido complexes are of interest for three major reasons:

1) there are very few examples of iridium phosphides,$^5,27,28$ despite the relatively large literature dealing with transition metal phosphido complexes.

2) our research group has been involved for a number of years with complexes containing the basic amide ligand, [N(SiMe$_2$CH$_2$PPh$_2$)$_2$]$^-$; $^{45,49-53}$ it was of interest to prepare complexes in which both the above mentioned
amide donor as well as another basic phosphide ligand bind to the same metal, and hence observe the competing reactivity of these two ligands. 3) except for one example of early transition metal phosphido complex, there are no other complexes known in which both an alkyl and a terminal phosphide ligand are bound to the same metal. Such complexes may provide some information regarding metal mediated carbon-phosphorus bond formation.

This thesis describes the syntheses of iridium(III) methyl diaryl-phosphido complexes, \( \text{Ir}(\text{CH}_3)(\text{PR}_2)[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{]} \) (\( R = \text{phenyl}, \text{m-tolyl} \)). The reactivity of the diphenylphosphido derivative was studied in detail. The nucleophilicity of the phosphido ligand in this complex, its reaction with dihydrogen along with carbon monoxide addition are presented.
2.1 Synthesis

The iridium(III) methyl diarylphosphido complexes, Ir(CH$_3$)(PR$_2$)-[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (2a: R = Ph, 2b: R = m-tol), were synthesized by transmetalation of the previously reported$^{52}$ square pyramidal iridium(III) methyl iodide derivative, Ir(CH$_3$)(I)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], 1, with stoichiometric amounts of the corresponding lithium diarylphosphide (Eq. 2.1). The reaction proceeds within minutes at room temperature with a dramatic colour change. The deep green colour of the methyl iodide derivative changes quickly to the dark purple of the phosphido complex. The visible spectrum of the diphenylphosphido derivative 2a shows a strong absorption band at 536 nm (ε = 3.11x10$^3$ M$^{-1}$ cm$^{-1}$). This band is presumably
a d-d transition, which is characteristic of most five coordinate d^6 molecules.\(^{52,55}\)

There likely exists some steric hindrance between the alkyl ligand on the metal and the aryl unit of the phosphide donor. For example, when the methyl ligand on the metal was replaced by a phenyl group, the starting material Ir(Ph)(I)[N(SiMe_2CH_2PPh_2)_2] \(^{56}\) failed to react with LiPPh_2 (Eq. 2.2).

![Reaction Scheme]

\[
\text{Me}_2\text{Si} \quad \text{Me}_2\text{Si} \\
\begin{array}{c}
\begin{array}{c}
\text{N} \\
\text{Ir} \\
\text{I}
\end{array} \\
\text{R} \\
\text{Ph} \\
\text{Ph}
\end{array} \quad \begin{array}{c}
\text{LiPR}_2'
\end{array} \\
\text{Toluene/THF} \\
\begin{array}{c}
\text{No Reaction}
\end{array}
\]

(2.2)

The \(^1\text{H NMR}\) spectra for the terminal phosphido complexes 2a and 2b are straightforward. The spectrum of 2a (Fig. 2.1) will serve to illustrate. The Si(CH_3)_2 resonances are observed as two sharp singlets of equal intensity indicating inequivalent environments above and below the metal tridentate plane. An AB quartet of virtual triplets\(^{57}\) for the CH_2P protons is indicative of a trans orientation of the chelating phosphine. Shaw\(^{57}\) has demonstrated that virtual coupling arises in such AA'BB'XX' spin systems when J_{XX'} is very large. For 2a and 2b, in which the
phosphines are strongly coupled, an apparent $A_2B_2X_2$ pattern is observed for

the CH$_2$P protons. Signals for the para and meta protons of the phenyl rings are observed as a multiplet and are separated from the signals for the ortho protons by 0.75 ppm. A chemical shift difference of 0.6 - 1.0 ppm between the ortho and para/meta protons of the phosphine phenyl groups (in deuterated aromatic solvents) is also indicative of trans disposed phosphines. 58
The above mentioned spectral data do not readily distinguish between the two basic geometries possible for the five coordinate molecule: (a) trigonal bipyramidal (tbp) or (b) square pyramidal (sqp). For the latter case, there is also uncertainty as to which ligand is apical: methyl (sqp 1), diphenylphosphide (sqp 2), or amide (sqp 3) (Fig. 2.2).

The $^1$H NMR spectrum (Fig. 2.1) readily rules out the sqp 3 geometry, as the methyl ligand would be expected to resonate as a doublet of triplets for this stereochemistry because of its larger trans coupling with the phosphide group than its cis coupling with the chelating phosphine donors; rather it is observed to be a four line pattern ($^3J_{CH_2PPh_2,H} = 6.0$ Hz, $^3J_{PPh_2,H} = 3.0$ Hz). A nuclear Overhauser effect difference (NOEDIFF) experiment (Fig. 2.3) was conducted in order to distinguish among the other three isomers. On irradiating the downfield methylene proton resonance of 2a, small enhancement of the methyl resonance is observed. Furthermore, no enhancement of the methyl protons occurs when the upfield methylene resonance is irradiated; therefore, the sqp 2 stereochemistry for which the methyl group is trans to the amide is eliminated.

Similar NOEDIFF experiments for the sqp 1 iridium(III) methyl bromide complex, Ir(CH$_3$)(Br)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], show a fairly large enhancement (~3x compared to that observed for the methyl protons of 2a) of the apical methyl protons; in comparison, the tbp iridium(III) dimethyl complex, Ir(CH$_3$)$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], displays no enhancement of the methyl resonance on irradiating the methylene protons. Thus the extent of enhancement observed for the methyl protons in the present study suggests
a) Trigonal bipyramidal

![Trigonal bipyramidal structure](image)

b) Square pyramidal

![Square pyramidal structures](image)

Fig. 2.2 Possible geometries for $\text{Ir}($CH$_3$)(PPh$_2$)$_2$(N(SiMe$_2$CH$_2$Ph)$_2$)$_2$, 2a
Fig. 2.3 (a) $^1$H NMR spectrum ($C_6D_6$, 400 MHz) and (b) NOEDIF spectrum of Ir(CH$_3$)(PPh$_2$)$_2$-[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], 2a
the complex \( \text{Ir(CH}_3\text{)(PPh}_2\text{)[N(SiMe}_2\text{CH}_2\text{PPh}_2\text{)]}_2 \) possesses a stereochemistry intermediate between the \textit{tbp} and \textit{sqp} 1 forms. However, in this thesis, this complex has been represented by the \textit{sqp} 1 form.

As pointed out earlier, the phosphido ligand in complexes 2\textit{a} and 2\textit{b} can possess either (a) pyramidal or (b) planar geometry (Fig. 2.4). So it was of interest to determine which applied in this work.

![Figure 2.4](image)

\( \text{Ir(CH}_3\text{)(PR}_2\text{)[N(SiMe}_2\text{CH}_2\text{PPh}_2\text{)]}_2 \) complex incorporating (a) a pyramidal phosphido ligand, or (b) a planar phosphido ligand

The respective \( ^{31}\text{P}\{^1\text{H}\} \) chemical shifts for pyramidal and planar phosphido complexes reported in the literature range from \(-270 - +420 \text{ ppm}\) and \(200 - 400 \text{ ppm}\) (See Appendix). The \( ^{31}\text{P}\{^1\text{H}\} \) shifts of 105.65 and 117.84 ppm for complexes 2\textit{a} and 2\textit{b}, respectively, although not conclusive in distinguishing the geometry at the phosphido ligand, point to the presence of a pyramidal phosphido donor in these complexes.

The ability of the phosphido group to act as a nucleophile also supports this view (See Section 2.2.3).
2.2 Reactivity

2.2.1 Thermolysis

The iridium(III) methyl diphenylphosphido complex, Ir(CH$_3$)(PPh$_2$)$_2$-[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], 2a, in the solid state is very temperature-sensitive as it decomposes to a black tar at temperatures above 60°C. The benzene solution of this complex, when heated at 60°C for five hours, affords a mixture of at least three complexes which is yet to be isolated and characterized. The high field resonance at -20 ppm in the $^1$H NMR spectrum (Fig. 2.5) of the mixture indicates that one of the complexes is a hydride containing species. Further work on this reaction was not pursued.

Fig. 2.5 $^1$H NMR spectrum (C$_6$D$_6$, 400 MHz) of the thermolysis products of Ir(CH$_3$)(PPh$_2$)$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], 2a
2.2.2 Photolysis

The iridium(III) methyl diphenylphosphido complex, \( \text{Ir(CH}_3\text{)}(\text{PPh}_2)-[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)_2] \), \( 2a \), in the solid form shows no photochemical reactivity on irradiation with a 275-W sunlamp; however, complete conversion to the corresponding iridium(I) methyldiphenylphosphine complex, \( \text{Ir(PCH}_3\text{Ph}_2)[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)_2] \), \( 3a \), occurs on photolysis of \( 2a \) in benzene solution for 24 hours (Eq. 2.3).

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Me}_2\text{Si} & \quad | \\
\text{N—Ir'—PPh}_2 & \quad \text{hv} \\
\text{Me}_2\text{Si} & \quad \text{24 h} \\
\text{C}_6\text{D}_6 & \\
\text{Me}, \text{Si} & \\
\text{Ph}, & \\
\text{Ph}, & \\
\text{Me}, \text{Si} & \\
\text{Ir} & \\
\text{COE} + \text{PCH}_3\text{Ph}_2 & \text{Toluene} \\
\text{-COE} & \text{(-COE)} \\
\text{Me}_2\text{Si} & \quad | \\
\text{N—Ir—PCH}_3\text{Ph}_2 & \quad \text{(2.4)}
\end{align*}
\]
At least two possible mechanistic pathways for the synthesis of 3a can be envisaged. The reaction may occur via either (a) an intramolecular mechanism or (b) an intermolecular reductive elimination with a second mole of iridium(III) phosphide, 2a. A crossover experiment was performed in order to distinguish between these two possibilities. A 50:50 mixture of the complexes Ir(CH$_3$)(PPh$_2$)(N(SiMe$_2$CH$_2$PPh$_2$)$_2$), 2a, and Ir(CD$_3$)(P(m-tol)$_2$)(N(SiMe$_2$CH$_2$PPh$_2$)$_2$), 2b, was photolyzed in benzene. The results observed are outlined in Scheme 2.1. The $^1$H, $^2$H($^1$H) and $^{31}$p($^1$H) NMR spectroscopy did not provide any information on examining the photolysis products of 2a and 2b since various nuclei within 3a and

Fig. 2.6 $^1$H NMR spectrum (C$_6$D$_6$, 400 MHz) of Ir(PCH$_3$Ph)$_2$[N(SiMe$_2$CH$_2$PPh)$_2$)$_2$, 3a
Scheme 2.1 Crossover experiment
3b resonate at approximately the same chemical shifts. Thus, it was decided to add CO to the photolysis products which generated the planar iridium(I) carbonyl complex, \( \text{Ir(CO)}[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)]_2 \),\(^{52}\) and free phosphines. Since both the carbonyl complex and the phosphines possess high solubility in benzene, their further reaction with methyl iodide was necessary. The carbonyl derivative reacted with methyl iodide to generate the previously reported complex \( \text{Ir(CH}_3\text{(I)(CO)}[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)]_2 \);\(^{52}\) the free phosphines reacted with methyl iodide to give phosphonium salts which precipitated from solution and were isolated. The FAB mass spectrum obtained for the latter showed two peaks at 215 and 246 mass units. These signals can clearly be assigned to the \( \text{P(CH}_3\text{)}_2\text{Ph}_2^+ \) and \( \text{P(CH}_3\text{)(CD}_3\text{)}-(\text{m-tol})_2^+ \) ions, respectively. No peaks for the possible crossover products \( \text{P(CH}_3\text{)(CD}_3\text{)Ph}_2^+ \) and \( \text{P(CH}_3\text{)}_2(\text{m-tol})_2^+ \) were observed; thus, the intermolecular mechanism (b) can be disregarded. Hence, the photolytic reaction (Eq. 2.3) involves an intramolecular pathway (a); no other information is available on the mechanism at this time, but a simple reductive elimination of the methyl and the phosphide ligands is reasonable. The formation of a metal mediated carbon-phosphorus bond is observed in this reaction.
2.2.3 Reaction with methyl iodide

The nucleophilic character of the phosphido ligand in the complex \( \text{Ir}(\text{CH}_3)(\text{PPh}_2)[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2] \), denoted as \( \text{2a} \), is illustrated by reaction with the electrophile methyl iodide (Eq. 2.5). The reaction proceeds within minutes at room temperature and affords an octahedral iridium(III) methyldiphenylphosphine complex \( \text{4} \).

\[
\text{Me}_2\text{Si} - \text{Ir} - \text{PPh}_2 + \text{CH}_3\text{I} \rightarrow \text{Toluene} \rightarrow \begin{array}{c}
\text{Me}_2\text{Si} - \text{Ir} - \text{PPh}_2 \\
\text{Me}_2\text{Si} - \text{Ir} - \text{PCH}_3\text{Ph}_2
\end{array}
\]

![Diagram of the reaction](attachment:reaction_diagram.png)

The \(^1\text{H}\) and \(^{31}\text{P}\{^1\text{H}\} \) NMR spectra show the formation of only one isomer in the reaction. The presence of virtual coupling for the methylene protons in the \(^1\text{H}\) NMR (Fig. 2.7) is consistent with trans phosphine donors.

Fig. 2.7 \(^1\text{H}\) NMR spectrum (C\(_6\)D\(_6\), 400 MHz) of \( \text{Ir}(\text{CH}_3)(\text{PCH}_3\text{Ph}_2)(\text{I})-\) \([\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2] \), \( \text{4} \)
of the tridentate ligand, thus establishing that the tridentate ligand is bound in a meridional fashion in the octahedral complex. Thus, there are only three possible stereoisomers for the structure of this complex in solution: o1, o2, or o3 (Fig. 2.8). The $^1$H NMR spectrum readily rules out the isomer o3, as the methyl ligand would be expected to resonate as a doublet of triplets for this stereochemistry because of its larger trans coupling with the methyldiphenylphosphine ligand than its cis coupling with the chelating phosphine donors; rather it is observed to be a four line pattern. Interestingly, the isomer o3 was prepared by a straightforward addition of methyldiphenylphosphine to the coordinatively unsaturated iridium(III) methyl iodide complex 1 (Eq. 2.6). The product is isomerically pure and as mentioned above has a doublet of triplets for the methyl resonance ($^3J_{PCH_3PH_2,H} = 20.0$ Hz, $^3J_{CH_2PH_2,H} = 6.0$ Hz).

Fig. 2.8 Possible stereochemistries for Ir(CH$_3$)(PCH$_3$PH$_2$)(I)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$]
A distinction between the isomers o1 and o2 was accomplished via an independent experiment. Given that the oxidative addition of alkyl halides proceeds kinetically to generate trans adducts, the reaction between CH$_3$I and the square planar complex Ir(PCH$_3$Ph$_2$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] should result in the formation of isomer o1 (Eq. 2.7). This, indeed, is the result observed. The $^1$H NMR spectrum of the product obtained from the reaction 2.7 was identical to that of 4, which allowed assignment of structure o1 to 4.

In order to discover the source of the methyl group in the methyldiphenylphosphine ligand for complex 4, the analogous reaction
with $\text{CD}_3\text{I}$ was carried out (Eq. 2.8).

This experiment showed that the methyl group in the methyldiphenylphosphine ligand originated from the intermolecular reaction with $\text{CD}_3\text{I}$, since the product observed in this reaction is $\text{Ir}($CH$_3)(\text{PCD}_3\text{Ph}_2)(\text{I})[\text{N}($SiMe$_2\text{CH}_2\text{PPh}_2)_2]$. The $^1\text{H}$ NMR spectrum for the product of equation 2.8 did not show the doublet at 1.58 ppm ($^2J_{\text{P,H}} = 10.6$ Hz) as observed for the $\text{PCH}_3\text{Ph}_2$ ligand in the analogous reaction with $\text{CH}_3\text{I}$; however, a broad peak centered at the same chemical shift was present in the $^2\text{H}^1\text{H}$ NMR spectrum, which is obviously assigned to the $\text{PCD}_3\text{Ph}_2$ moiety. This labelling experiment thus shows that the reaction of the phosphido complex 2a with $\text{CH}_3\text{I}$ involves nucleophilic attack of the phosphido ligand on the electrophile $\text{CH}_3\text{I}$ resulting in the formation of complex 4. Such nucleophilicity of pyramidal phosphido ligand is well documented (See Section 1.2.1).
2.2.4 Hydrogenation

At room temperature, the reaction of a toluene solution of \( \text{Ir} (\text{CH}_3)(\text{PPh}_2)[\text{N} (\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2] \), \( \text{2a} \), with one atm of dihydrogen produces a mixture of the iridium(III) dihydride complex 5 and the methyl hydride complex 6 in the ratio of 70:30 as determined by \(^1\text{H} \) NMR spectroscopy (Eq. 2.9). Upon stirring the mixture of 5 and 6 under excess dihydrogen for an additional 24 hours, the methyl hydride complex 6 is completely converted to the dihydride complex 5.

The \(^1\text{H} \) NMR spectrum provides an excellent handle on the identity and stereochemistry of these hydride species (Fig. 2.9). Once again, the methylene resonances, observed as an AB quartet of virtual triplets for
both 5 and 6, are indicative of trans disposed phosphines of the tridentate ligand. The diphenylphosphido ligand in 2a is converted to diphenylphosphine ligand in 5 and 6 by acquisition of a proton and the resonances are observed as doublets of triplets centered at 5.84 ppm \( (^{1_J}_{P,H} = 334.7 \text{ Hz, } ^{3_J}_{P,H} = 9.7 \text{ Hz}) \) for 5 and at 5.76 ppm \( (^{1_J}_{P,H} = 334.7 \text{ Hz, } ^{3_J}_{P,H} = 8.4 \text{ Hz}) \) for 6. The hydride resonance for the methyl hydride complex 6 is a doublet of triplets centered at -9.06 ppm \( (^{2_J}_{PHPh_2,H} = 150.0 \text{ Hz, } ^{2_J}_{CH_2PPh_2,H} = 10.1 \text{ Hz}) \). The dihydride complex 5 displays a doublet of triplets of doublets at -9.75 ppm \( (^{2_J}_{PHPh_2,H} = 140.4 \text{ Hz}) \).

Fig. 2.9 \(^1\text{H NMR spectrum (C}_6\text{D}_6, 400 \text{ MHz) of Ir(H)}_2(\text{PHPh}_2)[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)_2], \ 5, \text{ and Ir(CH}_3)(\text{H})(\text{PHPh}_2)[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)_2], \ 6\)
Hz, $^{2}J_{\text{CH}_2\text{PPh}_2,H} = 18.2$ Hz, and $^{2}J_{H,H} = 5.0$ Hz) for the hydride trans to the diphenylphosphine ligand, and a quartet of doublets at -19.17 ppm ($^{2}J_\text{P,H} = 15.1$ Hz, $^{2}J_{H,H} = 5.2$ Hz) for the hydride trans to the amide ligand. The hydride resonances in the region of -8 to -30 ppm have been reported for a number of rhodium and iridium amine and amide hydride complexes.$^{53}$ The IR stretches at 2220 cm$^{-1}$ for 5 and 2242 cm$^{-1}$ for 6 are also typical of late transition metal hydride complexes.$^{53}$

Complex 5 was also prepared by the addition of PHPh$_2$ to the coordinatively unsaturated iridium(III) dihydride complex, Ir(H)$_2$-$[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)_2]$ ($^{60}$Eq. 2.10).

\[
\begin{array}{c}
\text{Me}_2\text{Si} & \text{P} & \text{N} & \text{Ir} & \text{H} \\
\text{Me}_2\text{Si} & \text{P} & \text{H} & & \\
\end{array} + \text{Toluene} \quad \xrightarrow{\text{PHPh}_2} \quad \begin{array}{c}
\text{Me}_2\text{Si} & \text{P} & \text{N} & \text{Ir} & \text{H} \\
\text{Me}_2\text{Si} & \text{P} & & \text{PHPh}_2 & \\
\end{array} \quad (2.10)
\]

In order to obtain some information on the mechanism involved in the formation of the hydride complexes 5 and 6, the analogous reaction with one atm of D$_2$ was carried out (Scheme 2.2). Some very intriguing results were revealed. The $^{1}$H NMR spectrum for the reaction products still showed the PHPh$_2$ resonance for the methyl hydride complex; furthermore, the resonance of the iridium-methyl protons was broadened instead of the doublet of triplets observed for the previous reaction with H$_2$. The $^{2}$H($^{1}$H) NMR spectrum (Fig. 2.10) was also completely consistent with the
Scheme 2.2 Deuteration of Ir(CH$_3$)(PPh$_2$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], 2a
structures 7 and 8 shown in Scheme 2.2. The gaseous products evolved in this reaction were \( \text{CH}_{3}\text{D} \) and \( \text{CH}_{2}\text{D}_{2} \), as confirmed by mass spectroscopy.

The reaction of 2a with \( \text{D}_{2} \) was also followed by variable temperature \(^1\text{H}\) NMR spectroscopy. From -70°C to +10°C, only the starting phosphide was detected, but as the temperature was increased to 20°C, the complexes 7 and 8 appeared almost simultaneously in their respective yields of 70 and 30%. This experiment along with the previous deuterium-labelling study indicate that the methyl hydride complex is not an intermediate in the formation of the dihydride complex, even though it is ultimately converted to the dihydride complex upon being stirred under excess \( \text{H}_{2} \) for 24 hours.

Fig. 2.10 \(^2\text{H}\{^1\text{H}\} \) NMR spectrum (CH\(_3\)C\(_6\)H\(_5\), 40 MHz) of Ir(D)\(_2\)(PDPh\(_2\))[N(SiMe\(_2\)CH\(_2\)PPh\(_2\))]\(_2\), 7, and Ir(CH\(_2\)D)(D)(PHPh\(_2\))[N(SiMe\(_2\)CH\(_2\)PPh\(_2\))]\(_2\), 8
To account for the observed distribution of deuterium, an equilibrium between the methyl diphenylphosphide complex 2a and the methyldiene diphenylphosphine species 11 is proposed as shown in Scheme 2.3. Such an intramolecular proton transfer from a hydrocarbyl ligand to a phosphido donor is extremely rare. Although, there is no evidence for 11 at the present, the suggested reaction of D₂ across the iridium-carbon double bond would generate 8, the correct methyl hydride isotopomer. The sequence of reactions to convert 2a to the dideuteride 7 is speculative but draws on earlier observations of ancilliary ligand involvement in the activation of dihydrogen. In particular, addition of D₂ produces the amine deuteride 12 which can rearrange to the isomer 13 by amine dissociation, inversion at nitrogen, and reassociation; elimination of CH₃D from 13 to give the phosphido deuteride 14 followed by addition of D₂ generates the observed major product 7.

Some preliminary mechanistic studies have been done. It can be shown that the proposed phosphido deuteride 14 could not reductively eliminate to the iridium(I) diphenylphosphine complex Ir(PDPh₂)[N(SiMe₂CH₂PPh₂)₂] prior to D₂ addition, since reaction of the complex Ir(PHPh₂)[N(SiMe₂CH₂PPh₂)₂] with H₂ does not yield the mer-dihydride 5, rather fac-Ir(H)₂(PHPh₂)[N(SiMe₂CH₂PPh₂)₂] is the only product observed (Eq. 2.11). Attempts to prepare the proposed intermediate 11
Scheme 2.3 Mechanism proposed for deuteration of $\text{Ir(CH}_3\text{)(PPh}_2\text{)}_2$-$[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)_2]$, 2a
by either the addition of one equivalent of PHPh₂ to the previously reported methyldene complex, Ir(=CH₂)[N(SiMe₂CH₂PPh₂)]₂,⁶³ or by the reaction of CH₂N₂⁶⁴ with Ir(PHPh₂)[N(SiMe₂CH₂PPh₂)]₂ have been unsuccessful; in the former reaction, a complex mixture results, while in the latter case, the iridium(I) derivative Ir(PCH₃Ph₂)[N(SiMe₂CH₂PPh₂)]₂ is the only product. Clearly, neither of these procedures is kinetically feasible for accessing the proposed equilibrium in Scheme 2.3. Further studies are underway to provide evidence for the reversible intramolecular proton transfer from an alkyl to a terminal phosphide ligand.
2.2.5 Carbonylation

The coordinatively unsaturated phosphido complex $\text{Ir}($CH$_3$)(PPh$_2$)$_2$-$[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)_2]$, 2a, reacts under one atm of carbon monoxide within minutes at room temperature to afford an octahedral carbonyl derivative, $\text{Ir}($CH$_3$)(CO)(PPh$_2$)$_2$-$[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)_2]$, 9 (Eq. 2.12). Upon contact with CO, the intense purple colour of the starting material is lost leaving a yellow carbonyl complex.

The $^1\text{H}$ and $^{31}\text{P}$$^1\text{H}$ NMR spectra show the formation of only one isomer in the reaction. The presence of virtual coupling for the methylene protons in the $^1\text{H}$ NMR spectrum (Fig. 2.11) is consistent with the trans phosphine donors, thereby establishing that the tridentate ligand is bound
Fig. 2.11 $^1$H NMR spectrum ($C_6D_6$, 400 MHz) of $\text{Ir(CH}_3\text{(CO)}(\text{PPh}_2)_2\text{[N(SiMe}_2\text{CH}_2\text{PPh}_2)_2]}$, 9

Fig. 2.12 $^{13}$C{$^1$H} NMR spectrum ($C_6D_6$, 75 MHz) of $\text{Ir(CH}_3\text{)(}^{13}\text{CO)}(\text{PPh}_2)_2\text{[N(SiMe}_2\text{CH}_2\text{PPh}_2)_2]}$, 9
in a meridional fashion in the octahedral complex. The $^{13}$C($^1$H) NMR spectrum (Fig. 2.12) of the labelled complex, Ir(CH$_3$)($^{13}$CO)(PPh$_2$)$\cdot$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], displays a doublet of triplets at 173.2 ppm ($^{2}$$J_{CH_2PPh_2}$, $^{13}$C = 9.1 Hz, $^{2}$$J_{PPh_2}$$^{13}$C = 51.8 Hz), attributable to the carbonyl carbon atom. This observed shift is typical of late transition metal carbonyl complexes. Complex 9 exhibits a strong absorption at 2009 cm$^{-1}$ in benzene, which shifts to 1960 cm$^{-1}$ upon isotopic substitution with $^{13}$CO.

Completely different spectroscopic results are observed when the excess CO is pumped off from the reaction mixture. The $^1$H NMR spectrum in Fig. 2.13 will serve to illustrate this fact. The Si(CH$_3$)$_2$ resonances have shifted considerably in this spectrum when compared to that of complex 9; the methylene protons are at different chemical shifts, but still are observed as an AB quartet of virtual triplets, thus indicating a meridional arrangement of the tridentate ligand in the new complex. The most anomalous feature of this spectrum is that even in the presence of the three phosphorus containing ligands, the methyl resonance is only split into a triplet! The $^{13}$C($^1$H) NMR spectrum (Fig. 2.14) for the $^{13}$C-enriched carbonyl derivative displays a doublet of triplets at 177.5 ppm ($^{2}$$J_{CH_2PPh_2}$, $^{13}$C = 11.5 Hz, $^{2}$$J_{PPh_2}$, $^{13}$C = 656.8 Hz). The important features of this spectrum are i) the observed shift, which indicates that the CO is present as a terminal carbonyl ligand in the new complex, and ii) the very high $^{2}$$J_{PPh_2}$, $^{13}$C value, which suggests that the phosphide and the carbonyl
ligands are in a trans disposition. Further evidence for the presence of CO as a terminal carbonyl ligand comes from the strong absorption at 1944 cm\(^{-1}\) in the infrared spectrum.

These results suggest that the complex 10 is an isomer of complex 9 with the phosphido and carbonyl ligands trans to one another (Eq. 2.13). Complex 10 was also obtained when the previously characterized complex \(\text{Ir(CH}_3\text{)(CO)}(\text{I})[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)]\text{2}\) was reacted with one equivalent of LiPPh\(_2\) (Eq. 2.13).

An alternate formulation of 10 (shown below) is the product of CO insertion into the phosphide-metal bond. As mentioned earlier, such carbonyl insertion has been reported for a hafnium di-tert-butylphosphido
Fig. 2.13 $^1H$ NMR spectrum (C$_6$D$_6$, 400 MHz) of Ir(CH$_3$)(CO)(PPh$_2$)$_2$-\[N(SiMe$_2$CH$_2$PPh$_2$)$_2\]$_2$, 10

Fig. 2.14 $^{13}C\{^1H\}$ NMR spectrum (C$_6$D$_6$, 75 MHz) of Ir(CH$_3$)($^{13}$CO)(PPh$_2$)$_2$-\[N(SiMe$_2$CH$_2$PPh$_2$)$_2\]$_2$, 10
complex. This alternative does explain the presence of the methyl resonance as a triplet in the $^1$H NMR spectrum; however, it does not account for the $^{13}$C($^1$H) NMR and IR data.

The carbonylation of the phosphido complex 2a is summarized in Scheme 2.4. The conversion of the cis carbonyl-phosphido geometry in complex 9 to the trans carbonyl-phosphido arrangement in the complex 10 can be accounted for as follows: the carbonylation of 2a gives 9 as the kinetically favoured product, which rearranges to the more thermodynamically stable product 10 via CO dissociation, followed by reassociation when excess CO is removed. However, this reaction mechanism is no way clearly understood.

Both carbonyl derivatives 9 and 10 are unstable in solution at room temperature. Within minutes of their formation, they start converting to the planar iridium(I) complex, Ir(CO)-[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (which has been previously characterized) and free methyldiphenylphosphine (Scheme 2.4). Once again, the formation of a carbon-phosphorus bond is observed in this reaction.
Scheme 2.4 Carbonylation of Ir(CH$_3$)(PPh$_2$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], 2a
CHAPTER 3

CONCLUSIONS AND SOME SUGGESTIONS FOR FUTURE WORK

3.1 Conclusions

The iridium(III) methyl diarylphosphido complexes, $\text{Ir}(\text{CH}_3)(\text{PR}_2)^{-} [\text{N}($SiMe$_2$CH$_2$PPh$_2$)$_2]$ (2a: $R$ = Ph, 2b: $R$ = m-tol), were synthesized by treatment of the iridium(III) methyl iodide derivative, $\text{Ir}(\text{CH}_3)(\text{I})^{-} [\text{N}($SiMe$_2$CH$_2$PPh$_2$)$_2]$], with the corresponding lithium diarylphosphide. Based primarily on a nuclear Overhauser effect difference experiment, these complexes are assigned a stereochemistry intermediate between the square pyramidal and trigonal bipyramidal forms. The $^{31}\text{P}^{1\text{H}}$ chemical shifts for 2a and 2b indicate pyramidal geometry at the phosphido ligand.

The diphenylphosphido derivative 2a affords a mixture of at least three unidentified complexes upon thermolysis in benzene solution; however, clean formation of the planar iridium(I) complex, $\text{Ir}(\text{PCH}_3\text{Ph}_2)^{-} [\text{N}($SiMe$_2$CH$_2$PPh$_2$)$_2]$], 3a, takes place upon photolyzing a benzene solution of 2a. A crossover experiment indicates that the formation of 3a is achieved via an intramolecular mechanism. The formation of a carbon-phosphorus bond is observed in the latter reaction.

The nucleophilicity of the phosphido ligand is evident from the reaction of 2a with CH$_3$I; the product of this reaction is $\text{Ir}(\text{CH}_3)^{-} (\text{PCH}_3\text{Ph}_2)(\text{I})[\text{N}($SiMe$_2$CH$_2$PPh$_2$)$_2]$, 4. The labelling experiment with CD$_3$I shows that the reaction is intermolecular as the product observed in this reaction is $\text{Ir}(\text{CH}_3)(\text{PCD}_3\text{Ph}_2)(\text{I})[\text{N}($SiMe$_2$CH$_2$PPh$_2$)$_2]$. 

Exposure of 2a to one atm of H₂ at room temperature produces a mixture of the iridium(III) dihydride complex Ir(H)₂(PPh₂)₂[N(SiMe₂CH₂PPh₂)₂], 5, and the methyl hydride complex Ir(CH₃)(H)(PPh₂)₂[N(SiMe₂CH₂PPh₂)₂], 6, in 70 and 30% yields, respectively. The analogous reaction with one atm of D₂ reveals that the formation of the methyl hydride complex, 6, involves an intramolecular proton abstraction by the phosphide ligand from the bound methyl group, as the minor product observed in this reaction is Ir(CH₂D)(D)(PPh₂)₂[N(SiMe₂CH₂PPh₂)₂], 8. A mechanism is proposed which involves the formation of Ir(=CH₂)(PPh₂)[N(SiMe₂CH₂PPh₂)₂] followed by trapping with D₂ to give the methyl hydride complex. The dihydride complex observed in these reactions is produced by an apparent heterolytic cleavage of dihydrogen.

Under excess CO, at room temperature the complex 2a is converted to an octahedral carbonyl species Ir(CH₃)(CO)(PPh₂)[N(SiMe₂CH₂PPh₂)₂], 9; the carbonyl and the phosphido ligands in this complex are in cis proximity. Upon removing the excess CO from the reaction mixture, another stereoisomer, 10, of the complex 9 is formed in which the carbonyl ligand and the phosphido donor are trans to each other. It is suggested that the complex 9 is the kinetically favoured isomer in the carbonylation reaction, and it rearranges to the more thermodynamically stable isomer 10 via CO dissociation upon removal of the excess CO. Both 9 and 10 are unstable in solution at room temperature as they rearrange to the planar iridium(I) carbonyl complex, Ir(CO)₂[N(SiMe₂CH₂PPh₂)₂], and methylidiphenylphosphine. Once again, the
formation of a carbon-phosphorus bond is observed in this reaction.

3.2 Suggestions for Future Work

Studies to characterize the complexes observed in the thermolysis reaction as well as experiments to trap the proposed intermediate Ir(=CH₂)(PHP₂)[N(SiMe₂CH₂PPh₂)₂] in the hydrogenation reaction should be pursued. The preparation of the complex Ir(CH₃)(PHR)[N(SiMe₂CH₂PPh₂)₂] would be of particular interest, since this complex, upon its photolysis or thermolysis, might lead to the corresponding phosphinidene complex via loss of methane.
CHAPTER 4

EXPERIMENTAL

4.1 General Information

All manipulations were performed under pre-purified nitrogen in a Vacuum Atmospheres HE-533-2 glove box equipped with a MO-40-2H purification system, or in standard Schlenk-type glassware.

Iridium trichloride hydrate was obtained on loan from Johnson-Matthey and used directly in the synthesis of \([\text{Ir}(\eta^2-\text{C}_8\text{H}_{14})_2\text{Cl}]_2\)\(^{66}\). The complexes \(\text{Ir}(\eta^2-\text{C}_8\text{H}_{14})[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]\) and \(\text{Ir}(R)(\text{I})[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]\) (R = Me, Ph, CH\(_2\)Ph) were prepared by published procedures.\(^{52,56}\) LiPPh\(_2\) and LiP(m-tol)\(_2\)\(^{67}\) were prepared by the dropwise addition of n-butyllithium in hexane (1.6M, Aldrich) to a hexane solution of PHPh\(_2\) and PH(m-tol)\(_2\), respectively. After several washings with hexane, the resultant lemon-yellow powders were used directly in the preparation of \(\text{Ir}(\text{CH}_3)(\text{PPh}_2)_2\) \([\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]\) and \(\text{Ir}(\text{CH}_3)(\text{P}(\text{m-tol})_2)_2\) \([\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]\).

Toluene, hexane and diethyl ether were dried and deoxygenated by distillation from sodium benzophenone ketyl under argon. Tetrahydrofuran (THF) was pre-dried by refluxing over CaH\(_2\) and then distilled from sodium benzophenone ketyl under argon. H\(_2\) was purified by passing it through a column of molecular sieves and MnO.

\(^{13}\text{CH}_3\text{I}\) (99.7 atom % \(^{13}\text{C}\)), \(\text{CD}_3\text{I}\) (98 atom % D) and \(^{13}\text{CO}\) (90 atom % \(^{13}\text{C}\)) were obtained from MSD. \(\text{D}_2\) (99.8 atom % D) was obtained from Matheson. All these reagents were used as obtained. Deuterated benzene
(C₆D₆; 99.6 atom % D), purchased from MSD, was dried over activated 4Å molecular sieves, vacuum transferred and degassed by freeze-pump-thawing several times before being used.

Melting points were determined on a Mel-Temp apparatus in sealed capillaries under nitrogen and are uncorrected. Carbon, hydrogen and nitrogen analyses were performed by Mr. P. Borda of this department.

¹H NMR spectra were recorded on a Bruker WH-400 spectrometer in C₆D₆ and were referenced to C₆D₅H at 7.15 ppm. ³¹P{¹H} NMR spectra were run at 121.4 MHz on a Varian XL-300 or 109.1 MHz on a Nicolet HXS-270. All ³¹P chemical shifts were referenced to external P(OMe)₃ set at 141.00 ppm relative to 85% H₃PO₄. ¹³C{¹H} and ²H{¹H} NMR spectra were run at 75 MHz and 40 MHz, respectively, on a Varian XL-300, and were referenced to solvent peaks (¹³C: C₆D₆ at 128.0 ppm; ²H: CH₃C₆H₅ at 2.1 ppm). All chemical shifts (¹H, ²H, ¹³C and ³¹P) are reported in ppm with the coupling constants expressed in Hz. Infrared spectra were recorded on a Pye-Unicam SP-1100 spectrophotometer on solution samples. All infrared absorptions are given in cm⁻¹. UV-Vis spectra in hexane were recorded on a Perkin Elmer 5523A UV/VIS spectrophotometer.

4.2 Synthesis

4.2.1 Ir(CH₃)(PR₂)[N(SiMe₂CH₂PPh₂)₂]

A solution of LiPR₂ (R = Ph, m-tol) in THF (5 mL) was added dropwise with stirring to a solution of Ir(CH₃)(I)[N(SiMe₂CH₂PPh₂)₂] in toluene (10 mL) at room temperature. The initially deep green solution immediately
turned dark purple in colour. After stirring for an hour, the solution was filtered through Celite in order to remove LiI. The solvent was removed in vacuo and the resultant powder recrystallized from toluene/hexane at -30°C which yielded purple crystals of Ir(CH₃)(PR₂)[N(SiMe₂CH₂PPh₂)₂].

4.2.1a Ir(CH₃)(PPh₂)[N(SiMe₂CH₂PPh₂)₂] 2a

Ir(CH₃)(I)[N(SiMe₂CH₂PPh₂)₂] (0.24 g, 0.28 mmol); LiPPh₂ (0.05 g, 0.31 mmol). Anal. Calcd. for IrC₃H₉NP₃Si₂: C, 56.07; H, 5.36; N, 1.52. Found: C, 55.80; H, 5.35; N, 1.40. m.p. 123±2°C (decomp.). ³¹P{¹H} NMR (C₆D₆, 121.4 MHz): PPh₂, 105.65 (t, 2Jₚ,ₚ = 34.8); CH₂PPh₂, 10.28 (d). Yield: 0.18 g (70%).

4.2.1b Ir(CH₃){P(m-tol)₂}[N(SiMe₂CH₂PPh₂)₂] 2b

Ir(CH₃)(I)[N(SiMe₂CH₂PPh₂)₂] (0.22 g, 0.25 mmol); LiP(m-tol)₂ (0.05 g, 0.26 mmol). Anal. Calcd. for IrC₄H₉₆NP₃Si₂: C, 56.94; H, 5.63; N, 1.48. Found: C, 56.70; H, 5.62; N, 1.42. m.p. 118±2°C (decomp.). ³¹P{¹H} NMR (C₆D₆, 109.3 MHz): P(m-tol)₂, 117.84 (t, 2Jₚ,ₚ = 34.7); CH₂PPh₂, 15.48 (d). Yield: 0.18 g (75%).

4.2.2 Ir(PCH₄Ph₂)[N(SiMe₂CH₂PPh₂)₂] 3

Method 1. A C₆D₆ solution (5 mL) of Ir(CH₃)(PPh₂)[N(SiMe₂CH₂PPh₂)₂] (0.10 g, 0.11 mmol), sealed under N₂, was exposed to a 275-W sunlamp for 24 hours. The original deep purple solution turned orange-yellow as the photolysis proceeded. The solvent was removed in vacuo. The addition of hexane to the resultant oil yielded yellow crystals. Anal. Calcd. for IrC₄H₉₆NP₃Si₂: C, 56.07; H, 5.36; N, 1.52. Found: C, 55.80; H, 5.35; N, 1.40. ³¹P{¹H} NMR (C₆D₆, 121.4 MHz): CH₂PPh₂, 25.30 (d, 2Jₚ,ₚ = 22.8);
PCH$_3$Ph$_2$, -1.79 (t).

Method 2. A solution of PCH$_3$Ph$_2$ (0.01 g, 0.05 mmol) in toluene (2 mL) was added dropwise to a toluene solution (5 mL) of Ir(η$^2$-C$_8$H$_{14}$)-[N(SiMe$_2$CH$_2$PPh$_2$)$_2$]$^{53}$ (0.05 g, 0.06 mmol). After stirring for 0.5 hour, the solvent was removed *in vacuo*. Yellow crystals were obtained upon crystallization from hexane. Yield: 0.04 g (76%).

Method 3. A freshly prepared ether solution (2 mL) of CH$_2$N$_2$$^{70}$ was added dropwise to a toluene solution (5 mL) of Ir(PPh$_2$)$_2$-[N(SiMe$_2$CH$_2$PPh$_2$)$_2$]$^{62}$ (0.03 g, 0.04 mmol) at room temperature. After stirring for 0.5 hour, the solvent was removed *in vacuo*. Recrystallization of the resultant powder from hexane yielded yellow crystals. Yield: 0.02 g (68%).

cis

4.2.3 Ir(CH$_3$)(PCH$_3$Ph$_2$)(I)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] 4

Method 1. This preparation involved the vacuum transfer of an excess (at least five fold) of degassed CH$_3$I at -10°C to a toluene solution (10 mL) of Ir(CH$_3$)(PPh$_2$)$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (0.25 g, 0.27 mmol). The solution was allowed to warm to room temperature, during which time the original purple colour changed to light yellow. After stirring for 0.5 hour, the solvent was removed *in vacuo*. Recrystallization of the resultant powder from toluene yielded yellow crystals. Yield: 0.21 g (75%). Anal. Calcd. for IrC$_{44}$H$_{52}$NP$_3$Si$_2$I$_{1.25}$C$_7$H$_8$: C, 50.59; H, 5.01; N, 1.29. Found: C, 50.40; H, 5.08; N, 1.20. m.p. 190±2°C (decomp.). $^{31}$P($^1$H) NMR (C$_6$D$_6$, 121.4 MHz): CH$_2$PPh$_2$, -17.67 (d, $^2$J$_{P,P}$ = 18.6); PCH$_3$Ph$_2$, -36.60 (t).
Method 2. To a solution of \( \text{Ir(PCH}_3\text{Ph}_2)[\text{NSiMe}_2\text{CH}_2\text{PPh}_2]_2 \) (0.05 g, 0.05 mmol) in toluene (5 mL), excess (at least five fold) degassed \( \text{CH}_3\text{I} \) at \(-10^\circ\text{C} \) was vacuum transferred. The solution was stirred for 0.5 hour and the solvent removed \( \text{in vacuo} \) to give a yellow oil. The addition of toluene/hexane resulted in yellow crystals. Yield: 0.04 g (65%).

4.2.4 \( \text{Ir(CH}_3\text{)(PCH}_3\text{Ph}_2)(\text{I})[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2]_2 \)

A toluene solution (1 mL) of \( \text{PCH}_3\text{Ph}_2 \) (0.01 g, 0.05 mmol) was added dropwise to a toluene solution (5 mL) of \( \text{Ir(CH}_3\text{)(I})[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2]_2 \) (0.04 g, 0.05 mmol) at room temperature. The original green colour changed immediately to light yellow. The solvent was removed \( \text{in vacuo} \). Recrystallization of the resultant powder from toluene yielded yellow crystals. Yield: 0.04 g (70%). Anal. Calcd. for \( \text{IrC}_{44}\text{H}_{52}\text{NP}_3\text{Si}_2\text{I} \frac{1}{4}\text{C}_7\text{H}_8 \): C, 50.59; H, 5.01; N, 1.29. Found: C, 50.68; H, 5.42; N, 1.17.

4.2.5 \( \text{Ir(H}_2\text{)(PHPh}_2)[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2]_2 \) 5

Method 1. A solution of \( \text{Ir(CH}_3\text{)(PPh}_2)[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2]_2 \) (0.10 g, 0.11 mmol) in toluene (10 mL) was stirred under one atm of \( \text{H}_2 \) for 24 hours at room temperature. Within minutes, the purple solution turned light yellow. The solvent was removed \( \text{in vacuo} \), and the resultant pale yellow powder was recrystallized from toluene/hexane. Colourless crystals were obtained. Yield: 0.09 g (85%). Anal. Calcd. for \( \text{IrC}_{42}\text{H}_{49}\text{NP}_3\text{Si}_2 \): C, 55.49; H, 5.43; N, 1.54. Found: C, 55.83; H, 5.46; N, 1.49. m.p. 173±2°C (decomp.). \( ^{31}\text{P}(\text{H}) \) NMR (\( \text{C}_6\text{D}_6 \), 109.3 MHz): \( \text{CH}_2\text{PPh}_2 \), 10.70 (d, \( 2^J_{\text{P},\text{P}} = 15.8 \)); \( \text{PHPh}_2 \), -23.72 (t). IR (\( \text{CH}_2\text{Cl}_2 \), cm\(^{-1} \)): \( \nu_{\text{Ir-H}} = 2220 \) (s, br).
Method 2. A toluene solution (2 mL) of PHPh$_2$ (0.02 g, 0.13 mmol) was added dropwise to a Ir(H)$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$]$_6$ (0.09 g, 0.14 mmol) solution in toluene (10 mL). The reaction mixture was stirred for 0.5 hour. After removing the solvent in vacuo, the resultant brown powder was recrystallized from hexane at -30°C. Yield: 0.08 g (63%).

4.2.6 Ir(CH$_3$)(H)(PHPh$_2$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] 6

A solution of Ir(CH$_3$)(PPh$_2$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (0.10 g, 0.11 mmol) in toluene (10 mL) was stirred under one atm of H$_2$ for 5 min at room temperature. Upon solvent removal, the yellow powder was recrystallized from toluene/hexane. An analytically pure sample of this product was not obtained since it was always contaminated with the major dihydride complex 5. $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 109.3 MHz): CH$_2$PPh$_2$, 13.48 (d, $^2$J$_{P,P}$ = 15.3); PHPh$_2$, -33.90 (t). IR (CH$_2$Cl$_2$, cm$^{-1}$): $\nu_{Ir-H}$ = 2242 (m).

4.2.7 Deuteration Studies

The reactions to generate the complexes Ir(D)$_2$(PDPh$_2$)$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], 7, and Ir(CH$_2$D)(D)(PHPh$_2$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], 8, were carried out exactly as described above for the dihydride complex 5 and the methyl hydride complex 6 using D$_2$ (Matheson, 99.8% enriched).

4.2.8 fac-Ir(H$_2$)(PHPh$_2$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$]

A d$_6$-benzene solution (1 mL) of Ir(PHPh$_2$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (0.03 g, 0.04 mmol) was exposed to one atm of H$_2$ for 5 min at room temperature. The original yellow coloured solution immediately turned colourless. The
product was characterized by $^1\text{H}$ and $^{31}\text{P}$ NMR spectroscopy. $^{31}\text{P}$$\{^1\text{H}\}$ NMR (C$_6$D$_6$, 121.4 MHz): CH$_2$PPh$_2$, 5.72 (m); PPh$_2$, 0.07 (m).

4.2.9 Ir(CH$_3$)(CO)(PPh$_2$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] 9 and 10

A solution of Ir(CH$_3$)(PPh$_2$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (0.03 g, 0.03 mmol) in C$_6$D$_6$ (1 mL) was sealed under one atm of CO. The purple solution turned yellow immediately. $^{31}\text{P}$$\{^1\text{H}\}$ NMR (C$_6$D$_6$, 109.3 MHz): CH$_2$PPh$_2$, -22.30 (d, $^2J_{pP} = 26.0$); PPh$_2$, -61.73 (t). IR (C$_6$D$_6$, cm$^{-1}$): $\nu$$_{CO} = 2009$ (s). $^{13}\text{C}$$\{^1\text{H}\}$ NMR (C$_6$D$_6$, 75 MHz): $^{13}$CO, 173.2 (dt, $^2J_{\text{CH}_2\text{PPh}_2,^{13}\text{C}} = 9.1$, $^2J_{\text{PPh}_2,^{13}\text{C}} = 51.8$).

As the excess CO was pumped off from the yellow carbonyl solution, the complex isomerized to complex 10. $^{31}\text{P}$$\{^1\text{H}\}$ NMR (C$_6$D$_6$, 121.4 MHz): CH$_2$PPh$_2$, 25.88 (s); PPh$_2$, -5.51 (s). IR (C$_6$D$_6$, cm$^{-1}$): $\nu$$_{CO} = 1944$ (s). $^{13}\text{C}$$\{^1\text{H}\}$ NMR (C$_6$D$_6$, 75 MHz): $^{13}$CO, 177.5 (dt, $^2J_{\text{CH}_2\text{PPh}_2,^{13}\text{C}} = 11.5$, $^2J_{\text{PPh}_2,^{13}\text{C}} = 656.8$).

Both isomers were very unstable in solution, as they start converting within minutes to the previously reported complex Ir(CO)-[N(SiMe$_2$CH$_2$PPh$_2$)$_2$]$^{52}$ and free PCH$_3$Ph$_2$; therefore, it was not possible to obtain their elemental analyses.
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\text{Si(CH}_3\text{)}_2$</th>
<th>$\text{PCH}_2\text{Si}$</th>
<th>$\text{P(C}_6\text{H}_5\text{)}_2$</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ir(CH}_3\text{)(PPh}_2\text{)[N(SiMe}_2\text{CH}_2\text{PPh}_2\text{)}_2]$</td>
<td>-0.13(s)</td>
<td>1.82(dt, $J_{\text{app}}$ = 4.6, $J_{\text{gem}}$ = 12.0)</td>
<td>7.10(m,para/meta)</td>
<td>$\text{IrCH}<em>3$ 0.72(q, $J</em>{\text{P,H}}$ = 4.0) †</td>
</tr>
<tr>
<td></td>
<td>0.68(s)</td>
<td>2.36(dt, $J_{\text{app}}$ = 4.8)</td>
<td>7.85(m,ortho)</td>
<td></td>
</tr>
<tr>
<td>$\text{Ir(CH}_3\text{)(P(m-tol)}_2\text{)[N(SiMe}_2\text{CH}_2\text{PPh}_2\text{)}_2]$</td>
<td>-0.13(s)</td>
<td>1.75(dt, $J_{\text{app}}$ = 4.6, $J_{\text{gem}}$ = 13.3)</td>
<td>7.11(m,para/meta)</td>
<td>$\text{IrCH}<em>3$ 0.75(q, $J</em>{\text{P,H}}$ = 4.0) †</td>
</tr>
<tr>
<td></td>
<td>0.70(s)</td>
<td>2.36(dt, $J_{\text{app}}$ = 4.7)</td>
<td>7.90(m,ortho)</td>
<td>$\text{P(C}_6\text{H}_4\text{CH}_3\text{)}_2$ 2.10(s)</td>
</tr>
<tr>
<td>$\text{Ir(PCH}_3\text{Ph}_2\text{)[N(SiMeCH}_2\text{PPh}_2\text{)}_2]$</td>
<td>0.18(s)</td>
<td>1.87(t, $J_{\text{app}}$ = 5.3)</td>
<td>6.88(m,para/meta)</td>
<td>$\text{PCH}_3\text{Ph}<em>2$ 1.37(d, $J</em>{\text{P,H}}$ = 6.7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.65(m,ortho)</td>
<td></td>
</tr>
<tr>
<td>cis</td>
<td>$\text{Ir(CH}_3\text{(PCH}_3\text{Ph}_2\text{)(I)}-[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2\text{)}_2]$</td>
<td>0.52(s)</td>
<td>2.24(dt, $J_{\text{app}}$ = 6.6, $J_{\text{gem}}$ = 14.7)</td>
<td>7.07(m,para/meta)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.38(m,ortho)</td>
<td>$\text{PCH}_3\text{Ph}<em>2$ 1.58(d, $J</em>{\text{P,H}}$ = 10.6)</td>
</tr>
<tr>
<td>trans</td>
<td>$\text{Ir(CH}_3\text{(PCH}_3\text{Ph}_2\text{)(I)}-[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2\text{)}_2]$</td>
<td>0.46(s)</td>
<td>1.58(dt, $J_{\text{app}}$ = 6.6, $J_{\text{gem}}$ = 13.3)</td>
<td>7.33(m,para/meta)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.80(m,ortho)</td>
<td>$\text{PCH}_3\text{Ph}<em>2$ 1.92(d, $J</em>{\text{P,H}}$ = 6.7)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>8.06(m,ortho)</td>
<td></td>
</tr>
<tr>
<td>Complex</td>
<td>( \text{Si(CH}_3\text{)}_2 )</td>
<td>( \text{PCH}_2\text{Si} )</td>
<td>( \text{P(C}_6\text{H}_5\text{)}_2 )</td>
<td>Other</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>---------------------------------</td>
<td>------------------------------------------------</td>
<td>---------------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>( \text{mer-Ir(H)}_2(\text{PHPh}_2)[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)]_2 )</td>
<td>0.23(s) 0.67(s)</td>
<td>1.74(dt, ( J_{\text{app}} = 5.2 ), ( J_{\text{gem}} = 13.0 )) 1.91(dt, ( J_{\text{app}} = 5.2 ))</td>
<td>7.04(m, para/meta) 7.43(m, ortho) 8.32(m, ortho)</td>
<td>( \text{PHPPh}<em>2 5.84(\text{dt}, 1J</em>{P,H} = 334.7, 3J_{P,H} = 9.7) ) IrH(trans to ( \text{PHPh}<em>2 )) (-9.75(\text{dt}, 2J</em>{\text{PHPh}<em>2,H} = 140.4, 2J</em>{\text{CH}<em>2\text{PPh}<em>2,H} = 18.2, 2J</em>{H,H} = 5.0) ) IrH(trans to N) (-19.17(\text{qd}, 2J</em>{P,H} = 15.1, 2J_{H,H} = 5.2) )</td>
</tr>
<tr>
<td>( \text{Ir(CH}_3\text{)}(\text{H})(\text{PHPh}_2)[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)]_2 )</td>
<td>0.12(s) 0.63(s)</td>
<td>(~1.9 ) (obscured) 2.08(dt, ( J_{\text{app}} = 4.6 ), ( J_{\text{gem}} = \approx 13.0 ))</td>
<td>(~7.0) (m, para/meta) 8.72(m, ortho)</td>
<td>( \text{IrCH}<em>3 0.30(\text{dt}, 3J</em>{\text{CH}<em>2\text{PPh}<em>2,H} = 7.2, 3J</em>{\text{PHPh}<em>2,H} = 3.6) ) ( \text{PHPPh}<em>2 5.76(\text{dt}, 1J</em>{P,H} = 334.7, 3J</em>{P,H} = 8.4) ) IrH (-9.06(\text{dt}, 2J</em>{\text{PHPh}<em>2,H} = 150.0, 2J</em>{\text{CH}_2\text{PPh}_2,H} = 10.1) )</td>
</tr>
<tr>
<td>( \text{fac-Ir(H)}_2(\text{PHPh}_2)[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)]_2 )</td>
<td>0.58(s) 0.83(s)</td>
<td>1.68(m) 1.99(m)</td>
<td>6.90(m, para/meta) 7.43(m, ortho)</td>
<td>( \text{PHPPh}<em>2 6.17(\text{dt}, 1J</em>{P,H} = 346.7, 3J_{P,H} = 6.7) ) IrH (-10.43(m) )</td>
</tr>
<tr>
<td>( \text{Ir(PHPh}_2)[\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)]_2 )</td>
<td>0.29(s)</td>
<td>1.96(t, ( J_{\text{app}} = 4.7 ))</td>
<td>7.03(m, para/meta) 7.78(m, ortho)</td>
<td>( \text{PHPPh}<em>2 5.95(\text{dt}, 1J</em>{P,H} = 346.7, 3J_{P,H} = 11.3) )</td>
</tr>
<tr>
<td>Complex</td>
<td>Si(CH$_3$)$_2$</td>
<td>PCH$_2$Si</td>
<td>P(C$_6$H$_5$)$_2$</td>
<td>Other</td>
</tr>
<tr>
<td>---------</td>
<td>--------------</td>
<td>-----------</td>
<td>----------------</td>
<td>-------</td>
</tr>
<tr>
<td>cis</td>
<td>0.03(s)</td>
<td>1.86(dt, $J_{\text{app}}$ = 6.6; $J_{\text{gem}}$ = 13.3)</td>
<td>7.01(m, para/meta)</td>
<td>IrCH$<em>3$ 0.96(q, $J</em>{\text{p-H}}$ = 5.3) $^\dagger$</td>
</tr>
<tr>
<td></td>
<td>0.81(s)</td>
<td>2.73(dt, $J_{\text{app}}$ = 6.7)</td>
<td>7.38(m, ortho)</td>
<td></td>
</tr>
<tr>
<td>trans</td>
<td>0.34(s)</td>
<td>2.13(dt, $J_{\text{app}}$ = 6.3, $J_{\text{gem}}$ = 13.3)</td>
<td>7.04(m, para/meta)</td>
<td>IrCH$<em>3$ 0.56(t, $J</em>{\text{p-H}}$ = 5.3)</td>
</tr>
<tr>
<td></td>
<td>0.67(s)</td>
<td>2.44(dt, $J_{\text{app}}$ = 7.3)</td>
<td>7.51(m, ortho)</td>
<td></td>
</tr>
</tbody>
</table>

$^\dagger$ The IrCH$_3$ resonance in these complexes is observed to be a four line pattern and is indicated as "q"; however, a selective phosphorus decoupling experiment done on the complex Ir(CH$_3$)PPh$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] shows the methyl-resonance to be a triplet of doublets (see p. 21). Even though the $^{31}$P decoupling experiments were not performed on the rest of the complexes, it is assumed that the four line patterns in these complexes are triplet of doublets.
CHAPTER 5

REFERENCES


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413.
   b) ibid, p. 185.
61. To our knowledge, this is the first example of an intramolecular proton transfer from a hydrocarbyl ligand to a phosphido donor.
62. The complex Ir(PPh₂)[N(SiMe₂CH₂PPh₂)₂] was synthesized by addition of one equivalent of PPh₂ to the toluene solution of Ir(η²-C₈H₁₄)-[N(SiMe₂CH₂PPh₂)₂].
APPENDIX

Below is a comprehensive list of transition metal phosphide complexes reported in the literature along with the $^{31}P\{^1H\}$ chemical shift values and the assigned stereochemistry (wherever available) of the phosphide ligands. An asterisk denotes crystallographically characterized complexes.

Table 2 Transition metal phosphide complexes reported in the literature

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^3P{^1H}$ chemical shift (ppm) of the phosphide ligand</th>
<th>Phosphide ligand geometry</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(PR$_2^1$)(NR$_2^2$)$_3$</td>
<td>--</td>
<td>--</td>
<td>15</td>
</tr>
<tr>
<td>$R^1$=Et,SiMe$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$=Me,Et</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Li(DME)$_n$][M(PC$_2$)$_4$]</td>
<td>--</td>
<td>planar and bridging</td>
<td>9</td>
</tr>
<tr>
<td>$n=1$, M=Ti,V,Re</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n=2$, M=Nb</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cp$_2$M(PR$_2$)$_2$</td>
<td>at 25°C: a-f,</td>
<td>planar and pyramidal</td>
<td>12</td>
</tr>
<tr>
<td>$M$</td>
<td>$R$</td>
<td>(s)</td>
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</tr>
<tr>
<td>a. Zr</td>
<td>Et</td>
<td>100-160</td>
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</tr>
<tr>
<td>b. Zr</td>
<td>Cy</td>
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<td></td>
</tr>
<tr>
<td>c. Zr</td>
<td>Ph</td>
<td>at -126°C: e,</td>
<td></td>
</tr>
<tr>
<td>d. Hf</td>
<td>Et *</td>
<td>$P_A = 270.2$ (d)</td>
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</tr>
<tr>
<td>e. Hf</td>
<td>Cy</td>
<td>$P_B = -15.3$ (d)</td>
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</tr>
<tr>
<td>Compound</td>
<td>$^{31}$P/$^1$H chemical shift (ppm) of the phosphide ligand</td>
<td>Phosphide ligand geometry</td>
<td>Reference</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>-----------------------------------------------------------</td>
<td>---------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>$[\text{Li(DME)}][\text{M(PCy}_2\text{)}_5]$</td>
<td>--</td>
<td>planar and bridging</td>
<td>9</td>
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<tr>
<td>M=Zr</td>
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<tr>
<td>Hf *</td>
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<tr>
<td>$\text{Cp}^*\text{HfCl}_2{\text{P(CMe}_3\text{)}_2}$</td>
<td>209.9 (s)</td>
<td>planar</td>
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<tr>
<td>$\text{Cp}^*\text{HfCl}{\text{P(CMe}_3\text{)}_2}_2$</td>
<td>261.3 (s)</td>
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<td>$\text{Cp}^*\text{HfCl}(\text{R}){\text{P(CMe}_3\text{)}_2}_2$</td>
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<tr>
<td>R=CH$_2$CMe$_3$</td>
<td>213.6 (s)</td>
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<tr>
<td>CH$_2$Ph</td>
<td>222.2 (s)</td>
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<tr>
<td>Ph</td>
<td>216.2 (s)</td>
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<tr>
<td>$\text{Cp}^*\text{Hf(Me)}_2{\text{P(CMe}_3\text{)}_2}$</td>
<td>202.5</td>
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<td>33</td>
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<tr>
<td>$\text{Ta(H)(PPh}_2\text{)}_2\text{(dmpe)}_2^*$</td>
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<td>10</td>
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<tr>
<td>$\text{Cp(CO)}_3\text{M(PCl}_2\text{)}$</td>
<td></td>
<td>pyramidal</td>
<td>16a</td>
</tr>
<tr>
<td>M=Cr</td>
<td>421 (s)</td>
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</tr>
<tr>
<td>Mo</td>
<td>394 (s)</td>
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<tr>
<td>W</td>
<td>362 (s)</td>
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<tr>
<td>$\text{MeNCH}_2\text{CH}_2\text{N(Me)P-}$</td>
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<td>planar</td>
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<tr>
<td>$\text{MoCp(CO)}_2$ *</td>
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</table>
### Table: Characteristic Chemical Shifts of Phosphides

<table>
<thead>
<tr>
<th>Compound</th>
<th>(^{31}P{^1H} \text{ chemical shift (ppm) of the phosphide ligand})</th>
<th>Phosphide ligand geometry</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cp(CO)}_3\text{M(PPh}_2\text{)})</td>
<td>(\text{M}=\text{Mo})</td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>W</td>
<td>--</td>
<td>pyramidal</td>
<td></td>
</tr>
<tr>
<td>(-63.3,(d, ^{1}J_{PW}=52.0,\text{Hz}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Cp(CO)}_2\text{M(PMe}_3\text{)}\text{M(PPh}_2\text{)})</td>
<td>(\text{M}=\text{Mo})</td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>W</td>
<td>--</td>
<td>pyramidal</td>
<td></td>
</tr>
<tr>
<td>(-31.9,(s))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-55.9,(d, ^{1}J_{PW}=62.9,\text{Hz}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Mo(PCI}_2\text{)}_4)</td>
<td>*</td>
<td>--</td>
<td>9</td>
</tr>
<tr>
<td>(\text{1,2-M}_2{(\text{P}(t-\text{Bu})_2)\text{NMe}_2})</td>
<td>*</td>
<td>--</td>
<td>16b</td>
</tr>
<tr>
<td>(\text{W})</td>
<td></td>
<td>pyramidal</td>
<td></td>
</tr>
<tr>
<td>(\text{Cp(CO)}_2\text{M(P(R)(CH}=\text{PR})\})</td>
<td>(\text{R}=(2,4,6-t-\text{Bu}_3\text{C}_6\text{H}_2))</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>(\text{M}=\text{Mo})</td>
<td>*</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td></td>
<td>planar</td>
<td></td>
</tr>
<tr>
<td>(303.4,(d, ^{2}J_{PP}=55,\text{Hz}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(246.7,(dd, ^{2}J_{PP}=64,\text{Hz}, ^{1}J_{WP}=638,\text{Hz}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Cp(CO)}_2\text{W(PR}_2\text{)})</td>
<td>(\text{R}=\text{i-Pr})</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>(t-\text{Bu})</td>
<td>*</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>(401.9,(d, ^{1}J_{WP}=591,\text{Hz}))</td>
<td></td>
<td>planar</td>
<td></td>
</tr>
<tr>
<td>(373.4,(d, ^{1}J_{WP}=552,\text{Hz}))</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Compound | $^{31}\text{P}\{^1\text{H}\}$ chemical shift (ppm) of the phosphide ligand | Phosphide ligand geometry | Reference
--- | --- | --- | ---
$\text{Mn}_2\{\text{P(CH}_3\}_2\}_2\text{(CO)}_9$ | -- | -- | 38
$\text{Cp(NO)(PPh}_3\text{)Re(PPh}_2\}$ | -- | pyramidal | 19
$(\eta^5\text{-C}_5\text{H}_5\text{(CO)}_2\text{Fe-P}(\text{P(CF}_3\}_2\} | -- | pyramidal | 20
$[\text{MeNCH}_2\text{CH}_2\text{N}(\text{Me})\text{P-Fe(CO)}_4]^+\text{PF}_6^- | -- | -- | 21
$\text{Cp(CO)}_2\text{Fe(P(SiMe}_3\}_2\} | -265(\text{dd}, ^3J_{\text{PFeCH}=2.0} \text{ Hz}, \text{siCH}=4.0 \text{ Hz}) | pyramidal | 22
$\text{Cp}*\text{(CO)}_2\text{Fe(PR}_1\text{R}_2) | -- | pyramidal | 23
$\begin{array}{c}
\text{R}_1=\text{R}_2=\text{Ph} \\
\text{SiMe}_3 \\
\text{CMe}_3 \\
\text{R}_1=\text{CMe}_3, \text{R}_2=\text{SiMe}_3
\end{array} | -- | -- | 23
$\text{M(PRPh)(Cl)(CO)}_2^- (\text{PPh}_3)_2 | -- | pyramidal | 3, 24
$\begin{array}{c}
\text{M} \\
\text{Ru} \\
\text{Os} \\
\text{Os} \\
\text{Os} \\
\text{Os} \\
\text{Os}
\end{array} | \text{R} \\
\text{H} \\
\text{H} * \\
\text{Ph} \\
\text{I} \\
\text{OMe}
### Compound | $^{31}P\{^{1}H\}$ chemical shift (ppm) of the phosphide ligand | Phosphide ligand geometry | Reference
---|---|---|---
Os(PPh)(PH_{2}Ph)(Cl)-(CO)(PPh_{3})_{2} | -- | pyramidal | 24
Rh(PF_{2})(CO)(X)_{2}(PET_{3})_{2} | X=Br | 388.0(dd, $^{1}J_{PF}=1153$ Hz, $^{1}J_{PRh}=27$ Hz) | pyramidal | 26
 | I | 395.4(dd, $^{1}J_{PF}=1155$ Hz, $^{1}J_{PRh}=25$ Hz) | | |
Rh(PFCl)(CO)(Cl)_{2}-(PET_{3})_{2} | 369.8 (ABMXY pattern, $^{1}J_{PF}=1195$ Hz, $^{1}J_{PRh}=26$ Hz, $^{2}J_{PP}=3$ Hz) | pyramidal | 26
Ir(PF_{2})(CO)(X)_{2}(PET_{3})_{2} | X=Cl | 364.8(dd, $^{1}J_{PF}=1105$ Hz, $^{2}J_{PP}=9.2$ Hz) | pyramidal | 5b
<p>| Br | 363.3(dd, $^{1}J_{PF}=1108$ Hz, $^{2}J_{PP}=8.6$ Hz) | | |
| I | 364.8(dd, $^{1}J_{PF}=1112$ Hz, $^{2}J_{PP}=8.3$ Hz) | | |</p>
<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{31}\text{P}^{(1)}\text{H}$ chemical shift (ppm) of the phosphide ligand</th>
<th>Phosphide ligand geometry</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir(PF$_2$)(CO)(X)(H)- (PEt$_3$)$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X=Br</td>
<td>380.0(dd, $^1J_{PF}=1105$ Hz, $^2J_{PP}=26.4$ Hz)</td>
<td></td>
<td>5b</td>
</tr>
<tr>
<td>I</td>
<td>367.7(dd, $^1J_{PF}=1111$ Hz, $^2J_{PP}=25.9$ Hz)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ir(PF$_2$)(CO)(X)(Cl)- (PEt$_3$)$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X=Br</td>
<td>362.1(dd, $^1J_{PF}=1111$ Hz, $^2J_{PP}=8.6$ Hz)</td>
<td></td>
<td>5b</td>
</tr>
<tr>
<td>I</td>
<td>359.5(dd, $^1J_{PF}=1117$ Hz, $^2J_{PP}=7.5$ Hz)</td>
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<tr>
<td>Ir(PCl$_2$)(CO)(Cl)$_2$- (PEt$_3$)$_2$ *</td>
<td>304.0(d, $^2J_{PP}=34.0$ Hz)</td>
<td>pyramidal</td>
<td>5a</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td>Ir(PH$_2$)(CO)(X)(H)- (PEt$_3$)$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X=Cl</td>
<td>-217.9(d, $^1J_{PH}=172.4$ Hz)</td>
<td></td>
<td>28</td>
</tr>
<tr>
<td>Br</td>
<td>-219.3(d, $^1J_{PH}=172.8$ Hz)</td>
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<td></td>
</tr>
<tr>
<td>Ir(P$_a$H$_2$)(P$_b$H$_2$)(CO)- (H)(PEt$_3$)$_2$</td>
<td>$P_a$, -218.2(d, $^1J_{PH}=176$ Hz)</td>
<td>pyramidal</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>$P_b$, -239.4(d, $^1J_{PH}=164$ Hz)</td>
<td></td>
<td></td>
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<tr>
<th>Compound</th>
<th>$^{31}\text{P}^{(1)\text{H}}$ chemical shift (ppm) of the phosphide ligand</th>
<th>Phosphide ligand geometry</th>
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<tbody>
<tr>
<td>Cp(R)Ni{P(SiMe$_3$)$_2$}</td>
<td>-269 (dd, $^{3}J_{PSiCH} = 3.8$ Hz, $^{3}J_{PNiCH} &lt; 0.3$ Hz)</td>
<td>pyramidal</td>
<td>25</td>
</tr>
<tr>
<td>R=PPh$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>-236.5 (dd, $^{3}J_{PSiCH} = 4.4$ Hz, $^{3}J_{PNiCH} = 2.4$ Hz)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>