OLEFINIC TERTIARY PHOSPHINE COMPLEXES OF
NICKEL, PALLADIUM AND PLATINUM

BY

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ABSTRACT

The insertion of the olefinic moiety of the olefinic ligands $\ce{\text{o-CH_2=CHC_6H_4PPh}_2}$ (SP), $\ce{\text{o-CH_2=CHC_6H_4AsPh}_2}$ (SPAS) and $\ce{\text{o-CH_2=CHC_6H_4PMe}_2}$ (DMSP) into the platinum-hydride bond of various platinum(II) hydrido complexes trans-$\ce{[PtHClL_2]}$ ($L = \text{PPh}_3$, $\text{PET}_3$, $\text{P-i-Pr}_3$, AsPh$_3$) gives $\sigma$-alkyl complexes containing exclusively a five-membered metallocycle of general formula $\ce{[Pt(\text{o-CHMeC_6H_4ER}_2)Cl(L)]}$ ($E = \text{P}$, $\text{R} = \text{Ph}$, $L = \text{PPh}_3$, $\text{PET}_3$, $\text{P-i-Pr}_3$, AsPh$_3$; $E = \text{P}$, $\text{R} = \text{Me}$, $L = \text{PPh}_3$; $E = \text{As}$, $\text{R} = \text{Ph}$, $L = \text{PPh}_3$), no isomeric six-membered metallocyclic complexes being observed. This indicates that the regiochemistry of the insertion products of this type is independent of the electronic and steric properties of the olefinic ligands and of the Group V donor ligands present in the platinum(II) hydride complexes. However, the reaction rate depends strongly on these properties. Low temperature $^1\text{H}$ and $^{31}\text{P}$NMR spectroscopy shows that the first step of the insertion reaction of $\ce{\text{o-CH_2=CHC_6H_4PPh}_2}$ into the Pt-H bond of trans-$\ce{[PtHCl(PPh)_3]}$ is the formation of the four-coordinate cationic hydridocle intermediate $\ce{[PtH(PPh)_3(\text{o-CH_2=CHC_6H_4PPh}_2)]^+}$, formed by displacement of the ligand trans to hydride by the P-donor of the olefinic ligand.

Zerovalent metal complexes of general formula $\ce{M(SP)}_2$ ($M = \text{Ni, Pd, Pt}$; $\text{SP} = \ce{\text{o-CH_2=CHC_6H_4PPh}_2}$) have been synthesized. The Ni(SP)$_2$ and Pt(SP)$_2$ complexes are monomeric, tetrahedral complexes with both SP ligands coordinated through the P-donor and olefinic moiety. In contrast the palladium(0) analogue is trigonal planar with one coordinated vinyl group and one free vinyl group. This difference in structure suggests that the palladium-olefin bond is the weakest among this series. This is supported by the fact that while Ni(SP)$_2$
and Pt(SP)₂ are nonfluxional and dissociatively stable complexes, the palladium analogue is fluxional at room temperature. The 16-electron complex Pd(SP)₂ also reacts readily with additional SP to give Pd(SP)₃ in which all the vinyl groups are free, whereas the nickel and platinum analogues do not react with additional SP even under forcing conditions. Protonation of the M(SP)₂ complexes with HBF₄ or HPF₆ gives chelate σ-alkyl-olefin complexes of the divalent metals of general formula \[
\left[ M(o-\text{CHMeC}_6\text{H}_4\text{PPh}_2)(o-\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2) \right]^+.
\] The platinum and palladium complexes are air stable whereas the nickel complex is air-sensitive and readily decomposes in solution to form Ni(SP)₂, presumably via β-hydride elimination.

The mixed tertiary phosphine complexes of the zerovalent nickel triad of general formula M(PPh₃)₂(SP) (M = Pt, Pd) have been synthesized and spectroscopic evidence for the nickel analogue has been obtained. The palladium complex is immediately disproportionated in solution to give zerovalent palladium complexes containing tertiary phosphines Pd(SP)₂(PPh₃) and Pd(PPh₃)₃. In contrast the platinum analogue disproportionates at a much slower rate to give Pt(SP)₂ and Pt(PPh₃)₃. In solution at low temperature the nickel(0) and platinum(0) complexes are both tetrahedral, containing two triphenylphosphine ligands and one bidentate SP ligand, although at room temperature one of the triphenylphosphine ligands of Ni(PPh₃)₂(SP) undergoes reversible dissociation. In the platinum analogue, the coordinated vinyl group of SP dissociates reversibly above -30°C and at room temperature one of the tertiary phosphine ligands also dissociates. In general, the results compare well with the trend in behaviour towards σ-donor and π-acceptor ligands predicted from electron affinity and ionization potential data for the zerovalent metals of the nickel triad.
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ABBREVIATIONS

acac 2,4-pentanedionato
t-Bu tert-butyl
Cy cyclohexyl
COD cyclooctadiene
δ chemical shift
d doublet
DMSP o-vinylphenyldimethylphosphine
dppe bis(diphenylphosphino)ethane
Et ethyl
n hapto
IR infrared
i-Pr isopropyl
m multiplet or medium
Me methyl
M.P. melting point
M.W. molecular weight
NMR nuclear magnetic resonance
o ortho
Ph phenyl
ppm parts per million
q quintet
s strong
SP o-vinylphenyldiphenylphosphine
SPAS o-vinylphenyldiphenylarsine
t triplet
THF tetrahydrofuran
TMS tetramethylsilane
w weak
NOTE

$^{31}$P NMR spectra refers to $^{31}$P$^{1}$H NMR spectra
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CHAPTER ONE
INTRODUCTION

1.1 Objective and Scope of Investigation

Homogeneous catalysis using transition metal complexes plays an important role in several major industrial processes such as hydrogenation, polymerisation, isomerisation, hydroformylation and hydrosilation of olefins\textsuperscript{1-13}. Complexes of the nickel triad, especially those formed by tertiary phosphines, are very versatile and are widely used as homogeneous catalysts\textsuperscript{2,14,15b,16b,17}. Some typical examples of reactions catalysed by such complexes are summarized in Table 1.1. It has been established\textsuperscript{2} that these catalytic reactions involve the formation of metal-hydride, metal-olefin and metal-alkyl complexes as the key steps. The catalytic cycle for dimerisation of ethylene to 1-butene in Figure 1.1 illustrates these processes. Studies of the mechanism of catalytic reactions have frequently been hindered by the failure to identify the labile intermediates involved.

In order to stabilise metal-monoolefin complexes and to examine the reactions of an olefin in the vicinity of a metal ion, Nyholm and coworkers\textsuperscript{29-35} developed a series of chelating ligands containing Group V donor atoms and olefinic groups. The presence of a phosphorus or arsenic-containing donor group enhances metal-olefin $\pi$-back bonding, and chelation of the olefinic group reduces olefin dissociation and constrains it to the proximity of the metal atom. Consequently, the resulting chelate complexes are often more stable than complexes of simple olefins.
Table 1.1 Some examples of reactions catalysed by nickel triad complexes

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Example</th>
<th>Catalyst</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>double bond isomerisation</td>
<td>CH₂CHCH₂CH₂CH₃ → CH₃CH=CHCH₂CH₃</td>
<td>PdCl₂(NCPh)₂</td>
<td>18</td>
</tr>
<tr>
<td>polymerisation</td>
<td>CH₂=CHCH=CH₂ → polybutadienes</td>
<td>allyl Ni complexes</td>
<td>19, 20</td>
</tr>
<tr>
<td>dimerisation</td>
<td>2 + PhOH → PhO</td>
<td>Ni[P(OPh)₃]₄</td>
<td>21</td>
</tr>
<tr>
<td>hydrosilation</td>
<td>RCH=CH₂ → RCH(CH₃)SiR₃ + RCH₂CH₂SiR₃</td>
<td>Pt(PPMe₃)(C₆H₅)₂</td>
<td>22</td>
</tr>
<tr>
<td>&quot;Wacker process&quot; oxidation</td>
<td>C₂H₄ + O₂ → CH₃CHO</td>
<td>Pd(II) salts</td>
<td>23</td>
</tr>
<tr>
<td>skeletal isomerisation</td>
<td></td>
<td>NiHCl(P-t-Bu)₂</td>
<td>24</td>
</tr>
<tr>
<td>hydrocarboxylation</td>
<td>CH₂=CHCH₃ → (CH₃)₂CHCOOR</td>
<td>PdCl₂(PP₃)₂</td>
<td>25, 26</td>
</tr>
<tr>
<td>hydrogenation</td>
<td>1,5,9-Cyclododecatriene → Cyclodecene</td>
<td>[Pt(SnCl₅)]₃⁻</td>
<td>27</td>
</tr>
<tr>
<td>oligomerization</td>
<td></td>
<td>Ni(0), e.g. Ni(COD)₂</td>
<td>15b, 28</td>
</tr>
</tbody>
</table>
The aim of the work described in this thesis is to extend the chemistry of the olefinic tertiary phosphine complexes of the nickel triad. The main objective is to synthesize the types of complexes that are important in a catalytic cycle involving olefins and to study their reactivities and the mechanism of their formation. Two aspects of this area have been studied.

(1) Syntheses of platinum(II)-alkyl complexes by insertion of olefinic tertiary phosphines and of an olefinic tertiary arsine into the Pt-H bond. The main interest is the regiochemistry of the insertion products and the insertion mechanism (Chapter 2).

(2) Syntheses and reactivities of complexes of olefinic tertiary phosphines formed by zerovalent metals of the nickel triad (Chapter 3 and 4).

In the nickel triad, zerovalent olefinic complexes and divalent alkyl complexes are related by protonation and deprotonation reactions. These reactions model steps occurring in many catalytic cycles involving olefins (for example see Figure 1.1 and Figure 2.1).
1.2 Some Aspects of the Organometallic Chemistry of the Nickel Triad

In this introduction a brief overview of the organometallic chemistry of the nickel triad is given. Detailed descriptions of this chemistry are available in the literature\(^1,5\) a,\(^{16}\) a,\(^{17}, 36-38\).

In the nickel triad, the most common oxidation state is +2, \(M(\text{II})\), having a \(d^8\) electron configuration. Sixteen-electron complexes...
of this oxidation state are usually diamagnetic and square planar. The tendency to form diamagnetic five-coordinate 18-electron complexes and paramagnetic tetrahedral 16-electron complexes is much greater for nickel(II) than for palladium(II) and platinum(II). Five-coordinate palladium(II) and platinum(II) complexes usually have $\pi$-acceptor ligands such as $\text{SnCl}_3$ and ligands containing phosphorus, arsenic and antimony as donor atoms. The relative ability of the Group VB elements to stabilise a five-coordinate geometry is $\text{N} < \text{P} < \text{As} < \text{Sb}$, which parallels the $\pi$-bonding ability of these elements.

Zerovalent metal complexes of the nickel triad have coordination numbers ranging from four to two depending on the electronic properties of the metal and ligands, and on the steric properties of the ligands. The 18-electron four-coordinate complexes such as $\text{Pt(CO)(PPh}_3)_3$ and $\text{Pt(COD)}_2$ have a tetrahedral structure. The 16-electron three-coordinate complexes such as $\text{Pt(PPh}_3)_2$, $\text{Ni(PPh}_3)_2$, $\text{Pt(C}_2\text{H}_4)_3$ and $\text{Pt(C}_2\text{H}_4)\_3$ have a trigonal planar structure. The 14-electron two-coordinate complexes such as $\text{M[PPh(t-Bu)}_2]_2$ ($\text{M} = \text{Pd}, \text{Pt}$) have a linear structure.

The trend in the stability of complexes of the nickel triad metals in the zerovalent and in the divalent oxidation state depends on the ability of the central metal atom and the ligand to form $\sigma$- and $\pi$-bonds. Table 1.2 lists the electron affinities (EA), the ionization potential (IP) and the difference between these two quantities for metals of the zerovalent nickel triad. These parameters have been used to estimate the ability of each metal to participate in $\sigma$- and $\pi$-bonding. The $\sigma$-bond strength is related to the trend in EA i.e. $\text{Pt} > \text{Pd} = \text{Ni}$. The $\pi$-back bonding strength varies with IP and is in the order $\text{Ni} > \text{Pt} = \text{Pd}$. Hence nickel(0) is a strong $\pi$-bonder; platinum(0)
is a strong σ-bonder but palladium(0) is relatively weak in both bonding modes.

Table 1.2 Ionization potential (IP) and electron affinities (EA) of atoms of the nickel triad

<table>
<thead>
<tr>
<th>Metal</th>
<th>EA(eV)(^a)</th>
<th>IP(eV)(^b)</th>
<th>EA-IP(eV)</th>
</tr>
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<tbody>
<tr>
<td>Ni</td>
<td>1.2</td>
<td>5.81</td>
<td>- 4.6</td>
</tr>
<tr>
<td>Pd</td>
<td>1.3</td>
<td>8.33</td>
<td>- 7.0</td>
</tr>
<tr>
<td>Pt</td>
<td>2.4</td>
<td>8.20</td>
<td>- 5.8</td>
</tr>
</tbody>
</table>

\(a:\) \ EA = \Delta H \ for \ M^- (d^{10} s^1) \rightarrow M(d^{10}) + e^-  \\
\(b:\) \ IP = \Delta H \ for \ M(d^{10}) \rightarrow M^+ (d^9) + e^-  \\

Nickel readily forms a stable mononuclear tetracarbonyl, Ni(CO)\(_4\), by reaction of activated metallic nickel or nickel(II) salts with carbon monoxide at room temperature under one atmosphere of carbon monoxide\(^{15a,48}\). In contrast, Pd(CO)\(_4\)\(^{49,50}\) and Pt(CO)\(_4\)\(^{51}\) are extremely unstable, being formed in a rare gas matrix by the reaction of metal vapour with carbon monoxide at low temperature (< 30K). The decomposition temperatures of the M(PF\(_3\))\(_4\) compounds, Ni > 155°C; Pd > -20°C; Pt > 90°C show a similar trend\(^{52}\). Since both carbon monoxide and PF\(_3\) are strong π-acceptor ligands, these examples illustrate that nickel(0) has the best π-back bonding capacity in the nickel triad, in agreement with the prediction from IP and EA data. The enthalpies of activation for M-P bond rupture for a series of
zerovalent phosphite complexes, $\text{M}[\text{P(OC}_2\text{H}_5)_3]_4$, are in the order $\text{Ni} > \text{Pt} > \text{Pd}^{57}$ which is also consistent with this suggestion.

Molecular orbital calculations$^{53-56}$ and experimental evidence$^{15a,16a,17,36}$ suggest that $\pi$-back bonding in zerovalent metal complexes is more important than $\sigma$-bonding. In contrast, $\pi$-bonding is less important than $\sigma$-bonding in complexes of the divalent metals of the nickel triad with soft ligands such as olefins and phosphines$^{38c}$. A molecular orbital calculation by Akermark and coworkers supports this suggestion$^{58}$.

1.2.1 Olefin Complexes of Divalent Metals of the Nickel Triad

Olefin complexes are the oldest class of organometallic complexes known. The first complex of this type, Zeise's salt, $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)].\text{H}_2\text{O}$, was prepared in 1830$^{59}$. Olefin complexes of nickel(II) are rare, but those of palladium(II) and platinum(II) are relatively stable and have been extensively studied$^{15a,16a,17,60-67}$.

Contemporary understanding of the bonding in transition metal olefin complexes began with the molecular orbital model suggested by Dewar for silver(I) complexes$^{68}$. In this theory, which was extended by Chatt and Duncanson$^{69}$ to platinum(II) complexes, metal-olefin bonding has two components, a $\sigma$-bond from the filled $\pi$-orbital of the olefin to an empty hybrid orbital on the metal, and $\pi$-back donation of electron density from a filled hybrid orbital on the metal to the empty $\pi^*$-orbital on the olefin (Figure 1.2).
In platinum(II) complexes, the original molecular orbital treatment\textsuperscript{68,69} envisaged the formation of a \( \sigma \)-bond and a \( \pi \)-bond (Figure 1.2). The \( \sigma \)-bond is formed by donation of electron density from the filled \( p_{\pi} \)-orbital on the olefin to the empty \( 5d_{z^2}5d_{x^2-y^2}6s6p_z \) hybrid orbital on platinum, and the \( \pi \)-bond is formed by back donation of electron density from the \( 5d_{yz}6p_y \) hybrid orbital on platinum to the empty \( p_{\pi} \)* orbital on the olefin. This bonding scheme requires the olefin to be bound perpendicularly to the square plane containing platinum and the other ligands. Structural studies on Zeise's salt support this proposal\textsuperscript{70}.

Rotation of the olefin about the metal-olefin bond accounts for the temperature dependence of the NMR spectra of many complexes such as trans-[PtCl\(_2\)(olefin)(2,4,6-trimethylpyridine)] (olefin = styrene or...
t-butylethylene) \(^7\), and \([\text{PtCl(olefin)(acac)}]\) (olefin = propylene or cis-but-2-ene) \(^7\). The energy barrier to rotation lies between 10 and 15 Kcal/mol \(^7\). The rotation of the olefin can be explained using Dewar-Chatt-Duncanson theory. Favourable metal olefin bonding can occur in two orthogonal orientations, which allows olefin rotation. The perpendicular orientation of the olefin using the metal \(5d_{yz}6p_y\) hybrid is the most stable conformation, but the parallel orientation arising from overlap of the \(5d_{xz}\) orbital with the olefin \(p_{\pi^*}\) orbital is also accessible.

When an olefin is bonded to a transition metal, the following observable structural changes occur:

(1) A lengthening of the \(\text{C} = \text{C}\) bond distance, and a bending back of the substituents on the olefin away from the metal is shown by X-ray structural studies. The \(\text{C} = \text{C}\) stretching frequencies in the IR spectra are correspondingly reduced.

(2) The NMR parameters of the olefin change. The \textit{cis} and \textit{trans} proton-proton coupling constants decrease, and the \(^1\text{H}\) and \(^{13}\text{C}\) NMR resonances shift upfield.

Dewar-Chatt-Duncanson molecular orbital theory successfully accounts for all of these observations \(^7,6^4\). However, a detailed calculation \(^7^6\) for Zeise's anion, \([\text{PtCl}_3(\text{C}_2\text{H}_4)]^-\), indicates that the bonding of the olefin is more complicated than a simple \(\sigma-\pi\) type interaction. When the results are interpreted in terms of the Dewar-Chatt-Duncanson model, \(\sigma\)-bonding effects are found to be considerably more important than \(\pi\)-back bonding effects \(^7,3^8\).

Olefin complexes of divalent platinum and palladium are susceptible to nucleophilic attack. This reaction is generally supposed to be facilitated by the reduction of the electron density in the
π-bonding orbital which occurs on complexation\textsuperscript{77,78}. However, from molecular orbital calculations, Eisentein and Hoffmann\textsuperscript{79} have proposed a different explanation. The coordinated olefin is suggested to be activated towards nucleophilic attack by a slipping of the ML\textsubscript{n} fragment away from the olefin centre, along the C=C bond.

There are numerous examples of nucleophilic attack at a coordinated olefin e.g. Eq. 1.1. The addition of nucleophiles to palladium(II)-olefinic complexes is an important method of producing useful palladium(II) σ-bonded complexes and is a critical step in the Wacker process\textsuperscript{16a,80}.

\[
\text{M = Pd, Pt} \\
\text{Cl} = \text{dipentene, 1,5-cyclooctadiene} \\
\text{R} = \text{alkyl}
\]

Eq. 1.1

1.2.2 Hydride and Alkyl Complexes of the Divalent Metals of the Nickel Triad

The divalent metals of the nickel triad form an extensive series of square planar hydride and alkyl complexes which are stabilised by
ligands such as tertiary phosphines, $n^5$-cyclopentadienyl and carbon monoxide. The chemistry of these compounds is dominated by the high trans-influence of hydride and alkyl ligands. In general, the platinum(II) complexes are the most robust, both thermally and to air oxidation. There is a marked increase in the stability of transition metal hydrides and alkyls on descending the group. For example, the platinum(II) hydrido complexes, trans-$[\text{PtHXL}_2]$, are known for a variety of anionic ligands $X^-$, and for a range of tertiary phosphines and arsines. In contrast, the corresponding nickel(II) and palladium(II) compounds are thermally stable only when $L$ is a bulky tertiary phosphine. A recent review on transition metal hydrido complexes has appeared.

The monohydride complexes can be neutral ($\text{MHXL}_2$) or cationic ($\text{MHL}_3$)$^+$.$X^-$. Their syntheses are well documented and will not be considered in this summary. Their structures, determined by NMR and X-ray methods, are always four-coordinate square planar (16-electron complexes). With the exception of the complex $\text{[PtHCl(dppe)]}$, hydrides of the type ($\text{MHXL}_2$) adopt a trans configuration. Five-coordinate 18-electron hydride complexes of the divalent metals of the nickel triad are uncommon, the tendency to form them being highest for nickel(II). Most of the stable five-coordinate hydrides, such as $\text{[NiH(P(OEt)_3)}_4]^+\text{CF}_3\text{COO}^-$, $\text{[NiH(dppe)}_2]^+\text{AlCl}_4^-$, and $\text{[PtH(SnCl}_3\text{(C}_8\text{H}_16\text{)}(\text{PPh}_3)_2]}$ contain good π-acceptor ligands $[\text{P(OR)}_3$, $\text{SnCl}_3^-]$ or a bidentate ligand (dppe).

Methyl complexes such as $\text{[M(CH}_3\text{)XL}_2]}$ ($M = \text{Ni,Pd,Pt}$) preferentially adopt the trans geometry. In fact, a methyl complex with a cis configuration has only been isolated for platinum(II).

The homoleptic alkyl complex $\text{[Li}_2\text{Pt(CH}_3\text{)}_4]}$ is the only alkyl complex of the nickel triad metals which does not contain stabilising π-acid ligands. Platinum is the only member of the triad to form
stable dihydride complexes \(^{89-96}\).

As a consequence of their lability, nickel(II) and palladium(II) hydrides and alkyls are implicated in many catalytic processes involving these two metals. Studies of the corresponding platinum(II) compounds, which are more stable, have increased understanding of the nature of metal-ligand bonding and the trans-influence of ligands. Much of this information comes from NMR chemical shifts and coupling constants involving the spin-active nucleus \(^{195}\text{Pt}\) (I = \(\frac{1}{2}\), 34% abundance).

In general, methyl complexes of transition metals are more thermally stable than longer chain alkyl complexes. A low energy decomposition pathway for longer chain alkyl complexes is \(\beta\)-hydride elimination (Figure 1.3) \(^{97-101}\).

![Figure 1.3](image)

Figure 1.3 The \(\beta\)-hydride transfer-olefin elimination mechanism for decomposition of metal-alkyl complexes

Transition metals, in contrast to main group metals, possess partially filled d-valence shells and have variable oxidation states and coordination numbers. This property allows the formation of intermediates that involve a change in the oxidation state and coordination
number at the central metal atom, which would not otherwise be possible with the main group metals.

The role of bulky tertiary phosphine ligands in stabilising transition metal alkyl and hydride complexes is believed\(^{99}\) to be steric rather than electronic. Bulky ligands hinder access of reagents to the metal atom\(^ {38c}\).

Metal alkyl groups incorporated in a chelate ring are in general more stable than their open chain analogues because of the chelate effect\(^ {102,103}\) and the difficulty in adopting an appropriate geometry for \(\beta\)-hydrogen elimination\(^ {104}\). For example, a series of complexes bis[2-(diphenylphosphino)benzyl]nickel(II), palladium(II) and platinum(II) (Figure 1.4) was reported to be more stable than their nonchelate analogues\(^ {103}\).

![Figure 1.4 Bis[2-(diphenylphosphino)benzyl]M(II)](image)

\[M = \text{Ni, Pd, Pt}\]

1.2.3 Phosphine Complexes of Zerovalent Metals of the Nickel Triad

Stable zerovalent metal phosphine complexes of the nickel triad exist with coordination numbers of two, three or four, their total
number of valence electrons being 14, 16 and 18 respectively. Examples are Pt(PEt$_3$)$_4^{105}$, Pt(PPh$_3$)$_3^{106}$ and Pt(P-i-Pr$_3$)$_2^{107}$. The preferred coordination number is influenced by both steric and electronic factors$^{108}$.

A general characteristic of the four-coordinate species is their facile dissociation to form lower coordinated species in solution (Eq. 1.2). This behaviour is evident from the low molecular weight of these complexes in solution and the temperature dependence of their $^{31}$P NMR spectra. The extent of dissociation depends on the steric

\[ \begin{align*}
ML_4 & \rightleftharpoons ML_3 \rightleftharpoons ML_2 \rightleftharpoons (ML)_n \\
& \text{Eq. 1.2}
\end{align*} \]

and electronic properties of the ligands and metals. The interplay of electronic and steric factors is obvious from the following examples.

The dissociation of Pt(PEt$_3$)$_4$ was studied in n-heptane and THF by electronic spectroscopy$^{109}$. The $K_1$ value (Eq. 1.3) at 20°C is 0.5M in THF and 0.3M in n-heptane. Further dissociation to Pt(PEt$_3$)$_2$ is not detectable spectroscopically.

\[ \begin{align*}
\text{Pt(PEt}_3\text{)}_4 & \xrightleftharpoons{K_1} \text{Pt(PEt}_3\text{)}_3 + \text{PEt}_3 \\
& \text{Eq. 1.3}
\end{align*} \]

Under identical conditions, Pt(P-i-Pr$_3$)$_3$ is extensively dissociated; $K_2$ (Eq. 1.4) is $1.4 \times 10^{-1}$ M in THF and $4.0 \times 10^{-2}$ M in n-heptane. Approximately 94% of the complex Pt(P-i-Pr$_3$)$_3$ exists as Pt(P-i-Pr$_3$)$_2$ in THF solution in the absence of added phosphine$^{109}$. 
The extent of dissociation depends largely on steric factors, with bulkier phosphines favouring lower coordination numbers e.g. the cone angles of PET₃ and P-i-Pr₃ are 132 ± 4° and 160 ± 10° respectively (Appendix I). However, the electronic effects of the ligand cannot be ignored. For example, even though P-i-Pr₃ and P(0-2-C₆H₄CH₃)₃ have similar cone angles (160 ± 10° and 165 ± 10° respectively), Pt[P(0-2-C₆H₄CH₃)₃]₃ does not readily dissociate, whereas Pt(P-i-Pr₃)₃ dissociates extensively. The electronic properties of the metal ion also influence the preferred coordination number. For example, nickel(0) forms NiL₄ with P(0-2-C₆H₄CH₃)₃ whereas platinum(0) forms only PtL₃ with this ligand.

The importance of steric effects in determining the stability of zerovalent nickel phosphine and phosphite complexes has been studied in detail by Tolman using ¹H and ³¹P NMR spectroscopy. Tolman found that the degree of substitution of Ni(CO)₄ by members of a series of 24 phosphite and phosphine ligands correlates linearly with the cone angle of the ligands but not with their basicity. The basicity of phosphine and phosphite ligands was estimated from reduction of the carbon monoxide stretching frequencies of Ni(CO)₄L from Ni(CO)₄. It has been suggested by Ugo that excessive electron density on the metal promotes ligand dissociation and that trigonal planar tris(phosphine) complexes can participate in π-back bonding more readily than tetrahedral tetrakis(phosphine) complexes.

$$\text{Eq. 1.4}$$

$$\text{Pt(P-i-Pr}₃)₃ \xrightleftharpoons{K_2} \text{Pt(P-i-Pr}₃)₂ + \text{P-i-Pr}₃$$
The observation that \( \text{Ni}(\text{PPh}_3)_4 \) dissociates in solution whereas \( \text{Ni}(\text{PMe}_3)_4 \) does not dissociate can be explained by the small size of \( \text{PMe}_3 \) relative to \( \text{PPh}_3 \). This behaviour is inconsistent with the explanation given by Ugo \(^{113} \), if the usual assumption that \( \text{PMe}_3 \) is a better \( \sigma \)-donor than \( \text{PPh}_3 \) is made \(^{112b} \). However recent studies of the UV photoelectron spectra of a series of tertiary phosphine \( \text{PMe}_n\text{Ph}_3-n \) suggest that, contrary to this assumption, \( \text{PPh}_3 \) is a better \( \sigma \)-donor than \( \text{PMe}_3 \) \(^{114} \).

Because of the tendency of zerovalent tetrakis- and tris-(phosphine) complexes of the nickel triad to dissociate in solution, their characterisation in solution is a contentious issue. Nuclear magnetic resonance spectroscopy is the most widely used technique for this purpose. However, the NMR spectra are affected by dissociation of the compound in solution. Furthermore, in these systems, the NMR chemical shifts and coupling constants typically vary significantly with temperatures and solvents (Tables 1.3 and 1.5).

Attempts to characterise \( \text{Ni}(\text{PPh}_3)_n \) \((n = 3, 4) \) by \( ^{31} \text{P} \) NMR spectroscopy illustrate these difficulties. Tolman and coworkers \(^{115} \) reported that \( \text{Ni}(\text{PPh}_3)_3 \) shows no \( ^{31} \text{P} \) resonance at room temperature in toluene, but at \(-50^\circ \text{C} \) a broad resonance at \( \delta 21 \) was observed. This resonance sharpened and moved to \( \delta 23 \) at \(-75^\circ \text{C} \). At room temperature in the presence of excess \( \text{PPh}_3 \), the spectrum remained broad and showed no resonances. On cooling to \(-25^\circ \text{C} \), a broad resonance was observed at \( \delta 6-6 \), the position of free triphenylphosphine. At lower temperatures, this peak sharpened but did not move and no resonances due to \( \text{Ni}(\text{PPh}_3)_3 \) and \( \text{Ni}(\text{PPh}_3)_4 \) were observed. Tolman proposed \(^{115} \) that \( \text{Ni}(\text{PPh}_3)_4 \) can be represented as \( \text{Ni}(\text{PPh}_3)_3\text{PPh}_3 \), a triphenylphosphine solvate of the trigonal nickel(0) complex.
Wilke and coworkers\textsuperscript{116} subsequently showed by $^{31}$P NMR spectroscopy that the tetrahedral nickel(0) complex, Ni(PPh$_3$)$_4$, does in fact exist in solution. The $^{31}$P NMR spectrum of Ni(PPh$_3$)$_4$ at room temperature consists of a single broad resonance ($\delta$16.5, $\Delta\nu_{1/2} = 100$ Hz) which moves to lower field on reducing the temperature. Below -60°C, this signal becomes sharp and no longer migrates ($\delta$24.1 at -80°C, $\Delta\nu_{1/2} = 7$ Hz). The $^{31}$P NMR spectrum of Ni(PPh$_3$)$_3$ at 35°C in toluene is a sharp singlet at $\delta$20.5 which shifts to $\delta$21.8 at -80°C. On addition of one equivalent of PPh$_3$ to Ni(PPh$_3$)$_3$, spectra corresponding to those of Ni(PPh$_3$)$_4$ are observed. When the amount of free phosphine is reduced, separate signals assignable to Ni(PPh$_3$)$_3$ and Ni(PPh$_3$)$_4$ are observed in the same spectrum.

The behaviour of Pt(PPh$_3$)$_n$ ($n = 3,4$) in solution has been studied by several workers\textsuperscript{115,117}. The $^{31}$P NMR spectrum of Pt(PPh$_3$)$_3$ in toluene at room temperature is very broad\textsuperscript{115,117}. Sen and Halpern\textsuperscript{117} found that at -70°C the spectrum resolves into a 1:4:1 triplet ($\delta$49.9, $^1J$(PtP) = 4438 Hz in toluene). Addition of 0.5 equivalent of PPh$_3$ to Pt(PPh$_3$)$_3$ broadened the NMR resonance at -70°C. However at -100°C, the spectrum sharpened to give resonances due to Pt(PPh$_3$)$_3$ and Pt(PPh$_3$)$_4$ (Table 1.3), and no resonances due to free PPh$_3$. Hence at -100°C the equilibrium corresponding to the formation of Pt(PPh$_3$)$_4$ (Eq. 1.5) lies far to the right.

\[
\text{Pt(PPh}_3\text{)}_3 + \text{PPh}_3 \rightleftharpoons \text{Pt(PPh}_3\text{)}_4
\]

Eq. 1.5

The equilibrium between Pt(PPh$_3$)$_3$ and Pt(PPh$_3$)$_4$ at low temperature is also demonstrated by a reaction with ethylene\textsuperscript{117}. On saturation of
a toluene solution of Pt(PPh₃)₃ with ethylene at -80°C, the ³¹P NMR signal of Pt(PPh₃)₃ disappeared and only a broad resonance due to Pt(PPh₃)₂(C₂H₄) could be discerned. At -100°C, the spectrum sharpened to reveal two signals, each having ¹⁹⁵Pt satellites, which were assigned to Pt(PPh₃)₄ and Pt(PPh₃)₂(C₂H₄). These observations are consistent with the reaction in Eq. 1.6. Displacement of triphenylphosphine from Pt(PPh₃)₃ by ethylene at 25°C is unfavourable, with an equilibrium constant of 0.12[115]. The ability of ethylene to displace

$$2[\text{Pt}(\text{PPh}_3)_3] + \text{C}_2\text{H}_4 \rightarrow \text{Pt}(\text{PPh}_3)_4 + \text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$$

Eq. 1.6

triphenylphosphine from Pt(PPh₃)₃ at low temperature probably depends on scavenging of the displaced triphenylphosphine by Pt(PPh₃)₃, and therefore on the enhanced stability of Pt(PPh₃)₄ at low temperature[117].

Addition of two molar equivalents of triphenylphosphine to a solution of Pd(PPh₃)₃ gave resonances due to Pd(PPh₃)₄ and PPh₃ at -70°C[118].

The ³¹P NMR parameters of M(PPh₃)₃ and M(PPh₃)₄ (M = Ni, Pd, Pt) are listed in Table 1.3. It is interesting to note that whereas the chemical shifts of Pt(PPh₃)₄ and Pd(PPh₃)₄ are at higher field than their tris(phosphine) counterparts, the nickel system exhibits a reverse trend, i.e. the chemical shift of Ni(PPh₃)₄ is at lower field than that of Ni(PPh₃)₃.

In platinum(0) and palladium(0) phosphine complexes (Table 1.4 and 1.5) the general trend is that higher coordination numbers correspond to higher field resonances. The magnitude of the ¹⁹⁵Pt-³¹P coupling constants [¹⁹⁵J(PtP)] is valuable in determining the coordination
Table 1.3 $^{31}$P NMR parameters for $M(PPh_3)_n$ complexes; $n = 3, 4$
($M = Ni, Pd, Pt$) in toluene

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature $^\circ$C</th>
<th>$\delta P$(ppm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(PPh$_3$)$_3$</td>
<td>35</td>
<td>20.5</td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>-80</td>
<td>21.8</td>
<td>116</td>
</tr>
<tr>
<td>Ni(PPh$_3$)$_4$</td>
<td>35</td>
<td>16.5, $\Delta \nu_{1/2}$ 100 Hz</td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>-80</td>
<td>24.1, $\Delta \nu_{1/2}$ 7 Hz</td>
<td>116</td>
</tr>
<tr>
<td>Pd(PPh$_3$)$_3$</td>
<td>-70</td>
<td>22.6</td>
<td>118</td>
</tr>
<tr>
<td>Pd(PPh$_3$)$_4$</td>
<td>-70</td>
<td>18.4</td>
<td>118</td>
</tr>
<tr>
<td>Pt(PPh$_3$)$_3$</td>
<td>-70</td>
<td>49.9 [$^{1}J$(PtP) 4438 Hz]</td>
<td>117</td>
</tr>
<tr>
<td>Pt(PPh$_3$)$_3$</td>
<td>-50</td>
<td>55.0 [$^{1}J$(PtP) 4370 Hz]</td>
<td>115</td>
</tr>
<tr>
<td>Pt(PPh$_3$)$_4$</td>
<td>-100</td>
<td>9.2 [$^{1}J$(PtP) 3829 Hz]</td>
<td>117</td>
</tr>
<tr>
<td>L</td>
<td>PdL&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PdL&lt;sub&gt;3&lt;/sub&gt;</td>
<td>PdL&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>PMe&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-34.8</td>
<td></td>
<td></td>
</tr>
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</tr>
<tr>
<td>PMePh&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>PPh&lt;sub&gt;3&lt;/sub&gt;</td>
<td>+22.6&lt;sup&gt;b&lt;/sup&gt;</td>
<td>+18.4&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>PEt&lt;sub&gt;3&lt;/sub&gt;</td>
<td>+9.6</td>
<td></td>
<td>-1.5</td>
</tr>
<tr>
<td>P-n-Bu&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-1.4&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(CH&lt;sub&gt;2&lt;/sub&gt;Ph)&lt;sub&gt;3&lt;/sub&gt;</td>
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<td></td>
</tr>
<tr>
<td>P-i-Pr&lt;sub&gt;3&lt;/sub&gt;</td>
<td>+49.3&lt;sup&gt;d&lt;/sup&gt;</td>
<td>+39.0&lt;sup&gt;d&lt;/sup&gt;</td>
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</tr>
<tr>
<td>PCy&lt;sub&gt;3&lt;/sub&gt;</td>
<td>+38.7</td>
<td></td>
<td>+25.9</td>
</tr>
<tr>
<td>P-t-Bu&lt;sub&gt;2&lt;/sub&gt;Ph</td>
<td>+67.0</td>
<td></td>
<td></td>
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</tbody>
</table>

- Table 1.4: <sup>31</sup>P NMR chemical shifts of zerovalent palladium phosphine complexes (PdL<sub>n</sub>, n = 2-4), reproduced from reference 118.<sup>a</sup>

<table>
<thead>
<tr>
<th>L</th>
<th>PdL&lt;sub&gt;2&lt;/sub&gt;</th>
<th>PdL&lt;sub&gt;3&lt;/sub&gt;</th>
<th>PdL&lt;sub&gt;4&lt;/sub&gt;</th>
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<tr>
<td>PMe&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td>PMe&lt;sub&gt;2&lt;/sub&gt;Ph</td>
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</tr>
<tr>
<td>PMePh&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-4.2</td>
<td></td>
<td></td>
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<tr>
<td>PPh&lt;sub&gt;3&lt;/sub&gt;</td>
<td>+22.6&lt;sup&gt;b&lt;/sup&gt;</td>
<td>+18.4&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>PEt&lt;sub&gt;3&lt;/sub&gt;</td>
<td>+9.6</td>
<td></td>
<td>-1.5</td>
</tr>
<tr>
<td>P-n-Bu&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-1.4&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(CH&lt;sub&gt;2&lt;/sub&gt;Ph)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>+2.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-i-Pr&lt;sub&gt;3&lt;/sub&gt;</td>
<td>+49.3&lt;sup&gt;d&lt;/sup&gt;</td>
<td>+39.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>PCy&lt;sub&gt;3&lt;/sub&gt;</td>
<td>+38.7</td>
<td></td>
<td>+25.9</td>
</tr>
<tr>
<td>P-t-Bu&lt;sub&gt;2&lt;/sub&gt;Ph</td>
<td>+67.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Chemical shift (δ) measured in toluene containing 10% d<sub>8</sub>-toluene at -60°C, chemical shifts in ppm are relative to external 85% H<sub>3</sub>P<sub>0</sub>4.
- b at -70°C
- c at -100°C
- d at -80°C
Table 1.5 $^{31}$P NMR data for some zerovalent platinum complexes
(reproduced from reference 119)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp °C</th>
<th>Solvent</th>
<th>$\delta^{31}$P (ppm)</th>
<th>$^1J$(PtP) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(PMe$_3$)$_4$</td>
<td>-62</td>
<td>octane</td>
<td>-51.9</td>
<td>3838</td>
</tr>
<tr>
<td>Pt(PMe$_3$)$_4$</td>
<td>-74</td>
<td>toluene</td>
<td>-53.3</td>
<td>3828</td>
</tr>
<tr>
<td>Pt(PMe$_2$Ph)$_4$</td>
<td>-62</td>
<td>octane</td>
<td>-33.2</td>
<td>3809</td>
</tr>
<tr>
<td>Pt(PMe$_2$Ph)$_4$</td>
<td>-74</td>
<td>toluene</td>
<td>-34.2</td>
<td>3805</td>
</tr>
<tr>
<td>Pt(PMe$_2$)$_4$</td>
<td>-74</td>
<td>toluene</td>
<td>-14.8</td>
<td>3802</td>
</tr>
<tr>
<td>Pt[P(p-tolyl)$_3$]$_3$</td>
<td>-74</td>
<td>toluene</td>
<td>48.8</td>
<td>4443</td>
</tr>
<tr>
<td>Pt(PEt$_3$)$_4$</td>
<td>-74</td>
<td>toluene</td>
<td>-18.1</td>
<td>3723</td>
</tr>
<tr>
<td>Pt(PEt$_3$)$_3$</td>
<td>-74</td>
<td>toluene</td>
<td>41.3</td>
<td>4188</td>
</tr>
<tr>
<td>Pt(PEt$_3$)$_3$</td>
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<td>heptane</td>
<td>42.2</td>
<td>4231</td>
</tr>
<tr>
<td>Pt(PEt$_3$)$_3$</td>
<td>-48</td>
<td>octane</td>
<td>43.6</td>
<td>a</td>
</tr>
<tr>
<td>Pt(PEt$_3$)$_4$</td>
<td>-62</td>
<td>octane</td>
<td>-16.9</td>
<td>3729</td>
</tr>
<tr>
<td>Pt(P-n-Bu$_3$)$_4$</td>
<td>-74</td>
<td>toluene</td>
<td>-26.0</td>
<td>3700</td>
</tr>
<tr>
<td>Pt(P-n-Bu$_3$)$_3$</td>
<td>-74</td>
<td>toluene</td>
<td>31.8</td>
<td>4211</td>
</tr>
<tr>
<td>Pt[P(CH$_2$Ph)$_3$]$_3$</td>
<td>-74</td>
<td>toluene</td>
<td>34.5</td>
<td>4377</td>
</tr>
<tr>
<td>Pt(P-i-Pr$_3$)$_3$</td>
<td>-74</td>
<td>toluene</td>
<td>64.4</td>
<td>4260</td>
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<tr>
<td>Pt(P-i-Pr)$_3$</td>
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<td>octane</td>
<td>65.6</td>
<td>4271</td>
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<tr>
<td>Pt(P-i-Pr)$_3$</td>
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<tr>
<td>Pt(P-i-Pr)$_2$</td>
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<td>octane</td>
<td>72.8</td>
<td>4202</td>
</tr>
<tr>
<td>Pt(PCy$_3$)$_3$</td>
<td>-74</td>
<td>toluene</td>
<td>53.2</td>
<td>4228</td>
</tr>
<tr>
<td>Pt(PCy$_3$)$_3$</td>
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<td>heptane</td>
<td>54.5</td>
<td>4229</td>
</tr>
<tr>
<td>Pt(PCy$_3$)$_2$</td>
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<td>toluene</td>
<td>61.9</td>
<td>4120</td>
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<tr>
<td>Pt(PCy$_3$)$_2$</td>
<td>24</td>
<td>heptane</td>
<td>63.8</td>
<td>4227</td>
</tr>
<tr>
<td>Pt(PCy$_3$)$_2$</td>
<td>24</td>
<td>THF</td>
<td>63.6</td>
<td>4192</td>
</tr>
<tr>
<td>Pt(P-t-Bu$_2$Ph)$_2$</td>
<td>-74</td>
<td>toluene</td>
<td>83.6</td>
<td>4592</td>
</tr>
</tbody>
</table>

a: Owing to exchange too broad to be measured
number of the platinum complexes. The coupling constants are significantly less for PtL₄ than for PtL₃, probably because of the reduced s-character in the Pt-P bonds in the tetrakis complexes.

Mann and Musco¹¹⁹ have investigated the equilibrium and kinetic behaviour of PtLn (n = 2-4) in solution by ³¹P NMR spectroscopy (Table 1.5). They showed that the compounds [PtL₄] (L = PMe₃, PMe₂Ph, PMePh₂, PET₃ or P-n-Bu₃), [PtL₃] (L = PET₃, P-n-Bu₃, P(p-tolyl)₃, P(CH₂Ph)₃, P-i-Pr₃ or PCy₃) and [PtL₂] (L = P-i-Pr₃, PCy₃ or P-t-Bu₂Ph) exist in solution and undergo ligand exchange. The exchange mechanism is dissociative for Pt(PMe₃)₄, Pt(PMe₂Ph)₄, Pt(PMePh₂)₄, Pt(PET₃)₄, Pt(P-n-Bu₃)₄, Pt(P-i-Pr₃)₃ and Pt(PCy₃)₃, while for Pt(P-i-Pr₃)₂ and Pt(PCy₃)₂, associative exchange occurs. Both associative and dissociative exchange occur for Pt(PET₃)₃ and Pt(P-n-Bu)₃. The relative rates of these processes depend on the temperature and concentration of free tertiary phosphine. The rate of phosphine exchange of Pt(P-i-Pr₃)₂ and Pt(PCy₃)₂ is strongly affected by the presence of toluene, which may perhaps act as a ligand.

The ³¹P NMR spectroscopic investigation of the solution structure of PdLn by Mann and Musco¹¹⁸ (Table 1.4) showed that, at room temperature, PdL₄ complexes exist in solution for phosphines including PMe₃ and PMe₂Ph. Tris complexes PdL₃ are formed for the ligands PET₃, P-n-Bu₃, PPh₃, P(CH₂Ph)₃ and bis complexes PdL₂ are formed for P-i-Pr₃, PCy₃ and P-t-Bu₂Ph. At low temperature (-60°C to -100°C) additional species Pd(PMe₂Ph)₄, Pd(PPh₃)₄, Pd(PET₃)₄, Pd(P-n-Bu₃)₄, Pd(P-i-Pr₃)₃ and Pd(PCy₃)₃ have been identified. Hence, many complexes ML₂ (M = Pt, Pd), which are formally 14-electron species are stable in solution even in the presence of an excess tertiary phosphine.
The two-coordinate complex, Pt(\(\text{PPh}_3\))\(_2\) has been postulated as an intermediate in substitution reactions e.g. those of Pt(\(\text{PPh}_3\))\(_2\)(acetylene)\(^{120}\). However, monomeric Pt(\(\text{PPh}_3\))\(_2\) has not been successfully isolated\(^{108,117}\), although claims to the contrary have been made\(^{121,122}\).

By using bulky tertiary phosphines, a series of two-coordinate 14-electron complexes of zerovalent platinum and palladium has been prepared (Table 1.6). The steric bulk of the ligands plays a predominant role in stabilising the two-coordinate 14-electron systems. Otsuka\(^{108}\) suggested that ligands with a cone angle greater than 160° favour two-coordination. The complexes Pd(\(\text{P-t-Bu}_2\text{Ph}\))\(_2\)\(^{46,107}\) and Pt(\(\text{P-t-Bu}_2\text{Ph}\))\(_2\)\(^{107}\) are found by X-ray structure analysis to be almost linear with P-M-P angles of 176.6(1)° and 177.0(1)° respectively. However, Pd(\(\text{PCy}_3\))\(_2\) is bent with a P-M-P angle of 158.4(3)°\(^{46,126}\). A striking example of the importance of the steric factor in determining the reactivity of coordinatively unsaturated species has been demonstrated by Otsuka and coworkers\(^{161}\). While Pd(\(\text{P-t-Bu}_2\text{Ph}\))\(_2\) readily forms the dioxygen adduct [PdL\(_2\)O\(_2\)], the somewhat more crowded Pd(\(\text{P-t-Bu}_3\))\(_2\) is stable.

Dissociation of zerovalent metal tertiary phosphine complexes in solution forms coordinatively unsaturated species which behave as nucleophiles. These reactions with electrophiles are of two types. They are classified as oxidative addition if the bond in the electrophile is completely broken, or as ligand substitution if this bond is merely lengthened. Molecules that undergo oxidative addition include H-X, R-X, RCO-C1, RSO\(_2\)-C1, X\(_2\) and metal halide derivatives e.g. AuCl(\(\text{PPh}_3\)), HgCl\(_2\)\(^{36}\). The majority of \(\pi\)-bonding ligands, such as alkenes, alkynes, O\(_2\) and CS\(_2\) react with zerovalent metal phosphine complexes to give ligand substitution\(^{36}\).
### Table 1.6 Two coordinate complexes of the zerovalent nickel triad

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ligand</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>PCy_3(^a)</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>P(O-(\text{C}<em>{10}\text{H}</em>{17}))(_3)(^b)</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>P(O-o-(\text{C}<em>{6}\text{H}</em>{4}\text{C}<em>{6}\text{H}</em>{5}))(_3)</td>
<td>125</td>
</tr>
<tr>
<td>Pd</td>
<td>P-i-Pr(_3)</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>PCy_3</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>P-t-Bu(_2)Ph</td>
<td>126, 107</td>
</tr>
<tr>
<td></td>
<td>P-t-Bu(_3)</td>
<td>107</td>
</tr>
<tr>
<td>Pt</td>
<td>P-i-Pr(_3)</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>PCy_3</td>
<td>107, 127</td>
</tr>
<tr>
<td></td>
<td>P-t-Bu(_2)Me</td>
<td>128</td>
</tr>
<tr>
<td></td>
<td>P-t-Bu(_2)Ph</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>P-t-Bu(_3)</td>
<td>107</td>
</tr>
</tbody>
</table>

\(^a\) not isolated, detected spectroscopically

\(^b\) \text{C}_{10}\text{H}_{17} = \text{bornan-2-yl}

### 1.2.4 Zerovalent Metal Complexes of the Nickel Triad Containing Olefins as the only Ligands

Zerovalent complexes of the nickel triad containing olefins as the only ligands are thermally unstable, and much more so than the corresponding zerovalent phosphine complexes. Metal-olefin bonding in zerovalent metal complexes is adequately described using a modified Dewar-Chatt-Duncanson model. However there are some differences in
the bonding of olefins to divalent and zerovalent metal atoms. The contribution of π-back donation in electron-rich zerovalent metal complexes is more significant than that of σ-bonding. Molecular orbital calculations indicate that the strength of the zerovalent metal-olefin interaction is strongly dependent on the amount of π-back donation from the metal. Consequently the olefinic C=C double bond in the zerovalent metal complexes is weakened more than in divalent metal olefin complexes. This effect is shown by a greater lengthening of the C=C bond and by a greater bending of the olefinic substituents away from the metal atom in zerovalent complexes.

Zerovalent nickel triad complexes containing olefins as the only ligands can be classified into two types:

1. Tetrahedral complexes (18-electrons)
2. Trigonal planar complexes (16-electrons)

Tetrahedral olefin complexes of the zerovalent nickel triad are rare and are formed only by chelate diolefins, such as 1,5-cyclooctadiene (COD). The complexes M(COD)_2 (M = Ni, Pt) are important precursors for the syntheses of many complexes of zerovalent nickel and platinum. Bis(1,5-cyclooctadiene)nickel(0) was prepared as an air-sensitive yellow solid by reduction of bis(acetylacetonato)nickel(II) with triethylaluminium in the presence of 1,5-cyclooctadiene (Eq. 1.7).

\[
\text{Ni(acac)}_2 + \text{excess COD} \xrightarrow{\text{AlEt}_3} \text{Ni(COD)}_2
\]

Eq. 1.7

This synthesis probably goes through an unstable nickel-ethyl complex. This method fails for the preparation of Pt(COD)_2 because of the stability of the platinum-alkyl intermediate, although Pt(COD)_2 has
been prepared in low and erratic yields by irradiating the platinum(II) alkyl complex, Pt(i-Pr)$_2$(COD) in the presence of COD (Eq. 1.8$^{132}$).

In a more satisfactory synthesis of Pt(COD)$_2$ developed by Stone and coworkers$^{133,134}$, PtCl$_2$(COD) is reduced with dilithium cyclooctatetraene in ether at $-40^\circ$C in the presence of excess COD to give Pt(COD)$_2$ as a white solid in 40-60% yield (Eq. 1.9).

![Chemical reaction]

The complex Pt(COD)$_2$ is oxidatively and thermally more stable than the nickel analogue. The structures of both Ni(COD)$_2$ and Pt(COD)$_2$ have been determined by X-ray single crystal analysis$^{41,43}$. They are distorted tetrahedral complexes having four olefinic groups around the metal atom in a quasi-cubic arrangement (Figure 1.5b). Calculations by Hoffmann and Rosch$^{135}$ have shown that for the hypothetical tetrakis(ethylene)nickel(0) complex, the quasi-dodecahedral structure is the most favourable geometry to accommodate four ethylene ligands around the metal (Figure 1.5a). However, no tetrakis(olefin) complex of a freely rotating olefin has been made, so that the results of this calculation have not been confirmed. The quasi-cubic structure in bis(1,5-cyclooctadiene)metal(0), M(COD)$_2$ is probably a consequence of
quasi-cubic

quasi-dodecahedral

Figure 1.5 Two possible arrangements of tetrahedral tetrakis(olefin)metal complexes (reproduced from reference 135)

the chelate effect of the bidentate, 1,5-cyclooctadiene ligand (COD).

Other tetrakis(olefin) complexes \([\text{Ni(COD)}(\text{duroquinone})]\)\(^{136}\) and \(\text{Ni(duroquinone)}_2\)\(^{137}\) also adopt the quasi-cubic configuration.

The complex \(\text{Pd(COD)}_2\) has been synthesized from \(\text{PdCl}_2(\text{COD})\) in poor yield (30\%) by Stone and coworkers\(^{133}\) using a procedure adapted from the synthesis of \(\text{Pt(COD)}_2\). The preparation was carried out in the presence of propene to prevent deposition of palladium metal.
Whereas Pt(COD)$_2$ and Ni(COD)$_2$ are stable in the solid state at room temperature, Pd(COD)$_2$ is stable only below -20°C in the solid state. This reflects the relative weakness of the palladium-olefin bond and the poor π-bonding ability of palladium. It is therefore not practical to employ Pd(COD)$_2$ as a source of palladium(0) in synthesis.

The reaction of the 18-electron species Pt(COD)$_2$ with ethylene to give the 16-electron complex Pt(C$_2$H$_4$)$_3$ is an important result. It has been claimed that the driving force for this reaction is the relief of the strain in the coordination sphere induced by the small bite angle of COD(85°) relative to the ideal tetrahedral angle of 109°. However, this explanation appears to be inconsistent with the behaviour of Ni(COD)$_2$ which does not react with ethylene to give Ni(C$_2$H$_4$)$_3$. The lability of ethylene in Pt(C$_2$H$_4$)$_3$ allows the formation of Pt(PR$_3$)$_2$(C$_2$H$_4$) and Pt(PR$_3$)(C$_2$H$_4$)$_2$ by reaction with tertiary phosphines (Scheme 1.1). These complexes are synthetically useful sources of the Pt-(PR$_3$)$_n$ (n = 1,2) fragments.

The reaction of Pd(COD)$_2$ with ethylene gives Pd(C$_2$H$_4$)$_3$ which is stable only at low temperatures. This complex can also be prepared by cocondensation of metal atoms and ethylene.

The corresponding nickel complex, tris(ethylene)nickel(0) can be prepared by reaction of 1,5,9-cyclododecatriene nickel(0) [Ni(cdt)] and ethylene.
Neutron diffraction studies\textsuperscript{44} have shown that \( \text{Pt}(\text{C}_2\text{H}_4)_3 \) is trigonal planar with all \( \text{C} = \text{C} \) double bonds lying in the coordination plane. This geometry agrees with the calculations by Hoffmann and Rösch\textsuperscript{135} on the analogous nickel compound. These calculations show that as a consequence of the synergic effect of \( \sigma \)- and \( \pi \)-bonding, the trigonal planar structure is preferred over the alternative trigonal "upright" structure (Figure 1.6).

Figure 1.6 Two possible orientations of ethylene in the complex \( \text{Ni}(\text{C}_2\text{H}_4)_3 \) (reproduced from reference 135)
Reaction of zerovalent metal complexes with other ligands follows the pattern that binary complexes of π-acceptor ligands react smoothly with σ-donor ligands to give partial substitution (Eq. 1.10). In a similar manner, binary complexes of σ-donor ligands react with π-acceptor ligands (Eq. 1.11).  

\[
\text{M(olefin)}_3 + 2\text{PR}_3 \rightarrow \text{M(Pr)}_2\text{(olefin)}
\]  

Eq. 1.10

\[
\text{M(Pr)}_3 + \text{olefin} \rightarrow \text{M(Pr)}_2\text{(olefin)}
\]  

Eq. 1.11

The synergic effect in which the σ-donor ligand enhances the π-acceptor ability of the π-acceptor ligand and vice versa, stabilises the complexes. Although the π-acceptor or σ-donor ability of the ligands in these complexes cannot be measured precisely, it is possible to make a distinction between ligands which are predominantly π-acceptors and those which are predominantly σ-donors in a ternary complex. For example in Pt(PPh)_3(C_2H_4), PPh is the σ-donor and C_2H_4 is the π-acceptor.

There is a large class of zerovalent complexes of the nickel triad of the type M(Pr)_3(olefin) which have a combination of π-acceptor and σ-donor ligands. These complexes are more stable to dissociation than the corresponding M(Pr)_n (n = 3, 4) complexes, and are thermally more stable than the corresponding M(olefin)_3 complexes. They generally have a structure close to trigonal planar, with the olefin lying approximately in the trigonal plane. The C=C bond lengths in this class of complexes are significantly longer than in the free olefin, indicating considerable π-back bonding.
The equilibrium constant for the olefin-phosphine displacement reaction (Eq. 1.12) in benzene at 25°C is largest in nickel complexes and smallest in palladium complexes (Table 1.7)\textsuperscript{115}.

\[
M(PR_3)_3 + C_2H_4 \rightleftharpoons M(PR_3)_2(C_2H_4) + PR_3
\]

Eq. 1.12

<table>
<thead>
<tr>
<th>PR\textsubscript{3}</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh\textsubscript{3}</td>
<td>300</td>
<td>0.013</td>
<td>0.122</td>
</tr>
<tr>
<td>PEt\textsubscript{3}</td>
<td>30000</td>
<td>0.47</td>
<td>120</td>
</tr>
</tbody>
</table>

The behaviour of mixed ligand complexes in substitution reactions depends on electronic factors determined by the balance of π-acceptor and σ-donor strengths of the ligands, on the nature of the entering ligand, and to a certain extent on the solvent\textsuperscript{141}. In electron-rich mixed ligand complexes of the zerovalent nickel triad, π-acceptors generally substitute the π-acceptor ligand and σ-donors substitute the σ-donor ligand. Substitution only occurs when the incoming reagent is a stronger π-acceptor or a stronger σ-donor than the ligand to be replaced. For example, the reaction of Ni(COD)\textsubscript{2} with the strong π-acceptor ligand maleic anhydride (ma) gives Ni(COD)(ma). This complex is stabilised by the synergic effect of ma as a π-acceptor and COD as a predominantly σ-donor. Consequently, the total substitution of COD
by $\text{ma}$ to give $\text{Ni(ma)}_2$ cannot take place\textsuperscript{141,15a}. The complex $\text{Ni(ma)}_2$ can be prepared from $\text{Ni(CO)}_4$\textsuperscript{142} (Scheme 1.2).

Scheme 1.2 Formation of bis(maleic anhydride)nickel(0) from bis(1,5-cyclooctadiene)nickel(0)

The magnitudes of the $^{195}\text{Pt}-^{31}\text{P}$ coupling constants in trigonal phosphine stabilised olefinic complexes, $\text{Pt(PR}_3)_2(\text{olefin})$ (Table 1.8) are much smaller than those of the corresponding trigonal $\text{Pt(PR}_3)_3$ complexes (Table 1.5). These coupling constants are closer in magnitude to those in the corresponding tetrahedral $\text{Pt(PR}_3)_4$ complexes. This observation suggests that the hybridisation of platinum is closer to $\text{sp}^3$ than to $\text{sp}^2$ in trigonal complexes of type $\text{Pt(PR}_3)_2(\text{olefin})$. 

$\text{ma} = \text{maleic anhydride}$

$\text{Ni(ma)}_2$

$\text{ma}$

$\text{Ni(CO)}_4$

$\text{CO}$

$\text{Ni(COD)}_2$

$\text{Ni(COD)(ma)}$

$\text{ma}$
Table 1.8 $^{31}$P NMR parameters of some phosphine stabilised olefinic complexes of platinum(0)

<table>
<thead>
<tr>
<th>Compound</th>
<th>T(°C)</th>
<th>Solvent</th>
<th>$\delta P$</th>
<th>$J$(PtP)(Hz)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(PEt$_3$)$_2$(C$_2$H$_4$)</td>
<td>RT</td>
<td>cyclohexane</td>
<td>20.6</td>
<td>3551</td>
<td>143</td>
</tr>
<tr>
<td>Pt(PPh$_3$)$_2$(C$_2$H$_4$)</td>
<td>-80</td>
<td>toluene</td>
<td>32.5</td>
<td>3694</td>
<td>117</td>
</tr>
<tr>
<td>Pt(PMe$_3$)$_2$(C$_2$H$_4$)</td>
<td>RT</td>
<td>toluene</td>
<td>-19.5</td>
<td>3435</td>
<td>143</td>
</tr>
<tr>
<td>Pt(PEt$_3$)$_2$(propylene)</td>
<td>RT</td>
<td>cyclohexane</td>
<td>21.1, 18.5</td>
<td>3767, 3279$^a$</td>
<td>143</td>
</tr>
<tr>
<td>Pt(PEt$_3$)$_2$(cyclobutene)</td>
<td>RT</td>
<td>cyclohexane</td>
<td>20.1</td>
<td>3418</td>
<td>143</td>
</tr>
<tr>
<td>Pt(PPh$_3$)$_2$(cyclobutene)</td>
<td>RT</td>
<td>toluene</td>
<td>34.2</td>
<td>3604</td>
<td>143</td>
</tr>
</tbody>
</table>

$^a$: $J$(PP) = 66 Hz

1.3 Olefinic Tertiary Phosphine and Arsine Complexes of Transition Metals

Since Nyholm and coworkers reported a platinum(II) complex of dimethylpent-4-enylarsine [CH$_2$=CH(CH$_2$)$_3$AsMe$_2$] in 1961$^{29}$, many complexes of olefinic tertiary phosphines and arsines have been prepared. Comprehensive review articles describing complexes of olefinic ligands containing various combinations of donor atom (P, As, N, Te, Se, O, S and C) and olefin have been published$^{31-35}$.

In this project, the olefinic phosphine ligands $o$-vinylphenyl-diphenylphosphine ($o$-styryldiphenylphosphine, $o$-CH$_2$=CHC$_6$H$_4$PPh$_2$, abbreviated as SP) and its dimethylphosphine analogue ($o$-CH$_2$=CHC$_6$H$_4$PMe$_2$, abbreviated as DMSP) (Figure 1.7) have been used. The arsine analogue of SP, $o$-CH$_2$=CHC$_6$H$_4$AsPh$_2$ (abbreviated as SPAS) was used in one instance for comparison purposes (Figure 1.7).
These ligands have relatively simple $^1H$ NMR spectra and are sterically more constrained than ligands such as o-allyldiphenyldiphenyl phosphine or ligands in which the olefinic group is part of an aliphatic chain.

The monoolefin complexes $M(CO)_4(C_2H_4)$ ($M = Fe, Ru$) are unstable and air sensitive$^{144-146}$. Bennett and coworkers$^{147,148}$ used the olefinic tertiary phosphine (SP) to prepare zerovalent ruthenium and iron complexes containing a metal-olefin bond. The reaction of SP with freshly prepared Fe$_3$(CO)$_{12}$ in refluxing n-octane gives two air-stable products Fe(CO)$_3$(SP) (1.1) and Fe(CO)$_2$(SP)$_2$ (1.2). The analogous ruthenium complexes Ru(CO)$_3$(SP) (1.3) and Ru(CO)$_2$(SP)$_2$ (1.4) are obtained in a similar manner from Ru$_3$(CO)$_{12}$. These results illustrate the remarkable stabilising properties of the ligand SP. However, all of the stable zerovalent complexes of SP which have been prepared, contain CO as an additional stabilising ligand $^{[1.1-1.4]}$ and $M(CO)_4$(SP) for $M = Cr, Mo, W^{160}$. 

Figure 1.7 Olefinic ligands

SP : $E = P, R = Ph$
DMSP : $E = P, R = Me$
SPAS : $E = As, R = Ph$
The ability of the olefinic phosphine ligand to form olefinic complexes is greater than that of simple olefinic ligands, and a variety of stable olefinic complexes of these ligands has been reported\textsuperscript{31-35}. Some examples are given in Table 1.9. Two properties, chelation by the ligand and the synergic effect of the $\pi$-acid olefin and $\sigma$-donor phosphine moiety are probably important in stabilising these complexes.

In transition metal complexes containing olefinic tertiary phosphines and arsines, the ligand can function as a monodentate phosphine or arsine, or as a bidentate chelating or bridging ligand bound through both the olefin and the Group V donor (Table 1.9). A fourth possible mode of coordination, in which the olefin moiety alone is coordinated to the metal atom, has not been described in the literature. A number of factors appear to govern the mode of coordination of the particular ligand. The structure of the ligand itself, the metal atom and its oxidation state, the strength of the potential metal-
### Table 1.9 Complexes of olefinic tertiary phosphines and arsines

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Metal</th>
<th>Ligand</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Complex" /></td>
<td>Fe(0)</td>
<td>$\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$</td>
<td>147</td>
</tr>
<tr>
<td><img src="image2.png" alt="Complex" /></td>
<td>Ru(0)</td>
<td>$\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$</td>
<td>147, 148</td>
</tr>
<tr>
<td><img src="image3.png" alt="Complex" /></td>
<td>Fe(0)</td>
<td>$\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$</td>
<td>147, 148</td>
</tr>
<tr>
<td><img src="image4.png" alt="Complex" /></td>
<td>Ru(0)</td>
<td>$\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$</td>
<td>158</td>
</tr>
<tr>
<td><img src="image5.png" alt="Complex" /></td>
<td>V(0)</td>
<td>$\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$</td>
<td>159</td>
</tr>
<tr>
<td><img src="image6.png" alt="Complex" /></td>
<td>Cr(0)</td>
<td>$\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$</td>
<td>160, 163, 168</td>
</tr>
<tr>
<td><img src="image7.png" alt="Complex" /></td>
<td>Mo(0)</td>
<td>$\text{CH}_2=\text{CHC}_6\text{H}_4\text{AsMe}_2$</td>
<td>160, 163, 168</td>
</tr>
<tr>
<td><img src="image8.png" alt="Complex" /></td>
<td>W(0)</td>
<td>$\text{CH}_2=\text{CHC}_6\text{H}_4\text{AsMe}_2$</td>
<td>160, 163, 168</td>
</tr>
<tr>
<td><img src="image9.png" alt="Complex" /></td>
<td>Mn(1)</td>
<td>$\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$</td>
<td>162</td>
</tr>
<tr>
<td><img src="image10.png" alt="Complex" /></td>
<td>Re(1)</td>
<td>$\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$</td>
<td>162</td>
</tr>
</tbody>
</table>
**Table 1.9 continued**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Metal</th>
<th>Ligand</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="#">Diagram</a></td>
<td>Rh(I)</td>
<td>$\alpha$-CH$_2$=CHC$_6$H$_4$EPh$_2$ ($E = P, As$)</td>
<td>164</td>
</tr>
<tr>
<td><a href="#">Diagram</a></td>
<td>Ir(I)</td>
<td>$\alpha$-CH$_2$=CHC$_6$H$_4$EPh$_2$ ($E = P, As$)</td>
<td>165</td>
</tr>
<tr>
<td><a href="#">Diagram</a></td>
<td>Rh(I)</td>
<td>$\alpha$-CH$_2$=CHC$_6$H$_4$EPh$_2$ ($E = P, As$)</td>
<td>165</td>
</tr>
<tr>
<td><a href="#">Diagram</a></td>
<td>Pt(II)</td>
<td>$\alpha$-CH$_2$=CHC$_6$H$_4$PPh$_2$ $\alpha$-CH$_2$=CHC$_6$H$_4$AsMe$_2$ etc.</td>
<td>166, 167, 149</td>
</tr>
<tr>
<td><a href="#">Diagram</a></td>
<td>Ag(I)</td>
<td>$\alpha$-CH$_2$=CHCH$_2$C$_6$H$_4$AsMe$_2$</td>
<td>169</td>
</tr>
</tbody>
</table>
Table 1.10  X-ray single crystal data of some complexes containing olefinic tertiary phosphines or arsine

<table>
<thead>
<tr>
<th>Compound</th>
<th>M-C</th>
<th>C=C (Å)</th>
<th>α (degree)</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph₂P</td>
<td>a, 2.223(3)</td>
<td>1.403(7)</td>
<td>84</td>
<td>substituents bent back out of olefin plane away from Pt</td>
<td>149</td>
</tr>
<tr>
<td></td>
<td>b, 2.201(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph₂P</td>
<td>a, 2.290(5)</td>
<td>1.378(8)</td>
<td>81</td>
<td>substituent bent back 15° (Ph and H) and 11° (2 × H) out of olefin plane away from Pt</td>
<td>149</td>
</tr>
<tr>
<td></td>
<td>b, 2.245(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As₂P</td>
<td>a, 2.12</td>
<td>1.44</td>
<td>83.6</td>
<td></td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>b, 2.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeCO</td>
<td>2.100(5)mean</td>
<td>1.455(8)</td>
<td>6.65</td>
<td>trigonal bipyramidal with olefin in trigonal plane</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(coord)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.339(10)</td>
<td></td>
<td>148</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(uncoord)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoP</td>
<td>a, 2.45(2)</td>
<td>1.39(3)</td>
<td></td>
<td>octahedral with olefin lying approximately in the plane containing Mo, P and mid point of C=C bond</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>b, 2.52(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a: α is the angle which the C=C bond makes with the square plane about Pt(II).

b: α is the dihedral angle between the plane of the three-membered iron-olefin ring and the OC-Fe-CO plane.
olefin bond and the number and nature of other ligands on the metal centre are important.

Several olefinic tertiary phosphine and arsine complexes have been analysed by X-ray crystallography (Table 1.10). In the square planar platinum(II) complexes cis-[Pt(CR₃)₂(SP)] (R = H, F)¹⁴⁹ and [PtCl₂(o-CH₂=CHC₆H₄AsPh₂)]¹⁵⁰, the olefin is coordinated perpendicular to the square plane in agreement with the theoretical prediction for simple monoolefin complexes of platinum(II)⁶⁹.

In simple monoolefin complexes of iron(0) and in the trigonal planar bipyramidal molecule, Fe(CO₂(SP)₂ (₁₂)¹⁴⁷,¹⁴⁸, the coordinated olefin lies in the trigonal plane. The C=C double bond in ₁₂ is at right angles to the M-P-aromatic coordination plane. In contrast, the octahedral molybdenum(0) complex, Mo(CO)₄(o-CH₃CH=CHC₆H₄PPh₂)¹⁵¹ has both the coordinated olefin and the P-donor in the equatorial coordination plane.

Isomers of the octahedral molybdenum(0) and tungsten(0) complexes M(CO)₄(SP) (M = Mo, W)¹⁶³ are formed in solution, as shown by the IR spectra in the C=O stretching region. These isomers may differ in the orientation of the olefin, which can lie parallel to, or perpendicular to, the M-P coordination plane (Figure 1.8). These isomers rapidly interconvert on the NMR time scale and therefore they are undetectable by NMR spectroscopy.

The conversion of a metal-olefin complex to a metal-alkyl complex is a key step in many catalytic hydrogenation and isomerisation reactions of olefins. Olefinic tertiary phosphine complexes of transition metals can be converted to alkyl complexes by three routes: (1) electrophilic attack, (2) nucleophilic attack and (3) insertion of the olefinic tertiary phosphine into a metal-hydride bond. This insertion route will be discussed in detail in Chapter 2.
Figure 1.8 Two isomers of Mo(CO)$_4$(SP), (a) the olefin lies parallel to the P-Mo-CO axis (perpendicular to the CO-Mo-CO axis), (b) the olefin lies perpendicular to the P-Mo-CO axis (parallel to the CO-Mo-CO axis)

Electrophilic attack on a coordinated C=C double bond usually occurs with low valent transition metal complexes, whereas nucleophilic attack usually occurs on olefinic complexes of transition metals in higher oxidation states. This reactivity pattern is observed in complexes of chelating olefinic phosphine or arsine ligands.

Protonation of zerovalent iron and ruthenium olefinic tertiary phosphine complexes, M(CO)$_3$SP [M = Fe (1.1), M = Ru (1.3)] with HX (X = Cl, Br) in n-hexane gives octahedral chelate $\sigma$-alkyl complexes of the divalent metals, 1.5 and 1.6 respectively (Eq. 1.13)$^{152}$. 
The structure of 1.6b has been determined by X-ray single crystal analysis which confirms that it contains a five-membered metallocycle. In contrast, protonation of the monoolefin complexes of the type Fe(olefin)(CO)₄ with HCl or HBr results in decomposition to the alkane and Fe²⁺, possibly via an iron(II)-alkyl intermediate. This illustrates the stabilising effect of the chelate ring.

Hydride addition (NaBH₄/THF) to the π-olefin rhenium cation [Re(CO)₄SP]⁺ (1.7) gives the σ-alkyl complex [Re(o-CHMeC₆H₄PPh₂)(CO)₄]⁻ (1.8) (Eq. 1.14).
The reaction of PtCl₂(SP) (1.9) with methoxide ion gives the chelate \( \sigma \)-alkyl complex \([Pt(\sigma-\text{OMeCH}_2\text{CHC}_6\text{H}_4\text{PPh}_2)\text{Cl}]_2\) (1.10) (Equation 1.15).\(^{154}\)

The complex PtCl₂(\(\sigma-\text{CH}_2=\text{CHC}_6\text{H}_4\text{AsPh}_2\)), 1.11 reacts with methoxide ion to give a dimeric product containing a platinum carbon \( \sigma \)-bond, 1.12.\(^{155,156}\) The regiochemistry of the product (i.e. the ring size of the metallocycle) was unequivocally determined by a bridge splitting.
reaction with acetylacetonate or hexafluoroacetylacetonate to give highly soluble monomers 1.13 (Scheme 1.3). The X-ray crystal structure of 1.13b was also determined, confirming that it contains a five-membered metallocycle 156,157.

Scheme 1.3 Reaction of \([\text{PtCl}_2(\text{o-CH}_2=\text{CHC}_6\text{H}_4\text{AsPh}_2)]\) with \(\text{OMe}^-\) and the derivative reactions.
CHAPTER TWO

INSERTION OF OLEFINIC TERTIARY PHOSPHINE INTO THE Pt-H BOND

2.1 Introduction

2.1.1 The relationship of metal-hydride and metal-alkyl complexes as intermediates in catalytic processes

The insertion of an olefin into a metal-hydrogen bond has been postulated as the key step in many catalytic reactions involving olefins\(^1\text{-}^5\). Systems which have rhodium, palladium, platinum, nickel or iron complexes as catalysts commonly require a cocatalyst such as hydrogen or acid to promote the formation of the metal-hydride species. The importance of metal-hydride intermediates in the isomerisation of olefins has been discussed by Harrod and Chalk\(^{170}\) and by Cramer and Lindsey\(^{171}\) (Eq. 2.1).

\[
\begin{align*}
\text{M-H} + \text{RCH}_2\text{CH}==\text{CH}_2 & \rightarrow \left[ \begin{array}{c}
\text{RCH}_2\text{CHCH}_3 \\
\text{M}
\end{array} \right] & \rightarrow \text{RCH}==\text{CHCH}_3 + \text{M-H}
\end{align*}
\]

Eq. 2.1

Harrod and Chalk\(^{170}\) studied the isomerisation of deuterated olefins by group VIII metal complexes and suggested a reaction mechanism involving the rapid, reversible addition of a hydride to the coordinated olefin.

The roles of metal-hydride and metal-alkyl species in hydrogenation have been studied extensively\(^{172}\text{-}^{174}\). The mechanism of olefin hydrogenation with Wilkinson's catalyst, [RhCl(PPh\(_3\))\(_3\)] is known in some detail\(^{175}\text{-}^{182}\) and at least three mechanistic pathways
have been demonstrated. The kinetically dominant mechanism is shown in Scheme 2.1. The Rh(I) species in this catalytic cycle is probably a solvated three-coordinated complex formed by dissociation of a triphenylphosphine ligand from the parent compound. This Rh(I) species is a very reactive 14-electron coordinatively unsaturated species which oxidatively adds hydrogen to form a dihydride complex, in which the oxidation state of the metal is formally +3. When the concentration of triphenylphosphine is limited, a molecule of olefin coordinates to the metal and subsequent insertion of the olefin into the Rh-H bond produces an alkyl rhodium(III) hydride complex. This complex rapidly eliminates alkane and regenerates the catalytically active Rh(I) species to complete the cycle.

Scheme 2.1 A major mechanistic pathway for olefin hydrogenation by Wilkinson's catalyst (reproduced from reference 2).
Metal-hydride and metal-alkyl complexes also participate in the catalytic hydroformylation\textsuperscript{1,2,183} and hydrosilation\textsuperscript{1,2,184,185} of olefins.

2.1.2 Mechanism of insertion of a simple olefin into a Pt-H bond

Chatt and Shaw\textsuperscript{186} were the first to demonstrate that ethylene can be inserted reversibly into the Pt-H bond in trans-[PtHCl(PEt\textsubscript{3})\textsubscript{2}] (Eq. 2.2).

\[
\begin{align*}
\text{Pt} & \quad \text{PEt}_3 \quad \text{Et}_3\text{P} \quad \text{Cl} \\
+ & \quad \text{C}_2\text{H}_4 \\
\text{H} & \quad \text{C}_2\text{H}_5 \\
\end{align*}
\]

Eq. 2.2

At 95\textdegree C under ethylene (80 atmospheres), a 25\% conversion of the hydride complex into the ethyl complex was achieved after 20 hours, and the reverse reaction occurred when the ethyl complex was heated to 180\textdegree C. Chatt originally proposed that the reactions proceed via a five-coordinate \pi-olefin complex\textsuperscript{187}. It was also suggested that a hydrogen atom from the methyl group rather than one from the methylene group becomes the hydride ligand and the hydridic hydrogen becomes one of the methyl protons in the reverse process. In order to elucidate this point, the decomposition of trans-[PtCl(CD\textsubscript{2}CH\textsubscript{3})(PEt\textsubscript{3})\textsubscript{2}] and the reaction of trans-[PtXY(PEt\textsubscript{3})\textsubscript{2}] (X = H or D, Y = Cl or CN) with various olefins were studied\textsuperscript{187}. Upon heating trans-[PtBr(CD\textsubscript{2}CH\textsubscript{3})(PEt\textsubscript{3})\textsubscript{2}] a mixture of deuterated ethylenes is evolved, leaving a mixture of platinum hydride and deuteride complexes.
The scrambling of hydrogen atoms of the methyl and methylene groups occurs because $\beta$-hydrogen elimination is fast and reversible.

The forward reaction in Eq. 2.2 can be induced under milder conditions either catalytically$^{171,188}$, or by using a ligand with a weaker trans-influence than chloride$^{189-194}$. Examples of these reactions are illustrated in Eq. 2.3 to Eq. 2.6.

\[
\begin{align*}
\text{Eq. 2.3} & : & \text{H} & + & \text{Pt} & + & \text{C}_2\text{H}_4 & \overset{1\text{mol}\%\text{SnCl}_2}{\overset{29^\circ\text{C}, 1\text{atm}}{\longrightarrow}} & \text{C}_2\text{H}_5 & + & \text{Pt} \\
\text{L} & & \text{Cl} & & & & & & \text{L} & & \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{Eq. 2.4} & : & \text{H} & + & \text{Pt} & + & \text{C}_2\text{H}_4 & \overset{\text{RT, 1atm}}{\longrightarrow} & \text{C}_2\text{H}_5 & + & \text{Pt} \\
\text{L} & & \text{ONO}_2 & & & & & & \text{L} & & \text{ONO}_2
\end{align*}
\]

\[
\begin{align*}
\text{Eq. 2.5} & : & \text{H} & + & \text{Pt} & + & \text{C}_2\text{H}_4 & \overset{\text{RT, 1atm}}{\overset{\text{LiCl}}{\longrightarrow}} & \text{C}_2\text{H}_5 & + & \text{Pt} \\
\text{L} & & \text{acetone} & & & & & & \text{L} & & \text{Cl}
\end{align*}
\]
The forward reaction of Eq. 2.2 requires very vigorous conditions, but in the presence of a catalytic amount of SnCl₂, the reaction is complete within 30 minutes at 25°C under one atmosphere of ethylene (Eq. 2.3). It has been proposed that SnCl₂ promotes the formation of a five-coordinate hydrido-olefin trichlorostannate intermediate, \( \text{PtH(SnCl}_3\text{(C}_2\text{H}_4\text{)(PET}_3\text{)}_2\) \), and weakens the Pt-H bond. A claim for the isolation of an analogous five-coordinate intermediate, \( [\text{PtH(SnCl}_3\text{(C}_8\text{H}_16\text{)(PPh}_3\text{)}_2\) \) \( (C}_8\text{H}_16 \) = 1-octene) has been made.

When a weakly coordinating ligand (e.g. acetone, ONO₂⁻) is trans to the hydride, a mechanism involving olefin coordination after displacement of the trans ligand operates. This reaction proceeds via a cationic four-coordinate hydrido-olefin intermediate, \( \text{trans-}[\text{PtH(C}_2\text{H}_4\text{)(L}_2\text{)}]^+ \) 189-193.

The Ag⁺-assisted displacement of the trans chloride ligand also involves a dissociative route (Eq. 2.6) 189,190. In fact, the intermediate \( \text{trans-}[\text{PtH(C}_2\text{H}_4\text{(PET}_3\text{)}_2\text{]}\text{PF}_6 \) has been observed by \(^1\)HNMR spectroscopy at -10°C 191. The complex \( \text{trans-}[\text{PtH(C}_2\text{H}_4\text{(PET}_3\text{)}_2\text{]}\text{BPh}_4 \) has been isolated by Lewis and coworkers 195,196. The \(^1\)HNMR parameters [\( \delta-7.2\) (t, hydride), \( ^1\)J(PtH) = 908 Hz, \( ^2\)J(HP) = 12 Hz] confirm that
the hydride and ethylene ligands are mutually trans.

It has been suggested$^2,191$ that a prerequisite for a rapid insertion is a cis arrangement of the hydride and olefin ligands in the coordination sphere. Moreover, cis-[PtH(C$_2$H$_4$)(PET$_3$)$_2$]$^+$ has never been isolated, indicating that it is a highly reactive species, and suggesting that intramolecular migration of a hydride to an olefin is facile. Consequently, complexes which contain both olefin and hydride groups are rare$^3$, and those examples which have been isolated, such as trans-[PtH(C$_2$H$_4$)(PET$_3$)$_2$]$^+$ are stabilised by a kinetic barrier.

The rate of insertion of ethylene into the Pt-H bond was investigated by Clark and coworkers$^{193}$. A series of cationic trans-[PtHL(PET$_3$)$_2$]PF$_6$ (L = acetone, CO, PET$_3$, AsPh$_3$, P(OMe)$_3$, P(OPh)$_3$ and neutral trans-[PtHX(PET$_3$)$_2$] ($X^- = $Cl$^-$, NO$_3^-$, NO$_2^-$, CN$^-$) complexes were prepared and allowed to react with ethylene and PhC = CMe. The ease of formation of insertion products was a function of the trans ligand, L or X$^-$. Although PhC≡CMe is more reactive than ethylene towards insertion, the same order of reactivity is found for both ethylene and PhC≡CMe. Reactivity of the cationic hydrides decreases in the order:

L = acetone $>$ CO $>$ AsPh$_3$ $>$ P(OPh)$_3$, P(OMe)$_3$, PET$_3$

X = NO$_3^-$ $>$ Cl$^-$, NO$_2^-$, CN$^-$

In summary, when the trans ligand is loosely bound, e.g. NO$_3^-$ and acetone, the insertion reaction is fast and quantitative and the rate increases with the polarity of the medium (benzene $<$ acetone $<$ MeOH).
In these cases, the insertion probably proceeds via a four-coordinate intermediate, since the reaction rate is dependent on the lability of the trans ligand, and on the ability of the reaction medium to both stabilise the cationic intermediate and to solvate the leaving group. It also has been established that some neutral ligands, e.g. PET₃, P(OMe)₃, P(OPh)₃, AsPh₃ which are strongly coordinating, prevent insertion by blocking the vacant site.

Clark and coworkers also reported the reaction of trans-[PtH(CO)(PET₃)₃]PF₆ with ethylene in sealed tubes, to give the insertion product trans-[Pt(C₂H₅)(CO)(PET₃)₃]PF₆ after 2-3 days at 35°C. The same product is obtained by carbon monoxide quenching of the product from the reaction of trans-[PtH(acetone)(PET₃)₃]PF₆ with ethylene, or by treatment of trans-[PtCl(C₂H₅)(PET₃)₃] with carbon monoxide in the presence of AgPF₆ (Scheme 2.2).

\[ \text{Scheme 2.2 Formation of trans-[Pt(C₂H₅)(CO)(PET₃)₃]PF₆ by different routes.} \]
In a continuous-flow reactor designed to purge the system of carbon monoxide, the reaction of trans-[PtH(CO)(PEt$_3$)$_2$]PF$_6$ with ethylene also gives trans-[Pt(C$_2$H$_5$)(CO)(PEt$_3$)$_2$]PF$_6$. It is thus certain that the carbon monoxide ligand remains in the coordination sphere during insertion, implying that the reaction proceeds through a five-coordinate intermediate.

Thus, depending on the nature of the trans ligand, the insertion of ethylene into the Pt-H bond can proceed either through a neutral five-coordinate intermediate or through a cationic four-coordinate intermediate. Clark and coworkers$^{193}$ have described the insertion mechanism by a unified reaction scheme, wherein the fate of the initially formed five-coordinate species is determined largely by the ligand trans to hydride. Direct insertion (A), or insertion via a pathway involving preliminary substitution (B) can occur (Scheme 2.3).

\[
\begin{align*}
\text{[Pt(alkyl)XL$_2$]} \\
\quad \downarrow \\
\text{trans-[PtHXL$_2$] + OL} & \quad \leftrightarrow \quad \text{[PtHXL$_2$(OL)]} & \quad \leftrightarrow \quad \text{[PtH(OL)XL$_2$]} \\
\quad \downarrow \\
\text{cis H and OL} \\
\quad \downarrow \\
\text{X}^- + \text{trans-[PtH(OL)L$_2$]$^+$} & \quad \leftrightarrow \quad \text{X}^- + \text{cis-[PtH(OL)L$_2$]$^+$} \\
\quad \downarrow \\
\text{[Pt(alkyl)XL$_2$]}
\end{align*}
\]

**Scheme 2.3** The proposed reaction mechanism for the insertion of a simple olefin (OL) into a Pt-H bond.
For hydride complexes that contain a good leaving group trans to hydride, the square planar hydrido-olefin complexes formed by initial substitution provide a low energy pathway leading to insertion. When the ligand trans to hydride is a poorer leaving group, the direct insertion from the five-coordinate intermediate containing a bound olefin is expected to become a competitive pathway.

2.1.3 Insertion of olefinic tertiary phosphine into the metal-hydride bond

The reaction of MnH(CO)$_5$, 2.1 with SP at 35$^\circ$C in n-pentane$^{153}$ initially gives MnH(CO)$_4$(SP), 2.2 in which the SP ligand is P-bound and the vinyl group is uncoordinated. After heating the complex in cyclohexane under nitrogen, the hydride ligand migrates from the metal atom to the vinyl group to give a mixture of chelate Mn-C $\sigma$-bonded complexes 2.3 and 2.4 (Scheme 2.4). These compounds (2.3 and 2.4) could not be separated, but were identified by $^1$HNMR spectroscopy. Proton NMR data suggest that the major product (80-90%) is the five-membered metallocycle 2.3 arising from Markownikoff addition. The minor product 2.4 contains a six-membered metallocycle arising from anti-Markownikoff addition.

In contrast, the reaction of ReH(CO)$_5$, 2.5 with SP at 35$^\circ$C initially gives the hydride ReH(CO)$_4$(SP), 2.6 which rapidly isomerises to give the six-membered chelate complex 2.7 as the only detectable product (Scheme 2.5)$^{153}$. 
Scheme 2.4 Reaction of MnH(CO)₅ with α-vinylphenyldiphenylphosphine (SP).
Scheme 2.5 Reaction of ReH(CO$_5$) with o-vinylphenyldiphenylphosphine (SP).

It was suggested$^{153}$ that the difference in the direction of the addition of MnH(CO)$_5$ and ReH(CO)$_5$ to an olefin may result from a difference in acidity. The complex MnH(CO)$_5$ is a stronger acid than ReH(CO)$_5$ which may favour addition in the sense $M^- - H^+$ for manganese. A difference in the direction of addition of MnH(CO)$_5$ and ReH(CO)$_5$ to an olefin has been noted using CF$_2 = $ CFCl$^{199}$. 
Hydride abstraction from the alkyl chain of the mixture of complexes 2.3 and 2.4 and from 2.7 using Ph₃C⁺BF₄ gave the chelate olefinic cation [M(CO)₄SP]⁺ (M = Mn, 2.8; M = Re, 2.9) (Scheme 2.6 and 2.7). Hydride addition to 2.9 (NaBH₄/THF) gives the five-membered metallocyclic complex 2.10 (Scheme 2.7) which cannot be obtained from the reaction of SP and ReH(CO)₅ (Scheme 2.5).

Scheme 2.6 Reaction of Mn(α-CHMeC₆H₄PPh₂)(CO)₄, 2.3 and Mn(α-CH₂-CH₂C₆H₄PPh₂)(CO)₄, 2.4 with Ph₃C⁺BF₄

The reactions of trans-[PtHCl(PPh₃)₂] and SP were initially reported in a short communication by Brookes and Nyholm²⁰⁰, and later in a full paper by Brookes²⁰¹. Their results are summarized in Scheme 2.8.
Scheme 2.7  Formation of five-membered metallocycle 2.10 from the six-membered metallocycle 2.7 by hydride abstraction and re-addition.
Various insertion products of trans-[PtHCl(PPh₃)₂] and α-vinylphenyldiphenylphosphine (SP), reported by Brookes²⁰⁰,²⁰¹.
It was not possible to establish unequivocally whether the chelate ring in complexes 2.11, 2.12 and 2.13 is five-membered, \( \text{Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2) \) (Figure 2.1a), or six-membered, \( \text{Pt(o-CH}_2\text{-CH}_2\text{C}_6\text{H}_4\text{PPh}_2) \) (Figure 2.1b). Brookes favoured the former structure on the basis of infrared data. A band of medium to weak intensity at 1047 cm\(^{-1}\) could be reasonably assigned as a C-CH\(_3\) rocking vibration, and bands in the 1200 cm\(^{-1}\) region typical of CH\(_2\) rocking modes in Pt-CH\(_2\)-X complexes were not observed. A \(^1\)HNMR spectrum of 2.11 could not be obtained because of the low solubility of the complex. However, some structural information was obtained from the \(^1\)HNMR spectrum of the compound assigned structure 2.13. A complex

![Figure 2.1](image_url)
resonance was observed at δ0.65 with $^{195}$Pt satellites, $[J(\text{PtP}) = 36.5 \pm 1 \text{ Hz}]$. This resonance was assigned to the methyl protons, which have coincidentally equal couplings to the methine proton and to the trans phosphorus atom $[^4J(\text{CH}_3\text{P}_{\text{trans}}) = ^3J(\text{CH}_3\text{H}_{\text{methine}}) = 7.8 \pm 0.5 \text{ Hz} \text{ and } ^4J(\text{CH}_3\text{P}_{\text{cis}}) = 1.5 \pm 0.5 \text{ Hz}]$. The methine proton resonance, crucial to the structural determination, could not be located in the $^1$HNMR spectrum of 2.13.

The structures assigned to 2.11, 2.12 and 2.13 indicated that SP can displace triphenylphosphine from the coordination sphere, and coordinate to the metal as a monodentate phosphine ligand with a dangling vinyl group. The structures assigned to 2.11, 2.12 and 2.13 also suggest that in this planar platinum(II) system, SP does not readily behave as a bidentate chelate ligand.

An analogous reaction between SP and trans-$[\text{PtH(CO)(PEt}_3\text{)}_2]^+\text{ClO}_4^-$ resulted in olefin insertion, loss of carbon monoxide and a trans to cis rearrangement of the triethylphosphine ligands to give 2.14.

Brookes also postulated that the insertion of SP into trans-$[\text{PtHCl}(\text{PPh}_3)_2]$ goes through a cationic four-coordinate
intermediate \([\text{PtH(PPh}_3\text{)}(\text{SP})]^{+}\) but no evidence for this mechanism was
provided. 201

Although the electronic properties of triphenylphosphine and
SP as P donors are expected to be similar, the cone angle of SP
is estimated to be greater than 161° based on Tolman's definition
(Appendix I), while the cone angle of triphenylphosphine is 145°.
Consequently, SP acting as a monodentate P-donor is significantly
bulkier than triphenylphosphine. It has been demonstrated that
steric factors are important in determining the course of many
reactions at metal centres 202. Hence it is surprising that SP,
acting solely as a monodentate phosphine ligand, is capable of
displacing triphenylphosphine to form complexes 2.11, 2.12 and 2.13.

In summary, in Brookes' work, the regiochemistry of insertion
to give five-or six-membered metallocycle was not established with
certainty, the mechanism of insertion was not investigated and the
insertion products were not unequivocally identified.

The aim of the work described in this chapter was to study the
reaction of the olefinic tertiary phosphine, \(\alpha\)-vinylphenyldiphenylphosphine
\((\alpha\text{-CH}_2\text{=CHC}_6\text{H}_4\text{PPh}_2,\text{SP})\), its dimethylphosphine analogue
\((\alpha\text{-CH}_2\text{=CHC}_6\text{H}_4\text{PMe}_2,\text{DMSP})\) and its diphenylarsine analogue
\((\alpha\text{-CH}_2\text{=CHC}_6\text{H}_4\text{AsPh}_2,\text{SPAS})\) with \textit{trans-}[\text{PtHCl(PPh}_3\text{)}_2]\) and related
compounds in order to establish:

(1) the regiochemistry of the insertion products

(2) the possibility of displacement of triphenylphosphine by
P-bonded SP in this system; and

(3) the mechanism of the insertion reaction.
2.2 Results and Discussion

2.2.1 Reaction of o-vinylphenyldiphenylphosphine (SP) with 
\textit{trans-}[PtHCl(PPh}_{3}]_{2}\]

The reaction of \textit{trans-}[PtHCl(PPh}_{3}]_{2} with SP in either a 1:1 or 1:2 mole ratio in refluxing benzene gives an air-stable white solid, 2.15 in 88% yield, after addition of n-pentane (Scheme 2.9). This compound is insoluble in saturated hydrocarbons, diethylether and alcohols and only sparingly soluble in acetone, chloroform and dichloromethane. These poor solubility properties make high quality NMR spectra difficult to obtain. The hydride absorption at 2220 cm\(^{-1}\) in \textit{trans-}[PtHCl(PPh}_{3}]_{2} is absent from the infrared spectrum of product 2.15, indicating that insertion has taken place. Bands assignable to Pt-Cl stretching (289(m) cm\(^{-1}\)), Pt-C stretching (588(m) cm\(^{-1}\)) and C-CH\(_{3}\) rocking (1047(mw) cm\(^{-1}\)) frequencies are observed, in agreement with the data reported by Brookes\(^{200,201}\). However, the C=C double bond stretching frequency at 1620 cm\(^{-1}\) reported by Brookes, was not observed. [This band is predominantly due to \(\nu(\text{C=C})\)].

The \(^{31}\)PNMR spectrum indicates that 2.15 is a mixture of three species. The major product is the \textit{cis} isomer 2.15a. The minor products are the \textit{trans} isomer 2.15b (10-15%) and another \textit{cis} isomer 2.15a' (2-3%). In this description, the terms \textit{cis} and \textit{trans} refer to the relative disposition of the phosphorus atoms. In the solid state, the \textit{cis} isomer slowly isomerises to the \textit{trans} isomer over a period of 18 months. Isomerisation is more rapid in solution. Heating of a chloroform solution containing mainly the \textit{cis} isomer 2.15a for 24 hours at 50°C gives a ca 1:1 mixture of \textit{cis} and \textit{trans} isomers.
Further investigation of the course of the isomerisation and of the effect of solvents on this reaction has not been undertaken. The cis isomer is the kinetic product of the insertion reaction, whereas the trans isomer is the thermodynamic product. The high trans-influence
Figure 2.2 $^1$HNMR spectra (200 MHz) of $\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2\text{)}\text{Cl(PPh}_3\text{)}]$, 2.15 in $\text{CD}_2\text{Cl}_2$.

(A) $^1$HNMR spectrum

(B) $^1$H($^31$P)NMR spectrum
Figure 2.3 $^{31}$P NMR spectrum (80.99 MHz) of $[\text{Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2]\text{Cl(PPh}_3\text{)}]$, 2.15 in CD$_2$Cl$_2$. (The $^1$HNMR spectrum of the same sample is shown in Figure 2.2).
Figure 2.4  $^{31}$PNMR spectrum (80.99 MHz) of 2.15 generated in situ in CD$_2$Cl$_2$ from the reaction of trans-[PtHCl(PPh$_3$)$_2$] with o-CH$_2$=CHC$_6$H$_4$PPh$_2$ at room temperature.
Table 2.1 \(^1\)H NMR parameters of neutral insertion products\(^a\)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>N(^2)</th>
<th>Solv.</th>
<th>(\delta)CH(_3)</th>
<th>(^3)J(PtCH(_3))</th>
<th>(^3)J(CH(<em>3)H(</em>{\text{meth}}))</th>
<th>(^4)J(CH(_3)P(_y))</th>
<th>(^4)J(CH(_3)P(_x))</th>
<th>(\delta)methine</th>
<th>(^2)J(PtH(_{\text{meth}}))</th>
<th>(^3)J(H(_{\text{meth}})P(_y))</th>
<th>(^3)J(H(_{\text{meth}})P(_x))</th>
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<tr>
<td><img src="image1" alt="Compound 1" /></td>
<td>2.15(^b)</td>
<td>CO(_2)Cl(_2)</td>
<td>1.58(t)</td>
<td>30</td>
<td>7.5</td>
<td>8.1</td>
<td>0</td>
<td>3.98(qd)</td>
<td>97</td>
<td>7.2</td>
<td>2.2</td>
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<tr>
<td><img src="image2" alt="Compound 2" /></td>
<td>2.15(^a)</td>
<td>CO(_2)Cl(_2)</td>
<td>1.55(t)</td>
<td>30</td>
<td>7.5</td>
<td>8.1</td>
<td>0</td>
<td>3.98(qd)</td>
<td>97</td>
<td>7.2</td>
<td>2.2</td>
</tr>
<tr>
<td><img src="image3" alt="Compound 3" /></td>
<td>2.15(^b)</td>
<td>CO(_2)Cl(_2)</td>
<td>0.86(d)</td>
<td>57</td>
<td>7.3</td>
<td>0</td>
<td>0</td>
<td>2.85(m)</td>
<td>83</td>
<td>10.9</td>
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Table 2.1 continued

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<tr>
<th>Compounds</th>
<th>№</th>
<th>Solv.</th>
<th>δCH₃</th>
<th>3J(PtCH₃)</th>
<th>3J(CH₃&lt;sub&gt;meth&lt;/sub&gt;)</th>
<th>4J(CH₃Pₓ)</th>
<th>4J(CH₃Pᵧ)</th>
<th>Δmethine</th>
<th>2J(Pt&lt;sub&gt;meth&lt;/sub&gt;)</th>
<th>3J(H&lt;sub&gt;meth&lt;y&gt;&lt;/sub&gt;)</th>
<th>3J(H&lt;sub&gt;meth&lt;x&gt;&lt;/sub&gt;)</th>
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<td><img src="image1.png" alt="Diagram" /></td>
<td>2.17a</td>
<td>CDCl₃</td>
<td>0.88(d)</td>
<td>63</td>
<td>7.5</td>
<td>0</td>
<td>0</td>
<td>3.10(m)</td>
<td>70</td>
<td>11</td>
<td>0</td>
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<td>CDCl₃</td>
<td>1.49(t)</td>
<td>32</td>
<td>7.5</td>
<td>7.5</td>
<td>0</td>
<td>4.80(qd)</td>
<td>c</td>
<td>7.5</td>
<td>2</td>
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<td><img src="image3.png" alt="Diagram" /></td>
<td>2.20a&lt;sup&gt;d&lt;/sup&gt;</td>
<td>CDCl₃</td>
<td>1.70(t)</td>
<td>38</td>
<td>7.5</td>
<td>7.5</td>
<td>0</td>
<td>3.90(qd)</td>
<td>93</td>
<td>7.5</td>
<td>2</td>
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<td><img src="image4.png" alt="Diagram" /></td>
<td>2.20b&lt;sup&gt;e&lt;/sup&gt;</td>
<td>CDCl₃</td>
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<th>Solv.</th>
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<th>³J(PtCH₃)</th>
<th>³J(CH₃meth)</th>
<th>⁴J(CH₃Pₓ)</th>
<th>⁴J(CH₃Pᵧ)</th>
<th>δmethine</th>
<th>²J(PtHmeth)</th>
<th>³J(HmethPₓ)</th>
<th>³J(HmethPᵧ)</th>
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<td>7.5</td>
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<td>-</td>
<td>2.70(m)</td>
<td>c</td>
<td>10</td>
<td>-</td>
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<tr>
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<td>CDCl₃</td>
<td>1.65(d)</td>
<td>40</td>
<td>7.5</td>
<td>-</td>
<td>0</td>
<td>4.25(m)</td>
<td>100</td>
<td>-</td>
<td>2</td>
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<tr>
<td><img src="image3" alt="Compound 2.23" /></td>
<td>2.23</td>
<td>CD₂Cl₂</td>
<td>2.04(t)</td>
<td>34</td>
<td>7.5</td>
<td>7.5</td>
<td>0</td>
<td>3.61(m)</td>
<td>94</td>
<td>7.5</td>
<td>2</td>
</tr>
<tr>
<td><img src="image4" alt="Compound 2.25" /></td>
<td>2.25</td>
<td>CDCl₃</td>
<td>f</td>
<td>f</td>
<td>7.5</td>
<td>f</td>
<td>f</td>
<td>3.93(qd)</td>
<td>97</td>
<td>7.5</td>
<td>2</td>
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Table 2.1 continued

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<th>Compounds</th>
<th>N°</th>
<th>Solv.</th>
<th>δCH₃</th>
<th>3J(PtCH₃)</th>
<th>3J(CH₃₉meth)</th>
<th>4J(CH₃py)</th>
<th>4J(CH₃px)</th>
<th>δmethine</th>
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<td>1.44(t)</td>
<td>64.2</td>
<td>7.5</td>
<td>7.5</td>
<td>0</td>
<td>3.31(qd)</td>
<td>68</td>
<td>7.5</td>
<td>2</td>
</tr>
<tr>
<td>Ph₂</td>
<td>CD₃OD</td>
<td>1.95(t)</td>
<td>64.2</td>
<td>7.5</td>
<td>7.5</td>
<td>0</td>
<td>3.80(qd)</td>
<td>68</td>
<td>7.5</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>CD₃ODDCO₃</td>
<td>1.85(t)</td>
<td>64.2</td>
<td>7.5</td>
<td>7.5</td>
<td>0</td>
<td>3.75(qd)</td>
<td>68</td>
<td>7.5</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

a: ¹HNMR spectra were measured at room temperature. Chemical shifts (δ) are in ppm downfield of TMS. Coupling constants (J) are in Hz, d = doublet, t = triplet, m = multiplet and qd = quintet of doublets.
b: parameters obtained from computer simulation.
c: ¹⁹⁵Pt satellites are too broad to be observed.
d: δ1.26(d), δ1.0(d) methyl of DMSP, ²J(CH₃DMS) = 11 Hz, ³J(PtCH₃) = 47 Hz.
e: δ1.84(d), δ1.77(d) methyl of DMSP, ²J(CH₃DMS) = 11 Hz, ⁴J(CH₃py) = 1.5 Hz, ³J(PtCH₃) = 35 Hz.
f: obscured by other resonances.
Table 2.2  $^1$H NMR parameters of cationic insertion products

<table>
<thead>
<tr>
<th>Compounds</th>
<th>N°</th>
<th>Solv.</th>
<th>$^3J$(PtCH$_3$)</th>
<th>$^3J$(CH$<em>3$$</em>\text{meth}$)</th>
<th>$^4J$(CH$_3$$_y$)</th>
<th>$^4J$(CH$_3$$_x$)</th>
<th>$^6$methine</th>
<th>$^2J$(PtH$_\text{meth}$)</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>2.18</td>
<td>CD$_2$Cl$_2$</td>
<td>0.60(d)</td>
<td>37</td>
<td>7.5</td>
<td>0</td>
<td>0</td>
<td>3.25(m)</td>
<td>b</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>2.19a</td>
<td>CD$_2$Cl$_2$</td>
<td>0.78(d)</td>
<td>54</td>
<td>7.5</td>
<td>0</td>
<td>0</td>
<td>3.18(m)</td>
<td>86</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>2.19b</td>
<td>CD$_2$Cl$_2$</td>
<td>1.66(t)</td>
<td>28</td>
<td>7.5</td>
<td>7.5</td>
<td>0</td>
<td>3.58(m)</td>
<td>b</td>
</tr>
<tr>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>2.24</td>
<td>CD$_2$Cl$_2$</td>
<td>1.4(m)</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>3.28(m)</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compounds</td>
<td>( \mathbf{N} )</td>
<td>Solv.</td>
<td>( \delta \text{CH}_3 )</td>
<td>( ^3 \text{J(PtCH}_3) )</td>
<td>( ^3 \text{J(CH}<em>3\text{H}</em>{\text{meth}}) )</td>
<td>( ^4 \text{J(CH}_3\text{P}_x) )</td>
<td>( ^4 \text{J(CH}_3\text{P}_y) )</td>
<td>( ^2 \text{J(PtH}_{\text{meth}}) )</td>
<td>Others</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------</td>
<td>------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------</td>
</tr>
<tr>
<td><img src="image.png" alt="Image" /></td>
<td>2.26</td>
<td>CDCl(_3)</td>
<td>0.60(t)</td>
<td>35</td>
<td>7.5</td>
<td>8.0</td>
<td>0</td>
<td>3.15(m)</td>
<td>51</td>
</tr>
<tr>
<td><img src="image.png" alt="Image" /></td>
<td>2.27</td>
<td>CDCl(_3)</td>
<td>1.40(d)</td>
<td>60</td>
<td>7.5</td>
<td>-1</td>
<td>0</td>
<td>3.65(m)</td>
<td>75</td>
</tr>
</tbody>
</table>

\( \delta \): 1\(^{HNMR}\) spectra were measured at room temperature. Chemical shifts (\( \delta \)) are in ppm downfield of TMS. Coupling constants (\( J \)) are in Hz, t = triplet, d = doublet and m = multiplet.

b: too weak to be observed.

c: obscured by other resonances.

d: Vinyl proton resonances were measured from \( ^1\text{H}^{31}\text{P} \) NMR spectrum. The \(^{195}\text{Pt} \) satellites of the coordinated vinyl resonances were not observed.
Table 2.3 $^3$¹PNMR data for neutral insertion products

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$^3$¹N</th>
<th>Solv.</th>
<th>$\delta P_x$</th>
<th>$J(\text{PtP}_x)$</th>
<th>$\delta P_y$</th>
<th>$J(\text{PtP}_y)$</th>
<th>$J(P_xP_y)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₂P₂Cl₂PPh₃</td>
<td>2.15a</td>
<td>CH₂Cl₂</td>
<td>37.3</td>
<td>4650</td>
<td>24.1</td>
<td>1650</td>
<td>10</td>
</tr>
<tr>
<td>Ph₂P₂Cl₂PPh₃</td>
<td>2.15a'</td>
<td>CH₂Cl₂</td>
<td>35.8</td>
<td>4667</td>
<td>22.2</td>
<td>1583</td>
<td>10</td>
</tr>
<tr>
<td>Ph₂P₂Cl₂PPh₃</td>
<td>2.15b</td>
<td>CH₂Cl₂</td>
<td>40.8</td>
<td>4250</td>
<td>29.1</td>
<td>3313</td>
<td>429</td>
</tr>
<tr>
<td>Ph₂P₂Cl₂PPh₃</td>
<td>2.17a</td>
<td>CHCl₃</td>
<td>39.9</td>
<td>3092</td>
<td>27.0</td>
<td>3333</td>
<td>426</td>
</tr>
<tr>
<td>Ph₂P₂Cl₂PPh₃</td>
<td>2.17b</td>
<td>CHCl₃</td>
<td>38.8</td>
<td>4450</td>
<td>18.5</td>
<td>1660</td>
<td>10</td>
</tr>
<tr>
<td>Me₂P₂Cl₂PPh₃</td>
<td>2.20a</td>
<td>CHCl₃</td>
<td>7.8</td>
<td>4460</td>
<td>22.0</td>
<td>1640</td>
<td>8.5</td>
</tr>
<tr>
<td>Me₂P₂Cl₂PPh₃</td>
<td>2.20b</td>
<td>CHCl₃</td>
<td>22.5</td>
<td>3333</td>
<td>29.5</td>
<td>3000</td>
<td>435</td>
</tr>
<tr>
<td>Ph₂P₂Cl₂PPh₃</td>
<td>2.21</td>
<td>CH₂Cl₂</td>
<td>-</td>
<td>-</td>
<td>25.2</td>
<td>3887</td>
<td>-</td>
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</table>
### Table 3.2 continued

<table>
<thead>
<tr>
<th>Compounds</th>
<th>N°</th>
<th>Solv.</th>
<th>$\delta P_x$</th>
<th>$J(\text{PtP}_x)$</th>
<th>$\delta P_y$</th>
<th>$J(\text{PtP}_y)$</th>
<th>$J(\text{P}_x\text{P}_y)$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="" /></td>
<td>2.22</td>
<td>CHCl$_3$</td>
<td>34.7</td>
<td>4733</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><img src="image2" alt="" /></td>
<td>2.23</td>
<td>CH$_2$Cl$_2$</td>
<td>36.5</td>
<td>4608</td>
<td>14.0</td>
<td>1634</td>
<td>13</td>
</tr>
<tr>
<td><img src="image3" alt="" /></td>
<td>2.25</td>
<td>CHCl$_3$</td>
<td>35.3</td>
<td>4730</td>
<td>35.3</td>
<td>1692</td>
<td>-</td>
</tr>
<tr>
<td><img src="image4" alt="" /></td>
<td>2.30</td>
<td>CHCl$_3$</td>
<td>41.9</td>
<td>1919</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><img src="image5" alt="" /></td>
<td>2.30</td>
<td>C$_6$H$_5$CH$_3$</td>
<td>42.9</td>
<td>1929</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a: $^1$HNMR spectra were measured at room temperature. Chemical shifts ($\delta$), in ppm, are referenced to external 85% H$_3$PO$_4$ and are positive to low field. All coupling constants ($J$) are in Hz.
Table 2.4  $^{31}$PNMR data for cationic insertion products

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$^{31}$PNMR data for cationic insertion products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_2$CH$_2$CO + Pt$_2$Cl$_2$</td>
<td>$^{31}$PNMR spectra were measured at room temperature. Chemical shifts ($\delta$), in ppm, are referenced to external 85% H$_3$PO$_4$ and are positive to low field. All coupling constants ($J$) are in Hz.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$^3$PNMR data for cationic insertion products</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{74}$J (PP)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$^{31}$PNMR data for cationic insertion products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_2$CH$_2$CO + Pt$_2$Cl$_2$</td>
<td>$^{31}$PNMR spectra were measured at room temperature. Chemical shifts ($\delta$), in ppm, are referenced to external 85% H$_3$PO$_4$ and are positive to low field. All coupling constants ($J$) are in Hz.</td>
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<tr>
<th>Compounds</th>
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<tr>
<td>Ph$_2$CH$_2$CO + Pt$_2$Cl$_2$</td>
<td>$^{31}$PNMR spectra were measured at room temperature. Chemical shifts ($\delta$), in ppm, are referenced to external 85% H$_3$PO$_4$ and are positive to low field. All coupling constants ($J$) are in Hz.</td>
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<td>Ph$_2$CH$_2$CO + Pt$_2$Cl$_2$</td>
<td>$^{31}$PNMR spectra were measured at room temperature. Chemical shifts ($\delta$), in ppm, are referenced to external 85% H$_3$PO$_4$ and are positive to low field. All coupling constants ($J$) are in Hz.</td>
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<th>$^{31}$PNMR data for cationic insertion products</th>
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<td>$^{31}$PNMR spectra were measured at room temperature. Chemical shifts ($\delta$), in ppm, are referenced to external 85% H$_3$PO$_4$ and are positive to low field. All coupling constants ($J$) are in Hz.</td>
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<th>$^{31}$PNMR data for cationic insertion products</th>
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<td>Ph$_2$CH$_2$CO + Pt$_2$Cl$_2$</td>
<td>$^{31}$PNMR spectra were measured at room temperature. Chemical shifts ($\delta$), in ppm, are referenced to external 85% H$_3$PO$_4$ and are positive to low field. All coupling constants ($J$) are in Hz.</td>
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<td>Ph$_2$CH$_2$CO + Pt$_2$Cl$_2$</td>
<td>$^{31}$PNMR spectra were measured at room temperature. Chemical shifts ($\delta$), in ppm, are referenced to external 85% H$_3$PO$_4$ and are positive to low field. All coupling constants ($J$) are in Hz.</td>
</tr>
</tbody>
</table>
Table 2.5 $^1$H and $^{31}$PNMR parameters of the olefinic ligands SP, DMSP and SPAS

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Abbreviation</th>
<th>$\delta^1$H</th>
<th>$\delta^2$H</th>
<th>$\delta^3$H</th>
<th>$J(^1H^2H)$</th>
<th>$J(^1H^3H)$</th>
<th>$\delta P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP</td>
<td>c</td>
<td>5.14(d)</td>
<td>5.57(d)</td>
<td>11</td>
<td>18</td>
<td>-13.7</td>
<td></td>
</tr>
<tr>
<td>DMSP</td>
<td>c</td>
<td>5.16(d)</td>
<td>5.50(d)</td>
<td>11</td>
<td>18</td>
<td>-57.2</td>
<td></td>
</tr>
<tr>
<td>SPAS</td>
<td>c</td>
<td>5.13(d)</td>
<td>5.58(d)</td>
<td>11</td>
<td>18</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

- $^1$H and $^{31}$PNMR spectra were measured in CDC$_3$ at room temperature. For $^1$HNMR spectra, chemical shifts ($\delta$) are in ppm downfield of TMS. For $^{31}$PNMR spectra chemical shifts ($\delta$) in ppm are referenced to external 85% H$_3$PO$_4$ and are positive to low field. All coupling constants (J) are in Hz.

- a: 5.10 (d, methyl of DMSP), $J$(CH$_3$P) = 4Hz.

- b: Obscured by aromatic protons.
of the σ-carbon ligand probably contributes significantly to the relative thermodynamic stability of the trans isomer. This effect is observed in simple alkyl complexes of platinum(II), PtClR(PR₃)₂ where the trans isomer is more stable.

In agreement with Brookes' suggestion, the structure of 2.15 is established as a five-membered metallocycle, rather than the isomeric six-membered metallocycle, 2.16. The ¹H and ³¹P NMR spectra of 2.15 are crucial in defining its structure (Figures 2.2, 2.3 and 2.4; Table 2.1 and Table 2.3). The ¹H NMR spectra for both the cis and trans isomers 2.15 show no olefinic proton resonances.
in the region δ5 to δ6, indicating that a free vinyl group is absent.
The crucial resonances of the methyl and methine groups of a five-
membered metallocycle have been located. The spectrum indicates the
presence of three species. The resonance of the methyl protons of
the *cis* isomer 2.15a is an apparent triplet at δ1.58 with 195Pt
satellites [3J(PtCH₃) = 30 Hz]. The ideal triplet is distorted by an
overlapping resonance from the methyl group of another isomer (see
below). The multiplicity of the methyl resonance in 2.15a is due to
coincidentally similar couplings to the methine proton and to the
*trans* phosphorus nucleus (Pᵧ). Due to complicated spectral appearance,
the coupling constants were obtained by simulation [3J(CH₃Hₐ) = 7.5 Hz,
4J(CH₃Pᵧ) = 8.1 Hz, 4J(CH₃Pₓ) = 0 Hz] (for labelling of phosphorus
atoms see Table 2.1). The coupling constant of the methyl protons to
the phosphorus of the cyclometallated ring Pₓ is approximately zero.
The methyl resonance collapses to a doublet in the 3¹P-decoupled
¹HNMR spectrum. The methine proton resonance of 2.15a is a quintet
of doublets at δ3.98 flanked by 195Pt satellites [2J(PtHₐ) = 97 Hz].
The multiplicity is due to coincidentally similar couplings to the
methyl protons and to the *trans* phosphorus nucleus (Pᵧ). Spectral
simulation gives 7.5 Hz for 3J(HₐCH₃), 7.2 Hz for 3J(HₐPᵧ) and
2.2 Hz for 3J(HₐPₓ). As expected, the methine proton resonance
becomes a quartet on 3¹P decoupling.

In the *trans* isomer 2.15b, the proton resonance of the methyl
group is an apparent doublet at δ0.86 due to coupling with the methine
proton. Simulation gives 7.3 Hz for 3J(CH₃Hₐ) and couplings to
the two *cis* phosphorus nuclei of approximately zero
[4J(CH₃Pᵧ) = 0 Hz, 4J(CH₃Pₓ) = 0 Hz]. The value of 57 Hz for
3J(PtCH₃) for the *trans* isomer is almost twice the corresponding value
in the cis isomer, resulting from stronger trans-influence of the triphenylphosphine ligand compared to the chloride ligand\textsuperscript{81}. The resonance of the methine proton in the trans isomer is observed at \(\delta 2.85\) as a multiplet, due to coupling to the methyl protons and to one of the two cis phosphorus nuclei. On \(^{31}\text{P}\) decoupling the resonance becomes a quartet due to coupling to the methyl protons

\[
^{3}J(\text{H}^{\text{meth}}\text{CH}_{3}) = 7.3 \text{ Hz}
\]

Simulation gives values of 10.9 Hz for \(^{3}J(\text{H}^{\text{meth}}\text{Py})\) and 0 Hz for \(^{3}J(\text{H}^{\text{meth}}\text{Px})\). Of the two cis phosphorus atoms, only the phosphorus of the triphenylphosphine ligand is coupled to the methine proton. The magnitude of the cis phosphorus coupling constant, \(^{3}J(\text{H}^{\text{meth}}\text{Py})\) in 2.15b (10.9 Hz) is much larger than the cis phosphorus coupling constant, \(^{3}J(\text{H}^{\text{meth}}\text{Px})\) in 2.15a (2.2 Hz) and slightly larger than the methine to trans phosphorus coupling constants \(^{3}J(\text{H}^{\text{meth}}\text{Py})\) in 2.15a (7.2 Hz).

The two phosphorus nuclei in 2.15b are strongly coupled, resulting in these unusual couplings to the methine proton (see below)\textsuperscript{204}. The methine proton is coupled to \(^{195}\text{Pt}\) \([^{2}J(\text{Pt}^{\text{meth}}) = 83 \text{ Hz}]\), but less strongly than in the cis isomer \([^{2}J(\text{Pt}^{\text{meth}}) = 97 \text{ Hz}]\). This result is not consistent with the relative trans-influence of the trans ligand (PPh\textsubscript{3} > Cl\textsuperscript{-}). Hence these coupling constants may have opposite signs.

The \(^{31}\text{PNMR}\) spectrum of the cis isomer, 2.15a is a pair of doublets \([\delta 24.1, \delta 37.3, ^{2}J(\text{PP}) = 10 \text{ Hz}]\) and the spectrum of the trans isomer, 2.15b is an AB quartet \([\delta 29.1, \delta 40.8, ^{2}J(\text{PP}) = 429 \text{ Hz}]\). The resonances are accompanied by \(^{195}\text{Pt}\) satellites (Figure 2.3 and Table 2.3) and the chemical shifts are at lower field than those of free triphenylphosphine and free SP. The \(^{2}J(\text{PP})\) values are consistent with the cis and trans phosphorus couplings in square planar platinum(II)
The $^{31}$P resonance assigned to triphenylphosphine is observed at higher field than the $^{31}$P resonance assigned to the cyclometallated ring because of the expected large downfield shift ($+\Delta R$) arising from the five-membered cyclometallated ring \textsuperscript{205}. In contrast, in a six-membered ring complex, such as the hypothetical complex \textsuperscript{2.16} the $^{31}$P resonance of the cyclometallated ring is expected to be shifted upfield ($-\Delta R$) \textsuperscript{205}. Hence, the $^{31}$P chemical shifts in \textsuperscript{2.15} are consistent with a five-membered metallocyclic structure. The values of the $^1J$(PtP) coupling constants for the cis isomer are 1650 Hz for the triphenylphosphine ($P_y$) and 4650 Hz for the cyclometallated phosphine ($P_x$). These values are typical for one bond platinum-phosphorus coupling constants \textsuperscript{trans} to \(\sigma\)-carbon and chloride ligands respectively \textsuperscript{81,206,286}. The higher \textsuperscript{trans}-influence of the \(\sigma\)-carbon relative to triphenylphosphine is apparent from these platinum-phosphorus coupling constants. The values of $^1J$(PtP) in the \textsuperscript{trans} isomer \textsuperscript{2.15b} are 3133 Hz and 4250 Hz for triphenylphosphine ($P_y$) and cyclometallated phosphine ($P_x$) respectively. These values are typical for two mutually \textsuperscript{trans} phosphorus ligands in square planar platinum(II) complexes \textsuperscript{81,206,286}.

The reactions in Scheme 2.9 always give \textsuperscript{2.15a} and \textsuperscript{2.15b} as major products, and a third product \textsuperscript{2.15a'} in very small and variable yields (2-3\%). A careful examination of the methyl proton resonance of the cis isomer, \textsuperscript{2.15a} shows that it is not an ideal triplet, nor does it become an ideal doublet on $^{31}$P decoupling. This distortion is caused by an overlapping resonance of low intensity. In the $^{31}$P NMR spectrum of the mixture of \textsuperscript{2.15a} and \textsuperscript{2.15b} obtained from reaction of trans-[PtHCl(PPh$_3$)$_2$] and SP in benzene (Figure 2.3), a pair of doublets having similar chemical shifts to those of \textsuperscript{2.15a} was observed.
in very low intensity (2-3\%). However, the $^{195}$Pt satellites could not be located. The in situ analysis of the reaction of trans-$[\text{PtHCl}(\text{PPh}_3)_2]$ and SP (1:1 molar ratio) in CD$_2$Cl$_2$ rather than in benzene shows that a higher proportion of 2.15a' (30\%) was formed which enabled its $^{31}$P NMR parameters including location of the $^{195}$Pt satellites, to be obtained (Figure 2.4). The $^{31}$P NMR parameters of this compound 2.15a' [$\delta$35.8 ($P_X$), $\delta$22.2 ($P_Y$), $J(P_X,P_Y) = 10$ Hz, $1J(PtP_X) = 4667$ Hz, $1J(PtP_Y) = 1583$ Hz] are similar to those of 2.15a (Table 2.3), suggesting that they have similar structure. Hence, 2.15a' appears to be an isomer of 2.15a. The $^1$H and $^{31}$PNMR data exclude the possibility that this minor compound contains a six-membered metallocycle. Therefore it is probable that 2.15a' is a conformational isomer of 2.15a. The structure of this type of metallocycle has been determined crystallographically in the complexes, Ru($\omega$-CHMeC$_6$H$_4$PPh$_2$)Br(CO)$_3$ (1.6b)$^{152}$, Mn($\omega$-CHMeC$_6$H$_4$PPh$_2$)(CO)$_4$ (2.3)$^{207}$, Au[$\omega$-CH(CH$_2$Br)C$_6$H$_4$PPh$_2$]Br$_2$ $^{208}$ and Au[$\omega$-CH(CH$_2$OMe)C$_6$H$_4$PET$_2$]Br$_2$ $^{209}$. In all these cases, the five-membered ring is non-planar and has an envelope conformation. A similar structure is therefore proposed for complex 2.15a. In principle, the five-membered ring has two envelope conformations, which would be expected to interconvert rapidly$^{210a,211}$ (Figure 2.5). In fact, the complexes 2.15a and 2.15a' do not interconvert rapidly. Heating a solution of the mixture of 2.15a, 2.15a' and 2.15b results in cis to trans isomerisation at the platinum (2.15a to 2.15b) rather than the interconversion of 2.15a and 2.15a'. The interconversion may be slow for steric reason. A molecular model shows that the two cis phosphorus ligands are sterically crowded. This strain is relieved in the trans isomer 2.15b. This agrees with the observation that conformational isomerism is not observed in the
Figure 2.5 Two conformational isomers of cis-[Pt(o-CHMeC₆H₄PPh₂)Cl(PPh₃)], 2.15a and 2.15a'.
trans isomer (2.15b) presumably because the energy barrier between the conformers is very low.

In situ analysis of the reaction of trans-\([\text{PtHCl(PPh}_3\text{)}_2]\) and SP in benzene or toluene shows a very low concentration of 2.15a' (2-3\%) compared to that of 2.15a which is similar to that observed when the compound is precipitated from the reaction mixture in benzene with \(n\)-pentane. This illustrates that the difference in the ratio of 2.15a' to 2.15a when the reactions are carried out in benzene or toluene, and dichloromethane is genuine and not due to preferential crystallisation of 2.15a during isolation of the compounds from the reaction mixture.

In summary, the reaction of trans-\([\text{PtHCl(PPh}_3\text{)}_2]\) and SP in either 1:1 or 1:2 molar ratio gives \([\text{Pt}(o-\text{CHMeC}_6\text{H}_4\text{PPh}_2)\text{Cl(PPh}_3\text{)}]_5\), 2.15 as the sole product. The monodentate P-bonded SP is unable to displace triphenylphosphine under reaction conditions similar to those reported by Brookes\(^{200,201}\). These results disagree with the proposal that \(\text{cis-}[\text{Pt}(o-\text{CHMeC}_6\text{H}_4\text{PPh}_2)\text{Cl(SP)}]\), 2.11 is formed from the reaction of trans-\([\text{PtHCl(PPh}_3\text{)}_2]\) and SP in 1:2 molar ratio (Scheme 2.8), and therefore P-bonded SP can displace triphenylphosphine\(^{200,201}\).

On the contrary, the results described in this section indicate that in square planar platinum(II) complexes, triphenylphosphine is a better ligand than P-bonded SP. This result is as expected on the basis of the cone angles of these two ligands (see Appendix I).

The reaction of trans-\([\text{PtHI(PPh}_3\text{)}_2]\) and SP (1:1 molar ratio) in refluxing benzene gives compound 2.17a as a white solid in 89% yield on addition of \(n\)-pentane (Eq. 2.7). The \(^1\text{H}\) and \(^{31}\text{P}\) NMR data (Table 2.1 and 2.3) indicate that the insertion product 2.17a is exclusively the five-membered metallocycle having trans phosphorus...
The \(^1\)HNMR spectrum shows the characteristic methyl resonance at \(\delta 0.88\) as an apparent doublet with a \(^3\)J(PtCH\(_3\)) value of 63 Hz. The methine proton resonance is observed at \(\delta 3.10\) as a multiplet flanked by \(^{195}\)Pt satellites \([^2\text{J(PtH}_{\text{meth}}) = 70 \text{ Hz}].\)

The \(^{31}\)PNMR spectrum appears as an AB quartet \([\delta 27.0 (P_y), \delta 39.9 (P_x), ^2\text{J(P}_x\text{P}_y) = 426 \text{ Hz}]\) flanked by \(^{195}\)Pt satellites \([^1\text{J(PtP}_x) = 3092 \text{ Hz,} \quad ^1\text{J(PtP}_y) = 3333 \text{ Hz}]\). The appearance of this spectrum and the Pt-P coupling constants are characteristic of square planar platinum(II) complexes containing trans phosphorus atoms.

In contrast with the behaviour of trans-[PtHCl(PPh\(_3\))\(_2\)] and SP, the reaction of trans-[PtHI(PPh\(_3\))\(_2\)] and SP gives exclusively the trans isomer of the insertion product, 2.17a. Heating a solution of 2.17a in chloroform at 50\(^0\)C for 3 hours does not result in isomerisation to the cis isomer. Although this point has not been investigated, it seems likely that the cis isomer is formed initially in this reaction.
This isomer, which has been prepared by another method (see below, Eq. 2.15), isomerises to the trans isomer on heating.

The reactions of 2.15 with AgBF₄ in the presence of a neutral ligand (L = CO, p-CH₃C₆H₄NC) give the cationic derivatives 2.18 and 2.19 respectively, which are isolated as BF₄ salts (Eq. 2.8).

\[ \text{AgBF}_4, \text{L} \rightarrow \begin{array}{c} \text{acetone/CH}_2\text{Cl}_2 \\ \text{major} \end{array} \]

L = CO (2.18), p-CH₃C₆H₄NC (2.19)

Eq. 2.8

The \(^1\text{H}\) and \(^31\text{P}\) NMR data for 2.18 and 2.19 (Tables 2.2 and 2.4) indicate that 2.18 is the trans isomer, whereas 2.19 is a mixture of cis and trans isomers, with the trans isomer being the major product. Because the starting material (2.15) is predominantly the cis isomer 2.15a, cis-trans isomerisation must have occurred during the reaction.
2.2.2 Reaction of other olefinic ligands with trans-[PtHCl(PPh₃)₂]

The reaction of trans-[PtHCl(PPh₃)₂] with α-vinylphenyldimethylphosphine (DMSP) in a 1:1 molar ratio in refluxing benzene for two hours gives 2.20 in 80% yield as a white solid upon addition of n-pentane (Eq. 2.9). This compound is much more soluble in chloroform, dichloromethane and acetone than the diphenylphosphine analogue (2.15). The ¹H and ³¹PNMR spectra indicate that the product is a five-membered metallocycle consisting mainly of the cis isomer 2.20a, together with a small amount of the trans isomer 2.20b (2%). Heating the mixture of 2.20a and 2.20b in chloroform solution results in partial cis to trans isomerisation suggesting that the trans isomer is the thermodynamic product. The ¹HNMR parameters of 2.20a and 2.15a indicate that they have similar structures.

The ¹HNMR spectrum shows the resonance of the methyl protons in the chelate ring of the cis isomer, 2.20a at δ1.70 as an apparent triplet flanked by ¹⁹⁵Pt satellites [³J(PtCH₃) = 38 Hz]. The value of ³J(PtCH₃) is characteristic for a methyl group trans to a tertiary phosphine in this system. The multiplicity of the methyl resonance...
is due to coincidentally equal couplings to the methine proton and the trans phosphorus nucleus \( ^2 J(CH_3H_{\text{meth}}) = ^4 J(CH_3P_y) = 7.5 \text{ Hz} \).

As in the SP analogue 2.15a, the coupling between the methyl protons and the cis phosphorus nucleus \( (P_X) \) is approximately zero. The methine proton resonance of 2.20a appears as a quintet of doublets at \( \delta 3.90 \) due to coincidentally equal couplings to the methyl protons and to the trans phosphorus nucleus \( ^3 J(H_{\text{meth}}CH_3) = ^3 J(H_{\text{meth}}P_y) = 7.5 \text{ Hz} \), and to coupling to the cis phosphorus nucleus \( ^3 J(H_{\text{meth}}P_x) = 2 \text{ Hz} \). The methine proton resonance becomes a quartet, as expected, on \(^{31}P\) decoupling. The methine proton is also coupled to \(^{195}Pt\), giving a \( ^2 J(PtH_{\text{meth}}) \) value of 93 Hz.

The \(^{31}PNMR\) spectrum of 2.20a appears as a pair of doublets \([\delta 7.8 (P_x), \delta 22.0 (P_y), ^2 J(P_xP_y) = 8.5 \text{ Hz}] \) accompanied by \(^{195}Pt\) satellites \([^1 J(PtP_x) = 4460 \text{ Hz}, ^1 J(PtP_y) = 1640 \text{ Hz}] \). The magnitudes of \(^2 J(PP)\) and \(^1 J(PtP)\) are characteristic of a cis phosphine complex. The magnitudes of the coupling constants, \(^1 J(PtP)\) indicate that the \(P_x\) and \(P_y\) are trans to chloride and to \(\sigma\)-carbon respectively.

The \(^1HNMR\) spectrum of the trans isomer 2.20b has a methyl proton resonance at \( \delta 0.94 \) which appears as an apparent doublet flanked by \(^{195}Pt\) satellites \([^3 J(PtCH_3) = 63 \text{ Hz}] \). The magnitude of the \(^3 J(PtCH_3)\) of 2.20b is almost twice that observed in 2.20a, which results from the larger trans-influence of the triphenylphosphine ligand compared to the chloride ligand. The methine proton resonance of 2.20b is observed at \( \delta 2.68 \) as a multiplet with \(^{195}Pt\) satellites \([^2 J(PtH_{\text{meth}}) = 80 \text{ Hz}] \). The value of the \(^2 J(PtH_{\text{meth}})\) in the trans isomer, 2.20b is smaller than that observed in the cis isomer, 2.20a (93 Hz) following the same trend which was observed in the SP analogues (2.15a, 2.15b).
The $^{31}$PNMR spectrum of 2.20b, which is typical for a trans isomer, shows an AB quartet [$\delta$ 29.5 (P$_y$), $\delta$ 22.5 (P$_x$), $^2$J(P$_y$P$_x$) = 435 Hz] flanked by $^{195}$Pt satellites [$^1$J(PtP$_y$) = 3000 Hz, $^1$J(PtP$_x$) = 3333 Hz].

There is no reaction between trans-[PtHCl(PPh$_3$)$_2$] and o-vinylphenyldiphenylarsine (SPAS) when they are refluxed in benzene for two hours, and the starting materials are recovered. However, on heating the reagents in a mixture of toluene and acetone for 7 hours, an insertion product 2.21 is obtained in 82% yield as a white solid which was recrystallised from dichloromethane-diethylether (Eq. 2.10).

The $^1$HNMR spectrum of 2.21 is characteristic of a five-membered metallocycle. The methyl resonance is observed at $\delta$ 0.85 as an apparent doublet due to coupling to the methine proton [$^3$J(CH$_3$H$_{meth}$) = 7.5 Hz]. It is also coupled to $^{195}$Pt giving a $^3$J(PtCH$_3$) value of 50 Hz. Although the methine proton resonance appears at $\delta$ 2.70 as a multiplet, its $^{195}$Pt satellites could not be observed. The $^{195}$Pt satellites may be broadened because the methine proton is also coupled to the quadrupolar $^{75}$As nucleus. The $^1$HNMR data suggest that 2.21 has the phosphorus and arsenic atoms in a trans disposition.
The $^{31}$PNMR spectrum shows one singlet at δ25.2 with a $^1J$(PtP) value of 3887 Hz. The magnitude of the $^1J$(PtP) suggests that the triphenylphosphine ligand is trans to the arsenic rather than to the $\sigma$-carbon atom, 81,206 in agreement with the structure derived from $^1$HNMR data.

2.2.3 Reaction of $\alpha$-vinylphenyldiphenylphosphine (SP) with various platinum(II) hydrides

When a mixture of trans-[PtHCl(AsPh$_3$)$_2$] and SP in a 1:1 molar ratio was heated in benzene for two hours, an insoluble white solid was formed. This solid was isolated by centrifugation. It has not been characterised since its $^1$HNMR spectrum in CD$_2$Cl$_2$ is uninformative showing only resonances in the aromatic region.

Addition of n-pentane to the clear supernatant solution gave a white solid which was recrystallised from dichloromethane-diethylether to give compound 2.22 as a white solid in 61% yield (Eq. 2.11).

The $^1$H and $^{31}$PNMR spectra for 2.22 indicate that it is an insertion product containing a five-membered metallocycle. The $^1$HNMR spectrum shows
the methyl resonance at δ1.65 as a doublet \[^{3}\text{J(CH}_3\text{H}_{\text{meth}}) = 7.5 \text{ Hz}]\] with \[^{195}\text{Pt} \text{ satellites} \[^{3}\text{J(PtCH}_3) = 40 \text{ Hz}],\] indicating that
triphenylarsine is \textit{trans} to the \(\sigma\)-carbon ligand. Therefore, the
phosphorus and arsenic atoms are \textit{cis}. The methine proton resonance
appears at δ4.25 as a multiplet with \[^{195}\text{Pt} \text{ satellites} \[^{2}\text{J(PtH}_{\text{meth}}) = 100 \text{ Hz}],\] broadened by coupling to quadrupolar \(^{75}\text{As}.\) The \(^{31}\text{P} \text{NMR}\)
spectrum shows one singlet with \[^{195}\text{Pt} \text{ satellites} \[(δ34.7, \[^{1}\text{J(PtP) = 4733 \text{ Hz}]}\) confirming that the phosphorus atom in the cyclometallated ring is
\textit{trans} to the chloride ligand.

Reaction of \textit{trans-}[PtHCl(PEt\textsubscript{3})\textsubscript{2}] and SP (1:1 molar ratio) in
refluxing benzene gives an oil which is difficult to crystallise. It
has been characterised by \(^{1}\text{H} \text{ and} \(^{31}\text{P} \text{NMR spectroscopy as a mixture of}
a neutral five-membered metallocycle 2.23 and the chloride salt of
the cationic insertion product 2.24, with the former predominating
(Eq. 2.12). The PF\textsubscript{6} salt of 2.24 is obtained by addition

\[
\begin{align*}
\text{H} & \quad \text{PEt}_3 \\
\text{Pt} & \quad \text{Cl} \\
\text{Et}_3\text{P} & \quad \text{SP} \\
\text{C}_6\text{H}_6, 2 \text{hr} & \quad \xrightarrow{} \\
\text{2.23} & \quad \text{2.24}
\end{align*}
\]

\text{major}

of NH\textsubscript{4}PF\textsubscript{6} to the reaction mixture. The ClO\textsubscript{4} salt of 2.24 has been
reported by Brookes\textsuperscript{201} (section 2.1.3, compound 2.14). The Pt-C
stretching frequency (590 (m) cm\textsuperscript{-1}) observed is in agreement with
that reported by Brookes\textsuperscript{201}. The \textsuperscript{1}H and \textsuperscript{3}P NMR spectra of 2.23 are consistent with a cis isomer (Table 2.1 and 2.3). The \textsuperscript{1}HNMR spectrum of 2.23 shows the methyl proton resonance at \(\delta 2.04\) as a characteristic triplet with \(1^95\)Pt satellites \(\text{J}(\text{PtCH}_3) = 34\) Hz. The methine proton resonance of 2.23 appears as a multiplet at \(\delta 3.61\) flanked by \(1^95\)Pt satellites \(\text{J}(\text{PtHmeth}) = 94\) Hz. The \textsuperscript{3}PNMR spectrum appears as a pair of doublets \(\delta 36.5 (P_x), \delta 14.0 (P_y), 2\text{J}(P_xP_y) = 13\) Hz flanked by \(1^95\)Pt satellites \(\text{J}(\text{PtP}_x) = 4608\) Hz, \(\text{J}(\text{PtP}_y) = 1634\) Hz, which is characteristic of the insertion product containing cis phosphine ligands (Table 2.3). Compound 2.23 is difficult to obtain in analytically pure form. It is always contaminated by a small amount of the cationic product 2.24. The \textsuperscript{1}H and \textsuperscript{3}P NMR spectra of 2.24 are complicated and the \textsuperscript{1}HNMR data obtained are incomplete (Table 2.2). The \textsuperscript{3}PNMR spectrum of 2.24 is expected to be an ABCX spin system \((X = 1^95\)Pt). However the \textsuperscript{3}PNMR parameters for this compound were not obtained because the spectrum is complicated by overlapping resonances, rendering simulation impossible. The complexity of the NMR data of 2.24 may arise from the presence of impurities such as \([\text{PtH(PET}_3]_3^+\) which was detected by low temperature \textsuperscript{1}HNMR studies (section 2.2.6). The smaller and more basic triethylphosphine ligand probably competes with the chloride ligand and/or P-bonded SP to give \([\text{PtH(PET}_3]_3^+\) as an impurity.

No reaction took place when a mixture of trans-\([\text{PtHCl(P-i-Pr}_3]_2\) and SP in 1:1 molar ratio was refluxed in benzene for 2 hours, or in toluene for 16 hours. Treating trans-\([\text{PtHCl(P-i-Pr}_3]_2\) with excess SP in chloroform or dichloromethane at room temperature for 24 hours did not yield any insertion product and the starting materials were recovered unchanged. When the 1:1 mixture of trans-\([\text{PtHCl(P-i-Pr}_3]_2\)
and SP was refluxed in dichloromethane for 24 hours, a small amount of insertion product 2.25 was present among the starting materials, as shown by $^1$H and $^{31}$PNMR spectroscopy. A small amount of methanol (20%) was added to the reaction mixture, which was refluxed for a further 3 days. Monitoring the reaction by $^1$HNMR spectroscopy at one day intervals indicated that the reaction did not go to completion while decomposition of hydride took place. Hence, the reaction of SP with trans-[PtHCl(P-i-Pr$_3$)$_2$] is remarkably slow compared to the analogous reaction with trans-[PtHCl(PPh$_3$)$_2$]. The larger size of triisopropylphosphine (cone angle 160° ± 10°) compared to triphenylphosphine (cone angle 145° ± 2°) may contribute to this slow rate of insertion.

Compound 2.25 was not isolated in a pure state but was characterised by $^1$H and $^{31}$PNMR spectroscopy as a neutral insertion product containing a five-membered metallocycle, with the phosphine ligands being mutually cis.

The $^1$HNMR spectrum of the mixture containing 2.25 is complicated in the region δ0.5 - δ2.0 by proton resonances of the triisopropylphosphine in both the starting material and its decomposition products. Consequently, the metallocyclic methyl resonance is not observed. The methine proton resonance appears at δ3.93 as a multiplet with $^{195}$Pt satellites [$^2$J(PtH$_\text{meth}$) = 97 Hz]. The $^{31}$P chemical shifts of the phosphorus nucleus in the five-membered ring and of the triisopropylphosphine in 2.25 coincide at δ35.3 with $^1$J(PtP) values of 4730 Hz and 1692 Hz respectively. It is surprising that the cis isomer was isolated, in view of the bulkiness of the triisopropylphosphine (cone angle 160° ± 10°) which would be expected to favour a trans geometry, minimizing steric interaction between the phosphines.
2.2.4 Attempts to introduce another \( \sigma \)-vinylphenyldiphenylphosphine ligand (SP) into Pt(\( \sigma \)-CHMeC\(_6\)H\(_4\)PPh\(_2\))Cl(PPh\(_3\)), 2.15

The reactions of trans-[PtHCl(PPh\(_3\))\(_2\)] with SP in 1:2 or 1:3 molar ratios, followed by addition of AgBF\(_4\) or NH\(_4\)PF\(_6\) yield a mixture of the BF\(_4\) or PF\(_6\) salts of cations 2.26 and 2.27. The same mixture is obtained from reactions of the insertion product [Pt(\( \sigma \)-CHMeC\(_6\)H\(_4\)PPh\(_2\))Cl(PPh\(_3\))], 2.15 with SP in 1:1 or 1:2 molar ratios in the presence of AgBF\(_4\) or NH\(_4\)PF\(_6\) (Scheme 2.10).

The \(^1\)HNMR and \(^{31}\)PNMR spectra of the mixture of 2.26 and 2.27 are shown in Figures 2.6 and 2.7 respectively. The \(^1\)HNMR spectrum shows two methyl resonances, one a triplet (\(\delta\) 0.60) and the other a doublet (\(\delta\) 1.40), with \(^3\)J(PtCH\(_3\)) values of 35 Hz and 60 Hz respectively.

There are several sets of resonances in the region \(\delta\) 2.5 to \(\delta\) 5.5 which may arise from the methine proton and olefinic protons. The \(^{31}\)PNMR spectrum of the mixture is complicated but clearly suggests that a mixture of two compounds is present.

Successive recrystallisations from dichloromethane-methanol gave the less soluble product, 2.26 which was identified by \(^1\)HN and \(^{31}\)PNMR spectroscopy as [Pt(\( \sigma \)-CHMeC\(_6\)H\(_4\)PPh\(_2\))(PPh\(_3\))\(_2\)]\(^+\)X\(^-\) (X\(^-\) = PF\(_6\), BF\(_4\)).

Compound 2.26 was prepared independently by chloride abstraction from [Pt(\( \sigma \)-CHMeC\(_6\)H\(_4\)PPh\(_2\))Cl(PPh\(_3\))], 2.15 in the presence of triphenylphosphine (Eq. 2.13).
Scheme 2.10  Reactions of trans-[PtHCl(PPh\textsubscript{3})\textsubscript{2}] or \[\text{[Pt(\text{a-CHMeC\textsubscript{6}H\textsubscript{4}PPh\textsubscript{2}})Cl(PPh\textsubscript{3})]}\text{, 2.15 with SP in the presence of AgBF\textsubscript{4} or NH\textsubscript{4}PF\textsubscript{6}.}
Figure 2.6 \( ^1 \text{H NMR} \) spectrum (100 MHz, CDCl\(_3\)) of the mixture of 
\[
\begin{align*}
[\text{Pt}(\text{o-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]^+, 2.26 & \quad \text{and} \\
[\text{Pt}(\text{o-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{SP})]^+, 2.27 & \end{align*}
\]
from the reactions in Scheme 2.10.
Figure 2.7 $^{31}$PNMR spectra (24.28 MHz, CDC$_3$) of the mixture of 2.26 and 2.27, generated from reactions in Scheme 2.10 (B). The simulated spectrum for 2.26 (ABCX spin system, $X = ^{195}$Pt) is shown in (A).
The $^1$H and $^{31}$PNMR spectra of 2.26 from this independent synthesis are identical to those from one of the components of the mixture formed in the reactions shown in Scheme 2.10. The $^1$HNMR spectrum of 2.26 shows the methyl resonance at δ0.60 as an apparent broad triplet flanked by $^{195}$Pt satellites [$^{3}$J(PtCH$_3$) = 35 Hz] which is a characteristic value for a methyl group trans to phosphine ligand in this system (Tables 2.1, 2.2). The multiplicity of the methyl resonance is due to coincidentally equal couplings with the methine proton and the trans phosphorus nucleus [$^{4}$J(CH$_3$P$_y$) = $^{3}$J(CH$_3$H$_{meth}$) = 7.5 Hz]. The $^{31}$P decoupled spectrum shows the methyl resonance as a doublet as expected. The methine proton resonance is observed at δ3.15 as a multiplet with $^{195}$Pt satellites [$^{3}$J(PtH$_{meth}$) = 51 Hz]. The $^{31}$PNMR spectrum is complex but can be analysed as an ABCX system ($X = {^{195}}$Pt) by simulation. The chemical shifts and coupling constants were obtained by spectral simulation (Figure 2.7 and Table 2.4). The resonance at δ40.9 (P$_A$) is assigned to the phosphorus nucleus in the cyclometallated ring because of the characteristically large downfield coordination shift ($\Delta_R$)$. The values of $^2$J(P$_{A}P_{B}$), $^2$J(P$_{A}P_{C}$) and $^2$J(P$_{B}P_{C}$) [362 Hz, 21 Hz, 18 Hz respectively] are typical for trans, cis and cis P-P couplings respectively in square planar platinum(II) complexes.

No attempts were made to isolate the more soluble product 2.27 from this reaction mixture, since it was obtained more easily by protonation of the zerovalent platinum complex bis(o-vinylphenyldiphenylphosphine)platinum(0) (section 3.2.5) and independent synthesis.

Compound 2.27 was identified by $^1$H and $^{31}$PNMR spectroscopy as [Pt(o-CHMeC$_6$H$_4$PPh$_2$)(SP)]$^+$X$^-$ (X$^-$ = PF$_6^-$, BF$_4^-$). This complex was synthesized independently by displacement of triphenylarsine from the complex [Pt(o-CHMeC$_6$H$_4$PPh$_2$)Cl(AsPh$_3$)] (2.22) as shown in Eq. 2.14.
The $^1$H and $^{31}$PNMR data for the product 2.27 which was prepared from the reaction in Eq. 2.14 show that this complex is identical to the more soluble component of the mixture arising from the reactions in Scheme 2.10. The $^{31}$PNMR spectrum shows that two isomers of compound 2.27 are present in a 1:3 ratio, since they are overlapping AB quartets having very similar chemical shifts and identical coupling constants [$\delta 47.2$ (P$_x$), $\delta 33.9$ (P$_y$), J(PtP$_x$) = 2883 Hz, J(PtP$_y$) = 2883 Hz, J(pp) = 367 Hz for 2.27 and $\delta 48.2$ (P$_x$), $\delta 35.6$ (P$_y$), J(PtP$_x$) = 2883 Hz, J(PtP$_y$) = 2883 Hz, J(P$_x$P$_y$) = 367 Hz (Table 2.4). These $^{31}$PNMR parameters indicate that the phosphorus atoms are mutually trans in both isomers.

The $^1$H($^{31}$P) NMR spectrum of 2.27 shows resonances due to the coordinated vinyl group at $\delta 4.15$ ($d\text{,}H^3$), $\delta 5.15$ ($d\text{,}H^2$) and $\delta 5.45$ ($dd\text{,}H^1$), with $^3$J(H$^1$H$^3$) and $^3$J(H$^1$H$^2$) values of 15 and 8 Hz respectively (for numbering of protons see Eq. 2.14). The resonances of the coordinated vinyl protons are significantly shifted upfield from those in free SP, in agreement with theoretical predictions$^{38c}$. The $^{195}$Pt satellites of the coordinated vinyl protons were not located. The methyl proton resonance appears at $\delta 1.40$ as an apparent doublet.
Figure 2.8 Two diastereomers of trans-\([\text{Pt}(\text{o-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{o-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2)]^+\), 2.27
\[^3J(CH_3\text{meth}) = 7.5 \text{ Hz}\] flanked by \(^{195}\text{Pt}\) satellites \[^3J(\text{PtCH}_3) = 60 \text{ Hz}\].

The magnitude of \(^3J(\text{PtCH}_3)\) is as large as when the methyl group is trans to chloride, a ligand which has a low trans-influence. This suggests that the coordinated olefin has very low trans-influence in agreement with theoretical prediction\(^38\text{c}\). The methine proton resonance appears at 83.65 as a multiplet with \(^{195}\text{Pt}\) satellites \[^1J(\text{Ptmeth}) = 75 \text{ Hz}\].

Heating a chloroform solution of the two species of the trans isomers of 2.27 for 24 hours did not result in isomerisation to the cis isomer, suggesting that the more thermodynamically stable product has the trans configuration.

The two isomers of 2.27 are proposed to be diastereomers, arising from different dispositions of the coordinated olefin with respect to the chiral carbon atom in the metallocycle (Figure 2.8). This type of isomerism has been observed in \([\text{Ru}(\text{o-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{o-CH}_2\text{CHC}_6\text{H}_4\text{PPh}_2)\text{Cl(CO)}]^{212}\).

The mixture of 2.26 and 2.27 was recrystallised from dichloromethane-methanol to obtain predominantly 2.26. The reaction of this purified product with KI in acetone at room temperature gives \([\text{Pt}(\text{o-CHMeC}_6\text{H}_4\text{PPh}_2)\text{I(PPh}_3\text{)}], 2.17\text{b}\) as the only isolated product (Eq. 2.15). This reaction confirms the identity of compound 2.26.

\[
\begin{align*}
\text{2.26} & \quad \begin{array}{c}
\text{Ph}_2 \\
\text{P} \\
\text{C} \\
\text{CH}_3 \\
\text{H}
\end{array} \\
\text{Pt} & \quad \begin{array}{c}
\text{PPh}_3 \\
\text{Ph}_2 \\
\text{C} \\
\text{CH}_3 \\
\text{H}
\end{array}
\end{align*}
\quad \begin{array}{c}
\text{KI} \\
\text{acetone}
\end{array} \\
\begin{align*}
\text{2.17b} & \quad \begin{array}{c}
\text{Ph}_2 \\
\text{P} \\
\text{C} \\
\text{CH}_3 \\
\text{H}
\end{array} \\
\text{Pt} & \quad \begin{array}{c}
\text{PPh}_3 \\
\text{Ph}_2 \\
\text{C} \\
\text{CH}_3 \\
\text{H}
\end{array} \\
\text{I}
\end{align*}
\]

Eq. 2.15
Scheme 2.11 Proposed mechanism of formation of a mixture of compound $[\text{Pt}(\text{a-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]^+$, 2.26 and $\text{trans-}[\text{Pt}(\text{a-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{SP})]^+$, 2.27 from the reactions in Scheme 2.10.
Compound 2.17b was characterised by \(^1\)H and \(^{31}\)PNMR spectroscopy (Tables 2.1 and 2.3) and elemental analyses.

It is interesting to note that this reaction yields exclusively the cis isomer 2.17b, whereas the insertion reaction of trans-[PtH(PPh\(_3\))\(_2\)] and SP gives exclusively the trans isomer 2.17a (Eq. 2.7). The reaction in Eq. 2.7 was carried out in benzene, while reaction in Eq. 2.15 was carried out in the more polar solvent acetone. The polarity of the medium might affect the distribution of isomers, but this aspect was not investigated further. However, heating the dichloromethane solution of 2.17b results in partial cis to trans isomerisation indicating that the trans isomer is the thermodynamic product.

Scheme 2.11 illustrates the proposed mechanism of the formation of the mixture of 2.26 and 2.27 from trans-[PtHCl(PPh\(_3\))\(_2\)] or complex 2.15 with an excess of SP in the presence of AgBF\(_4\) or NH\(_4\)PF\(_6\). The crucial factors are the powerful chelating ability of SP, and the tendency of platinum(II) phosphine complexes containing similar, but different phosphine ligands to disproportionate (redistribute) to form more symmetrical complexes 213-216. The intermediates 2.28 and 2.29 (Scheme 2.11), which were not observed in this work, were reported by Brookes\(^{200,201}\) to be stable complexes (Scheme 2.8). However, these structural assignments are incorrect. Compound 2.28 is unlikely to exist as a stable compound because of steric factors and because of the tendency of platinum(II) mixed phosphine complexes to disproportionate\(^{213-216}\). Steric congestion and the powerful chelating tendency of the SP ligand undoubtedly contribute to the failure to isolate compound 2.29.
2.2.5 Preparation of the platinum(II) chelate bis(alkyl) complex

\[ \text{cis-}[\text{Pt}(\text{o-CHMeC}_6\text{H}_4\text{PPh}_2)_2], \text{2.30} \]

Coordinated olefins in platinum(II) complexes are activated towards nucleophilic attack (section 1.2.1). Nucleophilic attack on the double bonds of coordinated olefinic tertiary phosphines and arsines has also been reported (section 1.3). To substantiate the structure of compound 2.27, its reaction with nucleophiles was investigated. The reaction of 2.27 with sodium borohydride in aqueous acetone gives the chelate bis(alkyl) complex 2.30 in 80% yield (Eq. 2.16). This compound is isolated exclusively as the cis isomer. This isomer is presumably more stable than the trans isomer, which would be destabilised by the high trans-influence of the σ-carbon ligands.

Most dialkyl platinum(II) complexes of type \([\text{PtR}_2\text{L}_2]\) have a cis disposition of the \(σ\)-alkyl ligands. Examples include \(\text{cis-}[\text{Pt}(\text{CH}_3)_2(\text{PMe}_3)_2], \text{cis-}[\text{Pt}(\text{C}_2\text{H}_5)_2(\text{PMe}_3)_2], \text{cis-}[\text{Pt}(\text{CH}_3)_2(\text{PET})_3)_2], \text{cis-}[\text{Pt}(\text{C}_2\text{H}_5)_2(\text{PET}_3)_2]\) and \(\text{cis-}[\text{Pt}(\text{CH}_3)_2(\text{PMe}_2\text{Ph})_2]\).^87b,217

The \(^1\text{HNMR}\) spectrum of 2.30 in CDCl\(_3\) shows the methyl proton resonance at δ1.44 as an apparent triplet \(\int J(\text{CH}_3\text{H}_{\text{meth}}) = 4 J(\text{CH}_3\text{P}_{\text{trans}})\)
=7.5 Hz] flanked by $^{195}\text{Pt}$ satellites [$^3J(\text{PtCH}_3) = 64.2 \text{ Hz}$]. The methine proton resonance appears at $\delta 3.31$ as a quintet of doublets [$^3J(\text{methCH}_3) = ^3J(\text{methP}_{\text{trans}}) = 7.5 \text{ Hz}$, $^3J(\text{methP}_{\text{cis}}) = 2 \text{ Hz}$] accompanied by $^{195}\text{Pt}$ satellites [$^2J(\text{PtH}_{\text{meth}}) = 68 \text{ Hz}$]. The $^1\text{HNMR}$ spectra of 2.30 in $d_6$-benzene and $d_8$-toluene show significant solvent shifts relative to those in CDCl$_3$ (see Table 2.1).

The $^{31}\text{PNMR}$ spectrum of 2.30 in chloroform shows a singlet at $\delta 41.9$ with $^{195}\text{Pt}$ satellites [$^1J(\text{PtP}) = 1919 \text{ Hz}$]. This is a characteristic one bond $^{195}\text{Pt} - ^{31}\text{P}$ coupling constant for phosphorus trans to a $\sigma$-alkyl ligand $^{81,206}$. The $^{31}\text{PNMR}$ spectrum of 2.30 in toluene is also shifted slightly from that in chloroform (see Table 2.3). Because the $\alpha$-carbon atoms in the chelate rings are chiral centres, diastereomers of complex 2.30 exist. However, only one isomer has been detected.

Complex 2.30 is closely related to the chelate bis(alkyl) complexes $[\text{Pt(CH}_2\text{C}_6\text{H}_4\text{P(t-Bu)(o-toly))}_2]$ (2.31, 2.32) which have been prepared by cyclometallation of the bulky ligand bis(o-toly)t-butylphosphine (Scheme 2.12)$^{218}$. In this case, prolonged heating converts the trans isomer 2.31 to the cis isomer 2.32, indicating that it is the thermodynamic product.
2.2.6 The mechanism of the insertion reaction of the olefinic moiety of o-vinylphenyldiphenylphosphine (SP) into the Pt-H bond of trans-[PtHCl(PPh₃)₂].

The conditions required for the insertion of the olefinic moiety of SP into the Pt-H bond of trans-[PtHCl(PPh₃)₂] are mild compared with those required for the corresponding insertion of a simple olefin (section 2.1.2). A plausible reaction mechanism is shown in Scheme

Scheme 2.12 Formation of ±-cis and trans-[Pt(CH₂C₆H₄P(t-Bu)(o-tolyl)]₂}
Scheme 2.13 Possible pathways for the reaction of o-vinylphenyldiphenylphosphine (SP) and trans-[PtHCl(PPh₃)₂].
2.13. There are two important features of this scheme:

(1) Because of the high trans-influence of the hydride ligand, the chloride ion should be readily displaced by a tertiary phosphine, such as P-bonded SP (Step 1).

(2) An intermediate in which the olefinic moiety of the ligand SP and the hydride ligand are both coordinated to the metal is generated (Step 2).

The formation of the hydrido-olefin intermediate (Step 2) can occur either associatively via a five-coordinate intermediate (A) or dissociatively via a four-coordinate intermediate (B). The rate of this step appears to be enhanced when the olefin is part of a chelate ring such as in SP. When the phosphorus or arsenic donor atom of the olefinic ligand is coordinated, the olefinic moiety is constrained to lie close to the coordination sphere and olefin coordination becomes more likely. Consequently, the insertion of this type of olefinic ligand into Pt-H bond occurs much more readily than that of the corresponding simple olefin.

A series of NMR experiments was carried out in an effort to detect some of the intermediates postulated in Scheme 2.13.

In CD$_2$Cl$_2$, which is a more polar solvent than benzene, trans-[PtHCl(PPh$_3$)$_2$] and SP react readily at room temperature (Eq. 2.17). All three insertion products, i.e. the two isomeric neutral species cis and trans-[Pt(o-CHMeC$_6$H$_4$PPh$_2$)Cl(PPh$_3$)] (2.15a and 2.15b) and the cationic insertion product [Pt(o-CHMeC$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$]$^+$, 2.26, were observed. In this reaction the cis isomer (2.15a) of the neutral insertion product predominates.
The reaction of the nitrato complex trans-\([\text{PtH(NO}_2](\text{PPh}_3)_2]\) with SP in \(\text{CD}_2\text{Cl}_2\) at room temperature proceeds rapidly to give a different distribution of insertion products. In this reaction, the cationic species (2.26) predominates (Eq. 2.18).

The reaction of SP with the cationic hydride complex trans-\([	ext{PtH(acetone)}(\text{PPh}_3)_2]^+\) gives exclusively the cationic insertion product, as expected (Eq. 2.19).
Thus the insertion reaction proceeds faster in a more polar solvent (CH₂Cl₂ > benzene) and in the presence of more weakly bound ligands (acetone, ONO₂⁻ > Cl⁻) trans to hydride. This observation is consistent with formation of an intermediate cationic hydride, [PtH(PPh₃)₂(SP)]⁺.\(^{2.33}\)

2.2.6.1 Detection of the intermediate \(^{2.33}\) using low temperature \(^1\)HNMR and \(^{31}\)PNMR spectroscopy

The \(^1\)HNMR and \(^{31}\)PNMR spectra of an accurately weighed mixture of trans-[PtHCl(PPh₃)₂] and SP in 1:1 molar ratio were recorded in CD₂Cl₂ at -90°C immediately after the solvent had been added to the mixture of the solid reactants at -80°C. Subsequent spectra were obtained at -30°C, 0°C and 20°C. These \(^1\)HNMR spectra are shown in Figure 2.9 and the \(^{31}\)PNMR spectra are shown in Figure 2.10. The \(^1\)HNMR and \(^{31}\)PNMR spectra were recorded on separate samples, the conditions being kept as far as possible the same for the two series of measurements.

At -90°C, two hydride resonances can be observed in the region from δ0 to δ-30. One hydride resonance is due to the starting...
Table 2.6 $^1$HNMR data for some cationic platinum(II) hydrides

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta H$</th>
<th>$^1J$ (PtH)</th>
<th>$^2J_{(HP\text{cis})}$</th>
<th>$^2J_{(HP\text{trans})}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[PtH(PPh$_2$Me)acetone]PF$_6$</td>
<td>-23.60 (t)</td>
<td>1458</td>
<td>14.5</td>
<td>-</td>
<td>190</td>
</tr>
<tr>
<td>b trans-[PtH(PPh$_2$Me)A]PF$_6$</td>
<td>-7.20 (t)</td>
<td>1080</td>
<td>14.5</td>
<td>-</td>
<td>190</td>
</tr>
<tr>
<td>c trans-[PtH(PPh$_2$Me)B]PF$_6$</td>
<td>-6.53 (t)</td>
<td>1073</td>
<td>14.0</td>
<td>-</td>
<td>190</td>
</tr>
<tr>
<td>d trans-[PtH(PPh$_2$Me)(C$_2$H$_4$)]PF$_6$</td>
<td>-6.32 (t)</td>
<td>931</td>
<td>11.5</td>
<td>-</td>
<td>190</td>
</tr>
<tr>
<td>e [PtH(PPh$_2$Me)$_3$]PF$_6$</td>
<td>-5.39 (td)</td>
<td>840</td>
<td>18.0</td>
<td>167</td>
<td>190</td>
</tr>
<tr>
<td>f [PtH(PPh$_2$Me)$_3$]BPh$_4$</td>
<td>-5.90 (td)</td>
<td>788</td>
<td>15.0</td>
<td>158</td>
<td>219</td>
</tr>
<tr>
<td>e [PtH(PPh$_3$)$_2$(PMe$_3$)]BPh$_4$</td>
<td>-6.12 (td)</td>
<td>800</td>
<td>16.0</td>
<td>166</td>
<td>219</td>
</tr>
<tr>
<td>f [PtH(PPh$_3$)$_3$(PMe$_3$)]BPh$_4$</td>
<td>-13.8 (td)</td>
<td>490</td>
<td>-</td>
<td>150</td>
<td>219</td>
</tr>
<tr>
<td>g [PtH(PPh$_3$)$_2$(SP)]Cl (2.33)</td>
<td>-5.31 (td)</td>
<td>786.2</td>
<td>14.5</td>
<td>154.6</td>
<td>-</td>
</tr>
<tr>
<td>g [PtH(PPh$_3$)$_2$(SP)]Cl (2.34)</td>
<td>-7.1 (td)</td>
<td>902.7</td>
<td>14.8</td>
<td>167.4</td>
<td>-</td>
</tr>
<tr>
<td>g [PtH(PPh$_3$)$_2$(SP)]Cl (2.35)</td>
<td>-5.5 h</td>
<td>375.1</td>
<td>h</td>
<td>h</td>
<td>-</td>
</tr>
</tbody>
</table>

a: Chemical shifts ($\delta$) in ppm downfield from TMS, coupling constants ($J$) in Hz, all spectra measured at room temperature in CD$_2$Cl$_2$ unless otherwise stated.
b: A = 2-methylpyridine.
c: B = 2,4,6-trimethylpyridine.
d: C = CH$_3$C$_6$H$_4$NC
e: measured at -70°C
f: measured at -90°C
g: results from this work, measured at -90°C from in situ reaction.
h: the $^{31}$P couplings were not obtained because the resonance can only be located in the $^1$H($^{31}$P) NMR spectrum since it is obscured by resonances of 2.34 in $^1$HNMR spectrum.
material trans-[PtHCl(PPh$_3$)$_2$][δ-16.3(t), $^{1}$J(PtH) = 1229.8 Hz, $^{2}$J(HP) = 14.5 Hz], although its $^{195}$Pt satellites are broader than those of the pure material. The other hydride resonance is a triplet of doublets at δ-5.31 flanked by $^{195}$Pt satellites [$^{1}$J(PtH) = 786.2 Hz]. This multiplicity is due to coupling to the trans phosphorus nucleus [$^{2}$J(HP$_{\text{trans}}$) = 154.6 Hz] and to two cis phosphorus nuclei [$^{2}$J(HP$_{\text{cis}}$) = 14.5 Hz] indicating that the resonance belongs to a hydrido complex containing three phosphine ligands. The magnitude of $^{1}$J(PtH) and $^{2}$J(HP) and the $^{1}$H chemical shift compare well with those of square planar platinum(II) cationic hydrides, e.g. [PtH(PPh$_2$Me)$_3$]PF$_6$,$^{190}$ [PtH(PEt$_3$)$_3$]BPh$_4$,$^{219}$ and [PtH(PEt$_3$)$_2$(PMe$_3$)]BPh$_4$,$^{219}$ (Table 2.6). In contrast, five-coordinate platinum(II) hydrides e.g. [PtH(PEt$_3$)$_3$(PMe$_3$)]BPh$_4$,$^{219}$ show the hydride resonance at considerably higher field (δ-13.8) and the $^{1}$J(PtH) value of 490 Hz is much less than that of four-coordinate hydrides (Table 2.6). Therefore the peak at δ-5.3 is assigned to a cationic four-coordinate hydride in which the vinyl group of SP is not coordinated to the metal [PtH(PPh$_3$)$_2$(SP)]$^+$, 2.33 (Scheme 2.13).

The $^{1}$HNMR spectrum in the region δ0 to δ10 at -90°C is complex and broad. Although there are peaks in the region δ4.5 to δ6 characteristic of uncoordinated vinyl groups, they could not be assigned with certainty. However, the broad resonances due to methyl protons of the neutral cis isomer (2.15a, 2.15a') and the cationic product (2.26) at δ1.58 and δ0.60 respectively can be located. Furthermore, the methine proton resonance of 2.15a with $^{195}$Pt satellites at δ3.98 is discernible. Therefore the $^{1}$HNMR spectrum at
Figure 2.9a  

$^1H$ and $^1H(^{31}P)$NMR spectra (200 MHz, δ0 to δ-30) measured at -90°C of the species detected in the in situ reaction of trans-[PtHCl(PPh$_3$)$_2$] and SP in CD$_2$Cl$_2$ at -80°C.
Figure 2.9b Variable temperature $^1\text{H}$$^{31}\text{P}$NMR spectra (200 MHz, 80 to δ-30) of the species detected in the in situ reaction of trans-[PtHCl(PPh$_3$)$_2$] and SP in CD$_2$Cl$_2$ at -80°C.
Variable $^1$H($^{31}$P)NMR spectra (200 Hz, $\delta$0-810) of the species detected in the in situ reaction of trans-[PtHCl(PPh$_3$)$_2$] and SP in CD$_2$Cl$_2$ at -80°C.
Figure 2.10a Variable $^{31}$P{H}NMR spectra (80.99 MHz) of the species detected in the in situ reaction of trans-[PtHCl(PPh$_3$)$_2$] and SP in CD$_2$Cl$_2$ at -80°C.
Figure 2.10b Variable $^{31}$P{$^1$H}NMR spectra (80.99 MHz) of the species detected in the in situ reaction of trans-[PtHCl(PPh$_3$)$_2$] and SP in CD$_2$Cl$_2$ at -80°C.
-90°C indicates that the insertion reaction has already taken place to some extent. However, the starting hydride trans-[PtHCl(PPh₃)₂] and cationic hydride intermediate [PtH(PPh₃)₂(SP)]⁺ (2.33) are also present.

The ³¹PNMR spectrum at -90°C supports the formulation of the cationic hydride intermediate as [PtH(PPh₃)₂(SP)]⁺, 2.33. The major species shows a five-line pattern with ¹⁹⁵Pt satellites. There are also resonances due to the neutral cis insertion product 2.15a and the cationic insertion product 2.26. Another set of low intensity peaks (labelled xyz), which have an ABCX pattern (X = ¹⁹⁵Pt) are present at this temperature. These resonances, which have not been identified are absent from the spectrum at -30°C. A broad singlet of low intensity at δ-8.0 which is possibly due to free SP. Computer simulation of the five-line pattern with ¹⁹⁵Pt satellites (AB₂X spin system, X = ¹⁹⁵Pt) gives δ22.7 (P_A), δ24.1 (P_B), ²J(P_A,P_B) 18.2 Hz, ¹J(PtP_A) 2179 Hz, (P_A trans to hydride) and ¹J(PtP_B) 2816 Hz (P_B trans to P_B').

Comparison of the ³¹PNMR parameters, coordination shifts (Δ) and ²J(PP) of compound 2.33 to those of the four-coordinate and five-coordinate cationic hydride complexes listed in Table 2.7 confirms that the cationic hydride 2.33 is a four-coordinate species. The resonance due to the starting hydride trans-[PtHCl(PPh₃)₂] which is present in the ¹H NMR spectrum at -90°C, cannot be located in the ³¹PNMR spectrum, perhaps because of the slightly different composition of the starting materials in both samples. Although great care was taken to prepare identical ¹H and ³¹PNMR samples, the low solubility of the starting materials and products at -90°C makes this difficult
Table 2.7: $^{31}$PNMR data for some cationic platinum(II) hydrides\(^a\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>T (^\circ)C</th>
<th>(\delta)free P</th>
<th>(\Delta P) ((\delta))(^b)</th>
<th>J(PtP)</th>
<th>(\delta)free P'</th>
<th>(\delta P') ((\delta))(^b)</th>
<th>J(PtP')</th>
<th>J(PP')</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}^-)\text{Pt}+\text{PEt}_3\text{BPh}_4^-)</td>
<td>-80</td>
<td>-20.4</td>
<td>16.2 (36.6)</td>
<td>2495</td>
<td>-62.0</td>
<td>-20.6 (41.4)</td>
<td>1915</td>
<td>22</td>
<td>219</td>
</tr>
<tr>
<td>(\text{H}^-)\text{Pt}+\text{PEt}_3\text{BPh}_4^-)</td>
<td>-80</td>
<td>-20.4</td>
<td>15.59 (36.0)</td>
<td>2459</td>
<td>-20.4</td>
<td>12.80 (33.2)</td>
<td>2000</td>
<td>21</td>
<td>228</td>
</tr>
<tr>
<td>(\text{H}^-)\text{Pt}+\text{PEt}_3\text{BPh}_4^-)</td>
<td>-90</td>
<td>-20.4</td>
<td>-14.1 (6.3)</td>
<td>2667</td>
<td>-62.0</td>
<td>-56.3 (5.7)</td>
<td>2115</td>
<td>31</td>
<td>219</td>
</tr>
<tr>
<td>(\text{Ph}_3\text{P}^-)\text{Pt}+\text{PPh}_3\text{Cl}^-)</td>
<td>-90</td>
<td>-6</td>
<td>24.07 (30.1)</td>
<td>2816</td>
<td>-13.7</td>
<td>22.74 (36.4)</td>
<td>2179</td>
<td>18.2</td>
<td>c</td>
</tr>
</tbody>
</table>

\(^a\) $^{31}$PNMR spectra were measured in CD\(_2\)Cl\(_2\). Chemical shifts (\(\delta\)), in ppm, are referenced to external 85\% H\(_3\)PO\(_4\) and are positive to low field.

\(^b\) Coupling constants (\(J\)) are in Hz. P' is assigned to phosphorus trans to hydride.

\(^c\) Coordination shifts (\(\delta\)) = \(\delta P\)(free) - \(\delta P\)(coordinated).
since each sample contains a small amount of insoluble material and only the clear solutions are transferred to the NMR tubes.

The $^1$H($^{31}$P) NMR spectrum at -30°C shows the resonances due to the cationic hydride, 2.33, but their intensities are reduced and the lines are broadened compared to those observed at -90°C. The resonances due to the starting hydride trans-[PtHCl(PPh$_3$)$_2$] are also present although their $^{195}$Pt satellites become sharper. There are many resonances in the olefinic proton region δ4.5 to δ6 but assignment cannot be made with certainty. The methyl and methine proton resonances of the insertion products (2.15a, 2.15a' and 2.26) are sharper than at -90°C. In the $^{31}$PNMR spectrum at -30°C, the resonances due to insertion products (2.15a, 2.15a', 2.26) are more intense while the resonances due to the cationic hydride, 2.33 merge to a single broad peak with $^{195}$Pt satellites and the singlet at δ-8.0 is no longer visible. There is a good correlation between data obtained from both $^1$H and $^{31}$PNMR spectra at this temperature.

At 0°C, the $^1$HNMR spectrum indicates that the hydride resonance due to the cationic hydride, 2.33 at δ-5.31 has almost disappeared while the hydride resonance due to the starting hydride trans-[PtHCl(PPh$_3$)$_2$] is sharp and remains unchanged. The methyl and methine proton resonances of the insertion products (2.15a and 2.15a') are sharp and relatively more intensive than at lower temperatures while the methyl proton resonances due to cationic insertion product 2.26 are no longer visible. The $^{31}$PNMR spectrum at 0°C agrees with the $^1$HNMR spectrum. At 0°C, the major components in the $^{31}$PNMR spectrum are the neutral cis insertion product (2.15a, 2.15a') with a small
amount of cationic insertion product (2.26). The cationic hydride (2.33) resonances have now collapsed to a broad singlet with $^{195}\text{Pt}$ satellites and the intensity is greatly reduced. A singlet resonance at $\delta 28.0$ with no $^{195}\text{Pt}$ satellites is also visible. At room temperature the $^1\text{H NMR}$ spectrum shows no sign of the cationic hydride, 2.33 while the resonances due to the starting hydride trans-$[\text{PtHCl}(\text{PPh}_3)_2]$ remain unchanged. Only the resonances due to the isomers of the neutral cis insertion product (2.15a, 2.15a') are present. Several resonances in the olefinic proton region $\delta 4.5$ to $\delta 6$ cannot be assigned. The $^{31}\text{P NMR}$ spectrum at room temperature shows that the solution consists of mainly neutral cis insertion products (2.15a, 2.15a') together with minor species having resonances at $\delta 28.0$ and $\delta 14.5$. The identity of these two resonances is unclear. The stoichiometry of the reaction indicates that for every mole of the neutral insertion product 2.15 formed, one mole of free triphenylphosphine should be liberated. However, there is no peak in the region $\delta-6$ due to free triphenylphosphine. The resonance at $\delta 28.0$ could be due either to OOPh$_3$ or to the oxide of SP $(\text{o-CH}_2\text{-CH}_6\text{H}_4\text{POPh}_2)^{220,271}$ possibly arising from aerial oxidation. The resonance at $\delta 14.5$ cannot be assigned.

In summary, the low temperature $^1\text{H}$ and $^{31}\text{P NMR}$ experiments give evidence that the insertion of the olefinic moiety of o-vinylphenyldiphenylphosphine (SP) into the Pt-H bond of trans-$[\text{PtHCl}(\text{PPh}_3)_2]$ goes through a cationic hydride intermediate $[\text{PtH(PPh}_3)_2(\text{SP})]^+$, 2.33. This is the first step of the insertion mechanism proposed in Scheme 2.13, in which the chloride ligand which is trans to the hydride ligand is displaced by P-bonded SP to form a four-coordinate hydride $[\text{PtH(PPh}_3)_2(\text{SP})]^+$, 2.33.

It is interesting to observe that in this low temperature in situ experiment the ratio of the isomeric neutral cis insertion product
2.15a' to 2.15a is higher than that observed in the in situ reaction at room temperature (Figure 2.4).

In a preliminary low temperature $^1$HNMR study, a mixture of trans-[$\text{PtHCl(PEt}_3\text{)}_2$] and SP in CD$_2$Cl$_2$ at -90°C shows three hydride resonances. One of these hydrides is the starting material trans-[$\text{PtHCl(PEt}_3\text{)}_2$] [$\delta$-17.9, $^1$J(PtH) = 1353.6 Hz, $^2$J(HP$_\text{cis}$) = 12.0 Hz] 186. The major hydride resonance is a triplet of doublets at $\delta$-7.1, with $^{195}$Pt satellites [$^1$J(PtH) = 902.7 Hz]. The multiplicity of the hydride resonance is due to a large coupling to the trans phosphorus atom and small coupling to the two cis phosphorus atoms [$^2$J(HP$_\text{trans}$) = 167.4 Hz, $^2$J(HP$_\text{cis}$) = 14.8 Hz]. The third hydride resonance, which has low intensity, has a chemical shift of $\delta$-5.5 with $^{195}$Pt satellites [$^1$J(PtH) = 375.1 Hz]. As the temperature is raised to -30°C, an additional hydride resonance appears at $\delta$-6.2 [$^2$J(HP$_\text{trans}$) = 158.5 Hz, $^2$J(HP$_\text{cis}$) = 15.7 Hz, $^1$J(PtH) = 791.3 Hz]. This hydride belongs to [PtH(PEt$_3$)$_3$]$^+$ 228. At room temperature, the resonance of the hydride complexes [PtH(PEt$_3$)$_3$]$^+$ and trans-[$\text{PtHCl(PEt}_3\text{)}_2$] remain unchanged. However, the hydride resonances of the other two compounds disappear, presumably because these complexes react to form insertion products.

Spectral parameters for the hydride resonances of [PtH(PEt$_3$)$_2$(PMe$_3$)]$^+$ and [PtH(PEt$_3$)$_3$(PMe$_3$)]$^+$ are presented in Table 2.6, for comparison with data for the hydride intermediates. The major product is proposed to be the cationic four-coordinate hydride [PtH(PEt$_3$)$_2$(SP)]$^+$, 2.34 with the vinyl group of the SP ligand dangling freely. The minor hydride could be the five-coordinate complex [PtH(PEt$_3$)$_2$(SP)]$^+$, 2.35, with the SP coordinated through both the phosphorus donor and the vinyl group.
The cationic hydride \([\text{PtH(PEt}_3\text{)}_3]^+\) probably results from competition of the more basic and smaller triethylphosphine with P-bonded SP. Formation of this complex blocks olefin insertion. The additional triethylphosphine ligand which is required to form this complex can be generated before insertion occurs by formation of the cationic four-coordinate hydrido-olefin complex \([\text{PtH(PEt}_3\text{)(SP)}]^+,\text{2.36 (Eq. 2.20)}\). Alternatively, it can be displaced from the cationic insertion product 2.24 by a chloride ion (Eq. 2.21). The results obtained to date cannot distinguish between these two possibilities.
The $^1$HNMR spectra in the region $\delta 0$ to $\delta 10$ are complex containing a number of methylene and methyl resonances. These spectra are not useful in confirming the proposed structures of the intermediate hydride complexes. The $^{31}$PNMR spectra are also extremely complex, rendering definite assignment impossible. However, two cationic hydride intermediates $\text{2.34}$ and $\text{2.35}$ appear to be present, suggesting that the insertion of the olefinic moiety of SP into trans-$[\text{PtHCl(PEt}_3]_2$ may proceed partly through the five-coordinate cationic hydrido-olefin complex $\text{2.35}$ via initial formation of the four-coordinate cationic hydride $\text{2.34}$. 
2.2.7 Conclusion

The insertion products formed by reaction of olefinic ligands of the type \(\text{CH}_2=\text{CHC}_6\text{H}_4\text{ER}_2\) (E = P, R = Ph; E = P, R = Me; E = As, R = Ph) with platinum(II) hydrides \(\text{trans-}[\text{PtHClL}_2]\) (L = PPh\(_3\), AsPh\(_3\), PEt\(_3\), P-i-Pr\(_3\)) contain a five-membered metallocycle, irrespective of the steric bulk or basicity of the olefinic ligand or the ligands present in the hydrido complex. Bennett and Watt\(^{153}\) suggested that the difference in the direction of insertion of the olefinic moiety of SP into the metal-hydrogen bond in \(\text{MnH(CO)}_5\) and \(\text{ReH(CO)}_5\) to give a five-membered and six-membered metallocycle respectively may be connected with the fact that \(\text{ReH(CO)}_5\) is a weaker acid than \(\text{MnH(CO)}_5\), so that addition in the sense \(\text{M}^-\cdot\text{H}^+\) will be favoured for the manganese complex. The direction of insertion of olefinic moiety of the SP ligand into platinum-hydrogen bond in \(\text{trans-}[\text{PtHClL}_2]\) is the same as in the reaction of \(\text{MnH(CO)}_5\) and SP, implying that the Pt-H bond in \(\text{trans-}[\text{PtHCl(PPh}_3)_2]\) polarised in such a way that the H ligand carries a positive charge. This is consistent with the suggestion by Chatt and Leigh\(^{221}\) from dipole moment measurements that the H ligand in \(\text{trans-}[\text{PtHCl(PPh}_3)_2]\) is slightly positive. Furthermore, low temperature NMR studies suggest that the reactions of SP and \(\text{trans-}[\text{PtHCl(PPh}_3)_2]\) goes through a cationic hydride intermediate \([\text{PtH(PPh}_3)_2(\text{SP})]^+\), \(^{2.33}\) in which the H ligand would be expected to be even more positively charged than in the neutral starting hydride.

The polarisation of the metal-hydrogen bond in transition metal hydrido complexes is a controversial issue\(^{222-223}\). Recent matrix isolation studies\(^{222}\) using infrared spectroscopy and X-ray photoelectron...
spectroscopy\textsuperscript{224} of MnH(CO)_5 suggest that the H ligand may carry a partial negative charge. It has been suggested that the acidity of the hydrides is a reflection of the weakness of the metal-hydrogen bond rather than a function of the charge on hydrogen\textsuperscript{222}. Thus the original assumption of Bennett and Watt\textsuperscript{153} that Mn-H bond is polarised in the sense Mn\textsuperscript{-} - H\textsuperscript{+} is in doubt. At this stage the factors that control the direction of insertion of olefins into metal-hydrogen bonds are not clearly understood.

Brookes\textsuperscript{200,201} suggested that SP can displace triphenylphosphine from the coordination sphere of platinum(II) to give stable mixed ligand complexes containing P-bonded SP and triphenylphosphine. The work reported in this chapter shows that although such a complex may be formed as an intermediate, it is not stable and disproportionates rapidly to give more symmetrical complexes.

The four-coordinate cationic hydride [PtH(PPh\textsubscript{3})\textsubscript{2}(SP)]\textsuperscript{+}, 2.33 which is postulated as an intermediate in the reaction of SP and trans-[PtHCl(PPh\textsubscript{3})\textsubscript{2}] (Scheme 2.13) has been detected by $^1$H and $^{31}$PNMR spectroscopy at -90°C. Therefore, the first step of the insertion is the displacement of the chloride ligand by P-bonded SP to form the cationic hydride 2.33. However, an intermediate in which both hydride and olefin are coordinated to the platinum could not be detected. Insertion may be fast compared with olefin coordination, and as a result the intermediate with both the hydride and olefin coordinated to the metal is never present in observable concentration.

Direct evidence indicating whether the insertion takes place via a four- or five-coordinate hydrido-olefin complex has not been obtained. However, the work presented in this chapter provides some
indirect evidence. The formation of the complex \(^{\text{trans}}\)[Pt(o-CHMeC\(_6\)H\(_4\)PPh\(_2\)]\(^+\) (SP)]\(^+\), 2.27 (Scheme 2.11) indicates the powerful chelate effect of the SP ligand. It is possible that the olefinic moiety of the SP ligand in the cationic hydride intermediate 2.33 is able to displace an adjacent triphenylphosphine ligand to form a four-coordinate hydrido-olefin complex (Scheme 2.13, B). The displacement of one of the triphenylphosphine ligands by the olefinic moiety of SP could relieve some of the steric congestion around the platinum atom, and provide a pathway for insertion to take place.

The reaction of SP with \(^{\text{trans}}\)[PtHCl(P-i-Pr\(_3\))]\(_2\) is extremely slow (section 2.2.3), probably because the steric bulk of the trisopropylphosphine hinders the approach of the P-donor in SP. The cationic hydride 2.37 analogous to 2.33 is likely to be sterically very crowded. The much slower rate of reaction of \(^{\text{trans}}\)[PtHCl(PPh\(_3\))]\(_2\) with \(_{\circ}\)-vinylphenyldiphenylarsine (SPAS) compared with SP (section 2.2.2, Eq. 2.10) is probably due to the weaker donor properties of the arsine ligand, which results in a slower rate of formation of the cationic hydride intermediate 2.38. The reaction of SP and \(^{\text{trans}}\)[PtHCl(PEt\(_3\))]\(_2\] has been shown by preliminary low temperature
$^1$HNMR studies to proceed through at least two intermediates. The first stage of the reaction is probably the formation of the four-coordinate cationic hydride $[^{\text{PtH(PET}}_3]_2^{\text{(SP)}}]^+$, 2.34 which was detected spectroscopically. However it seems unlikely that the vinyl group of SP would displace a small and basic phosphine such as triethylphosphine from the platinum(II) complex. Therefore the insertion is more likely to proceed through a five-coordinate hydrido-olefin intermediate, 2.35 (Table 2.6). This complex 2.35 has previously been postulated by Clark and Jablonski as the intermediate for the reaction of SP and trans-$[^{\text{PtHCO(PET}}_3]_2^{\text{2+}}$.

In summary, insertion of the $\text{C=C}$ double bond of a chelating olefinic tertiary phosphine (SP, DMSP) or arsine (SPAS) into a Pt-H bond in complexes of the type trans-$[^{\text{PtHClL}}_2^{\text{2}}$ (L = PPh$_3$, PET$_3$, P-i-Pr$_3$, AsPh$_3$) initially goes through a four-coordinate cationic hydride where the donor atom of the olefinic ligand displaces the ligand trans to hydride. The subsequent step, which precedes insertion, is coordination of the olefin which may or may not involve dissociation of one of the tertiary phosphine or arsine ligands on the hydride complex. No direct evidence has been obtained to distinguish these possible routes. However the nature of the insertion reaction clearly depends on a balance of electronic and steric properties of the olefinic ligands and of the ligands on the hydride complexes.
2.3 Experimental

Unless otherwise stated, all reactions were carried out in an atmosphere of dry nitrogen or argon. However, the products were isolated in air since they are air-stable in the solid state.

Benzene and toluene were of analytical reagent grade and were distilled from sodium and benzophenone in a nitrogen atmosphere. All other solvents were of analytical reagent grade and were used without further purification. All other substances besides those listed as starting materials were obtained commercially and used without further purification.

Microanalyses and osmometric molecular weight measurements (Knauer vapour pressure osmometer) were carried out by the Research School of Chemistry Microanalytical Service (Miss Brenda Stevenson and associates). Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected.

Infrared spectra in the range 4000 - 250 cm\(^{-1}\) were recorded on Perkin-Elmer 225, Perkin-Elmer 457 and Perkin-Elmer 683.

Nuclear magnetic resonance spectra were measured using the following instruments:

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<tr>
<th>nucleus</th>
<th>instrument</th>
<th>frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\text{H})</td>
<td>Varian Associates HA100</td>
<td>100 MHz</td>
</tr>
<tr>
<td></td>
<td>Bruker CXP 200</td>
<td>200 MHz</td>
</tr>
<tr>
<td></td>
<td>Jeol FX 200</td>
<td>200 MHz</td>
</tr>
<tr>
<td>(^{31}\text{P})</td>
<td>Bruker B-KR 322S</td>
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<td></td>
<td>Bruker CXP 200</td>
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<td>(^{13}\text{C})</td>
<td>Jeol FX 200</td>
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<tr>
<td></td>
<td>Bruker CXP 200</td>
<td>50.3 MHz</td>
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Table 2.8 Analytical data and decomposition points of the insertion products. Calculated values are in parentheses.

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<tr>
<th>Compound</th>
<th>No</th>
<th>%C</th>
<th>%H</th>
<th>%P</th>
<th>% other</th>
<th>M.W.</th>
<th>Decomp. Point</th>
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<tr>
<td>cis- and trans-([Pt(\text{CHMeC}_6\text{H}_4\text{PPh}_2)\text{Cl}(\text{PPh}_3)])</td>
<td>2.15</td>
<td>58.02 (58.35)</td>
<td>4.19 (4.25)</td>
<td>7.67 (7.92)</td>
<td>4.52 (Cl, 4.53)</td>
<td>782 (771)</td>
<td>220-222</td>
</tr>
<tr>
<td>trans-([Pt(\text{CHMeC}_6\text{H}_4\text{PPh}_2)\text{I}(\text{PPh}_3)])</td>
<td>2.17a</td>
<td>51.94 (52.24)</td>
<td>3.78 (3.81)</td>
<td>7.24 (7.07)</td>
<td></td>
<td>870 (873)</td>
<td>248-250</td>
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<tr>
<td>cis-([Pt(\text{CHMeC}_6\text{H}_4\text{PPh}_2)\text{I}(\text{PPh}_3)])</td>
<td>2.17b</td>
<td>53.17 (52.24)</td>
<td>3.91 (3.81)</td>
<td>6.83 (7.09)</td>
<td></td>
<td></td>
<td>240-242</td>
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<tr>
<td>trans-([Pt(\text{CHMeC}_6\text{H}_4\text{PPh}_2)\text{I}(\text{PPh}_3)\text{CO}]\text{BF}_4)</td>
<td>2.18</td>
<td>54.78 (54.37)</td>
<td>3.92 (3.86)</td>
<td>7.16 (7.19)</td>
<td></td>
<td></td>
<td>140-145</td>
</tr>
<tr>
<td>cis- and trans-([Pt(\text{CHMeC}_6\text{H}_4\text{PPh}_2)\text{I}(\text{PPh}_3)(p\text{-tolNC})]\text{BF}_4)</td>
<td>2.19</td>
<td>58.17 (58.12)</td>
<td>4.35 (4.24)</td>
<td>6.61 (6.52)</td>
<td>1.26 (N, 1.47)</td>
<td>657 (658)</td>
<td>222-225</td>
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<td>cis- and trans-([Pt(\text{CHMeC}_6\text{H}_4\text{PMe}_2)\text{Cl}(\text{PPh}_3)])</td>
<td>2.20</td>
<td>51.25 (51.11)</td>
<td>4.60 (4.44)</td>
<td>9.20 (9.41)</td>
<td>(5.62)(Cl, 5.39)</td>
<td>657 (658)</td>
<td>222-225</td>
</tr>
<tr>
<td>trans-([Pt(\text{CHMeC}_6\text{H}_4\text{AsPh}_2)\text{Cl}(\text{PPh}_3)])</td>
<td>2.21</td>
<td>55.67 (55.25)</td>
<td>4.24 (4.03)</td>
<td>4.15 (3.75)</td>
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<td></td>
<td>781 (826)</td>
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Table 2.8 continued

<table>
<thead>
<tr>
<th>Compound</th>
<th>No</th>
<th>%C</th>
<th>%H</th>
<th>%P</th>
<th>%other</th>
<th>M.W. a</th>
<th>Decomp. Point (°C)</th>
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<tr>
<td>cis-[Pt(o-CHMeC₆H₄PPh₂)Cl(AsPh₃)]b</td>
<td>2.22</td>
<td>52.89 (53.24)</td>
<td>4.26 (3.95)</td>
<td>8.83 (As, 8.63)</td>
<td>190-195</td>
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<tr>
<td>cis-[Pt(o-CHMeC₆H₄PPh₂)Cl(PEt₃)]</td>
<td>2.23</td>
<td>47.91 (48.94)</td>
<td>5.35 (5.21)</td>
<td>10.44 (9.71)</td>
<td>607 (638)</td>
<td>135-140</td>
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<tr>
<td>[Pt(o-CHMeC₆H₄PPh₂)(PEt₃)₂]PF₆</td>
<td>2.24</td>
<td>44.20 (45.40)</td>
<td>5.42 (5.60)</td>
<td>14.00 (14.31)</td>
<td>190-200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Pt(o-CHMeC₆H₄PPh₂)(PPh₃)₂]PF₆ c</td>
<td>2.26</td>
<td>57.69 (57.49)</td>
<td>4.32 (4.16)</td>
<td>11.06 (10.54)</td>
<td>9.45 (9.67)</td>
<td>225-230</td>
<td></td>
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<tr>
<td>trans-[Pt(o-CHMeC₆H₄PPh₂)(SP)]BF₄ c</td>
<td>2.27</td>
<td>54.96 (54.89)</td>
<td>4.16 (4.06)</td>
<td>7.39 (7.03)</td>
<td>197-205</td>
<td></td>
<td></td>
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<tr>
<td>cis-[Pt(o-CHMeC₆H₄PPh₂)₂]c</td>
<td>2.30</td>
<td>60.97 (60.81)</td>
<td>4.77 (4.63)</td>
<td>7.77 (7.79)</td>
<td>784 (774)</td>
<td>230-240</td>
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a: molecular weights by osmometry in dichloromethane at 25°C
b: calculated from M.W. + ½CH₂Cl₂
c: calculated from M.W. + ¼CH₂Cl₂
$^{1}H$ and $^{13}C$ NMR spectra were referenced to internal TMS. All $^{31}P$ NMR spectra, regardless of their temperature, were referenced to external 85% $H_{3}PO_{4}$ at room temperature. Computer simulations of NMR spectra were performed using Laocoon 3, an iterative method. Elemental analyses and melting points are listed in Table 2.8.

2.3.1 Preparation of starting materials

2.3.1.1 Preparation of olefinic ligands

The olefinic ligands $o$-vinylphenyldiphenylphosphine (SP) and $o$-vinylphenyldiphenylarsine (SPAS) were prepared by a literature method, from the reaction of the Grignard reagent of $o$-bromostyrene with chlorodiphenylphosphine and chlorodiphenylarsine respectively in THF. The ligands are white solids with melting point 90-100°C for SP and 68-70°C for SPAS.

The dimethyl analogue of SP, $o$-vinylphenyldimethylphosphine (DMSP) was prepared by a method adapted from that used for SP. The Grignard reagent prepared from $o$-bromostyrene in THF and chlorodimethylphosphine gave DMSP as an air-sensitive colourless liquid (B.P. 60-62°C at 0.7mm Hg) in 80% yield.

The $^{1}H$ and $^{31}P$ NMR data of these olefinic ligands are listed in Table 2.5. The $^{13}C$ NMR data for SP and DMSP are listed in Table 3.5.
2.3.1.2 Preparation of hydrides

The complex \textit{trans}-[PtHCl(PPh\textsubscript{3})\textsubscript{2}] was prepared by reduction of \textit{cis}-[PtCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] with hydrazine in ethanol\textsuperscript{226}. Its iodo analogue, \textit{trans}-[PtI(PPh\textsubscript{3})\textsubscript{2}] was prepared by heating \textit{trans}-[PtHCl(PPh\textsubscript{3})\textsubscript{2}] with NaI in acetone\textsuperscript{186}. The nitrato derivative was prepared by halide abstraction of \textit{trans}-[PtHCl(PPh\textsubscript{3})\textsubscript{2}] with AgBF\textsubscript{4} in MeOH followed by addition of NaNO\textsubscript{3}. The triphenylarsine complex \textit{trans}-[PtHCl(AsPh\textsubscript{3})\textsubscript{2}] was prepared by reaction of the zerovalent platinum complex Pt(AsPh\textsubscript{3})\textsubscript{4} with methanolic hydrochloric acid\textsuperscript{227}. The \textsuperscript{1}HNMR spectrum of \textit{trans}-[PtHCl(AsPh\textsubscript{3})\textsubscript{2}] has not been reported previously; the hydride resonance is at $\delta$-19.0, with $^{1}J$(PtH) value of 1040 Hz. The $^{195}$Pt satellites are very broad because of coupling to the quadrupolar $^{75}$As nuclei.

The complex \textit{trans}-[PtHCl(P\textit{Et}\textsubscript{3})\textsubscript{2}] was prepared by reduction of \textit{cis}-[PtCl\textsubscript{2}(P\textit{Et}\textsubscript{3})\textsubscript{2}] with hydrazine\textsuperscript{186}. The complex \textit{trans}-[PtHCl(P-i-Pr\textsubscript{3})\textsubscript{2}] was prepared by reduction of \textit{trans}-[PtCl\textsubscript{2}(P-i-Pr\textsubscript{3})\textsubscript{2}] with hydrazine\textsuperscript{91}. The complex \textit{trans}-[PtH(acetone)(PPh\textsubscript{3})\textsubscript{2}]BF\textsubscript{4} was prepared by abstraction of the chloride ligand from \textit{trans}-[PtHCl(PPh\textsubscript{3})\textsubscript{2}] using AgBF\textsubscript{4} in acetone, a method adapted from that of Clark and Jablonski\textsuperscript{191}.

2.3.2 Preparation of [Pt(\textit{o}-CHMeC\textsubscript{6}H\textsubscript{4}PPh\textsubscript{2})Cl(PPh\textsubscript{3})], \textsuperscript{2.15}

A solution containing \textit{trans}-[PtHCl(PPh\textsubscript{3})\textsubscript{2}] (0.200g, 0.265mmol) and SP (0.080g, 0.278mmol) in benzene (10ml) was refluxed for 2 hours, then n-pentane (15-20ml) was added to the reaction mixture. The resulting white solid was filtered off and washed with n-pentane (30ml).
The product was dried in vacuo to give 2.15 (0.182g, 88%). Compound 2.15 is almost insoluble in benzene, toluene and saturated hydrocarbons but is more soluble in dichloromethane and chloroform.

2.3.3 Preparation of trans-[Pt(o-CHMeC₆H₄PPh₂)I(PPh₃)]I, 2.17

The complex trans-[PtH(PPh₃)₂] (0.163g, 0.193mmol) and SP (0.065g, 0.225mmol) were dissolved in benzene (10ml). The reaction mixture was refluxed for 2 hours then allowed to cool to room temperature. Addition of n-pentane gave a white solid. The product 2.17 was filtered off, washed with n-pentane (3 x 5ml) then diethyl ether (10ml) and dried in vacuo (0.15g, 89%).

2.3.4 Preparation of [Pt(o-CHMeC₆H₄PPh₂)(PPh₃)(CO)]BF₄, 2.18

The complex [Pt(o-CHMeC₆H₄PPh₂)Cl(PPh₃)], 2.15 (0.127g, 0.162mmol) was stirred in dichloromethane (15ml) while carbon monoxide was bubbled through the solution for 15 minutes. A solution of AgBF₄ (0.036g, 0.185mmol) in acetone (2ml) was added to the reaction mixture. A white precipitate of AgCl formed immediately and it was removed by centrifugation. The clear solution was evaporated to dryness and the residue was recrystallised from dichloromethane-diethyl ether to give 2.18 (0.12g, 83%). The infrared spectrum (Nujol mull) shows ν(C≡O) at 2100(m) cm⁻¹.
2.3.5 Preparation of $[\text{Pt}(\text{o-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})]\text{BF}_4$, 2.19

The complex $[\text{Pt}(\text{o-CHMeC}_6\text{H}_4\text{PPh}_2)\text{Cl}(\text{PPh}_3)]$, 2.15 (0.164g, 0.209mmol) and p-toluonitrile (0.395g, 3.37mmol) were dissolved in dichloromethane (30ml) and AgBF$_4$ (0.051g, 0.262mmol) in acetone (2ml) was added. A white precipitate of AgCl formed instantly and was removed by centrifugation. The clear solution was evaporated to dryness and the product was recrystallised from dichloromethane-diethylether to give 2.19 as a white solid (0.122g, 78%). The infrared spectrum (Nujol mull) shows $v(\text{C}≡\text{N})$ at 2260 cm$^{-1}$.

2.3.6 Preparation of $[\text{Pt}(\text{o-CHMeC}_6\text{H}_4\text{PMe}_2)\text{Cl}(\text{PPh}_3)]$, 2.20

The ligand o-vinylphenyldimethylphosphine (DMSP) (0.022g, 0.134mmol) was added via syringe to a solution of trans-$[\text{PtHCl}(\text{PPh}_3)_2]$ (0.103g, 0.130mmol) in benzene (15ml). The reaction mixture was refluxed for 2 hours and allowed to cool to room temperature. Addition of n-pentane (40ml) gave a white precipitate on cooling to 0°C. The white solid was filtered off, washed with n-pentane (3 × 10ml) and dried in vacuo to yield 2.20 (0.069g, 80%). The compound can be recrystallised from chloroform-diethylether.

2.3.7 Preparation of $[\text{Pt}(\text{o-CHMeC}_6\text{H}_4\text{AsPh}_2)\text{Cl}(\text{PPh}_3)]$, 2.21

A solution of o-vinylphenyldiphenylarsine (SPAS) (0.047g, 0.133mmol) in acetone (1ml) was added to a solution of trans-$[\text{PtHCl}(\text{PPh}_3)_2]$ (0.066g, 0.133mmol) in toluene (15ml). The reaction mixture was refluxed for 7 hours, the solvent was evaporated to dryness and the product was recrystallised from chloroform-diethylether to give 2.21 as a white
solid (0.059g, 82%).

2.3.8 Preparation \( \text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2)\text{Cl(AsPh}_3\text{)]} \), 2.22

A solution containing \( \text{trans-[PtHCl(AsPh}_3\text{)]}_2 \) (0.133g, 0.157mmol) and \( \text{SP} \) (0.048g, 0.166mmol) in benzene (10ml) was refluxed for two hours. The reaction mixture became cloudy due to formation of an insoluble white solid which was removed by centrifugation. Addition of \( n \)-pentane (20ml) to the clear supernatant solution gave a white solid which was recrystallised from dichloromethane-diethylether to give 2.22 (0.079g, 61%).

2.3.9 Reaction of \( \text{o-vinylphenyldiphenylphosphine (SP)} \) with \( \text{trans-[PtHCl(PET}_3\text{)]}_2 \)

A solution of \( \text{trans-[PtHCl(PET}_3\text{)]}_2 \) (0.070g, 0.149mmol) and \( \text{SP} \) (0.052g, 0.180mmol) in benzene (5ml) was refluxed for two hours. The reaction mixture was reduced to ca 1ml, \( n \)-pentane was added and the mixture was cooled to give a white oil. The mixture was evaporated to dryness and trituration of the oily mass with diethylether gave a white solid, which was recrystallised from dichloromethane-ether to give predominantly \( \text{cis-[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2)\text{Cl(PET}_3\text{)]} \), 2.23 (0.057g, 60%).

A similar reaction was carried out again, but after the period of reflux, the reaction mixture was evaporated to dryness. The residue was redissolved in acetone in the presence of a stoichiometric amount of \( \text{NH}_4\text{PF}_6 \). A white precipitate of \( \text{NH}_4\text{Cl} \) formed immediately and was
removed by centrifugation. The clear solution was evaporated to dryness and recrystallised from dichloromethane-methanol giving

\[ \text{[Pt}(\text{a-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{PET}_3)_2]\text{PF}_6 \] (2.24) in 80% yield.

2.3.10 Reaction of \( \text{o-vinylphenyldiphenylphosphine (SP)} \) with \( \text{trans-[PtHCl(P-Pr}_3)_2] \)

A solution containing \( \text{trans-[PtHCl(P-i-Pr}_3)_2] \) (0.141g, 0.256mmol) and SP (0.074g, 0.256mmol) in dichloromethane (4ml) was refluxed for 24 hours. At this stage the \(^1\text{H}NMR\) spectrum showed a small amount of insertion product and a large amount of unchanged starting materials. After refluxing in dichloromethane-methanol (4ml/1ml) for another three days, with continuous monitoring of the \(^1\text{H}NMR\) spectrum, the reaction did not go to completion while the starting hydride slowly decomposed.

2.3.11 Reaction of \( \text{trans-[PtHCl(PPh}_3)_2] \) with two equivalents of \( \text{o-vinylphenyldiphenylphosphine (SP)} \) in the presence of \( \text{NH}_4\text{PF}_6 \)

A suspension of \( \text{trans-[PtHCl(PPh}_3)_2] \) (0.176g, 0.233mmol) and SP (0.142g, 0.492mmol) in acetone (30ml) was refluxed for one hour. The resulting clear solution was cooled, then \( \text{NH}_4\text{PF}_6 \) (0.050g, 0.306mmol) in acetone (2ml) was added. The solution turned cloudy immediately and was stirred for one hour. The white precipitate of \( \text{NH}_4\text{Cl} \) was removed by centrifugation. The clear solution was evaporated to dryness, the residue was dissolved in dichloromethane and the solution was filtered to remove insoluble material (excess \( \text{NH}_4\text{PF}_6 \)).
Crystallisation of the product was induced by addition of diethylether (0.180g). The $^1$H and $^{31}$PNMR spectra (section 2.2.4) indicate that this product is not the reported compound $\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{SP})(\text{PPh}_3))]PF_6$, 2.12 but rather a mixture of $\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]PF_6}$, 2.26 and $\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{SP})]PF_6}$, 2.27. However elemental analyses cannot distinguish between these possibilities. Selective crystallisations from dichloromethane-methanol gave predominantly 2.26, presumably the less soluble component.

For purified mixture found: C 57.19; H 4.32, P 10.50
Calc. for $\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{SP})(\text{PPh}_3))]PF_6}$ (2.12), C$_{58}$H$_{50}$P$_4$F$_6$Pt requires: C 59.04; H 4.27; P 10.50; F 9.66
Calc. for $\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2)\text{SP}]PF_6}$ (2.27), C$_{40}$H$_{35}$P$_3$F$_6$Pt requires: C 52.35; H 3.84; P 10.13; F 12.42
Calc. for $\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]PF_6}$ (2.26), C$_{56}$H$_{48}$P$_4$F$_6$Pt requires: C 58.29; H 4.19; P 10.74; F 9.88.

2.3.12 Reaction of $\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2)\text{Cl}(\text{PPh}_3)]}$, 2.15 with one equivalent of $\text{o-vinylphenyldiphenyolphosphine (SP)}$ in the presence of $\text{AgBF}_4$

Complex $\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2)\text{Cl}(\text{PPh}_3)]}$, 2.15 (0.481g, 0.615mmol) and SP (0.178g, 0.618mmol) were suspended in acetone (40ml) and refluxed for one hour, then $\text{AgBF}_4$ (0.1239, 0.633mmol) was added to the reaction mixture. The precipitate of AgCl was removed by centrifugation. The solution was evaporated to dryness, the residue was redissolved in dichloromethane and the solution was filtered.
Addition of diethylether to the clear solution gave a white solid (0.50g). The $^1$H and $^{31}$PNMR spectra (section 2.2.4) indicate that it is not the compound [Pt(o-CHMeC$_6$H$_4$PPh$_2$)(SP)(PPh$_3$)]BF$_4$, $^{2.12}$ but a mixture of [Pt(o-CHMeC$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$]BF$_4$, $^{2.26}$ and [Pt(o-CHMeC$_6$H$_4$PPh$_2$)(SP)]BF$_4$, $^{2.27}$. However, elemental analysis cannot distinguish between these possibilities. Successive recrystallisations from dichloromethane-methanol gave predominantly [Pt(o-CHMeC$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$]BF$_4$. For the purified mixture found: C 59.74; H 4.47; P 7.87; F 6.75

Calc. for [Pt(o-CHMeC$_6$H$_4$PPh$_2$)(SP)(PPh$_3$)]BF$_4$ (2.12), C$_{58}$H$_{50}$P$_3$BF$_4$Pt requires: C 62.10; H 4.49; P 8.28; F 6.77

Calc. for [Pt(o-CHMeC$_6$H$_4$PPh$_2$)(SP)]BF$_4$ (2.27), C$_{40}$H$_{35}$P$_2$BF$_4$Pt requires: C 55.89; H 4.10; P 7.21; F 8.84

Calc. for [Pt(o-CHMeC$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$]BF$_4$ (2.26), C$_{56}$H$_{48}$P$_3$BF$_4$Pt requires: C 61.38; H 4.41; P 8.48; F 6.93.

2.3.13 Reaction of trans-[PtHCl(PPh$_3$)$_2$] with three equivalents of o-vinylphenyldiphenylphosphine (SP) in the presence of NH$_4$PF$_6$

A suspension of trans-[PtHCl(PPh$_3$)$_2$] (0.100g, 0.132mmol) and SP (0.118g, 0.410mmol) in acetone (30ml) was refluxed for one hour, yielding a clear solution. Addition of NH$_4$PF$_6$ (0.030g, 0.184mmol) to the reaction mixture caused a white precipitate to form instantly. The mixture was stirred for one hour and the white precipitate of NH$_4$Cl was removed by centrifugation. The resulting clear solution was evaporated to dryness, the residue was redissolved in
dichloromethane and the solution was filtered. Addition of
diethylether to the clear solution gave a white solid (0.12g). The
$^1$H and $^{31}$P NMR data indicate that it is not the complex
$$\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2](SP)\text{]}PF_6, 2.13$$
but a mixture of
$$\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2](PPh}_3\text{)}\text{]}PF_6, 2.26$$
and $$\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2](SP)\text{]}PF_6, 2.27$$
(section 2.2.4). Elemental analysis cannot distinguish between these
possibilities. Successive recrystallisation from dichloromethane-
methanol gave predominantly 2.26. For the purified mixture found:

C 58.99; H 4.26; P 10.97
Calc. for $$\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2](SP)\text{]}PF_6 (2.13), C_{60}H_{52}P_4F_6Pt$$
requires: C 59.75; H 4.35; P 10.27
Calc. for $$\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2](PPh}_3\text{)}\text{]}PF_6 (2.27), C_{40}H_{35}P_3F_6Pt$$
requires: C 52.35; H 3.84; P 10.13
Calc. for $$\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2](PPh}_3\text{)}\text{]}PF_6 (2.26), C_{56}H_{48}P_4F_6Pt$$
requires: C 58.29; H 4.19; P 10.74.

2.3.14 Reaction of $$\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2]Cl(PPh}_3\text{)}, 2.15$$ with two
equivalents of $\sigma$-vinylphenyldiphenylphosphine (SP) in the
presence of $\text{AgBF}_4$

A solution of $$\text{[Pt(o-CHMeC}_6\text{H}_4\text{PPh}_2]Cl(PPh}_3\text{)}, 2.15 (0.106g, 0.136mmol)$$
and SP (0.095g, 0.329mmol) in dichloromethane (20ml) was refluxed for
30 minutes and then allowed to cool to room temperature. A solution
of $\text{AgBF}_4$ (0.029g, 0.147mmol) in acetone (2ml) was added to the reaction
mixture. A white precipitate of AgCl formed instantly and was removed
by centrifugation. The resulting clear solution was evaporated to
dryness, the residue was dissolved in dichloromethane and the solution
was filtered. Addition of diethylether gave a white product (0.12g).
The $^1$H and $^{31}$PNMR data indicate that it is not the complex

$$\text{[Pt(o-CHMeC}_6^\text{H}_4\text{PPh}_2\text{)(SP)}\text{_2]BF}_4, 2.13$$

but a mixture of

$$\text{[Pt(o-CHMeC}_6^\text{H}_4\text{PPh}_2\text{)(PPh}_3\text{_2]BF}_4, 2.26$$

and

$$\text{[Pt(o-CHMeC}_6^\text{H}_4\text{PPh}_2\text{)(SP)]BF}_4, 2.27.$$  

However, elemental analysis cannot distinguish between these possibilities and successive recrystallisations from dichloromethane-methanol gave predominantly 2.26.

For the purified mixture found: C 60.05; H 4.93

Calc. for \([\text{Pt(o-CHMeC}_6^\text{H}_4\text{PPh}_2\text{)(SP)}\text{_2]BF}_4, 2.13, C_{60.52}H_{52}P_{3}BF_4Pt\) requires:

C 62.78; H 4.57

Calc. for \([\text{Pt(o-CHMeC}_6^\text{H}_4\text{PPh}_2\text{)(SP)]BF}_4, 2.27, C_{40.35}H_{35}P_{2}BF_4Pt\) requires:

C 55.89; H 4.10

Calc. for \([\text{Pt(o-CHMeC}_6^\text{H}_4\text{PPh}_2\text{)(PPh}_3\text{_2]BF}_4, 2.26, C_{61.38}H_{48}P_{3}BF_4Pt\)

requires: C 61.38; H 4.41

2.3.15 Reaction of \([\text{Pt(o-CHMeC}_6^\text{H}_4\text{PPh}_2\text{)(PPh}_3\text{_2]PF}_6, 2.26 with potassium iodide\)

A solution of KI (0.012g, 0.072mmol) in acetone (10ml) was added to a solution of \([\text{Pt(o-CHMeC}_6^\text{H}_4\text{PPh}_2\text{)(PPh}_3\text{_2]PF}_6, 2.26 (0.072g, 0.062mmol) in acetone (5ml). A white precipitate formed instantly and the reaction mixture was refluxed for 15 minutes. The white precipitate was filtered off and washed with dichloromethane (3 x 10ml). The dichloromethane washings were evaporated to small volume and addition of n-pentane gave a white solid (0.030g, 56%). The $^1$H and $^{31}$PNMR and elemental analyses data indicate that the product is \(\text{cis-[Pt(o-CHMeC}_6^\text{H}_4\text{PPh}_2\text{I(PPh}_3\text{)]}, 2.17b.\)
2.3.16 Preparation of $[\text{Pt}(\sigma-\text{CHMeC}_6\text{H}_4\text{PPh}_2)\text{Cl}(\text{PPh}_3)]PF_6$, 2.28

A solution containing $[\text{Pt}(\sigma-\text{CHMeC}_6\text{H}_4\text{PPh}_2)\text{Cl}(\text{PPh}_3)]$, 2.15 (0.161g, 0.206mmol) and triphenylphosphine (0.060g, 0.229mmol) in a mixture of dichloromethane (5ml) and acetone (5ml) was treated with a solution of $\text{NH}_4\text{PF}_6$ (0.035g, 0.215mmol) in acetone (2ml). The initially clear solution turned cloudy instantly. The reaction mixture was stirred at room temperature for 4 hours. A white precipitate of $\text{NH}_4\text{Cl}$ was removed by centrifugation. The clear solution was evaporated to dryness, the residue was redissolved in dichloromethane and the solution was filtered. The solution was reduced in volume and addition of methanol gave a white crystalline solid on cooling. The product was filtered off, washed with diethylether (3 x 5ml) and dried in vacuo to give 2.26 (0.20g, 84%).

2.3.17 Preparation of trans-$[\text{Pt}(\sigma-\text{CHMeC}_6\text{H}_4\text{PPh}_2)\text{SP})\text{BF}_4]$, 2.27

A solution of cis-$[\text{Pt}(\sigma-\text{CHMeC}_6\text{H}_4\text{PPh}_2)\text{Cl}(\text{AsPh}_3)]$, 2.22 (0.099g, 0.120mmol) in acetone (20ml) was treated with a solution of $\text{AgBF}_4$ (0.034g, 0.175mmol) in acetone (2ml). The clear reaction mixture turned cloudy instantly because of the formation of $\text{AgCl}$. The ligand $\text{SP}$ (0.070g, 0.243mmol) was added and the reaction mixture was refluxed for 0.5 hour. After cooling the mixture to room temperature, $\text{AgCl}$ was removed by centrifugation. The resulting clear solution was evaporated to dryness, the residue was redissolved in dichloromethane (3ml) and the solution was filtered. Addition of diethylether to the solution gave a white solid. The product was filtered off, washed with diethylether (3 x 5ml) and dried in vacuo to give 2.27 (0.070g, 68%).
2.3.18 Preparation of cis-[Pt(o-CHMeC₆H₄PPh₂)₂]BF₄, 2.30

Sodium borohydride (0.009g, 0.238mmol) in water (0.5ml) was added to the solution of [Pt(o-CHMeC₆H₄PPh₂)(SP)]BF₄, 2.27 (0.07g, 0.081mmol) in acetone (10ml), resulting in the instantaneous formation of a white solid. The reaction mixture was stirred for 4 hours. The suspension was evaporated to dryness, the residue was taken up in chloroform and the solution was filtered. The clear filtrate was evaporated to dryness. Recrystallisation of the residue from dichloromethane-methanol gave 2.30 as a white crystalline solid (0.05g, 80%).

2.3.19 Low temperature in situ NMR experiments on the reaction of trans-[PtHCl(PPh₃)₂] with o-vinylphenyldiphenylphosphine (SP)

A mixture of trans-[PtHCl(PPh₃)₂] (0.100g, 0.132mmol) and SP (0.038g, 0.132mmol) was dissolved in CD₂Cl₂ (4ml) in a Schlenck flask under a dry nitrogen atmosphere at -75°C to -80°C (dry ice-ether bath). The mixture was vigorously stirred at this temperature for 10 minutes, then about 1ml of the reaction mixture was transferred via a cannula capped at one end by a small piece of filter paper into a capped NMR tube cooled in a dry ice-ether bath. The solution was transferred by applying a small amount of suction at the receiving end, while pressurising the other end with nitrogen. The ¹H NMR spectra of this sample were recorded immediately from -90°C to -30°C, 0°C and then at room temperature. The results are discussed in section 2.2.6. A similar technique was used to study the ³¹P NMR spectra at low temperature.

During the experiment at low temperature, it was very difficult to dissolve the reactants completely. It was also difficult to observe
the solution because the reaction flask was submerged in the dry ice-ether bath. Hence despite the care in weighing out stoichiometric amounts of reactants, it is possible that the reactants in the NMR tube were not present in exactly a 1:1 molar ratio.

As discussed in Section 1.2.3, zerovalent metal complexes of the nickel triad may have tetrahedral, trigonal planar or linear geometries, depending on the metal and on the electronic and steric properties of the ligands. Complexes of this triad containing a bifunctional, potentially chelating ligand such as p-vinylphenylidiphosphino-phosphine should provide an excellent opportunity to study the interplay of these factors.

The objective of this work was therefore to synthesise complexes of the zerovalent nickel triad containing p-vinylphenylidiphosphino-phosphine (VP) as the only ligand and to examine their structures and reactivities towards acids.

3.1.1 Synthesis of stabilized palladium and platinum complexes

In this section, the major literature methods to prepare zerovalent nickel, palladium and platinum complexes are briefly surveyed. These synthetic methods are:

1. Reduction of the divalent metal complexes by appropriate reducing agents, including metals, sodium borohydride, hydrazine and aluminium alkyls (Eq. 3.1 to Eq. 3.5).
CHAPTER THREE
COMPLEXES OF OLEFINIC TERTIARY PHOSPHINES WITH ZEROVALENT
NICKEL, PALLADIUM AND PLATINUM

3.1 Introduction

As discussed in section 1.2.3, zerovalent metal complexes of the nickel triad may have tetrahedral, trigonal planar or linear geometries, depending on the metal and on the electronic and steric properties of the ligands. Complexes of this triad containing a bifunctional, potentially chelating ligand such as \( \alpha \)-vinylphenyldiphenylphosphine should provide an excellent opportunity to study the interplay of these factors.

The objective of this work was therefore to synthesize complexes of the zerovalent nickel triad containing \( \alpha \)-vinylphenyldiphenylphosphine (SP) as the only ligand and to examine their structures and reactivities towards acids.

3.1.1 Syntheses of nickel(0), palladium(0) and platinum(0) complexes

In this section, the major literature methods to prepare zerovalent nickel, palladium and platinum complexes are briefly surveyed. These synthetic methods are:

(1) Reduction of the divalent metal complexes by appropriate reducing agents, including metals, sodium borohydride, hydrazine and aluminium alkyls (Eq. 3.1 to Eq. 3.6).
\[
\text{trans-[PtCl}_2(\text{PCy}_3)_2] \rightarrow_{1\% \text{Na/Hg}}^{\text{THF}} \text{Pt(PCy}_3)_2
\]

Eq. 3.1 \textsuperscript{107}

\[
\text{NiCl}_2 + \text{PPh}_3 \text{ excess} \rightarrow_{\text{C}_2\text{H}_4, \text{Zn}}^{\text{THF}} \text{Ni(PPh}_3)_2(\text{C}_2\text{H}_4)
\]

Eq. 3.2 \textsuperscript{229}

\[
[\text{Pt(PPh}_3)_2(\text{CO}_3)] \rightarrow_{\text{NaBH}_4, \text{ethanol}} \text{Pt(PPh}_3)_2(\text{C}_2\text{H}_4)
\]

Eq. 3.3 \textsuperscript{230}

\[
\text{cis-[PtCl}_2(\text{PPh}_3)_2] \rightarrow_{\text{N}_2\text{H}_4, \text{H}_2\text{O}}^{\text{EtOH, PPh}_3} \text{Pt(PPh}_3)_3
\]

Eq. 3.4 \textsuperscript{106}

\[
\text{PdCl}_2 + \text{PPh}_3 \text{ excess} \rightarrow_{\text{DMSO}}^{\text{N}_2\text{H}_4, 140^\circ\text{C}} \text{Pd(PPh}_3)_4
\]

Eq. 3.5 \textsuperscript{231}

\[
\text{Pd(acac)}_2 + \text{PPh}_3 \text{ excess} + \text{C}_2\text{H}_4 \rightarrow_{\text{toluene/Et}_2\text{O}} \text{Al(OEt)(Et)}_2 \rightarrow \text{Pd(PPh}_3)_2(\text{C}_2\text{H}_4)
\]

Eq. 3.6 \textsuperscript{232}
(2) Ligand exchange using an appropriate source of zerovalent metal complexes (Eq. 3.7 to Eq. 3.9)

\[
\begin{align*}
\text{Pt(COD)}_2 & + \text{C}_2\text{H}_4 & \rightarrow & \text{Pt(C}_2\text{H}_4)_3 \\
\text{Pt(C}_2\text{H}_4)_3 & + \text{PCy}_3 & \rightarrow & \text{Pt(PCy}_3\text{(C}_2\text{H}_4)_2}
\end{align*}
\]

Eq. 3.7

\[
Pd_2\text{dba}_3 + L + L' & \rightarrow PdL'\]

dba = dibenzylideneacetone
\[L = 1,5\text{-cyclooctadiene, norborndiene}\]
\[L' = \text{maleic anhydride}\]

Eq. 3.8

\[
\text{Ni(COD)}_2 + 2\text{P(p-tol)}_3 + \text{PhCH=CHPh} & \rightarrow \text{Ni[P(p-tol)}_3\text{]}_2(\text{PhCH=CHPh})
\]

Eq. 3.9

(3) Reductive elimination of stable molecules from an organo-derivative of the divalent metal (Eq. 3.10 - Eq. 3.12).

\[
\begin{align*}
\left\langle \begin{array}{c}
\downarrow \\
M \\
\end{array} \right\rangle & + \text{PR}_3 & \rightarrow & \text{M(PPh}_3\text{)}_4
\end{align*}
\]

\[R = \text{Ph, Et, } M = \text{Ni}; \quad R = \text{Ph, } M = \text{Pd}\]

Eq. 3.10
(4) Direct synthesis from the metal (Eq. 3.13)

\[
\text{Ni(II)oxalate} \xrightarrow{\Delta} \text{Ni(metal)} + 4L \quad \text{NiL}_4
\]

\[
L = \text{PF}_3, \text{CF}_3\text{CF}_2, \text{CCl}_3\text{PF}_2.
\]

146.

3.1.2 Protonation of zerovalent metal complexes of the nickel triad

Low valent metal complexes are susceptible to attack by electrophiles, including protonic acids. These reactions are a model for the behaviour of low valent metal complexes in catalytic...
oxidation-reduction reactions and in hydrogenation\textsuperscript{1,2,13}.

The reaction of Pt(PPh\textsubscript{3})\textsubscript{3} with HX results in the formation of a platinum(II) hydride complex\textsuperscript{241}. This species can be cationic, [PtH(PPh\textsubscript{3})\textsubscript{3}]\textsuperscript{+}X\textsuperscript{-}, or neutral, trans-[PtHX(PPh\textsubscript{3})\textsubscript{2}], depending on the nature of the anion (X) and on the reaction medium. The cationic platinum(II) complexes containing noncoordinating anions such as ClO\textsubscript{4}\textsuperscript{-}, BF\textsubscript{4}\textsuperscript{-} or HSO\textsubscript{4}\textsuperscript{-} can be isolated as the appropriate salts. Neutral platinum(II) complexes with a trans geometry are obtained for anions such as CN\textsuperscript{-} with a higher nucleophilicity towards platinum (Eq. 3.14). If the anion is chloride, the reaction product is dependent on the solvent. Polar solvents favour the formation of the ionic species whereas non-polar solvents give the neutral complexes.

Protonation of the zerovalent metal olefin complex, Pt(COD)\textsubscript{2} with HBF\textsubscript{4} or HPF\textsubscript{6} gives the cyclooctenyl complex (Eq. 3.15)\textsuperscript{242}.

\[
\text{Pt(COD)\textsubscript{2} + HX} \xrightarrow{X = \text{BF}_4/\text{PF}_6} \text{[Cyclooctenyl]}^+ \xrightarrow{\text{X}^\text{-}} \text{trans-[PtHX(PPh\textsubscript{3})\textsubscript{2}]} \]

Eq. 3.14
The palladium and nickel complexes, M(PPh$_3$)$_4$ do not give the corresponding hydrides on reaction with acids at room temperature. Dihalo complexes are isolated and hydrogen is evolved. A mechanism proposed for these reactions is shown in Scheme 3.1. Oxidative addition of acid to the initially formed hydride complex, MHX(PPh$_3$)$_2$ forms a tetravalent metal dihydride complex, which reductively eliminates hydrogen.$^{38b}$

$$
M(PPh_3)_4 \rightarrow M(PPh_3)_3 + HX \\
\text{MH}(X)(PPh_3)_2 \\
M(PPh_3)_2 + H_2 \leftarrow \text{MH}_2(X)(PPh_3)_2
$$

Scheme 3.1 Mechanism for protonation of M(PPh$_3$)$_4$ (M = Ni, Pd)

Kudo and coworkers$^{243}$ have reported that both Pd(CO)(PPh$_3$)$_3$ and Pd(PPh$_3$)$_4$ react with HCl at -50°C in diethylether to give the hydride $^{\text{trans-}[PdHCl(PPh_3)_2]}$ (Table 3.1). Van der Linde$^{244}$ has observed a similar reaction with the 14-electron complex, Pd(PC$_3$)$_2$ (Table 3.1). Protonation of nickel(0) complexes, e.g. Ni(diphos)$_2$ or Ni[P(OR)$_3$]$_4$, containing ligands which do not readily dissociate in
Table 3.1 Oxidative addition of inorganic acids, HX to zerovalent complexes of the nickel triad.

<table>
<thead>
<tr>
<th>Complex</th>
<th>X</th>
<th>Product</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(PPh$_3$)$_4$</td>
<td>Cl</td>
<td>trans-[PdCl$_2$(PPh$_3$)$_2$]</td>
<td>241</td>
</tr>
<tr>
<td>Pd(CO)(PPh$_3$)$_3$</td>
<td>Cl</td>
<td>trans-[PdHCl(PPh$_3$)$_2$]</td>
<td>243</td>
</tr>
<tr>
<td>Pd(PPh$_3$)$_4$</td>
<td>Cl</td>
<td>trans-[PdHCl(PPh$_3$)$_2$]</td>
<td>243</td>
</tr>
<tr>
<td>Pd(olefin)(PPh$_3$)$_2$</td>
<td>Cl</td>
<td>trans-[PdHCl(PPh$_3$)$_2$]</td>
<td>246</td>
</tr>
<tr>
<td>Pd(PCy$_3$)$_2$</td>
<td>Cl</td>
<td>trans-[PdHCl(PCy$_3$)$_2$]</td>
<td>244</td>
</tr>
<tr>
<td>Pt(PPh$_3$)$_3$</td>
<td>ClO$_4$</td>
<td>[PtH(PPh$_3$)$_3$]ClO$_4$</td>
<td>241</td>
</tr>
<tr>
<td></td>
<td>BF$_4$</td>
<td>[PtH(PPh$_3$)$_3$]BF$_4$</td>
<td>241</td>
</tr>
<tr>
<td></td>
<td>HSO$_4$</td>
<td>[PtH(PPh$_3$)$_3$]HSO$_4$</td>
<td>241</td>
</tr>
<tr>
<td></td>
<td>CN</td>
<td>trans-[PtH(CN)(PPh$_3$)$_2$]</td>
<td>241</td>
</tr>
<tr>
<td></td>
<td>NCS</td>
<td>trans-[PtH(NCS)(PPh$_3$)$_2$]</td>
<td>241</td>
</tr>
<tr>
<td>Ni[P(OEt)$_3$]$_4$</td>
<td>Cl</td>
<td>[NiH(P(OEt)$_3$)$_4$]Cl</td>
<td>84, 85, 245</td>
</tr>
<tr>
<td>Ni(diphos)$_2$</td>
<td>Cl</td>
<td>[NiH(diphos)$_2$]Cl</td>
<td>84, 85, 245</td>
</tr>
<tr>
<td>Ni(PCy$_3$)$_3$</td>
<td>Cl</td>
<td>NiHCl(PCy$_3$)$_2$</td>
<td>247</td>
</tr>
</tbody>
</table>

- a: at $-50^{\circ}C$
- b: olefin = styrene, ethyl methacrylate, methyl methacrylate, methacrylonitrile, methyl acrylate or dimethyl maleate
solution gives five-coordinate hydrido nickel(II) complexes (Table 3.1). 

3.2 Results and Discussion

3.2.1 Syntheses of bis(o-vinylphenyldiphenylphosphine)platinum(0) and its nickel analogue

Initial attempts to prepare bis(o-vinylphenyldiphenylphosphine) platinum(0) [Pt(SP)₂, 3.1] by reduction of the divalent platinum complex PtCl₂(SP), 3.2 with hydrazine or with zinc dust did not give the desired product.

The complex Pt(SP)₂ was prepared for the first time by reduction of PtCl₂(SP), 3.2 with 1% sodium amalgam in the presence of one equivalent of SP in THF at -30°C (Eq. 3.16). The yield in this reaction is variable (10-50%) and a mixture of products including Pt(SP)₂ and polymeric material is formed. This synthetic method is unsatisfactory, perhaps because the starting material 3.2 is poorly soluble, thus causing
difficulties in controlling temperature and stoichiometry. When
the reaction was carried out at room temperature, extensive
decomposition to metallic platinum occurred.

A more effective method of preparing Pt(SP)$_2$ is from
bis(1,5-cyclooctadiene)platinum(O), Pt(COD)$_2$. Ligand exchange of
Pt(COD)$_2$ with two equivalents of SP gives Pt(SP)$_2$, 3.1 as a bright
yellow solid in quantitative yield (Eq. 3.17).

\[
\text{Pt(COD)$_2$ + 2 SP} \xrightarrow{\text{toluene RT}} \text{Pt(SP)$_2$ + 2 COD}
\]

Eq. 3.17

This complex is slightly air-sensitive in the solid state and is
soluble in benzene, toluene, diethylether and THF. It is insoluble
in saturated hydrocarbons and alcohols.

The nickel analogue, Ni(SP)$_2$, 3.3, a bright yellow air-
sensitive solid, is prepared in quantitative yield by a similar
method from Ni(COD)$_2$ and two equivalents of SP. It can also be
prepared in excellent yield (91%) by direct reduction of anhydrous
bis(acetylacetonato)nickel(II), Ni(acac)$_2$ with triethylaluminium
(AlEt$_3$) in the presence of two equivalents of SP in toluene at \(-30^\circ\text{C}\)
(Scheme 3.2).

\[
\text{Ni(COD)$_2$ + 2 SP} \xrightarrow{\text{Et$_2$O -30^\circ\text{C}}} \text{Ni(SP)$_2$} \xleftarrow{\text{AlEt$_3$ \text{Toluene -30^\circ\text{C}}}} \text{Ni(acac)$_2$ + 2 SP}
\]

Scheme 3.2 Synthetic routes to prepare Ni(SP)$_2$
The complexes Pt(SP)$_2$ and Ni(SP)$_2$ were characterised by $^1$H, $^{31}$P and $^{13}$C NMR spectroscopy, infrared spectroscopy and elemental analyses. A molecular weight measurement by osmometry in toluene at 37°C indicates that Pt(SP)$_2$ is a monomeric complex and this result is confirmed by its mass spectrum which shows a molecular ion at m/e = 771. The nickel analogue, Ni(SP)$_2$, is also monomeric as suggested by its mass spectrum which shows a molecular ion (m/e = 634). The osmometric molecular weight determination of Ni(SP)$_2$ was not attempted because the complex is extremely air-sensitive in solution.

Infrared spectra of both Ni(SP)$_2$ and Pt(SP)$_2$ in the solid state show no C=C stretching bands, which typically occur around 1620 cm$^{-1}$ and therefore the olefinic moiety of both SP ligands is coordinated to the metal (Figure 3.2).

The $^1$H and $^{31}$PNMR spectra of Pt(SP)$_2$ and Ni(SP)$_2$ are invariant over the temperature range from room temperature to -80°C.

The $^1$HNMR spectrum of Pt(SP)$_2$ (Figure 3.1 and Table 3.2) shows three multiplets accompanied by $^{195}$Pt satellites in the region $\delta$2.5 to $\delta$4.1. They are assigned to the olefinic protons of the SP ligand. These resonances exhibit $^{31}$P couplings, as well as interproton couplings. Computer simulation of this spectrum gives the values of $J(H^1H^3)$ 9.35 Hz, $J(H^3P^1)$ 4.23 Hz, $J(H^3P^2)$ 1.44 Hz, $J(H^1H^2)$ 8.25 Hz, $J(H^2P^1) = J(H^2P^2)$ = 4.13 Hz, $J(H^1P^1) = J(H^1P^2)$ = 3.45 Hz. On $^{31}$P decoupling, each of the three multiplets collapse, giving a doublet($\delta$2.47,$H^3$), a doublet($\delta$3.33,$H^2$) and a doublet of doublets($\delta$4.05,$H^1$). The resonances of the olefinic protons are shifted significantly upfield from those of free SP (Table 3.2). This trend is usually observed both in simple olefinic complexes and in complexes of the olefinic tertiary phosphine SP (Tables 3.3 and 3.4). The resonance of $H^3$ (protons numbered as shown
Table 3.2 $^{1}H(31p)$ and $^{31}p(1H)$ NMR parameters for Pt(SP)$_2$, Ni(SP)$_2$, Pt(DMSP)$_2$.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\delta H^1$</th>
<th>$\delta H^2$</th>
<th>$\delta H^3$</th>
<th>$^{3}J(H^1H^2)$</th>
<th>$^{3}J(H^1H^3)$</th>
<th>$\delta P$</th>
<th>$\Delta c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(SP)$_2$</td>
<td>4.05(dd)</td>
<td>3.33(d)</td>
<td>2.47(d)</td>
<td>8.3</td>
<td>9.4</td>
<td>17.6</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>[43.3]</td>
<td>[60.6]</td>
<td>[57.2]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(DMSP)$_2$</td>
<td>4.45(dd)</td>
<td>3.38(d)</td>
<td>2.72(d)</td>
<td>8.7</td>
<td>11.8</td>
<td>42.5</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>[42.6]</td>
<td>[59.3]</td>
<td>[55.1]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(DMSP)$_2$</td>
<td>3.98(dd)</td>
<td>3.24(d)</td>
<td>2.30(d)</td>
<td>8.2</td>
<td>9.1</td>
<td>-24.1</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>[42.6]</td>
<td>[59.3]</td>
<td>[55.1]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Chemical structure](image)

Ni(SP)$_2$: 4.05(dd), 3.33(d), 2.47(d), 8.3, 9.4, 17.6, 31
Pt(DMSP)$_2$: 4.45(dd), 3.38(d), 2.72(d), 8.7, 11.8, 42.5, 56
Pt(DMSP)$_2$: 3.98(dd), 3.24(d), 2.30(d), 8.2, 9.1, -24.1, 33

$a$: $^1$HNMR spectra were measured in d$_8$-toluene with chemical shifts ($\delta$) in ppm downfield of TMS. $^{31}$PNMR spectra were measured in toluene/d$_8$-toluene, chemical shifts ($\delta$) are referenced to external 85% H$_3$PO$_4$ and are positive to low field. All coupling constants ($J$) are in Hz. All spectra were measured at room temperature unless otherwise stated.

$b$: measured at -50°C

$c$: coordination shifts ($\delta$) = $\delta P$(free) - $\delta P$(coordinated)
### Table 3.3 \(^1\)HNMR parameters of some SP containing complexes\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta H^1)</th>
<th>(\delta H^2)</th>
<th>(\delta H^3)</th>
<th>(J(H^1H^2))</th>
<th>(J(H^1H^3))</th>
<th>(J(H^2H^3))</th>
<th>other coupling constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(CO)(_4)(SP)</td>
<td>5.06(7)</td>
<td>3.25(dd)</td>
<td>2.86(dd)</td>
<td>9.0</td>
<td>13.0</td>
<td>0</td>
<td>(J(\text{PH}^2) = J(\text{PH}^3) = 5.0)</td>
</tr>
<tr>
<td>Fe(CO)(_3)(SP)</td>
<td>4.0(8)</td>
<td>2.73(7)</td>
<td>1.94(td)(^b)</td>
<td>8.5</td>
<td>9.8</td>
<td>2.3</td>
<td>(J(\text{PH}^1) = 4.55)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(J(\text{PH}^2) = 5.55)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(J(\text{PH}^3) = 9.35)</td>
</tr>
<tr>
<td>Ru(CO)(_3)(SP)</td>
<td>3.96(6)</td>
<td>2.45(7)</td>
<td>1.62(td)(^b)</td>
<td>8.5</td>
<td>9.0</td>
<td>3.0</td>
<td>(J(\text{PH}^1) = 3.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(J(\text{PH}^2) = 5.0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(J(\text{PH}^3) = 8.0)</td>
</tr>
<tr>
<td>Fe(CO)(_2)(SP)(_2), free</td>
<td>c</td>
<td>5.10(d)</td>
<td>5.50(d)</td>
<td>10.0</td>
<td>17.0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>coordinated</td>
<td>2.98(m)</td>
<td>2.3(m)</td>
<td>2.3(m)</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>Ru(CO)(_2)(SP)(_2), free</td>
<td>c</td>
<td>5.10(d)</td>
<td>5.50(d)</td>
<td>11.0</td>
<td>17.0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>coordinated</td>
<td>2.84(m)</td>
<td>1.9(m)</td>
<td>1.9(m)</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>d</td>
</tr>
</tbody>
</table>

\(^a\): \(^1\)HNMR spectra measured in C\(_6\)D\(_6\) at room temperature with chemical shifts (\(\delta\)) in ppm downfield of TMS, coupling constants (\(J\)) in Hz, protons are numbered as in Table 3.2, reproduced from reference 147.

\(^b\): 1:2:1 triplet of doublets.
\(^c\): obscured by aromatic protons.
\(^d\): spectrum too complex to obtain coupling constants.
Table 3.4 $^1$H and $^{13}$CNMR data of some platinum(0) olefin complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$HNMR</th>
<th>$^{13}$CNMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solv.</td>
<td>T(°C)</td>
</tr>
<tr>
<td>Pt(COD)$_2$</td>
<td>C$_6$D$_6$</td>
<td>RT</td>
</tr>
<tr>
<td>Pt(C$_2$H$_4$)$_3$</td>
<td>C$_6$H$_6$</td>
<td>18</td>
</tr>
<tr>
<td>tris(bicyclo[2.2.1]heptene)Pt(0)</td>
<td>C$_6$D$_6$</td>
<td>RT</td>
</tr>
<tr>
<td>tris(trans-cyclo-octene)Pt(0)</td>
<td>C$_6$D$_6$</td>
<td>RT</td>
</tr>
<tr>
<td>Pt(PEt$_3$)$_2$(C$_2$H$_4$)</td>
<td>C$_6$D$_6$</td>
<td>RT</td>
</tr>
<tr>
<td>Pt(PCy$_3$)(C$_2$H$_4$)$_2$</td>
<td>C$_6$D$_6$</td>
<td>RT</td>
</tr>
</tbody>
</table>

a: chemical shifts (δ) in ppm downfield of TMS, coupling constants (J) in Hz.
Figure 3.1 $^1$HNMR spectra (200 MHz) of Pt(α-CH$_2$=CHC$_6$H$_4$PPh$_2$)$_2$[Pt(SP)$_2$, 3.1] in d$_8$-toluene at room temperature

(A) $^1$HNMR spectrum
(B) $^1$H($^3$P)NMR spectrum
(X) residual toluene
Infrared spectra (KBr disk) of SP (A), Pt(SP)₂ (B), Ni(SP)₂ (C).

Figure 3.2
in Table 3.2) is shifted upfield more than that of $H^2$, and becomes
the highest field olefinic proton. However, in free SP, $H^2$ is the
highest field olefinic proton. This trend is also observed in the
NMR spectra of the zerovalent metal complexes Fe(CO)$_3$(SP), 1.1 and
Ru(CO)$_3$(SP), 1.3 (Table 3.3)$^{147}$. The magnitudes of the interproton
coupling constants also change from their values in the free ligand.
The trans-proton coupling constant $^3J(H^1H^3)$ is reduced significantly
from 18.0 Hz to 9.4 Hz, whereas the cis-proton coupling constant
$^3J(H^1H^2)$ is reduced only slightly from 11.0 Hz to 8.3 Hz. As a result,
the magnitudes of the cis and trans coupling constants between the
olefinic protons in Pt(SP)$_2$ are comparable [$^3J(H^1H^2) = 8.3$, $^3J(H^1H^3) = 9.4$ Hz].
The values of the coupling constants of the olefinic protons to $^{195}$Pt are
43.3 Hz for $^1J$($PtH^1$), 60.6 Hz for $^1J$($PtH^2$) and 57.2 Hz for $^1J$($PtH^3$). These
values are comparable with those in other zerovalent platinum olefin
complexes such as Pt(COD)$_2$ (55 Hz)$^{133}$, Pt(C$_2$H$_4$)$_3$ (57 Hz)$^{133}$, Pt(PEt$_3$)$_2$(C$_2$H$_4$)
(55 Hz)$^{143}$ etc. (Table 3.4).

The $^{31}$PNMR spectrum shows a sharp singlet with $^{195}$Pt satellites
at 17.6 [$^1J$(PtP) = 3130 Hz]. Hence at room temperature the two
phosphorus nuclei are equivalent. Upon coordination, the $^{31}$P resonance
of SP is shifted downfield as expected, compared with its position in
the free ligand [coordination shift ($\Delta$) = 31 ppm]. The magnitude of
$^1J$(PtP) in Pt(SP)$_2$ (3130 Hz) is smaller than that in the tetrahedral
complex, Pt(PPh$_3$)$_4$ (3829 Hz) (Table 1.3)$^{117}$. Therefore, the olefins
exert a considerable electronic effect on the Pt-P bonds. The values
of $^1J$(PtP) in the trigonal planar complexes Pt(PPh$_3$)$_3$ (4438 Hz) (Table
1.3)$^{117}$ and Pt(PPh$_3$)$_2$(C$_2$H$_4$) (3694 Hz) (Table 1.8)$^{117}$ show a similar
trend, in that coordination of olefin considerably reduces the $^1J$(PtP)
Table 3.5 $^{13}$CNMR parameters for M(SP)$_2$ complexes for M = Ni, Pd and Pt$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solv. temp.</th>
<th>$\delta C_\alpha$ (o C)</th>
<th>$J(C_\alpha P)$ (Hz)</th>
<th>$\delta C_\beta$ (o C)</th>
<th>$J(C_\beta P)$ (Hz)</th>
<th>$J(C_\alpha H)$</th>
<th>$J(C_\beta H)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP:</td>
<td>CD$_2$Cl$_2$ RT</td>
<td>125.7</td>
<td>4.3</td>
<td>115.9</td>
<td>1.7</td>
<td>156, 156</td>
<td></td>
</tr>
<tr>
<td>Pt(SP)$_2$</td>
<td>CD$_2$Cl$_2$ RT</td>
<td>64.8$^b$</td>
<td>37.0</td>
<td>32.1$^c$</td>
<td>0</td>
<td>154, 154</td>
<td></td>
</tr>
<tr>
<td>Ni(SP)$_2$</td>
<td>THF RT</td>
<td>82.7</td>
<td>23.6</td>
<td>54.7</td>
<td>0</td>
<td>156, 156</td>
<td></td>
</tr>
<tr>
<td>Pd(SP)$_2$</td>
<td>THF RT</td>
<td>109.8</td>
<td>d</td>
<td>81.5</td>
<td>d</td>
<td>151.7, 158.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>THF -80</td>
<td>106.2</td>
<td>d</td>
<td>78.3</td>
<td>d</td>
<td>e</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>122.5</td>
<td>d</td>
<td>115.5</td>
<td>d</td>
<td>e</td>
<td></td>
</tr>
</tbody>
</table>

$^a$: chemical shifts (o C) in ppm downfield of TMS, coupling constants (J) in Hz.

$^b$: $J(PtC_\alpha) = 168.0$ Hz.

$^c$: $J(PtC_\beta) = 196.1$ Hz.

$^d$: resonance too broad to observe fine couplings.

$^e$: not measured.

$^f$: coordination shifts (o C) = $\delta C$(free) - $\delta C$(coordinated).
values for the phosphine ligands.

The $^{13}$C NMR spectrum of Pt(SP)$_2$ (Table 3.5) shows two olefinic carbon resonances accompanied by $^{195}$Pt satellites. The doublet is assigned to C$\alpha$ and the singlet is assigned to C$\beta$ [$\delta$64.8(C$\alpha$), $J^{13C\alpha}_{31P}$ = 37.0 Hz, $J^{195Pt^{13C\alpha}}$ = 168.0 Hz; $\delta$32.1(C$\beta$), $J^{13C\beta}_{31P}$ = 0 Hz, $J^{195Pt^{13C\beta}}$ = 196.1 Hz]. As is usually observed for zerovalent metal olefin complexes (Table 3.4), these resonances are shifted significantly upfield upon coordination compared with their position in the free ligand (Table 3.5). The magnitudes of the $^{195}$Pt-$^{13}$C coupling constants are comparable with those reported for platinum(0)-olefin complexes e.g. Pt(COD)$_2$ (143 Hz), Pt(C$_2$H$_4$)$_3$ (113 Hz), tris(bicyclo[2.2.1]heptene)platinum(0) (189 Hz) and tris(trans-cyclooctene)platinum(0) (154 Hz)$^{133}$. The $^1$H, $^{31}$P and $^{13}$CNMR data for Pt(SP)$_2$ suggest that the SP ligands are symmetrically coordinated.

The $^1$HNMR spectrum of Ni(SP)$_2$ is similar to that of Pt(SP)$_2$ and at room temperature shows a set of three multiplets due to coordinated vinyl protons (Figure 3.3 and Table 3.2). The multiplicity is due to interproton couplings and phosphorus couplings. On $^{31}$P decoupling, the olefinic proton resonances become a doublet ($\delta$2.72, H$^3$), a doublet ($\delta$3.38, H$^2$) and a doublet of doublets ($\delta$4.45, H$^1$) as expected (for numbering of protons see Table 3.2, Figure 3.3). However the $^{31}$P coupled multiplet resonances were not analysed to obtain $J$(PH) values. The $^1$H chemical shifts of the nickel complex Ni(SP)$_2$ are very similar to those of the platinum analogue, though the magnitude of the coordination shifts (\(\Delta\)) is slightly less for Ni(SP)$_2$ than for Pt(SP)$_2$. This may indicate that the strength of the metal-olefin bond in Pt(SP)$_2$ is greater than in Ni(SP)$_2$. The smaller reduction of $^3J$(H$^1$H$^3$) in Ni(SP)$_2$ compared to Pt(SP)$_2$ is consistent with the above suggestion (Table 3.2).
Figure 3.3  $^1$HNMR spectra (200 MHz) of Ni(o-CH$_2$=CHC$_6$H$_4$PPh$_2$)$_2$[Ni(SP)$_2$, 3.3] in d$_8$-toluene at room temperature.

(A) $^1$HNMR spectrum  
(B) $^1$H($^31$P)NMR spectrum  
(X) impurity (diethylether)
Figure 3.4  Two possible structures of M(SP)_2

(a) tetrahedral

(b) trigonal planar
The $^{31}$PNMR spectrum of Ni(SP)$_2$ shows a sharp singlet at $\delta 42.5$ at room temperature which shows little change in chemical shift or line width at -80°C.

The $^{13}$CNMR spectrum of Ni(SP)$_2$ shows two olefinic carbon resonances $[\delta C_\alpha 82.7, J^{13}C_\alpha^{31}P) = 23.6$ Hz, $\delta C_\beta^{31}P) = 54.7, J^{13}C_\beta^{31}P) = 0$ Hz] (Table 3.5). They are shifted upfield from those of SP, as expected (Table 3.5). However, the magnitudes of the coordination shifts ($\Delta$) of the olefinic carbon resonances in Ni(SP)$_2$ are smaller than the corresponding values observed in Pt(SP)$_2$ (Table 3.5). This follows the same trend as their $^1$HNMR data (Table 3.2).

In summary, $^1$H, $^{31}$P and $^{13}$CNMR data suggest that in solution at room temperature Ni(SP)$_2$ and Pt(SP)$_2$ contain two symmetrically coordinated SP ligands with both of the phosphorus donors and the olefinic groups attached to the metal atom, giving a tetrahedral structure (Figure 3.4a). A structure in which both olefinic groups are coordinated agrees with solid state infrared data.

The NMR data do not exclude the possibility that the compounds adopt a trigonal planar structure in solution (Figure 3.4b) in which the free and coordinated vinyl groups exchange rapidly on the NMR time scale, even at -80°C. However this is considered unlikely because the magnitudes of $J^{135}$Pt$^1$H) for Pt(SP)$_2$ are similar to those of other platinum(0)-olefin complexes.

3.2.2 Synthesis of bis(o-vinylphenyldiphenylphosphine)palladium(0)

The complex bis(o-vinylphenyldiphenylphosphine)palladium(0), Pd(SP)$_2$, (3.4) was more difficult to synthesize than its platinum and
and nickel analogues. Reduction of the palladium(II) complex, PdCl₂(SP) with 1% sodium amalgam in the presence of an excess of SP at -30°C in THF formed metallic palladium. A similar reaction using zinc dust as the reducing agent gave no characterisable product. The reduction of the palladium(II) complex PdCl₂(SP) with hydrazine in the presence of SP in DMSO at 140°C gave a brown solution from which Pd(SP)₂ could not be isolated, although this procedure is a standard method for preparing Pd(PPh₃)₄. The reduction of bis(acetylacetonato)-palladium(II) with diethylethoxyaluminium (AlEt₂OEt) in the presence of excess SP gave a mixture of products including Pd(SP)₂, 3.4 and Pd(SP)₃, 3.5 (see below). The ligand exchange of SP with Pd₂dba₃dba (dba = dibenzylideneacetone) in toluene also resulted in a mixture of products including 3.4 and 3.5.

The reaction of Pd(η³-C₃H₅)(η⁵-C₅H₅) with an excess of SP at -70°C in toluene gave an air-sensitive and thermally unstable yellow solid 3.6 upon addition of n-pentane at -70°C (Scheme 3.3). This compound has the empirical formula Pd(C₅H₅)(C₃H₅)(SP), 3.6 on the basis of complete elemental analyses (C,H,P,Pd). The infrared spectrum of 3.6 in a KBr disk at 0°C shows an absorption at 1620 cm⁻¹ indicating the presence of free vinyl groups. The ¹H and ³¹PNMR spectra of 3.6 are complicated and temperature dependent. Owing to the low thermal stability of 3.6 in solution, the spectra are not reproducible, and they have not been completely interpreted. Two coordinated cyclopentadienyl resonances and two sets of allylic resonances are discernible.

Werner and coworkers have used a combination of kinetic measurements and low temperature NMR studies to show that the reaction of Pd(η³-allyl)(η⁵-C₅H₅) with tertiary phosphines or phosphites (L)
Scheme 3.3 Reaction of Pd(η^3-C_3H_5)(η^5-C_5H_5) with SP, all reactions in toluene.

...goes through an intermediate 1:1 adduct, Pd(η^1-allyl)(η^5-C_5H_5)L to give PdL_4 (Scheme 3.4). Using the 2-chloroallyl precursor the reaction can be stopped at the first stage to isolate Pd(C_5H_5)(2-ClC_3H_4)L complexes.^253
Scheme 3.4  Mechanism of the reaction of Pd(\(\eta^3\)-allyl)(\(\eta^5\)-C\(_5\)H\(_5\))
and tertiary phosphines or phosphites(L).

It is possible that in the solid state, complex 3.6 is a 1:1
adduct of Pd(C\(_3\)H\(_5\))(C\(_5\)H\(_5\)) and SP having the structure,
Pd(\(\eta^1\)-C\(_3\)H\(_5\))(\(\eta^5\)-C\(_5\)H\(_5\))(SP) analogous to those reported by Werner and
coworkers\(^{250-253}\).
Reaction of 3.6 with exactly one equivalent of SP in toluene at room temperature initially gave a clear red solution which then changed colour to yellow and finally precipitated a yellow solid within one hour. The time course of these changes depends on concentration. A complete elemental analysis showed this precipitate to be Pd(SP)$_2$, 3.4.

Although complex 3.6 is a convenient precursor of Pd(SP)$_2$, this compound can be prepared directly from Pd($\eta^3$-C$_3$H$_5$)($\eta^5$-C$_5$H$_5$) and exactly two equivalents of SP at room temperature. The molar ratio of the reactants are crucial in this case, because if excess of SP is present, Pd(SP)$_3$, 3.5 is also formed (see section 3.2.4). For this reason, this reaction is only satisfactory for relatively large scale preparations of Pd(SP)$_2$. On a very small scale, errors introduced in weighing the volatile starting material Pd($\eta^3$-C$_3$H$_5$)($\eta^5$-C$_5$H$_5$) interfere with the preparation.
The complex Pd(SP)$_2$ is almost insoluble in toluene and is poorly soluble in diethylether and benzene. In contrast, Pt(SP)$_2$ and Ni(SP)$_2$ are soluble in toluene, diethylether and benzene. Despite its unexpected solubility properties, Pd(SP)$_2$ is not aggregated. A molecular weight determination in toluene by osmometry, and the X-ray single crystal structure (section 3.2.3) show that Pd(SP)$_2$ is monomeric. The mass spectrum of Pd(SP)$_2$ shows a fragment due to SP ligand. No parent ion peak is observed, possibly due to the low thermal stability and involatility of this complex. The infrared spectrum in a KBr disk shows a weak absorption at 1620 cm$^{-1}$ indicating the presence of an uncoordinated vinyl group (Figure 3.5).

Figure 3.5  Infrared spectrum of Pd(SP)$_2$ in a KBr disk at room temperature.
The NMR spectroscopic behaviour of Pd(SP)₂ is complicated. Variable temperature \(^1\)H and \(^{31}\)PNMR spectra measured in CD₂Cl₂ are shown in Figure 3.6 and Figure 3.7 respectively. At room temperature the \(^1\)HNMR spectrum shows two broad resonances at \(\delta 4.0\) and \(\delta 6.2\) in an approximate 2:1 ratio. At \(-50^\circ C\) the spectrum is broader but at \(-80^\circ C\) the spectrum resolves into many sets of resonances in the region between \(\delta 7.0\) and \(\delta 3.5\). These resonances are still broad, and the limiting spectrum was not obtained. There appears to be more than one set of coordinated vinyl proton resonances. These resonances have chemical shifts of \(\delta 3.85, \delta 4.05, \delta 5.80, \delta 6.05, \delta 6.15\) and \(\delta 6.60\) and are at lower field than the coordinated vinyl proton resonances of Pt(SP)₂ and Ni(SP)₂ (Table 3.2). In addition, there are resonances at \(\delta 5.10\) and \(\delta 5.60\) which can be assigned to a free vinyl group. The \(^1\)H\(^{1}\)H NMR spectra show that the two doublets at \(\delta 3.85\) and \(\delta 4.05\) are not coupled to each other and hence they belong to different coordinated vinyl groups.

The \(^{13}\)CNMR spectrum at room temperature shows two broad singlets at \(\delta 109.8\) and \(\delta 81.5\) which are at much lower field than the olefinic carbon resonances in Pt(SP)₂ and Ni(SP)₂ but which are at higher field than the corresponding resonances in free SP ligand (Table 3.5). At \(-80^\circ C\) the spectrum shows four broad singlets, a pair at \(\delta 106.2\) and \(\delta 78.3\) and another pair at \(\delta 122.5\) and \(\delta 115.5\). These two pairs of resonances are unequal in intensity, the ratio being approximately 1.5:1. The latter pair is assigned to uncoordinated vinyl carbon resonances and the former pair to coordinated vinyl carbon resonances.

The \(^1\)H and \(^{13}\)CNMR spectra at \(-80^\circ C\) thus indicate the presence of both free and coordinated vinyl groups in Pd(SP)₂ and show that at room temperature on warming, these groups exchange rapidly on the NMR
Figure 3.6 $^1$HNMR spectra (200 MHz) of Pd(SP)$_2$, 3.4 in CD$_2$Cl$_2$ at room temperature (A), -50°C (B), -80°C (D) and $^1$H$^{31}$P NMR spectrum at -80°C (C) ($X$ = impurities).
Figure 3.7 Variable temperature $^{31}$PNMR spectra (80.99 MHz) of Pd(SP)$_2$, 3.4 in CD$_2$Cl$_2$. 
time scale.

The $^{31}$PNMR spectrum at room temperature shows a singlet at $\delta 25.0$ which broadens slightly as the temperature decreases to $-30^\circ C$. At $-50^\circ C$, a four-line AB pattern appears to the low frequency side of the singlet. These resonances sharpen at $-80^\circ C$ and the intensity of the AB pattern increases relative to that of the singlet. The AB spin system $[\delta 21.0(P_A), \delta 20.4(P_B), J_{AB} = 37 \text{ Hz}]$ corresponds to an isomer of Pd(SP)$_2$ with inequivalent phosphorus atoms. This isomer probably has one P-bonded SP and one bidentate SP which corresponds to the structure found by X-ray single crystal analysis (section 3.2.3). The resonance at $\delta 25.0$ is assigned to a second isomer containing symmetrically bound SP, both vinyl groups either being coordinated (giving an 18-electron species) or free (giving a 14-electron species).

On the basis of $^1H$, $^{31}P$ and $^{13}C$ chemical shifts at room temperature and at $-80^\circ C$, it is most reasonable to postulate that the species having symmetrically coordinated SP is a tetrahedral complex having both vinyl groups coordinated. If this interpretation is correct, it is remarkable that the unsaturated species having an AB pattern in the $^{31}$PNMR spectrum is formed as the temperature is lowered. The opposite trend, in which the saturated species is favoured at low temperature is generally observed in zerovalent metal phosphine complexes of the nickel triad (section 1.2.3).

In summary, at least two processes are responsible for the fluxional behaviour of Pd(SP)$_2$. Free and coordinated vinyl groups exchange intramolecularly. In addition, there are two exchanging isomeric species, a tetrahedral complex in which both vinyl groups are coordinated and a trigonal species in which only one vinyl group is coordinated.
In the solid state under argon at 5°C, Pd(SP)₂, a yellow compound, decomposes over several months to a pale yellow solid which is insoluble in toluene and THF.

In contrast to the freshly prepared Pd(SP)₂, this compound does not react with one equivalent of SP to give Pd(SP)₃, (section 3.2.4). The infrared spectrum of this complex is different from that of freshly prepared Pd(SP)₂ in that the absorption at 1620 cm⁻¹ characteristic of free vinyl group is no longer present. The compound may polymerise under these conditions, but this possibility has not been fully investigated.

3.2.3 X-ray single crystal structures of Ni(SP)₂, Pd(SP)₂ and Pt(SP)₂

The X-ray single crystal structures of Ni(SP)₂, Pd(SP)₂ and Pt(SP)₂ were determined by Dr. G.B. Robertson and Mrs. Uncharee Tooptakong in the Research School of Chemistry, Australian National University. The crystal data and the structural data are presented in Tables 3.6 and 3.7 respectively. The molecular structures of Ni(SP)₂, Pt(SP)₂ and Pd(SP)₂ are shown in Figures 3.8, 3.10 and 3.12 respectively. Schematic presentations of selected bond lengths and bond angles of the olefins in Ni(SP)₂, Pt(SP)₂ and Pd(SP)₂ are shown in Figures 3.9, 3.11 and 3.13 respectively. Table 3.8 lists relevant X-ray single crystal structural data of some zerovalent nickel, palladium and platinum complexes of olefins and one acetylene complex for comparison purposes.
Table 3.6  Crystal data for M(SP)$_2$ complexes (M = Ni, Pd, Pt; SP = $\text{-C}_2\text{H}_5$CH$\text{C}_6\text{H}_4$PPh$_2$)

<table>
<thead>
<tr>
<th></th>
<th>Ni(SP)$_2$</th>
<th>Pd(SP)$_2$</th>
<th>Pt(SP)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>a</td>
<td>13.432(2) $\text{Å}$</td>
<td>a = 21.456(3) $\text{Å}$</td>
<td>a = 11.245 $\text{Å}$</td>
</tr>
<tr>
<td>b</td>
<td>11.486(2) $\text{Å}$</td>
<td>b = 9.483(2) $\text{Å}$</td>
<td>b = 14.126 $\text{Å}$</td>
</tr>
<tr>
<td>c</td>
<td>21.630(3) $\text{Å}$</td>
<td>c = 9.202(2) $\text{Å}$</td>
<td>c = 14.417 $\text{Å}$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>104.34(1)$^\circ$</td>
<td>$\alpha = 60.84(1)^\circ$</td>
<td>$\alpha = 119.05^\circ$</td>
</tr>
<tr>
<td></td>
<td>$V = 3233.10 \text{ Å}^3$</td>
<td>$V = 1614.12 \text{ Å}^3$</td>
<td>$V = 1822.88 \text{ Å}^3$</td>
</tr>
<tr>
<td>$D_m$</td>
<td>1.32 g cm$^{-3}$</td>
<td>$D_m = 1.40 g \text{ cm}^{-3}$</td>
<td>$D_m = 1.49 g \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>Z = 2</td>
<td>Z = 2</td>
</tr>
<tr>
<td>$D_c$</td>
<td>1.31 g cm$^{-3}$</td>
<td>$D_c = 1.41 g \text{ cm}^{-3}$</td>
<td>$D_c = 1.41 g \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>space gr.</td>
<td>$P_2_1/n$</td>
<td>space gr. $P\bar{1}$</td>
<td>space gr. $P\bar{1}$</td>
</tr>
<tr>
<td>R</td>
<td>0.041, $R_w = 0.048$</td>
<td>R = 0.032, $R_w = 0.036$</td>
<td>R = 0.026, $R_w = 0.030$</td>
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</table>
Table 3.7  Selected bond lengths and bond angles for Ni(SP)$_2$, Pt(SP)$_2$ and Pd(SP)$_2$
(numbering of atoms as in Figures 3.8, 3.10 and 3.12 respectively)

<table>
<thead>
<tr>
<th></th>
<th>Ni(SP)$_2$</th>
<th>Pd(SP)$_2$</th>
<th>Pt(SP)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bond distance (Å)</strong></td>
<td>Ni-P1 2.194(1)</td>
<td>Pd-P1 2.302(7)</td>
<td>Pt-P1 2.278(1)</td>
</tr>
<tr>
<td></td>
<td>Ni-P2 2.204(1)</td>
<td>Pd-P2 2.3054(7)</td>
<td>Pt-P2 2.290(1)</td>
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<tr>
<td></td>
<td>Ni-C19 2.033(4)</td>
<td>Pd-C39 2.141(7)</td>
<td>Pt-C19 2.139(4)</td>
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<tr>
<td></td>
<td>Ni-C20 2.038(5)</td>
<td>Pd-C40 2.213(4)</td>
<td>Pt-C20 2.165(7)</td>
</tr>
<tr>
<td></td>
<td>Ni-C39 2.059(4)</td>
<td>Pd-C19 3.470(3)</td>
<td>Pt-C39 2.152(4)</td>
</tr>
<tr>
<td></td>
<td>Ni-C40 2.034(5)</td>
<td>Pd-C20 4.466(4)</td>
<td>Pt-C40 2.179(7)</td>
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<tr>
<td></td>
<td>C19-C20 1.397(6)</td>
<td>C19-C20 1.293(5)</td>
<td>C19-C20 1.404(11)</td>
</tr>
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<td></td>
<td>Ni-CA 1.912</td>
<td>Pd-CA 2.063</td>
<td>Pt-CA 2.035</td>
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<td></td>
<td>Ni-CB 1.923</td>
<td></td>
<td>Pt-CB 2.044</td>
</tr>
<tr>
<td><strong>Bond angle (degree)</strong></td>
<td>C19-Ni-C20 40.1(2)</td>
<td>C39-Pd-C40 37.1(1)</td>
<td>C19-Pt-C20 38.1(3)</td>
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<td></td>
<td>C39-Ni-C40 40.0(2)</td>
<td>P1-Pd-P2 121.36(3)</td>
<td>C39-Pt-C40 38.5(3)</td>
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<tr>
<td></td>
<td>P1-Ni-P2 109.30(4)</td>
<td>CA-Pd-P2 100.3</td>
<td>P1-Pt-P2 110.08(4)</td>
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<tr>
<td></td>
<td>CA-Ni-CB 113.2</td>
<td>[P1-Pd-P2][C40-Pd-C39] 24.7</td>
<td>CA-Pt-CB 112.1</td>
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<tr>
<td></td>
<td>CA-Ni-P1 95.5</td>
<td></td>
<td>CA-Pt-P1 90.6</td>
</tr>
<tr>
<td></td>
<td>CB-Ni-P2 91.6</td>
<td></td>
<td>CB-Pt-P2 88.7</td>
</tr>
<tr>
<td></td>
<td>[Ni-CA-CB][Ni-P1-P2] 69.0</td>
<td></td>
<td>[Pt-CA-CB][Pt-P1-P2] 61.8</td>
</tr>
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</table>
Table 3.8  Selected X-ray single crystal data of some zerovalent metal complexes of the nickel triad\(^a\)

<table>
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<tr>
<th>Compounds</th>
<th>ref</th>
<th>geometry</th>
<th>C=C</th>
<th>M-C</th>
<th>M-P</th>
<th>dihedral angle [P-M-P][C-M-C]</th>
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<tr>
<td>Ni(COD)(_2)</td>
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<td>tetrahedral</td>
<td>1.385 (mean)</td>
<td>2.124 (mean)</td>
<td>-</td>
<td></td>
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<tr>
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<td>41</td>
<td>tetrahedral</td>
<td>1.398(9)</td>
<td>2.211(7)</td>
<td>-</td>
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<tr>
<td>Ni(PPh(_3))(_2)(C(_2)H(_4))</td>
<td>43</td>
<td>trigonal</td>
<td>1.391(5)</td>
<td>1.978(5)</td>
<td>2.148(4)</td>
<td>5(^b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.959(6)</td>
<td>2.158(4)</td>
<td></td>
</tr>
<tr>
<td>Pt(PPh(_3))(_2)(C(_2)H(_4))</td>
<td>255</td>
<td>trigonal</td>
<td>1.434(13)</td>
<td>2.106(8)</td>
<td>2.265(2)</td>
<td>1.6</td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td>2.116(9)</td>
<td>2.270(2)</td>
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<tr>
<td>Pt(PPh(_3))(_2)(C(_2)(CN)(_4))</td>
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<td>trigonal</td>
<td>1.49(5)</td>
<td>2.10(3)</td>
<td>2.288(8)</td>
<td>8.3</td>
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<td>2.12(3)</td>
<td>2.291(9)</td>
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<tr>
<td>Pt(PPh(_3))(_2)(C(_2)Cl(_4))</td>
<td>257</td>
<td>trigonal</td>
<td>1.62(3)</td>
<td>2.02(3)</td>
<td>2.278(8)</td>
<td>12.3</td>
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<td>2.05(3)</td>
<td>2.292(7)</td>
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<tr>
<td>Pd(dbca)(_3)</td>
<td>258</td>
<td>trigonal</td>
<td>1.38(2)</td>
<td>2.223(2)</td>
<td>-</td>
<td>21(3), 16(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(coordinated)</td>
<td>(mean)</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>1.26(2)</td>
<td></td>
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<td>16(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(uncoordinated)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Pd(C(_2)(CO(_2)Me)(_2))(PPh(_3))(_2)</td>
<td>259</td>
<td>trigonal</td>
<td>1.28(1)(^c)</td>
<td>2.074(6)</td>
<td>2.321(2)</td>
<td>9.7(4)</td>
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<td></td>
<td>2.051(6)</td>
<td>2.330(2)</td>
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</tr>
</tbody>
</table>

\(^{a}\) bond lengths in Å and dihedral angles in degrees.

\(^{b}\) dihedral angle was reported by Nyburg et al.\(^{260}\) however Dreissig and Dietrich stated that this value is not valid.

\(^{c}\) acetylenic C=C bond length.
Figure 3.8  Molecular structure of Ni(o-CH$_2$=CHC$_6$H$_4$PPh$_2$)$_2$

[Ni(SP)$_2$, 3.3].
Figure 3.9  Bond lengths and bond angles of the coordinated vinyl groups in Ni(SP)$_2$. 

$\alpha = 36^\circ, \beta = 71^\circ, \beta' = 73^\circ$

$\alpha = 37^\circ, \beta = 73^\circ, \beta' = 71^\circ$
Figure 3.10 Molecular structures of Pt(o-CH₂=CHC₆H₄PPh₂)$_2$

[Pt(SP)$_2$, 3.1].
Figure 3.11  Bond lengths and bond angles of the coordinated vinyl groups in Pt(SP)$_2$
Figure 3.12  Molecular structure of $\text{Pd}(\sigma$-$\text{CH}_2$-$\text{CHC}_6\text{H}_4\text{PPh}_2)_2 \text{[Pd(SP)_2, 3.4]}$. 
Figure 3.13 Bond lengths and bond angles of the coordinated vinyl group in Pd(SP)₂.
The single crystals used in these determinations were grown by vapour diffusion of \( \text{n-hexane} \) into toluene solutions of the complexes in a nitrogen atmosphere and the crystals were coated with Araldite before mounting.

The nickel(0) and platinum(0) complexes, Ni(SP)\(_2\) and Pt(SP)\(_2\) are isomorphous, four-coordinate complexes containing two tertiary phosphine ligands and two vinyl groups in a distorted tetrahedral geometry. The palladium(0) complex Pd(SP)\(_2\) differs from its analogues. It is an approximately trigonal planar complex containing one coordinated vinyl group and two tertiary phosphine ligands. All the complexes in this series are monomeric. The crystal structures of Ni(SP)\(_2\) and Pt(SP)\(_2\) agree with those derived from NMR\((^1\text{H}, ^{31}\text{P}, ^{13}\text{C})\) data in solution and from solid state infrared data.

Distortion from an ideal tetrahedral structure is indicated by the dihedral angle between the plane containing the metal and the two phosphorus atoms and the plane containing the metal and the two olefinic midpoints. This angle, which should be 90\(^\circ\) for an ideal tetrahedral geometry is 69.0\(^\circ\) for Ni(SP)\(_2\) and 61.8\(^\circ\) for Pt(SP)\(_2\). The angles formed by the two olefinic midpoints with metal as the vertex and by the two phosphorus atoms with the metal as the vertex are 113.2\(^\circ\) and 109.3\(^\circ\) in Ni(SP)\(_2\) and 112.1\(^\circ\) and 110.1\(^\circ\) in Pt(SP)\(_2\).

The C=C double bond distances of the coordinated vinyl groups in Ni(SP)\(_2\) are equal \([1.397(6)\AA\) and 1.402(6)\AA\]. These distances are significantly longer than in a free C=C double bond \([1.337(6)\AA]\)\(^{261}\) but shorter than in a C-C single bond \([1.541(3)\AA]\)\(^{262}\). They are comparable with the C=C bond lengths of 1.391(5)\AA\ and 1.385\AA\ found
in \( \text{Ni} (\text{PPh}_3)_2 (\text{C}_2\text{H}_4) \)\textsuperscript{43} and \( \text{Ni(COD)}_2 \)\textsuperscript{254} respectively.

The C=C double bond lengths of the coordinated vinyl groups in \( \text{Pt(SP)}_2 \) \([1.404(11)\text{Å}, 1.429(11)\text{Å}, \text{mean} = 1.417\text{Å}] \) are comparable with the C=C double bond lengths in \( \text{Pt(COD)}_2 \) \([1.398(9)\text{Å}] \)\textsuperscript{41} and \( \text{Pt(PPh}_3)_2 (\text{C}_2\text{H}_4) \) \([1.434(13)\text{Å}] \)\textsuperscript{255}. However, they are shorter than the C=C double bond distances in \( \text{Pt(PPh}_3)_2 [\text{C}_2(\text{CN})_4] \) \([1.49(5)\text{Å}] \)\textsuperscript{256} and \( \text{Pt(PPh}_3)_2 (\text{C}_2\text{Cl}_4) \) \([1.62(3)\text{Å}] \)\textsuperscript{257}. 

The lengths of the coordinated olefinic bond, \( \text{Ni(SP)}_2 \) and \( \text{Ni(SP)}_2 \), are comparable with the corresponding bond length in \( \text{Fe(CO)}_2 (\text{SP})_2 \), \([1.455(8)\text{Å}] \) (Table 1.10)\textsuperscript{147,148}.

In \( \text{Ni(SP)}_2 \), the vinyl group of one \( \text{SP} \) ligand is symmetrically coordinated \([\text{Ni-C19} = 2.033(4)\text{Å}, \text{Ni-C20} = 2.038(5)\text{Å}] \). However, in the vinyl group of the other \( \text{SP} \) ligand, the \( \beta \)-carbon atom (C40) is closer to the nickel atom than is the \( \alpha \)-carbon atom (C39) \([\text{Ni-C39} = 2.059(4)\text{Å}, \text{Ni-C40} = 2.034(5)\text{Å}, \Delta/\sigma = 3.9]. \) This type of asymmetry is also observed in the platinum(II) complexes \( \text{Pt(CH}_3)_2 (\text{SP}) \) and \( \text{Pt(CF}_3)_2 (\text{SP}) \) (Table 1.10)\textsuperscript{149}. The \( \text{Ni-C} \) bond lengths in \( \text{Ni(SP)}_2 \) are similar to those reported for \( \text{Ni(PPh}_3)_2 (\text{C}_2\text{H}_4) \) \([1.978(5)\text{Å}, 1.959(6)\text{Å}] \)\textsuperscript{43} and \( \text{Ni(COD)}_2 \) \([\text{mean Ni-C} = 2.124\text{Å}] \)\textsuperscript{254}.

The distances between the nickel atom and the two phosphorus atoms are approximately equal \([\text{Ni-P1} = 2.194(1)\text{Å}, \text{Ni-P2} = 2.204(1)\text{Å}] \) and are longer than those found in \( \text{Ni(PPh}_3)_2 (\text{C}_2\text{H}_4) \) \([2.148(4)\text{Å}, 2.158(4)\text{Å}] \)\textsuperscript{43}.

Each vinyl group is not symmetrically coordinated to platinum in \( \text{Pt(SP)}_2 \) \([\text{Pt-C19} = 2.139(4)\text{Å}, \text{Pt-C20} = 2.165(7)\text{Å}, \Delta/\sigma = 3.2; \text{Pt-C39} = 2.152(4)\text{Å}, \text{Pt-C40} = 2.179(7)\text{Å}, \Delta/\sigma = 3.3]. \) The \( \alpha \)-carbon atom is closer to the platinum atom than the \( \beta \)-carbon atom in both vinyl groups. This is opposite to what is observed in the asymmetric vinyl group in \( \text{Ni(SP)}_2 \).
However these values are similar to those observed in
$\text{Pt(COD)}_2$ [2.211(7)$\text{Å}$, 2.106(8)$\text{å}$, 2.116(9)$\text{Å}$] and $\text{Pt(PPh}_3)_2$[2.02(3)$\text{Å}$, 2.05(3)$\text{Å}$] and $\text{Pt(PPh}_3)_2[\text{C}_2\text{(CN)}_4]$
[2.10(3)$\text{Å}$, 2.12(3)$\text{Å}$].

The distances between the platinum atom and the two phosphorus atoms in $\text{Pt(SP)}_2$ [2.278(1)$\text{Å}$, 2.290(1)$\text{Å}$] are comparable to those found in $\text{Pt(PPh}_3)_2[\text{C}_2\text{H}_4]$ [2.265(4)$\text{Å}$, 2.270(4)$\text{Å}$], $\text{Pt(PPh}_3)_2[\text{C}_2\text{Cl}_4]$
[2.278(8)$\text{Å}$, 2.292(7)$\text{Å}$] and $\text{Pt(PPh}_3)_2[\text{C}_2\text{(CN)}_4]$
[2.288(8)$\text{Å}$, 2.291(9)$\text{Å}$].

The "bite angles" of the bidentate SP ligands (defined as the angles Pl-M-CA and P2-M-CB where CA and CB are the hypothetical carbon atoms at the midpoint between C19-C20 and C39-C40 respectively) in $\text{Ni(SP)}_2$ and $\text{Pt(SP)}_2$ are comparable in magnitude, being 95.5$^0$ and 91.6$^0$ in $\text{Ni(SP)}_2$, and 90.6$^0$ and 88.7$^0$ in $\text{Pt(SP)}_2$. They are smaller than the ideal tetrahedral angle (109$^0$). This deviation indicates some strain in these two molecules induced by coordination of the bidentate SP ligands. The bite angles of SP in tetrahedral complexes $\text{Ni(SP)}_2$ and $\text{Pt(SP)}_2$ are slightly larger than the bite angle of 1,5-cyclooctadiene in $\text{Pt(COD)}_2$ (85$^0$).41

In the trigonal planar complex, $\text{Pd(SP)}_2$ only one vinyl group is coordinated to the metal. The distances between the palladium atom and the other vinyl group $\text{Pd-C19}$ [3.470(3)$\text{Å}$] and $\text{Pd-C20}$ [4.466(4)$\text{Å}$] indicate that there is no interaction between the palladium atom and these two olefinic carbon atoms. The olefin is coordinated asymmetrically to the palladium atom [$\text{Pd-C39} = 2.141(3)$Å, $\text{Pd-C40} = 2.213(4)$Å] with the palladium atom being closer to the $\alpha$-carbon atom (C39) than to the $\beta$-carbon atom (C40) of the vinyl group. Thus, in contrast to $\text{Ni(SP)}_2$ and $\text{Pt(CHR}_3)(\text{SP})$ (R = H, F)149, the $\beta$- rather than the $\alpha$-carbon atom is closer to the metal centre. This asymmetry is also found in $\text{Pt(SP)}_2$.41
The C=C bond length of the coordinated olefin in Pd(SP)$_2$ [C39-C40 = 1.387(5)Å] is comparable with the corresponding value in Pd(dba)$_3$C$_6$H$_6$ [1.38(2)Å]$^{258}$. The C=C bond length of the uncoordinated vinyl group in Pd(SP)$_2$, [C19-C20 = 1.293(5)Å] is, as expected, significantly shorter than that of the coordinated olefinic bond and is comparable with the corresponding value found in Pd(dba)$_3$C$_6$H$_6$ [1.26(6)Å]$^{258}$. Surprisingly, these values are shorter than the normal value for a free C=C double bond [1.337(6)Å]$^{261}$ and for the free vinyl bond distance in Fe(CO)$_2$(SP)$_2$ [1.339(10)Å] (Table 1.10)$^{147,148}$.

In Pd(SP)$_2$ the dihedral angle between the planes [P1-Pd-P2] and [C39-Pd-C40] is 24.7°. The palladium atom is 0.22Å above the plane formed by P1-P2-CA where CA is the midpoint between the two carbon atoms (C39, C40) of the coordinated olefin. Therefore, the coordinated olefin deviates from the ideal trigonal plane. This behaviour has been observed in many trigonal complexes of the zerovalent metals of the nickel triad containing olefins (dihedral angles in parenthesis) e.g. Pd(dba)$_3$C$_6$H$_6$[21(3)°,16(3)°,16(3)°]$_{258}$, Pt(PPh$_3$)$_2$(C$_2$H$_4$)(1.6°)$^{255}$, Pt(PPh$_3$)$_2$[C$_2$(CN)$_4$](8.3°)$^{256}$, Pt(PPh$_3$)$_2$(C$_2$Cl$_4$)(12.3°)$^{257}$.

The palladium-phosphorus bond lengths in Pd(SP)$_2$ are essentially equal [Pd-P1 = 2.3029(7)Å, Pd-P2 = 2.3054(7)Å]. These values are comparable with those reported for Pd[C$_2$(CO$_2$Me)$_2$](PPh$_3$)$_2$ [2.321(2)Å, 2.330(2)Å]$^{259}$. In contrast, in Fe(CO)$_2$(SP)$_2$, the Fe-P bond length to the bidentate SP ligand [2.205(2)Å] is shorter than to the monodentate SP ligand [2.239(2)Å]$^{147,148}$. 


The bite angle of the bidentate SP in Pd(SP)$_2$ [CA-Pd-P2 = 100.3°] is larger than the corresponding values in Pt(SP)$_2$ (90.6°, 88.7°) and Ni(SP)$_2$ (95.5°, 91.6°). However it is considerably smaller than the ideal trigonal planar angle of 120°, which indicates the presence of strain in the coordination sphere. This strain may influence the reactivity of the complexes. For example the reaction of the 18-electron complex Pt(COD)$_2$ with ethylene to form the 16-electron complex Pt(C$_2$H$_4$)$_3$ $^{44,133}$ has been claimed to be driven by the relief of the strain in the coordination sphere imposed by bidentate chelate 1,5-cyclooctadiene ligand (bite angle = 85°)$^{41}$.

Structural evidence for the degree of π-back bonding in a metal-olefin bond is provided by the lengthening of the olefinic bond and bending back of the olefinic substituent groups away from the metal atom$^{129}$. The differences in the coordinated C=C bond lengths in the M(SP)$_2$ complexes for nickel, palladium and platinum (Table 3.7) are not statistically significant, although there is an apparent trend for the C=C bond lengths to increase in the order Pd < Ni < Pt.

Useful measures of the degree of bending back are the α and β angles defined in Figure 3.1$^{129}$. The angle α is the angle between the normals to the planes defined by the substituent groups; β and β' are the angles between the olefin bond and the normals to these planes. As the substituents bend back, α increases from 0°, and β and β' decrease from 90°. The sum of the three angles need not be 180° unless substituents bend back so that the normals to the two planes and the C=C bond remain coplanar. It is generally found that the sum of these angles is near 180°. In the M(SP)$_2$ complexes three of the four substituents on the vinyl group are hydrogen atoms which are difficult
to locate with certainty. The values of $\alpha$, $\beta$ and $\beta'$ for the coordinated olefins in the M(SP)$_2$ complexes are $\alpha = 47(6)^\circ$, 51(5)$^\circ$; $\beta = 63^\circ$, 65$^\circ$; $\beta' = 71^\circ$, 64$^\circ$ for Pt(SP)$_2$; $\alpha = 36(4)^0$, 37(4)$^\circ$; $\beta = 71^\circ$, 73$^\circ$; $\beta' = 73^\circ$, 71$^\circ$ for Ni(SP)$_2$ and $\alpha = 32(3)^0$, $\beta = 74^\circ$, $\beta' = 75^\circ$ in Pd(SP)$_2$ (Figures 3.9, 3.11, 3.13). Owing to the large inherent errors in determining hydrogen atom positions from X-ray data, the differences are statistically insignificant, although again the general trend is for the angles to increase in the order Pd $<$ Ni $<$ Pt. The trends in the coordinated C=C bond lengths and the degree of bending back of substituents in the coordinated C=C bonds correlate well with each other.
3.2.4 Reaction of bis(o-vinylphenyldiphenylphosphine)metal(0) complexes of the nickel triad with o-vinylphenyldiphenylphosphine

The tris(o-vinylphenyldiphenylphosphine) complexes of the zerovalent nickel triad \([M(SP)_3; M = Ni, Pd, Pt]\) are expected to have a structure similar to that of \(Pt(PPh_3)_3\), which is trigonal planar. In this geometry, the three \(SP\) ligands would be coordinated to the metal through the phosphorus donors only, leaving three uncoordinated vinyl groups (Figure 3.15). Because this structure is sterically crowded, these complexes are expected to be unstable. However, in early efforts to prepare the \(Pd(SP)_2\) complex, \(Pd(SP)_3\) was also formed. Attempts were therefore made to develop reliable syntheses of the \(M(SP)_3\) complexes of the nickel triad.

![Figure 3.15 Possible structure of \(M(SP)_3\) for \(M = Ni, Pd, Pt\)](image-url)
The $^{31}$PNMR spectrum of a 1:1 mixture of Pt(SP)$_2$ and SP at room temperature shows two broad resonances at δ18.0 due to Pt(SP)$_2$ and at δ-14.2 due to the free SP ligand. However, the former resonance does not show the usual $^{195}$Pt satellites and this, together with the broadness of the peaks, indicates that an intermolecular exchange reaction is occurring between SP and Pt(SP)$_2$. When the temperature was lowered to -75°C the spectrum sharpened and the resonances due to Pt(SP)$_2$ flanked by $^{195}$Pt satellites [δ18.0, $^1J$(PtP)=3132 Hz] and the free SP (δ-14.7) were observed. This result indicates that the free and the coordinated SP exchange but there is no net reaction at room temperature. The reaction mixture was heated for 3 hours in toluene at 50°C and the $^{31}$PNMR spectrum, recorded at room temperature, was broad, indicating that an exchange process was occurring. However at -75°C, a sharp spectrum was obtained, suggesting that the exchange process had been frozen. The spectrum shows that the major products are the starting materials Pt(SP)$_2$ and SP. A singlet at δ28.3 is also observed as a minor product. This resonance is assigned to $\omega$-vinylphenyldiphenylphosphine oxide (SP oxide, $\omega$-CH$_2$=CHC$_6$H$_4$POPh$_2$) by comparison with the $^{31}$PNMR spectrum of an authentic sample. The formation of SP oxide in this system is possibly catalysed by the presence of the zerovalent platinum complex Pt(SP)$_2$.

The mechanism for exchanging free SP ligand and coordinated SP in Pt(SP)$_2$ probably involves intramolecular dissociation of one of the vinyl groups to form a 16-electron Pt(SP)$_2$ complex, 3.7 as an intermediate. The 16-electron Pt(SP)$_2$, 3.7 then undergoes intermolecular associative ligand exchange with free SP ligand, resulting in a loss of spin-spin coupling between $^{195}$Pt and $^{31}$P (Scheme 3.5). The proposed intermediate 3.7 contains one P-bonded
Scheme 3.5 Possible mechanism for ligand exchange between Pt(SP)$_2$ and and SP

SP and one bidentate SP and thus has an analogous structure to that found by X-ray structure analysis of Pd(SP)$_2$, 3.4.

Attempts to prepare Pt(SP)$_3$ by reduction of the platinum(II) complex, PtCl$_2$(SP), 3.2 with 1% sodium amalgam in the presence of excess SP ligand at -30°C in THF resulted in a mixture of products including polymeric materials. Nuclear magnetic resonance ($^1$H and
and infrared data indicate that the mixture consisted mainly of 
Pt(SP)$_2$, SP and SP oxide. The infrared spectrum of the product from 
this reaction in a KBr disk shows absorption at 1620 (w) cm$^{-1}$ and 
1185 (bs) cm$^{-1}$ assigned to v(C=C) and v(P=O) respectively. The $^{1}$HNMR 
resonances assigned to SP oxide occur at δ7.73 (dd, H$_1$), δ4.85 (d, H$_2$) 
and δ5.30 (d, H$_3$) with J(H$_1$H$_2$) and J(H$_1$H$_3$) being 11.0 and 17.5 Hz 
respectively. When a larger amount of SP was used, more polymeric 
products were formed, presumably by an alkali metal initiated 
polymerisation of the vinyl group in SP$^{263}$. 

An obvious alternative method of preparing Pt(SP)$_3$ is the reaction 
of Pt(COD)$_2$ with three equivalents or with a large excess of SP. 
However, at room temperature this reaction gives only Pt(SP)$_2$. The 
reaction mixture was refluxed for three days and was continuously 
monitored by $^{1}$H and $^{31}$P NMR spectroscopy. It was found that the 
reaction at elevated temperature does not give Pt(SP)$_3$ but instead 
seems to give a platinum(II) complex which has not yet been identified 
conclusively. 

In conclusion, a synthetic route to Pt(SP)$_3$ has not been found. 
The preparation always preferentially produces Pt(SP)$_2$, even in the 
presence of excess SP. Under forcing conditions side reactions 
become competitive. 

The reaction of Ni(SP)$_2$ with SP in a 1:1 molar ratio was monitored 
by $^{31}$P NMR spectroscopy. There is no reaction at room temperature. The 
$^{31}$P NMR spectrum at room temperature shows two sharp singlets assigned 
to Ni(SP)$_2$ and SP suggesting that the exchange between Ni(SP)$_2$ and SP 
is very slow on the NMR time scale compared to the corresponding 
exchange in Pt(SP)$_2$. This result implies that nickel(0)-olefin bonding
is much more favourable than nickel(0)-tertiary phosphine bonding, which is consistent with the trend predicted from electron affinities and ionization potential data that nickel(0) is a good \( \pi \)-bonder but a poor \( \sigma \)-bonder (Table 1.2, section 1.2). Heating the reaction mixture at 80\(^\circ\)C in toluene for 16 hours does not yield any Ni(SP)\(_3\) and the starting materials, Ni(SP)\(_2\) and SP are recovered unchanged.

Ligand exchange of Ni(COD)\(_2\) with an excess of SP in toluene at room temperature and at 80\(^\circ\)C does not give Ni(SP)\(_3\) even on prolonged heating (24 hours). Several attempts to reduce bis(acetylacetonato) nickel(II) with triethylaluminium in the presence of excess SP gave only Ni(SP)\(_2\). These experiments suggest that Ni(SP)\(_2\) is a very stable species and even under forcing conditions in the presence of a large excess of SP, no Ni(SP)\(_3\) is formed.

In contrast with the behaviour of the nickel and platinum analogues, the palladium(0) complex Pd(SP)\(_2\) reacts readily with SP at room temperature to give a new compound, formulated as Pd(SP)\(_3\), Eq. 3.5. It can also be prepared directly from reaction of either Pd(\( \eta^3\)-C\(_3\)H\(_5\))(\( \eta^5\)-C\(_5\)H\(_5\)) or of the unstable intermediate Pd(C\(_3\)H\(_5\))(C\(_5\)H\(_5\))(SP), Eq. 3.6 with a stoichiometric quantity or with an excess of SP (Scheme 3.3). This compound is a yellow air-sensitive solid. It is soluble in toluene, benzene, THF and diethylether but insoluble in saturated hydrocarbons. It is much more soluble in toluene than is Pd(SP)\(_2\). The complex can be obtained in an analytically pure form by recrystallisation from toluene-n-pentane. The mass spectrum shows no molecular ion, but only peaks due to SP. An osmometric molecular weight measurement gives a very low value (found 471, calc. 971). Although the latter observation
Figure 3.16 $^1$HNMR spectra (100 MHz) of Pd(SP)$_3$ in d$_8$-toluene at room temperature.

(A) $^1$HNMR spectrum
(B) $^1$H($^{31}$P)NMR spectrum
appears to indicate complete dissociation, the result may be due to irreversible oxidation in solution. The infrared spectrum of Pd(SP)$_3$ in a KBr disk shows absorption at 1620 cm$^{-1}$ which indicates the presence of free vinyl groups.

The $^1$HNMR spectrum of Pd(SP)$_3$ (Figure 3.16) shows resonances assignable to vinyl protons at $\delta$7.58 (dd,$H^1$), $\delta$4.72 ($d,H^2$), $\delta$5.06 ($d,H^3$) with $J(H^1H^2)$ and $J(H^1H^3)$ values of 11.0 and 17.5 Hz respectively. The chemical shifts and coupling constants of the vinyl protons in Pd(SP)$_3$ indicate that the vinyl groups are not coordinated to the palladium. However different samples, even though analytically pure, give rise to slightly different chemical shifts and line widths. This may be due to exchange with trace amounts of free SP, but this question has not been investigated.

The $^{31}$PNMR spectrum of Pd(SP)$_3$ at room temperature appears as a broad resonance ($\Delta\nu$ = 250 Hz) at $\delta$ca 11-18, the chemical shift varying with different samples. In addition, a sharp singlet is usually observed at $\delta$28, its intensity being less than that of the broad resonance. When the temperature is lowered to -80$^\circ$C the broad resonance sharpens slightly ($\Delta\nu$ = 85 Hz) and moves slightly downfield (ca 18-20) and in one case a resonance due to free SP at $\delta$-15 was observed. The peak at $\delta$28 remains unchanged at -80$^\circ$C and is tentatively assigned to SP oxide, which may be formed by adventitious palladium(0) catalysed air oxidation of SP.$^{271}$ At this stage these results cannot be interpreted and it would clearly be worthwhile to examine the effect on the $^{31}$PNMR spectrum of Pd(SP)$_2$ of additional SP.
3.2.5 Protonation of the bis(o-vinylphenyldiphenylphosphine) complexes of zerovalent platinum, palladium and nickel

Treatment of Pt(SP)\(_2\) with one equivalent of HBF\(_4\) or HPF\(_6\) in diethylether at room temperature yields the chelate \(\sigma\)-alkyl platinum(II) complex \([Pt(o\text{-CHMeC}_6\text{H}_4\text{PPh}_2)(SP)]^+X^- (X^- = BF_4^-, PF_6^-)\), \(3.8\) formed by addition of a proton to one of the coordinated vinyl groups (Eq. 3.18). The trans isomer of this compound, \(3.8a\) was isolated during the study of the reactions of trans-[PtHCl(PPh\(_3\))\(_2\)] and trans-[PtHCl(AsPh\(_3\))\(_2\)] with SP in the presence of AgBF\(_4\) or NH\(_4\)PF\(_6\) (complex 2.27, section 2.2.4). In contrast, the protonation of Pt(SP)\(_2\) always gives a mixture of cis and trans isomers, \(3.8b\) and \(3.8a\) respectively, in different proportions. Prolonged heating of the mixture of cis and trans isomers in dichloromethane gives the trans isomer which is therefore the thermodynamically stable product. The spectral properties and characterisation of the trans isomer, \(3.8a\) have been described in section 2.2.4 (complex 2.27). NMR spectral
Table 3.9 $^1$H$^3$P$^1$H NMR parameters for [M(o-CHMeC$_6$H$_4$Ph$_2$)(SP)]$^+$ for M = Pd, Pt

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<th>$\delta$H$^2$</th>
<th>$\delta$H$^3$</th>
<th>J(H$^1$H$^2$)</th>
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$^a$: $^1$HNMR spectra were measured in CDCl$_3$ with chemical shifts (δ) in ppm downfield of TMS and $^{31}$PNMR spectra were measured in CDCl$_3$/CHCl$_3$ and are referenced to external 85% H$_3$PO$_4$ and are positive to low field. All coupling constants (J) are in Hz. All spectra were measured at room temperature.

$d$: doublet, $q$: quartet

$b$: obscured by aromatic proton resonances.

$c$: not observed.

$d$: it appears as a triplet in the $^1$HNMR spectrum.
data for the cis isomer 3.8b are listed in Table 3.9. The $^1$HNMR spectrum of 3.8b shows a methyl proton resonance at $\delta 1.65$ as an apparent triplet flanked by $^{195}$Pt satellites [$^3J({\text{PtCH}}_3) = 30$ Hz]. The multiplicity is due to coincidentally equal couplings to the methine proton and trans phosphorus nucleus (Py), $^3J({\text{CH}_3}_{\text{meth}}) = ^4J({\text{CH}_3}_{\text{Py}}) = 7.5$ Hz (Table 3.9). The methine proton resonance appears as a multiplet at $\delta 3.50$ with $^{195}$Pt satellites [$^2J({\text{PtH}}_{\text{meth}}) = 68$ Hz]. The olefinic proton resonances, $^1H({}^{31}P)$, are at $\delta 5.85$ (d, H$^2$) and $\delta 4.80$ (d, H$^3$) accompanied by $^{195}$Pt satellites [$^1J({\text{PtH}}^2) = 63$ Hz, $^1J({\text{PtH}}^3) = 59$ Hz] (for numbering of protons see Table 3.9). The resonance of the olefinic proton H$^1$ is not observed, presumably because it is obscured by the aromatic peaks.

The $^{31}$PNMR spectrum of 3.8b appears as a pair of doublets with a $^2J(PP)$ value of 16 Hz. The doublet at $\delta 44.1$ is assigned to the phosphorus in the metallocycle (P$^x$) because of its large downfield shift on coordination due to formation of the ring ($\Delta R)^{205}$. The doublet at $\delta 30.0$ is assigned to the phosphorus of the triphenylphosphine ligand (Py). The values of $^1J({\text{PtP}}^x)$ and $^1J({\text{PtPy}})$ are 4200 Hz and 1633 Hz respectively, indicating that $P^x$ and $P^y$ are trans to the olefin and $\sigma$-carbon atom respectively. This result is also consistent with the structure derived from $^1$HNMR spectroscopy. In the product mixture, there is another minor isomer 3.8b' (12%) having similar chemical shifts and identical coupling constants to the major isomer 3.8b. It is probably the diastereomer of 3.8b arising from coordination of different faces of the olefin with respect to the chiral $\sigma$-carbon atom. This kind of isomerism has been observed for the trans isomer 3.8a (complex 2.2.7, section 2.2.4).
The complex 3.8 is not deprotonated by KOt-Bu to regenerate Pt(SP)₂ even on heating.

Treatment of Pd(SP)₂ with one equivalent of aqueous HBF₄ in diethylether at -30°C instantly precipitates an off-white solid (Eq. 3.19). This compound is air-stable and soluble in dichloromethane, chloroform and acetone. The ¹H and ³¹PNMR spectra (Table 3.9) suggest that it is a chelate o-alkyl palladium(II) complex, 3.9 containing a five-membered metallocycle having a structure analogous to that of trans-[Pt(₇CHMeC₆H₄PPh₂)(SP)]⁺, 3.8a. In contrast with the corresponding reaction of Pt(SP)₂, the palladium complex 3.9 is always isolated as the trans isomer and there is no evidence for the intermediacy of a cis isomer. Palladium(II) complexes are more labile than their platinum analogues, and hence cis to trans isomerisation is more rapid. Consequently, only the thermodynamic product is isolated.

The ³¹PNMR spectrum of 3.9 is an AB quartet with 2J(PP) value of 326 Hz, characteristic of a complex containing mutually trans phosphines (Table 3.9). The ³¹PNMR spectrum shows no sign of the diastereomer which is observed for the platinum analogue. The ¹HNMR spectrum shows characteristic methyl and methine proton resonances at δ1.10(d) and δ4.20(m).
respectively with a $^3J(CH_3H_{meth})$ value of 7.5 Hz. The olefinic proton resonances, $^1H\{^{31}P\}$, appear at $\delta5.50(d)$ and $\delta4.70(d)$ and are assigned to $H^2$ and $H^3$ respectively (for numbering of protons see Table 3.9). The interproton coupling constants $^3J(H^1H^2)$, $^3J(H^1H^3)$ are 8 and 15 Hz respectively. The olefinic proton $H^1$ is not observed and is presumably obscured by the aromatic proton resonances.

Protonation of Pd(SP)$_2$ with HBF$_4$ at room temperature, rather than at $-30^\circ C$ gave a yellow solid which is different from 3.9. This product has not been identified.

Reaction of one equivalent of aqueous HBF$_4$ with Ni(SP)$_2$ in diethyl ether at $-30^\circ C$ was attempted. Generally, white paramagnetic solids were obtained. These solids were not identified. On one occasion, an air-sensitive orange precipitate, 3.10 was obtained. This product, which was insoluble in toluene and diethylether dissolved in dichloromethane, chloroform, chlorobenzene and acetone to give air-sensitive solutions which rapidly blackened. The complex 3.10 may be a rare example of a cationic nickel(II)-olefin complex, but it could not be adequately characterised. The only known example of a cationic nickel(II)-olefin complex is the trigonal bipyramidal complex $[Ni(CH_2=CHCH_2CH_2)As(CH_2CH_2CH_2AsMe_2)_2]X$ (X = Cl, Br) 265. The infrared spectrum of the orange solid, 3.10 in a KBr disk at 0°C was broad but has a similar absorption pattern to that of trans-[Pt(o-CHMeC$_6$H$_4$PPh$_2$)(SP)]BF$_4$, 3.8a (Figure 3.17). The absence of absorptions in the region 1700-2000 cm$^{-1}$suggests that the compound is not a hydride complex. The microanalytical and infrared data suggest that 3.10 may be the chelate nickel(II) $\sigma$-alkyl complex trans-[Ni(o-CHMeC$_6$H$_4$PPh$_2$)(SP)]BF$_4$ analogous to the platinum(II), 3.8a and the palladium(II), 3.9 complexes. The $^1H$ and $^{31}P$NMR
Figure 3.17 Infrared spectra of the protonation products of Ni(SP)$_2$ and Pt(SP)$_2$ at 0°C in a KBr disk.

(A) trans-[Ni(o-CHMeC$_6$H$_4$PPh$_2$)(SP)]BF$_4$

(B) trans-[Pt(o-CHMeC$_6$H$_4$PPh$_2$)(SP)]BF$_4$
spectra in chlorobenzene and acetone could not be obtained at room temperature because the compound decomposed to metallic nickel.

At -90°C in d_6-acetone, the $^{31}$PNMR spectra showed that the solution consists of mainly Ni(SP)$_2$ and decomposition products. It is possible that this $\sigma$-alkyl-olefin-containing complex, 3.10 undergoes $\beta$-hydrogen elimination to form Ni(SP)$_2$ in solution which subsequently decomposes.

If this argument is correct, complex 3.10 is a rare example of a cationic nickel(II)-olefin complex.

3.2.6 Reactivity of the zerovalent metal complexes of bis(2-vinylphenylidiphenylphosphine), M(SP)$_2$ ($M = Ni, Pd, Pt$)

In situ NMR studies of the reactivities of the M(SP)$_2$ complexes towards ethylene, carbon monoxide, triphenylphosphine and methyl iodide were carried out at room temperature.

No colour change was observed when ethylene was bubbled for 30 minutes into solutions of Ni(SP)$_2$ or Pt(SP)$_2$ in d$_8$-toluene or into a solution of Pd(SP)$_2$ in CD$_2$Cl$_2$. The $^1$HNMR spectra which were recorded immediately afterwards, showed unchanged starting material and a peak due to free ethylene at $\delta$5.25. Thus, under these conditions, ethylene does not react with any compound in the series M(SP)$_2$ ($M = Ni, Pd, Pt$).

In contrast, under the same conditions carbon monoxide reacts immediately with all three complexes, as shown by colour changes of yellow to pale yellow (Ni), yellow to orange (Pt) and yellow to pale yellow to dark brown (Pd). The $^1$HNMR spectra show no resonances due to the coordinated vinyl group in the region $\delta$2.0 to $\delta$5.0. Many overlapping resonances in the region of the free vinyl group ($\delta$5.0 to $\delta$6.0) are
present. The infrared spectra in \textit{n}-hexane of the products isolated by addition of \textit{n}-pentane to the reaction mixture show a broad band in the region \textit{ca} 2000 cm$^{-1}$ probably due to overlapping carbonyl absorptions in various species. These data indicate that a mixture of products was formed for each metal, and these products were not characterised.

Addition of approximately one equivalent of triphenylphosphine to solutions of Ni(SP)$_2$ and Pt(SP)$_2$ in d$_8$-toluene and to the solution of Pd(SP)$_2$ in CD$_2$Cl$_2$ causes their $^1$H NMR spectra to broaden. This preliminary investigation indicates that triphenylphosphine can partially or wholly displace SP, but whether the olefinic group or the phosphorus donor is displaced, has not been determined.

No reaction occurs between Pt(SP)$_2$ and an excess of methyl iodide in toluene at room temperature. In contrast, solutions of Pd(SP)$_2$ in dichloromethane and Ni(SP)$_2$ in toluene react instantly with an excess of methyl iodide to yield red solids which are insoluble in most organic solvents. These products have not been characterised.

3.2.7 \textit{Attempts to prepare zerovalent platinum complexes of} \textit{o-vinylphenyldimethylphosphine (DMSP)}

It is interesting to study this series of compounds to see whether the ligand DMSP, which is less bulky and more basic than SP, will also form chelate olefin complexes of the d$^{10}$ nickel triad.

All attempts to prepare the complex Pt(DMSP)$_2$ and Pt(DMSP)$_3$ resulted in mixtures. The complexes were characterised by spectral comparison with the SP analogues (sections 3.2.1 and 3.2.4).
Figure 3.18: $^1$H-$^{31}$P NMR spectrum (200 MHz) of a mixture containing predominantly Pt(DMSP)$_2$ in $d_8$-toluene at room temperature ($Y = \text{unknown species}, X = \text{impurity}$).
Attempts to prepare Pt(DMSP)$_2$ by sodium amalgam reduction of PtCl$_2$(DMSP) with one equivalent of DMSP at -50°C in THF resulted in extensive decomposition to metallic platinum. Ligand exchange of Pt(COD)$_2$ with two equivalents of DMSP gives an oily product consisting mainly of Pt(DMSP)$_2$, 3.12 (70%). The $^1$HNMR spectrum of the mixture at room temperature (Figure 3.18) shows resonances characteristic of a coordinated vinyl group accompanied by $^{195}$Pt satellites. The chemical shifts $\delta$3.98(dd,H$^1$), $\delta$3.24(d,H$^2$) and $\delta$2.30(d,H$^3$) and coupling constants $^3$J(H$^1$H$^2$) 8.2 Hz, $^3$J(H$^1$H$^3$) 9.1 Hz, $^1$J(PtH$^1$) 42.6 Hz, $^1$J(PtH$^2$) 59.3 Hz and $^1$J(PtH$^3$) 55.1 Hz are comparable to those observed in Pt(SP)$_2$ (Table 3.2), suggesting that Pt(DMSP)$_2$ and Pt(SP)$_2$ have similar structures.

The $^{31}$PNMR spectrum of this mixture shows a major singlet at $\delta$-24.1 with $^{195}$Pt satellites [$^1$J(PtP) = 3065 Hz], and a minor singlet at $\delta$29.3 with no $^{195}$Pt satellites. The $^{31}$PNMR parameters of the major species, $^1$J(PtP) (3065 Hz) and the coordination shift (33 ppm) are comparable to those observed in Pt(SP)$_2$ (3130 Hz, 31 ppm respectively). Therefore, on the basis of $^1$H and $^{31}$PNMR data, the major component of this mixture is Pt(DMSP)$_2$ which has an analogous structure to Pt(SP)$_2$, 3.1.

At -50°C the $^1$HNMR spectrum of Pt(DMSP)$_2$ broadens, whereas the $^{31}$PNMR spectrum changes from a singlet to an AB quartet pattern which is also flanked by $^{195}$Pt satellites [$\delta$-14.2 (P$_A$), $\delta$-18.3 (P$_B$), $^3$J(P$_AP_B$) = 50 Hz, $^1$J(PtP$_A$) = 3337 Hz, $^1$J(PtP$_B$) = 3384 Hz]. Therefore at -50°C the symmetric tetrahedral structure is no longer retained. This may arise from the coordination of the two olefinic moieties to the platinum centre in different orientations with respect to each other. This kind of asymmetry has been observed in many compounds that contain two bidentate
olefinic tertiary phosphines, such as Ru(CO)(SP)$_2^{264}$, [Ir(CO)(SP)$_2^{+165}$, [Rh(CO)(SP)$_2^{+165}$, RhCl(SP)$_2^{165}$ and IrCl(SP)$_2^{165}$. Surprisingly, this behaviour is not observed in the SP analogue Pt(SP)$_2$. A significant temperature shift of the $^{31}$P resonances of Pt(DMSP)$_2$ is also observed.

The minor component of this mixture gives rise to broad $^1$HNMR resonances at $\delta 5$ to $\delta 6$ (Figure 3.18) and a $^{31}$P resonance as a sharp singlet at $\delta 29.3$. It is not known whether this is due to o-vinylphenyldimethylphosphine oxide or to Pt(DMSP)$_3$. If it is the latter, it is not clear why $^{195}$Pt satellites should not be observed, even at -80°C. Ligand exchange reaction (either dissociative or associative) is generally responsible for the loss of spin-spin coupling between $^{195}$Pt and $^{31}$P nuclei in zerovalent metal phosphine complexes of the nickel triad, however this process is normally frozen out at -80°C or higher temperature (section 1.2.3).

Reduction of PtCl$_2$(DMSP) in the presence of an excess of DMSP with 1% sodium amalgam at -50°C in THF or ligand exchange of Pt(COD)$_2$ and excess DMSP at room temperature give a very air-sensitive yellow oil. $^{31}$PNMR studies indicate that this oil consisted mainly of the complex that gives rise to a sharp singlet at $\delta 29.3$ which is observed as a minor component in the previous reaction. The $^1$HNMR spectrum of this species at room temperature shows broad resonances in the region of uncoordinated vinyl groups, $\delta 7.87$ (dd, $H^1$), $\delta 5.14$ (dd, $H^2$), $\delta 5.46$ (dd, $H^3$), $^3J(H^1H^2) = 11$ Hz, $^3J(H^1H^3) = 17$ Hz].
Zerovalent metal complexes of general formula M(SP)$_2$ (SP = o-vinylphenyldiphenylphosphine) for M = Ni, Pd, Pt have been synthesized. They represent the first examples of zerovalent metal complexes containing olefinic tertiary phosphines as the only ligands. The platinum(0) and nickel(0) complexes are monomeric, having a distorted tetrahedral structure, each SP ligand being coordinated through the P-donor and the olefinic moiety. In contrast the Pd(SP)$_2$ complex in the solid state is trigonal planar with one SP coordinated through the P-donor and the olefinic moiety, and one monodentate P-bonded SP. The Pt(SP)$_2$ and Ni(SP)$_2$ complexes are nonfluxional and dissociatively stable, however the palladium analogue is fluxional at room temperature, apparently owing to interconversion of an 18-electron Pd(SP)$_2$ and a 16-electron Pd(SP)$_2$ species and interconversion of free and coordinated olefins in the 16-electron Pd(SP)$_2$ complex. The different structure adopted by Pd(SP)$_2$ compared with its nickel and platinum analogues and its fluxional behaviour suggest that in zerovalent complexes palladium-olefin bonding is unfavourable, compared with that of nickel and platinum.

The upfield shifts of the vinylic protons and carbon nuclei and the decrease in the interproton coupling constants on coordination in the M(SP)$_2$ series increase in the order Pd < Ni < Pt, which may represent the order of metal-olefin bond strengths in this triad. The same trend is apparent from a comparison of both the coordinated C=C bond lengths and of the bend back angles of the substituents on the vinyl group, although it must be admitted that
the differences in each set of parameters are not statistically significant.

Ionization potential and electron affinity data (section 1.2, Table 1.2) have been taken to indicate that platinum(0) is the best σ-bonder, nickel(0) is the best π-bonder and palladium(0) is relatively weak in both bonding modes. Therefore the strength of the palladium-olefin bond in Pd(SP)₂ is predicted to be the weakest in this M(SP)₂ series, in good agreement with results observed in this work. The comparison of Pt(SP)₂ with Ni(SP)₂ is apparently inconsistent with the predictions above, and it may be that the greater σ-bonding between platinum(0) and the P-donor of SP synergically enhances π-back donation from platinum(0) to the olefinic moiety of SP.

The high reactivity of the 16-electron complex Pd(SP)₂ is illustrated by its instantaneous reaction with SP to form the trigonal planar tris-complex Pd(SP)₃. In contrast the corresponding reactions do not occur in the 18-electron Ni(SP)₂ and Pt(SP)₂ complexes, even under forcing conditions.

The 18-electron complex Pt(SP)₂, 3.1 undergoes a ligand exchange reaction at room temperature with SP. This reaction probably proceeds via the 16-electron complex Pt(SP)₂, 3.7 containing one P-bonded SP and one bidentate SP. In contrast the exchange of Ni(SP)₂ with SP is too slow to be detected on the NMR time scale at room temperature. These ligand exchange results depend on the relative affinity of nickel(0) and platinum(0) for olefins and for tertiary phosphines, and they suggest that the platinum-olefin and platinum-phosphorus bond strengths in Pt(SP)₂ are comparable whereas in Ni(SP)₂ the
nickel-olefin bond is stronger than the nickel-phosphorus bond. This conclusion is also supported by the results obtained from the series of M(PPh₃)₂(SP) complexes of the nickel triad reported in Chapter 4.

Protonation of the M(SP)₂ complexes with HBF₄ gives divalent metal σ-alkyl complexes containing a five-membered metallocycle and a coordinated vinyl group, [M(o-CHMeC₆H₄PPh₂)(o-CH₂=CHC₆H₄PPh₂)]⁺ for M = Ni, Pd and Pt. For the platinum(II) complex both the kinetic and thermodynamic products, the cis and trans isomers respectively, can be isolated. However for the palladium(II) complex, only the thermodynamic product, the trans isomer, is obtained, consistent with the greater lability of palladium(II) relative to platinum(II). In contrast to the palladium(II) and platinum(II) analogues, the cationic nickel(II) σ-alkyl complex is air-sensitive and thermally very unstable in solution, decomposing to Ni(SP)₂, presumably by β-hydrogen elimination. If the tentative structural assignment for the nickel(II) σ-alkyl complex [Ni(o-CHMeC₆H₄PPh₂)(o-CH₂=CHC₆H₄PPh₂)]⁺ is correct, then it is a rare example of nickel(II) olefinic complex.
3.3 Experimental

All reactions and isolations of products were carried out in an atmosphere of dry nitrogen or argon using standard Schlenk techniques.

All solvents used were of analytical grade. Toluene, benzene, diethylether and THF were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. n-Pentane and n-hexane were dried over sodium wire and degassed before use. Deuterated solvents for NMR samples were degassed via freeze/thaw cycles. Compounds other than those prepared in section 3.3.1 were obtained as analytical grade reagents commercially.

Microanalyses and osmometric molecular weight measurements (Knauer vapour pressure osmometer) were carried out by the Research School of Chemistry Microanalytical Service (Miss Brenda Stevenson and associates). Melting points were obtained on Gallenkamp melting point apparatus in sealed capillaries and are uncorrected.

Infrared spectra and NMR spectra were recorded on the instruments listed in section 2.3. Calibrations and computer simulations of the NMR spectra were carried out as described in section 2.3. Mass spectra were recorded on VG-Micromass 7070F medium resolution mass spectrometer.

Elemental analyses and melting points are given in Table 3.10.

3.3.1 Preparation of starting materials

The olefinic tertiary phosphine ligands o-vinylphenyldiphenylphosphine (SP) and its dimethylphosphine analogue (DMSP) were prepared
Table 3.10  Elemental analyses and melting point data

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<th>%H</th>
<th>%SP</th>
<th>%Metal</th>
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a: molecular weight by osmometry at 37\(^{oC}\) in toluene
b: measured by mass spectrometry
c: calculated with 0.25 mole of CH\(_2\)Cl\(_2\) which is evident in the \(^1\)HNMR spectrum
d: this compound cannot be recrystallised (see text).
as described in section 2.3.1.1. The complex PtCl₂(SP), 3.2 was prepared\(^{267}\) by refluxing anhydrous PtCl₂ with SP in chloroform for 24 hours. The mixture was filtered and the off-white product was obtained by precipitation with \(n\)-pentane. The palladium analogue, PdCl₂(SP) and the DMSP analogue, PtCl₂(DMSP) were prepared similarly\(^{225}\).

The complex Pt(COD)₂ was prepared by reduction of PtCl₂(COD) with dilithium cyclooctatetraene in the presence of excess COD\(^{133,134}\). The nickel analogue, Ni(COD)₂, was prepared by reduction of anhydrous bis(acetylacetonato)nickel(II) [Ni(acac)₂] with triethylaluminium in the presence of COD\(^{131}\). The complex Ni(acac)₂ was prepared by a literature method\(^{269}\). The anhydrous bis(acetylacetonato)nickel(II) was prepared by azeotropic distillation of water from a suspension of the hydrated compound in toluene\(^{131}\). The highly volatile complex Pd(\(n^3\-C_3H_5\))(\(n^5\-C_5H_5\)) was prepared\(^{268}\) by reaction of sodium cyclopentadienide and bis(\(n^3\)-allyl)di-\(\mu\)-chlorodipalladium(II).

3.3.2 Preparation of bis(o-vinylphenyldiphenylphosphine)platinum(O), \(\text{Pt(SP)}_2\), 3.1

3.3.2.1 Reduction of PtCl₂(SP) with 1\% sodium amalgam in the presence of SP

A suspension of PtCl₂(SP) (1.3g, 2.3mmol) and SP (0.07g, 2.3mmol) in THF (50ml) was added to 1\% sodium amalgam, (64.6g, 27.8mmol Na). The reaction mixture was vigorously stirred at -30°C in a dry ice-acetone
bath for 3 hours. After allowing the mixture to warm to room
temperature, the sodium amalgam was removed by centrifugation.
The clear yellow solution was evaporated to dryness and redissolved
in diethylether (40ml). The white diethylether-insoluble solid
was removed and the diethylether solution was passed through a
short column of alumina (Grade 2, 2 × 5cm) and evaporated to
dryness. Recrystallisation from either diethylether or toluene-n-
hexane gave a bright yellow crystalline solid, Pt(SP)₂ in variable
yield (10-50%).

3.3.2.2 Ligand exchange of Pt(COD)₂ and SP

A solution of Pt(COD)₂ (0.09g, 0.22mmol) in toluene (5ml) was
added to a solution of SP (0.13g, 0.44mmol) in toluene (5ml), and
the mixture immediately turned yellow. The reaction mixture was
stirred for 3 hours, evaporated to dryness and dried in vacuo
for 3 hours to give a yellow solid. Recrystallisation from
toluene-n-hexane gave Pt(SP)₂ as a bright yellow crystalline
solid (0.15g, 88%). This complex is soluble in toluene, benzene,
THF and diethylether. It is insoluble in n-pentane, n-hexane,
methanol or ethanol. Solutions in chloroform and dichloromethane
decomposed slowly within several hours. This complex is moderately
air-sensitive in solution but appears to be only slightly air-
sensitive in the solid state.
3.3.3 Preparation of bis(o-vinylphenyldiphenylphosphine)nickel(0), \( \text{Ni}(\text{SP})_2 \), 3.3

3.3.3.1 Ligand exchange of \( \text{Ni}(\text{COD})_2 \) and SP

A solution of \( \text{Ni}(\text{COD})_2 \) (4.7g, 17.0mmol) in diethylether (50ml) was added slowly to a solution of SP (9.8g, 34.1mmol) in diethylether (250ml) at \(-50^\circ\text{C}\). The reaction mixture was allowed to warm to room temperature, and was stirred overnight. The reaction mixture was reduced to half its volume, and was cooled to \(-70^\circ\text{C}\). A bright yellow crystalline solid formed. The solid was filtered off, washed with \( n \)-pentane (3 x 40ml) and dried in vacuo to give the bright yellow compound, \( \text{Ni}(\text{SP})_2 \) (9.5g, 89%).

3.3.3.2 Reduction of \( \text{Ni}(\text{acac})_2 \) with triethylaluminium in the presence of SP

Anhydrous \( \text{Ni}(\text{acac})_2 \) (2.08g, 8.1mmol) and SP (4.69g, 16.3mmol) were dissolved in toluene (10ml) and cooled to \(-50^\circ\text{C}\). Approximately 3ml of butadiene, dried by passing through a U-trap containing molecular sieves (Type 3A), was admitted to the reaction mixture. With rapid stirring, triethylaluminium (3ml, 21.9mmol) in toluene (3ml) was added slowly to the reaction mixture. The temperature of the reaction mixture was maintained at below \(-20^\circ\text{C}\) during the addition of triethylaluminium. The reaction mixture was left to stir overnight and slowly warmed up to room temperature. The resulting yellow mixture was cooled slowly to \(-70^\circ\text{C}\). Addition of \( n \)-hexane (60ml) instantly gave a bright yellow precipitate. The product was filtered off, washed with \( n \)-hexane (3 x 20ml) and cold diethylether (10ml) and
dried in vacuo to give Ni(SP)<sub>2</sub> (4.7g, 91%).

The complex Ni(SP)<sub>2</sub> is air-sensitive, decomposing over a few hours to a greenish white solid, presumably containing nickel(II). However it can be transferred in air quickly without appreciable decomposition. It is soluble in toluene, benzene and THF to give very air-sensitive solutions but is significantly less soluble in diethylether. It is insoluble in n-pentane and n-hexane. It oxidatively decomposes rapidly in dichloromethane and chloroform.

3.3.4 Preparation of bis(o-vinylphenyldiphenylphosphine)palladium(O), Pd(SP)<sub>2</sub>, 3.4

3.3.4.1 Reaction of Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) with SP

A clear dark red solution containing Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) (2.85g, 13.8 mmol) and SP (7.73g, 26.8 mmol) in toluene (5ml) was stirred vigorously for 15 minutes. A pale yellow precipitate formed, resulting in a very thick suspension. The reaction mixture was stirred for 3 hours. The pale yellow precipitate was isolated by filtration, washed with n-pentane (3 x 10ml) and dried in vacuo to give Pd(SP)<sub>2</sub> (5.95g, 65%).

The complex Pd(SP)<sub>2</sub> is not very soluble in toluene and diethylether but is more soluble in THF. It is very soluble in dichloromethane and chloroform. It is stable in dichloromethane at room temperature for 10-15 hours and for longer periods of time at lower temperatures. It is soluble in n-pentane, n-hexane and ethanol. It is moderately air-
sensitive in the solid state, but much more air-sensitive in solution.

3.3.4.2 Reaction of Pd(η\textsuperscript{3}-C\textsubscript{3}H\textsubscript{5})(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}) and SP to give Pd(C\textsubscript{3}H\textsubscript{5})(C\textsubscript{5}H\textsubscript{5})(SP), 3.6

A solution of Pd(η\textsuperscript{3}-C\textsubscript{3}H\textsubscript{5})(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}) (0.64g, 3.01mmol) and SP (5g, 17.34mmol) in toluene (30ml) at -70\degree C (dry ice-acetone bath) was stirred for one hour. Addition of n-hexane (40ml) at -70\degree C gave a bright yellow precipitate which was filtered off at -70\degree C to give 3.6 (1.3g, 85\%). The solid is not very soluble in toluene and gives a reddish solution. It is air-sensitive and extremely unstable thermally. The solution decomposes at room temperature within one hour under argon atmosphere.

3.3.4.3 Reaction of Pd(C\textsubscript{3}H\textsubscript{5})(C\textsubscript{5}H\textsubscript{5})(SP), 3.6 with SP

Toluene (2ml) was added to a mixture of the solid, Pd(C\textsubscript{3}H\textsubscript{5})(C\textsubscript{5}H\textsubscript{5})(SP), 3.6 (0.215g, 0.43mmol) and SP (0.124g, 0.43mmol) to give a clear dark red solution. After stirring for 1 hour, a yellow solid precipitated. The product was filtered off, washed with n-hexane (3 x 10ml) and dried in vacuo to give 3.4 (0.19g, 65%).
3.3.5 Attempted preparation of tris(o-vinylphenyldiphenylphosphine)platinum(0)

3.3.5.1 Ligand exchange of Pt(COD)$_2$ and SP

A solution of Pt(COD)$_2$ (0.079g, 0.18mmol), in toluene (4ml) was added to a solution of SP (0.23g, 0.80mmol) in toluene (5ml). The colourless solution turned yellow immediately. The reaction mixture was refluxed overnight. Addition of n-hexane gave a pale yellow solid which was filtered off, washed with n-hexane (3 × 10ml) and diethylether (3 × 10ml) and dried in vacuo. This solid was shown by $^1$H and $^{31}$PNMR spectroscopy and by elemental analysis to be a mixture of Pt(SP)$_2$, SP oxide and SP.

3.3.5.2 Reduction of PtCl$_2$(SP), 3.2 and an excess of SP with 1% sodium amalgam

Sodium amalgam (90.9g, 1%Na, 39.1mmol Na) was added to a suspension of PtCl$_2$(SP) (1.47g, 2.6mmol) and SP (1.7g, 5.9mmol) in THF (40ml) at -30°C. The reaction mixture was stirred vigorously for 3 hours and the sodium amalgam was removed by centrifugation. The yellow liquid was evaporated to dryness and recrystallised from diethylether to give a pale yellow solid (1.1g). Elemental analyses, $^1$H and $^{31}$PNMR spectroscopy indicate that the solid is a mixture of Pt(SP)$_2$, SP oxide and SP.
3.3.6 Preparation of \( \text{tris(o-vinylphenyldiphenylphosphine)palladium(O)} \), \( \text{Pd(Sp)}_3 \), 3.5

A clear red solution \( \text{Pd}(\eta^3-\text{C}_3\text{H}_5)(\eta^5-\text{C}_5\text{H}_5) \) (0.22g, 0.44mmol) in toluene (5 ml) was added to the colourless solution of SP (0.51g, 1.77mmol) in toluene (5ml). The reaction mixture turned yellow instantly and was stirred overnight. The reaction mixture was reduced to half and addition of \( n \)-pentane (20ml) gave a yellow precipitate. The product was filtered off, washed with \( n \)-pentane (3 \times 10ml) and dried in vacuo to give \( \text{Pd(Sp)}_3 \) (0.35g, 81%). This compound can be recrystallised from toluene-\( n \)-pentane. It is soluble in toluene, benzene, diethylether and THF and insoluble in saturated hydrocarbons.

3.3.7 Attempted preparation of \( \text{tris(o-vinylphenyldiphenylphosphine)nickel(O)} \), \( \text{Ni(Sp)}_3 \)

3.3.7.1 Reduction of \( \text{Ni(acac)}_2 \) with triethylaluminium in the presence of SP

Anhydrous \( \text{Ni(acac)}_2 \) (2.71g, 10.5mmol) and SP (10.3g, 35.7mmol) were dissolved in toluene (10ml) and cooled to -50°C in a dry ice-acetone bath. Approximately 3ml of butadiene, dried by passing through a U-trap containing molecular sieves (Type 3A) was admitted to the reaction mixture. With rapid stirring, triethylaluminium (4.0ml, 29.1mmol) was added slowly to the reaction mixture. The temperature of the reaction mixture was maintained below -20°C during the addition of
triethylaluminium. The reaction mixture was left to stir overnight and allowed to warm up slowly to room temperature. The yellow reaction mixture, was cooled slowly to -70°C. Addition of n-hexane (60 ml) gave a bright yellow precipitate. The product was filtered off, washed with n-hexane (3 x 30 ml) and cold diethylether (2 x 10 ml) and dried in vacuo. The yellow solid was shown by 1H and 31PNMR spectroscopy and microanalysis to be Ni(SP)₂ (6.5 g).

3.3.7.2 Ligand exchange of Ni(COD)₂ and SP

A yellow solution of Ni(COD)₂ (0.71 g, 2.6 mmol) in toluene (25 ml) was added slowly to a colourless solution of SP (2.7 g, 9.4 mmol) in toluene (25 ml). The reaction mixture turned yellow and was refluxed for 24 hours. It was then cooled to room temperature and evaporated to dryness. The residue was dried in vacuo for 5 hours. The resulting yellow solid was recrystallised from toluene–n-hexane to give a bright yellow solid. This solid was filtered off and washed with cold diethylether (3 x 10 ml). Elemental analysis and NMR (1H and 31P) spectroscopy show that this product is Ni(SP)₂.

3.3.8 Protonation of bis(o-vinylphenyldiphenylphosphine)platinum(0) with HBF₄ or HPF₆

Aqueous HBF₄ (43% w/w, 0.03 ml) was added to a clear yellow solution of Pt(SP)₂ (0.15 g, 0.19 mmol) in diethylether (10 ml). A white precipitate formed instantly and it was filtered off. The product was washed with
diethylether (3 × 5ml) and dried in vacuo to give the BF₄ salt of the cation 3.8, [Pt(o-CHMeC₆H₄PPh₂)(SP)]BF₄ (0.12g, 72%).

The white air-stable solid is soluble in chloroform, dichloromethane and acetone but insoluble in n-pentane, n-hexane, ethanol, methanol, diethylether, benzene and toluene.

The protonation of Pt(SP)₂ with HPF₆ was carried out in a similar manner to give [Pt(o-CHMeC₆H₄PPh₂)(SP)]PF₆ in 75% yield.

3.3.9 Protonation of bis(o-vinylphenyldiphenylphospine)palladium(0) with HBF₄

A solution of Pd(SP)₂ (0.050g, 0.073mmol) in diethylether (20ml) was cooled to -30°C in a dry ice-acetone bath. Aqueous HBF₄ (43% w/w, 0.02ml) was added to the cooled reaction mixture, to give a white precipitate on warming to room temperature. The product was filtered off, washed with diethylether (3 × 5ml) and dried in vacuo to give trans[Pd(o-CHMeC₆H₄PPh₂)(SP)]BF₄, 3.9 (0.45g, 80%). This air-stable complex is soluble in dichloromethane, chloroform, acetone but insoluble in n-pentane, n-hexane, diethylether, benzene and toluene.

3.3.10 Protonation of bis(o-vinylphenyldiphenylphosphine)nickel(0) with HBF₄

A solution of Ni(SP)₂ (1.00g, 1.57mmol) in diethylether (50ml) was cooled to -30°C in a dry ice-acetone bath. Aqueous HBF₄ (43% w/w,
0.15 ml) was added to give an orange precipitate on warming to room temperature. The product was filtered off, washed with diethylether (3 x 20 ml) and then dried in vacuo to give [Ni(o-CHMeC₆H₄PPh₂)(SP)]BF₄, 3.10 (0.79 g, 70%). The orange solid is insoluble in toluene and diethylether but soluble in acetone, chlorobenzene, dichloromethane and chloroform. It is highly air-sensitive and thermally unstable in solution. It turns black instantly in chlorinated solvents at room temperature. This compound decomposed to metallic nickel during attempts at recrystallisation.

3.3.11 Attempted preparation of bis and tris(o-vinylphenyldimethylphosphine)platinum(0), Pt(DMSP)₂ and Pt(DMSP)₃

3.3.11.1 Reduction of PtCl₂(DMSP) with 1% sodium amalgam in the presence of DMSP

Sodium amalgam (40.4 g, 1% Na, 17.4 mmol Na) was added to a suspension of PtCl₂(DMSP) (0.50 g, 1.2 mmol) and DMSP (0.19 g, 1.2 mmol) in THF (60 ml) at low temperature (-30°C to -50°C; dry ice-acetone bath). The reaction mixture was stirred vigorously for 3 hours at -50°C. After allowing the reaction mixture to warm to room temperature, the sodium amalgam was removed by centrifugation. The resulting solution is still dark even after filtration with celite. Apparently decomposition had taken place to form very fine particles of metallic platinum.
Similarly the reduction of PtCl₂(DMSP) in the presence of excess DMSP with 1% sodium amalgam was attempted. The product, which is an air-sensitive yellow oil, was shown by ¹H and ³¹P NMR spectroscopy to be a mixture of Pt(DMSP)₂ and an unknown species (see text).

3.3.11.2 Ligand exchange of Pt(COD)₂ and DMSP

A solution of Pt(COD)₂ (0.14g, 0.33mmol) in toluene (40ml) was added to the solution of DMSP (0.11g, 0.67mmol) in toluene (10ml). The colourless solution turned yellow immediately and it was stirred at room temperature for 3 hours. The reaction mixture was evaporated to dryness and the residue was dried in vacuo for 3 hours to give a yellow oil. Attempts to crystallise the product using toluene-n-hexane or diethylether-n-hexane were unsuccessful. The oily product was triturated with n-hexane and the solvents were evaporated to leave a yellow very air-sensitive oil. The ¹H and ³¹P NMR spectroscopy indicate that it is a mixture of products, containing predominantly Pt(DMSP)₂, 3.11.

Similarly the reaction of Pt(COD)₂ with an excess of DMSP gave an air-sensitive yellow oil which was shown by ¹H and ³¹P NMR spectroscopy to be a mixture of Pt(DMSP)₂ and an unknown species (see text).
4.1 Introduction

Transition metal complexes containing different tertiary phosphines are rare because they tend to disproportionate to give a mixture of more symmetrical complexes. Metal complexes of low symmetry containing mixed ligands with a variety of electronic and steric parameters can assist studies of the catalytic activity of metal complexes and of the asymmetric syntheses catalysed by metal complexes. Consequently the studies of mixed ligand metal complexes are important. The complexes PtLL'Cl₂ (L = PPh₃, L' = sulphides, amines) are reported to be more effective catalysts than either PtL₂Cl₂ or PtL₂Cl₂ for the hydrogenation of styrene to ethylbenzene in the presence of SnCl₂.2H₂O. Clark and coworkers have reported the preparation of platinum(II) complexes of the type PtLLX₂ and PtLLXY with mixed unidentate ligands (L' = PEt₃, L = PPh₃, PMePh₂, P-i-Pr₃, PCy₃, AsPh₃ or SbPh₃; X = Cl and Y = Cl, H or Me). This series of complexes is stable towards disproportionation and exhibits an extensive chemistry.

There are few reports of platinum(0) complexes containing different tertiary phosphine ligands. A difficulty in the preparation of these complexes is the tendency of zerovalent platinum complexes containing tertiary phosphine ligands to dissociate in
solution\textsuperscript{36}. By using the tridentate triphosphine ligand CH\textsubscript{3}C(CH\textsubscript{2}PPh\textsubscript{2})\textsubscript{3} (abbreviated as triphos), a series of dissociatively stable platinum(0)-tetrakis phosphine complexes of the type Pt(triphos)L [L = PPh\textsubscript{3}, P(p-tolyl)\textsubscript{3}, PPh\textsubscript{2}Me, P(OCH\textsubscript{2})\textsubscript{3}CCH\textsubscript{3}, PF\textsubscript{2}NMe\textsubscript{2}, P(OPh)\textsubscript{3}, PF\textsubscript{3}, CO] has been prepared by Meek and coworkers\textsuperscript{278}. The \textsuperscript{31}P NMR spectra of these complexes are interesting (Table 4.1), as the magnitude of \textsuperscript{1}J(PtP) for the triphos ligand is significantly smaller than that for the monodentate tertiary phosphine or phosphite.

The major factor which influences the magnitude of the directly bonded \textsuperscript{195}Pt-\textsuperscript{31}P coupling constants is assumed to be the s-character of the Pt-P bond\textsuperscript{280-282}. Meek and coworkers reported\textsuperscript{278} that the difference in coupling constants in Pt(triphos)L complexes may be that the s-character of the Pt-P bond of the monodentate ligand is larger than that of the Pt-P bond of the triphos ligand. The restricted "bite angle" of the P-Pt-P bonds (93-94°) imposed by the triphos should decrease the s-character of the Pt-P bonds of this

\[
P P P = \text{triphos} = CH_3C(CH_2PPh_2)_3
\]

Figure 4.1 Structure of Pt(triphos)L (see Table 4.1)
Table 4.1 $^{31}$PNMR data for the mixed phosphine platinum(0) complexes Pt(triphos)L$^a$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{1}J$(PtP) (triphos)</th>
<th>$^{2}J$(PP')</th>
<th>$^{1}J$(PtP') L</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(triphos)PPh$_3$</td>
<td>3096</td>
<td>51</td>
<td>5400</td>
<td>278</td>
</tr>
<tr>
<td>Pt(triphos)P(p-tolyl)$_3$</td>
<td>3098</td>
<td>51</td>
<td>5380</td>
<td>278</td>
</tr>
<tr>
<td>Pt(triphos)PPh$_2$Me</td>
<td>3075</td>
<td>51</td>
<td>5370</td>
<td>278</td>
</tr>
<tr>
<td>Pt(triphos)P(OCH$_2$)$_3$CCH$_3$</td>
<td>2990</td>
<td>68</td>
<td>6787</td>
<td>278</td>
</tr>
<tr>
<td>Pt(triphos)PF$_2$NMe$_2$</td>
<td>2893</td>
<td>83</td>
<td>8838</td>
<td>278</td>
</tr>
<tr>
<td>Pt(triphos)P(OPh)$_3$</td>
<td>2883</td>
<td>87</td>
<td>9150</td>
<td>278</td>
</tr>
<tr>
<td>Pt(triphos)PF$_3$</td>
<td>2867</td>
<td>95</td>
<td>9500$^b$</td>
<td>278</td>
</tr>
<tr>
<td>Pt(triphos)PF$_3$</td>
<td>2867</td>
<td>95.2</td>
<td>10200$^b$</td>
<td>283</td>
</tr>
<tr>
<td>Pt(triphos)CO</td>
<td>2837</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(triphos)PF$_2$(OPh)</td>
<td>2875</td>
<td>88.1</td>
<td>9766</td>
<td>283</td>
</tr>
</tbody>
</table>

$^a$: coupling constants (J) in Hz

$^b$: very low solubility of this complex prevents direct observation of $^{195}$Pt satellites. The value was obtained by extrapolation.
ligand. Therefore these three triphos Pt-P bonds will have a smaller s-character than ideal tetrahedral Pt-P bonds (ideal tetrahedral angle = 109°). Thus the remaining Pt-P bond will be rehybridized to include more s-character, and would be expected to exhibit a larger coupling constant. An inverse relationship between $^{1}J$(PtP) and $^{1}J$(PtP') in the Pt(triphos)L complexes (Table 4.1) provides support for such a rehybridisation and redistribution of s-character. The magnitude of the coupling constant, $^{1}J$(PtP') is also increased as more electronegative substituents are attached to phosphorus. This work has been extended by Nixon and coworkers, who have observed the same trend in the series in Pt(triphos)L (L = PF(CF$_3$)$_2$, PPhCl$_2$, PF$_2$(OPh), PCl$_3$, PF$_2$CHCl$_2$).

The objective of the work described in this chapter was to synthesize and characterize zerovalent nickel, palladium and platinum complexes containing different tertiary phosphine ligands, o-vinylphenyldiphenylphosphine (SP) and triphenylphosphine having the empirical formula $M$(PPh$_3$)$_2$(SP).

These studies complement those described in Chapter 3 and provide an interesting comparison of the relative abilities of the three metals to bind olefins and tertiary phosphines.

4.2 Results and discussion

4.2.1 Synthesis and characterisation of $Pt$(PPh$_3$)$_2$(SP), 4.1

The moderately air-sensitive bright yellow complex, $Pt$(PPh$_3$)$_2$(SP), 4.1 was prepared either from the reaction of $Pt$(PPh$_3$)$_2$(C$_2$H$_4$) with one equivalent of SP or by treatment of $Pt$(COD)$_2$ with two equivalents of
triphenylphosphine and one equivalent of SP at room temperature (Scheme 4.1).

\[ \text{Pt(PPh}_3\text{)}_2(\text{SP}) \]

\[ \text{Pt(PPh}_3\text{)}_2(\text{C}_2\text{H}_4) + \text{SP} \]

\[ \text{Pt(COD)}_2 + 2\text{PPh}_3 + \text{SP} \]

Scheme 4.1 Synthesis of Pt(PPh$_3$)$_2$(SP), 4.1

Elemental analyses agree with the empirical formula Pt(PPh$_3$)$_2$(SP). However osmometric molecular weight measurements in toluene at 37°C gave only half the expected value for a monomer (found 491; calc. 1008) indicating either dissociation or irreversible oxidation of the complex. The infrared spectrum in a KBr disk has no absorption in the region ca 1620 cm$^{-1}$, suggesting the absence of a free vinyl group.

The $^1$H and $^{31}$PNMR spectra of 4.1 at room temperature are broad which suggests that some dynamic processes are operating. The variable temperature $^{31}$PNMR spectra were recorded from room temperature to -117°C (Figure 4.2 and Figure 4.3). At room temperature the $^{31}$PNMR spectrum comprises two broad resonances at $\delta$23 and $\delta$17 with no apparent $^{195}$Pt satellites. As the temperature is lowered to -30°C a five-line pattern
Variable temperature $^3$PNMR spectra (24.28 MHz) for Pt(PPh$_3$)$_2$(SP) in d$_8$-toluene/toluene. X and Y are impurities OPPh$_3$ and Pt(PPh$_3$)$_3$ respectively.
Figure 4.3 Variable temperature $^{31}$PNMR spectra (80.99 MHz) of Pt(PPh$_3$)$_2$(SP) in $d_8$-THF/THF. The compounds OPPh$_3$(X), Pt(SP)$_2$(Y) and Pt(PPh$_3$)$_3$(Z) are impurities arising from disproportionation and subsequent reactions. (O) is an unknown impurity.
accompanied by $^{195}$Pt satellites appears. These resonances continue to sharpen as the temperature is lowered to -70°C. At this temperature, the five-line pattern with $^{195}$Pt satellites is sharp and can be analysed as an $A_2BX$ spin system ($X = ^{195}$Pt) [$\delta 16.5(P_A)$, $\delta 8.1(P_B)$, $2J(P_A,P_B) = 50$ Hz, $^1J(PtP_A) = 4209$ Hz, $^1J(PtP_B) = 2411$ Hz]. However, further cooling to -90°C causes the spectrum to broaden. At -117°C, the spectrum shows an eleven-line pattern accompanied by $^{195}$Pt satellites, which can be analysed as an ABCX spin system ($X = ^{195}$Pt). Simulation gives $\delta 19.3(P_A)$, $\delta 17.6(P_B)$ and $\delta 13.9(P_C)$ with $^2J(P_A,P_B) = 26.8$ Hz, $^2J(P_A,P_C) = 34.5$ Hz and $^2J(P_B,P_C) = 61.0$ Hz. The values of $^1J(PtP_A)$, $^1J(PtP_B)$ and $^1J(PtP_C)$ are 4009 Hz, 4305 Hz and 2501 Hz respectively. Peaks due to three other species, $\text{Pt(SP)}_2$ [$\delta 21.1$, $^1J(PtP) = 3106$ Hz], $\text{Pt(PPh}_3)_3$ [$\delta 53.0$] and a singlet at $\delta 26.6$ with no apparent $^{195}$Pt satellites are present in this spectrum. The singlet at $\delta 26.6$ is assignable to triphenylphosphine oxide$^{220}$. The additional compounds $\text{Pt(SP)}_2$ and $\text{Pt(PPh}_3)_3$ which are detected at low temperatures are formed in the slow disproportionation reaction (Eq. 4.1).

A solution of $\text{Pt(PPh}_3)_2(\text{SP})$ in toluene disproportionates completely within one week at room temperature to $\text{Pt(SP)}_2$, $\text{Pt(PPh}_3)_3$ and triphenylphosphine (identified by $^{31}$PNMR spectroscopy).

$$2\text{Pt(PPh}_3)_2(\text{SP}) \xrightarrow{\text{RT, <7 days}} \text{Pt(PPh}_3)_3 + \text{Pt(SP)}_2 + \text{PPh}_3$$

Eq. 4.1

The triphenylphosphine oxide found in the $^{31}$PNMR samples is formed by air oxidation of the triphenylphosphine liberated from the disproportionation reaction (Eq. 4.1). The formation of
triphenylphosphine oxide in this system is probably catalysed by the presence of platinum(0) phosphine complexes in the mixture. The complex Pt(PPh₃)₂(SP) was dissolved in d₈-toluene/toluene and 31PNMR spectra were measured between room temperature and -90°C. The sample was found to contain no disproportionation products (Figure 4.2). However, when Pt(PPh₃)₂(SP) was dissolved in d₈-THF/THF and 31PNMR spectra measured at below -100°C, disproportionation products were found (Figure 4.3). Therefore it is likely that the disproportionation reaction is faster in THF than in toluene.

The ¹HNMR spectrum of Pt(PPh₃)₂(SP) at room temperature is broad and uninformative and there are no resonances in the region δ6 to δ0. At -50°C, the spectrum sharpens and shows two sets of typical coordinated vinyl resonances of unequal intensity in a ca 1:5 ratio. The resonances of the minor component were assigned to Pt(SP)₂ on the basis of chemical shifts and coupling constants. The ¹H(³¹P)NMR spectrum shows resonances due to the major component at δ4.85 (dd, H¹), δ3.93 (d, H²) and δ2.83 (d, H³) with ¹⁹⁵Pt satellites [J(PtH¹) = 52 Hz, J(PtH²) = 60 Hz and J(PtH³) = 40 Hz] (for numbering of protons see Figure 4.4). The presence of coordinated vinyl resonances at -50°C suggests that this compound contains a coordinated vinyl group. Further cooling to -100°C does not result in sharp spectra, partly due to a decrease in resolution.

Three possible structures for the complexes of the type M(PPh₃)₂(SP) for M = Ni, Pd, Pt are shown in Figure 4.4. The tetrahedral structure (Figure 4.4a) contains a bidentate SP where the vinyl group is coordinated to the metal. There are two trigonal planar structures.
The presence of characteristic vinyl proton resonances and absence of free vinyl proton resonances in Figure 4.4a preclude the possibility that M(PPh₃)₂(SP) is a complex with the steric hindrance of the Ph₃P ligands and the P(SP) ligands in the vicinity of the vinyl group. The steric hindrance of the Ph₃P ligands in the vicinity of the vinyl group might favor the trigonal plane structures, Figure 4.4b or Figure 4.4c, respectively (section 4.5).

The stereochemical configuration (Figure 4.4a) shows the steric hindrance of the Ph₃P ligands and the P(SP) ligands in the vicinity of the vinyl group, which are similar to those of Figure 4.2b and Figure 4.2c, respectively (section 4.5).

Figure 4.4 Possible structures of M(PPh₃)₂(SP)
In one structure, the SP ligand is P-bonded (Figure 4.4b) and in the other structure (Figure 4.4c), the SP ligand is bonded via its vinyl group. The steric constraint (chelate effect) of the olefinic tertiary phosphine ligand SP, which forces the vinyl group to be in the vicinity of the coordination sphere, should favour the tetrahedral configuration (Figure 4.4a). However the steric bulk of the ligands (cone angles of PPh$_3$ = 145°, SP > 161°, see Appendix I) might favour the trigonal planar structures, Figure 4.4b or Figure 4.4c, which are similar to those adopted by Pt(PPh$_3$)$_3$ and Pt(PPh$_3$)$_2$(C$_2$H$_4$)$_2$ respectively (section 1.2.3 and 1.2.4).

The presence of coordinated vinyl proton resonances and absence of free vinyl proton resonance at -50°C preclude the possibility that Pt(PPh$_3$)$_2$(SP) is a trigonal planar trisphosphine complex with the olefinic moiety of the SP ligand dangling free (Figure 4.4b). This conclusion is supported by the absence of the infrared absorption at ca 1620 cm$^{-1}$ characteristic of free vinyl groups. Moreover, the three phosphorus nuclei have $^{195}$Pt satellites in the $^{31}$PNMR spectra and are mutually coupled, indicating that the structure with an uncoordinated phosphorus atom (Figure 4.4c) is unlikely. These data suggest that complex 4.1 is a tetrahedral complex containing three coordinated tertiary phosphines and one vinyl group (Figure 4.4a). In such a structure, the two triphenylphosphine ligands should be inequivalent, owing to the non-planarity of the chelate ring formed by coordination of SP. This inequivalence is observed at -117°C giving the ABCX spin system ($X = ^{195}$Pt) of the $^{31}$PNMR spectrum (Figure 4.3). In this spectrum of the tetrahedral complex, $P_A$ and $P_B$, which have similar chemical shifts
(δ19.3 and δ17.6 respectively) and $^{195}_{\text{Pt}}-^{31}_{\text{P}}$ coupling constants
$[^{1}J(\text{PtP}_{A}) = 4009 \text{ Hz}, \; ^{1}J(\text{PtP}_{B}) = 4305 \text{ Hz}]$ are assigned to the two triphenylphosphine ligands and $P_{c}$ (δ13.9) with $^{1}J(\text{PtP}_{c})$ value of 2501 Hz is assigned to the SP ligand.

The $^{31}_{\text{P}}$NMR spectrum of $\text{Pt(PPPh}_{3})_{2}(\text{SP})$ at -70°C is an $A_{2}BX$ spin system ($X = 195_{\text{Pt}}$), in which the $^{31}_{\text{P}}$ resonance at δ16.5 ($P_{A}$) is assigned to two equivalent triphenylphosphine ligands and the resonance at δ8.1 is assigned to SP. The equivalence of the two triphenylphosphine ligands of $\text{Pt(PPPh}_{3})_{2}(\text{SP})$ at -70°C or higher possibly arises from the dissociation of the coordinated vinyl group forming a trigonal planar trisphosphine intermediate, 4.2 (Scheme 4.2).

Scheme 4.2 A possible mechanism for equilibration of the two triphenylphosphine ligands in $\text{Pt(PPPh}_{3})_{2}(\text{SP})$. 
The $^{31}\text{P}$ chemical shift of the SP ligand in 4.1 at -70°C (§8.1) shows a significant temperature shift when compared to the corresponding value at -117°C (§13.9).

The magnitudes of $^1\text{J}(\text{PtP})$ for SP and triphenylphosphine differ greatly, although the corresponding values at -117°C and -70°C are comparable in magnitude which indicates no significant structural difference between these two temperatures. The values of the $^{195}\text{Pt}-^{31}\text{P}$ coupling constants in the triphenylphosphine ligands of Pt(PPh$_3$)$_2$(SP) are larger than that reported for tetrahedral Pt(PPh$_3$)$_4$ but not as large as that for Pt(PPh$_3$)$_3$ (Table 1.3), whereas the value of the $^{195}\text{Pt}-^{31}\text{P}$ coupling constant in the bidentate SP ligand is much smaller than that found for tetrahedral Pt(SP)$_2$ complex (Table 3.2). However, the value of $^2\text{J}(\text{P}_A\text{P}_B)$ of 50 Hz is normal for nonequivalent phosphines in tetrahedral platinum(0) complexes (Table 4.1). The SP ligand restricts the P-Pt-olefin angle ("bite angle") to around $90^\circ$-$100^\circ$, the "bite angle" of SP as found in the X-ray single structures of the M(SP)$_2$ series (M = Ni, Pd, Pt; section 3.2.3). Therefore this Pt-P bond will have a smaller s-character than a Pt-P bond in a normal tetrahedral complex, consequently the $^1\text{J}(\text{PtP})$ value of the bidentate SP ligand in Pt(PPh$_3$)$_2$(SP) will be smaller than that expected for an ideal tetrahedral complex. The remaining Pt-P bonds to the triphenylphosphine ligands will be rehybridised to include more s-character and would be expected to exhibit larger coupling constants. This trend is also observed in the series of dissociatively stable platinum(0) triphos complexes, Pt(triphos)L, discussed in section 4.1 (Table 4.1) 278, 283.
The complex Pt(PPh$_3$)$_2$(SP) is fluxional at room temperature, this may arise from dissociation of either of the tertiary phosphine ligands. This behaviour is a characteristic of zerovalent platinum complexes containing phosphines of similar bulk (section 1.2.3$^{119}$). Owing to the ease of disproportionation at high temperature, the spectra at temperature higher than room temperature were not attempted.

4.2.2 Synthesis and characterisation of Pd(PPh$_3$)$_2$(SP), 4.3

The complex Pd(PPh$_3$)$_2$(C$_2$H$_4$) reacts with one equivalent of SP at -70°C to give Pd(PPh$_3$)$_2$(SP), 4.3 as a pale yellow, air-sensitive solid which is unstable at room temperature (Eq. 4.2).

\[
\text{Pd(PPh}_3\text{)$_2$(C}_2\text{H}_4\text{)} + \text{SP} \xrightarrow{\text{toluene}} \text{Pd(PPh}_3\text{)$_2$(SP)} \quad \text{(Eq. 4.2)}
\]

Although satisfactory elemental analyses for 4.3 were obtained, the molecular weight determined by osmometry gave only half the value expected for a monomer (found 503; calc. 919). The infrared spectrum in a KBr disk has a weak absorption in the region 1620 cm$^{-1}$, suggesting that the complex contains free vinyl groups.

The $^1$HNMR spectra of 4.3 in the temperature range from room temperature to -90°C are broad and uninformative. The $^{31}$PNMR spectrum of 4.3 shows two species which are present in approximately a 1:1 ratio
Figure 4.5  Variable temperature $^{31}$PNMR spectra (24.28 MHz) of Pd(PPh$_3$)$_2$(SP) in d$_8$-toluene/toluene.
at -70°C. At room temperature, the spectrum consists of one large singlet at δ22.5 and a small broad resonance at δ12.5. However as the temperature is lowered to -70°C the broad resonance at δ12.5 resolves into a sharp five-line pattern which can be analysed as an $A_2X$ spin system. Simulation gives values of δ26.2 (d) and δ9.2 (t) for $P_A$ and $P_X$ respectively, with a $^2J(P_A^PP_X)$ value of 36 Hz.

The singlet at δ22.5, which can be observed from room temperature to -70°C, is assigned to Pd(PPh$_3$)$_3$ by spectral comparison with an authentic sample (Table 1.3). This result suggests that Pd(PPh$_3$)$_2$(SP) disproportionates completely in solution. Reaction stoichiometry and analytical data for 4.3 suggest that the other compound is Pd(PPh$_3$)(SP)$_2$, 4.4 since neither Pd(SP)$_2$ nor Pd(SP)$_3$ is observed (Eq. 4.3). There are

$$2\text{Pd(PPh}_3\text{)}_2(\text{SP}) \rightarrow \text{Pd(PPh}_3\text{)}_3 + \text{Pd(PPh}_3\text{)}(\text{SP})_2$$

Eq. 4.3

three possible structures for Pd(PPh$_3$)(SP)$_2$, 4.4, a trigonal planar structure with three coordinated tertiary phosphines and two uncoordinated vinyl groups (Figure 4.6a), a tetrahedral structure with three coordinated tertiary phosphines, one coordinated vinyl group and one uncoordinated vinyl group (Figure 4.6b) or a trigonal planar structure with two coordinated tertiary phosphines and one coordinated vinyl group from a SP ligand having its P-donor dangling freely (Figure 4.6c).
The static structures in Figure 4.6a and Figure 4.6b would be expected to give an $A_2X$ and an AMX spin system respectively in the $^{31}$PNMR spectra. For the static structure in Figure 4.6c the uncoordinated tertiary phosphine would exhibit a resonance at very high field in the position close to that of the free SP ligand ($\delta-13.7$). 

On the basis of $^{31}$PNMR and infrared data, complex 4.4 may possibly have a trigonal planar structure with three coordinated tertiary phosphines and two uncoordinated vinyl groups (Figure 4.6a). The complex Pd(PPh$_3$)(SP)$_2$ is fluxional at room temperature on the NMR time scale. The fluxional process may possibly result from dissociation...
of the tertiary phosphine ligand which is a characteristic of zerovalent metal complexes containing tertiary phosphines of similar bulk e.g. $M(P-i-Pr_3)_3$ ($M = Pt, Pd$; section 1.2.3).

The method of synthesis of $Pd(PPh_3)_2(SP)$, 4.3 (Eq. 4.2) should proceed by simple displacement of ethylene by the SP ligand, therefore it is likely that $Pd(PPh_3)_2(SP)$ was the initial reaction product. However, this compound disproportionates at a faster rate than its platinum analogue. Consequently $Pd(PPh_3)_2(SP)$ cannot be detected by NMR spectroscopy. Different disproportionation products are also formed from each complex 4.1 and 4.3 (Scheme 4.3).

![Diagram]

Scheme 4.3  Different disproportionation products of $Pt(PPh_3)_2(SP)$ and $Pd(PPh_3)_2(SP)$

4.2.3.  *Synthesis and characterisation of $Ni(PPh_3)_2(SP)$, 4.5*

The reaction of $Ni(PPh_3)_2(C_2H_4)$ with one equivalent of SP in toluene at room temperature gives an air-sensitive orange-red solution which gives an orange solid upon addition of n-hexane. The reaction of
Figure 4.7 ¹H NMR spectra (200 MHz) of the mixture from the reaction of Ni(COD)₂ + 2PPh₃ + SP in d₈-toluene at room temperature (Δ = impurities).

(a) ¹H NMR spectrum
(b) ¹H(³¹P) NMR spectrum
Ni(COD)$_2$ and stoichiometric amounts of SP and triphenylphosphine also
gives a similar product.

Elemental analyses of the orange solid do not correspond to the
formula Ni(PPh$_3$)$_2$(SP). The carbon analysis is lower than the calculated
value (found 71.99, calc. 77.17), although the hydrogen, phosphorus
and nickel analyses are satisfactory (H: found 5.35, calc. 5.43; P: found
10.11, calc. 10.66; Ni: found 6.93, calc. 6.74). The infrared spectrum
in a KBr disk shows no absorption in the region ca 1620 cm$^{-1}$ indicating
that free vinyl groups are absent. The $^1$HNMR spectrum at room temperature
shows two sets of coordinated vinyl resonances of unequal intensity and
one set of free vinyl resonances (Figure 4.7). By comparison with the
$^1$HNMR spectra of the authentic sample, one set of the coordinated vinyl
resonances is assignable to Ni(SP)$_2$.

The set of free vinyl resonances is probably due to the oxide of
SP ($\alpha$-CH$_2$=CHC$_6$H$_4$POPh$_2$)$_{271}$. The other set of coordinated vinyl resonances
is tentatively assigned to the mixed ligand nickel(0) complex,
Ni(PPh$_3$)$_2$(SP), 4.5. The $^1$H($^{31}$P)NMR spectrum shows resonances due to
$\delta$ at $\delta$4.55(dd,$\delta^1$), $\delta$3.45(d,$\delta^2$) and $\delta$2.95(d,$\delta^3$) with $^3$J($\delta^1$$\delta^2$) and
$^3$J($\delta^1$$\delta^3$) values of 8.9 and 11.7 Hz respectively (for numbering of
protons see Figure 4.4).

The variable temperature $^{31}$PNMR spectra of this product indicates
that it is a mixture of Ni(PPh$_3$)$_2$(SP), Ni(SP)$_2$ ($\delta$43.6), free
triphenylphosphine ($\delta$-6.8), Ni(PPh$_3$)$_3$ ($\delta$22.5), Ni(PPh$_3$)$_4$ ($\delta$25.1) and
Figure 4.8  Variable temperature $^{31}$PNMR spectra (80.99 MHz) of the mixture from reaction of Ni(COD)$_2$ + 2PPh$_3$ + SP in $d_8$-toluene/toluene.
the oxide of SP (δ28.9). The ratio of the resonances due to
Ni(PPh₃)₂(SP), 4.5 and the other products [Ni(SP)₂, Ni(PPh₃)₃,
Ni(PPh₃)₄, PPh₃ and SP oxide] varies between samples.

In the ³¹PNMR spectrum at room temperature (Figure 4.8),
resonances due to Ni(PPh₃)₂(SP) appear as three separate peaks, a
doublet at δ40.4, a very broad singlet at δ36.0 and a broad doublet
at δ17.9. There is no resonance assignable to free triphenylphosphine.
As the temperature is lowered to -7°C the resonances due to Ni(PPh₃)₂(SP)
sharpen to a seven-line pattern which can be analysed as an AMX spin
system. A signal due to free triphenylphosphine also appears at δ-6.8.
The parameters characterising the AMX spin system are
δ18.4(P_A), δ35.5(P_M) and δ40.0(P_X) with ²J(P_A,P_M) and ²J(P_A,P_X) values
of 33.2 Hz and 35.6 Hz respectively. The ³¹P-³¹P coupling constant
between P_M and P_X is approximately zero. The ³¹P resonances P_M and P_X,
which have similar chemical shifts, are assigned to the two nonequivalent
triphenylphosphine ligands, and the ³¹P resonance P_A is assigned to the
phosphorus nucleus of the bidentate SP ligand. The presence of three
nonequivalent phosphorus nuclei and the values of ²J(PP) are consistent
with a tetrahedral nickel(0) complex, Ni(PPh₃)₂(SP), 4.5 having a
structure analogous to that of Pt(PPh₃)₂(SP), 4.1.

The ³¹PNMR spectrum of 4.5 at room temperature shows broadening
of the resonance at δ35.5(P_M) assigned to one of the nonequivalent
triphenylphosphine ligands, disappearance of the signal assignable
to free triphenylphosphine, and a change in the fine structure of the
resonance at δ18.4(P_A) from an apparent triplet to a broad doublet.
This observation suggests that one of the triphenylphosphine ligands
of Ni(PPh₃)₂(SP) dissociates at room temperature to form a trigonal
planar complex Ni(PPh₃)(SP), 4.6 (Eq. 4.4).
In summary, the reaction of Ni(PPh$_3$)$_2$(C$_2$H$_4$) and one equivalent of SP or the reaction of Ni(COD)$_2$ with two equivalents of triphenylphosphine and one equivalent of SP gave a mixture containing Ni(PPh$_3$)$_2$(SP), 4.5 as the major product, together with Ni(SP)$_2$, Ni(PPh$_3$)$_3$, Ni(PPh$_3$)$_4$, SP and triphenylphosphine in various ratios. The presence of SP oxide in the $^1$H and $^{31}$PNMR spectra is probably due to oxidation of free SP ligand being catalysed by nickel(0) complexes\textsuperscript{272}. Disproportionation of Ni(PPh$_3$)$_2$(SP) appears to be more complicated than for the palladium and platinum analogues (Eq. 4.5).

\begin{align*}
\text{Ni(PPh}_3\text{)}_2\text{(C}_2\text{H}_4\text{) + SP} & \xrightarrow{\text{toluene, RT}} \text{Ni(PPh}_3\text{)}_2\text{(SP) + Ni(SP)}_2 + \text{Ni(PPh}_3\text{)}_3 + \\
\text{Ni(COD)}_2 + 2\text{PPh}_3 + \text{SP} & \xrightarrow{\text{RT}} \text{major product Ni(PPh}_3\text{)}_4 + \text{SP} + \text{PPh}_3
\end{align*}

Equation 4.5
4.2.4 Attempts to prepare dissociatively stable tetrahedral complexes of the type Pt(P\textsubscript{2}P)\textsubscript{2}(SP)

The reaction of Pt(COD)\textsubscript{2} and one equivalent each of SP and bis(diphenylphosphino)ethane (dppe) in toluene at room temperature gave a bright yellow solid upon addition of n-pentane. This product was shown by \textsuperscript{31}PNMR spectroscopy to consist of a mixture of Pt(dppe)\textsubscript{2} [\delta 31.4, \textbf{J}(\text{PtP}) = 3795 Hz] and Pt(SP)\textsubscript{2} [\delta 17.5, \textbf{J}(\text{PtP}) = 3130 Hz] in a 1:1 ratio and no complex containing different tertiary phosphine ligands was isolated (Eq. 4.6). The driving force of this reaction is perhaps the stability of Pt(dppe)\textsubscript{2}.

\begin{equation}
2\text{Pt(COD)}_2 + 2\text{dppe} + 2\text{SP} \rightarrow \text{Pt(dppe)}_2 + \text{Pt(SP)}_2
\end{equation}

Eq. 4.6

Attempts to prevent the formation of the Pt(P\textsubscript{2}P)\textsubscript{2} complex by using a more bulky diphosphine ligand, which would make the formation of Pt(P\textsubscript{2}P)\textsubscript{2} sterically unfavourable, were unsuccessful. The reaction of Pt(PCy\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}PCy\textsubscript{2})(C\textsubscript{2}H\textsubscript{4})\textsuperscript{285} with either one equivalent or an excess of SP is extremely slow and more than 75\% of the starting materials were recovered unchanged after three hours reaction time. The mixture of products, formed in low yield in this reaction, was not identified.

4.2.5 Conclusion

Zerovalent metal complexes of the nickel triad containing different tertiary phosphine ligands, M(PPh\textsubscript{3})\textsubscript{2}(SP) (M = Pd, Pt) were prepared,
and the nickel(O) analogue was detected spectroscopically. The nickel(O) and platinum(O) complexes were characterised by NMR spectroscopy. However no NMR spectroscopic data was obtained for the palladium analogue, presumably because of a rapid disproportionation reaction.

The nickel(O) and platinum(O) complexes have analogous structures at low temperature. They are tetrahedral complexes containing two triphenylphosphine ligands and one bidentate SP ligand. However, these complexes dissociate at room temperature, in contrast to the corresponding M(SP)_2 complexes which are dissociatively stable (section 3.2.1). The dissociative process occurring in Ni(PPh_3)_2(SP) is different from that of the platinum analogue. In Ni(PPh_3)_2(SP) at room temperature, one of the triphenylphosphine ligands dissociates whereas in the corresponding platinum analogue the coordinated vinyl group of SP dissociates at temperatures above -30°C, in addition to dissociation of one of the tertiary phosphine ligands at room temperature. This behaviour is consistent with the trend predicted from electron affinity and ionization potential data (section 1.2, Table 1.2) that nickel(O) has a higher affinity for a good π-acceptor ligand such as an olefin than has platinum(O).

For palladium(O), the result that the disproportionation products of Pd(PPh_3)_2(SP) contain no olefinic complex (Eq. 4.3) is also consistent with prediction from electron affinity and ionization potential data that palladium(O) should have the lowest affinity for π-acceptor ligands such as olefins (section 1.2, Table 1.2).

The ease of formation of the metal-olefin bond in this M(PPh_3)_2(SP) series is in the order Ni > Pt > Pd which is paralleled by that observed for the reactions of M(PR_3)_3 and C_2H_4 to form M(PR_3)_2(C_2H_4) (M = Ni, Pd, Pt; R = Ph, Et; Table 1.7)^115.
4.3 Experimental

All reactions were carried out in an atmosphere of dry nitrogen or argon using standard Schlenk techniques. All solvents were purified as described in section 3.3. Elemental analyses and molecular weight measurements are described in section 3.3. The instruments used for measuring NMR and infrared spectra are described in section 2.3. Calibrations and computer simulations of NMR spectra were carried out as described in section 2.3.

4.3.1 Preparation of starting materials

The olefinic ligand o-vinylphenyldiphenylphosphine (SP) was prepared by a literature method (section 2.3.1)\textsuperscript{160}. The slightly air-sensitive compound ethylene bis(triphenylphosphine) platinum(0), Pt(PPh\textsubscript{3})\textsubscript{2}(C\textsubscript{2}H\textsubscript{4}) was prepared by reduction of carbonato bis(triphenylphosphine) platinum(II), Pt(PPh\textsubscript{3})\textsubscript{2}(CO\textsubscript{3}) with sodium borohydride in ethanol\textsuperscript{230}. The highly air-sensitive and thermally unstable palladium analogue, Pd(PPh\textsubscript{3})\textsubscript{2}(C\textsubscript{2}H\textsubscript{4}) was prepared by reduction of bis(acetylacetonato) palladium(II), Pd(acac)\textsubscript{2} with ethoxydiethylaluminium, Al(OEt)\textsubscript{2}, in the presence of ethylene at 0\textdegree C\textsuperscript{232}. The highly air-sensitive compound Ni(PPh\textsubscript{3})\textsubscript{2}(C\textsubscript{2}H\textsubscript{4}) was prepared by reduction of anyhydrous bis(acetylacetonato)nickel(II), Ni(acac)\textsubscript{2} with ethoxydiethylaluminium in the presence of ethylene\textsuperscript{284}. The complex ethylene bis(dicyclohexylphosphino)ethaneplatinum(0), Pt(PCy\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}PCy\textsubscript{2})(C\textsubscript{2}H\textsubscript{4}) was prepared by sodium amalgam reduction of the platinum(II) complex PtCl\textsubscript{2}(PCy\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}PCy\textsubscript{2}) in the presence of ethylene at room temperature\textsuperscript{285}. 

The complex Pt(PCy\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}PCy\textsubscript{2}) and PtCl\textsubscript{2} were prepared according to literature procedures.
The compounds Pt(COD)$_2$ and Ni(COD)$_2$ were prepared according to the procedures described in section 3.3. The compounds Ni(acac)$_2$ and Pd(acac)$_2$ were prepared by literature methods$^{269,270}$. To obtain ethanol which was sufficiently dry to use in triethylaluminium reactions, the ethanol was distilled from magnesium according to a literature method$^{266}$.

4.3.2 Preparation of bis(triphenylphosphine) o-vinylphenyldiphenylphosphine platinum(0), Pt(PPh$_3$)$_2$(SP), 4.1

4.3.2.1 By reaction of Pt(PPh$_3$)$_2$(C$_2$H$_4$) and SP

Solid Pt(PPh$_3$)$_2$(C$_2$H$_4$) (0.83 g, 1.11 mmol) was added to a solution of SP (0.32 g, 1.11 mmol) in toluene (100 ml) at room temperature. The initially colourless solution turned yellow and gas was evolved immediately. The solution was stirred at room temperature for 0.5 hour, then evaporated to ca 40 ml and n-hexane was added to precipitate a bright yellow crystalline solid. After cooling the mixture in a dry ice-acetone bath, the solid was filtered off and washed with n-hexane (3 x 25 ml). The resulting bright yellow solid was dried in vacuo for 3 hours to give 4.1 (0.85 g, 82%).

Found C 66.62; H 4.73; P 9.47
C$_{56}$H$_{47}$P$_3$Pt requires: C 66.73; H 4.73; P 9.22
M.W. (toluene, 37°C) 491 (calc. 1008).

4.3.2.2 By reaction of Pt(COD)$_2$ with SP and triphenylphosphine

A solution of Pt(COD)$_2$ (0.05 g, 0.12 mmol) in toluene (10 ml) was added to a solution containing SP (0.035 g, 0.12 mmol) and triphenylphosphine (0.064 g, 0.24 mmol) in toluene (10 ml). The initially colourless solution turned yellow instantly and the reaction mixture was stirred
at room temperature for 0.5 hour, then evaporated to dryness and dried in vacuo for 3 hours. The resulting yellow solid was recrystallised from toluene-n-hexane to give a yellow crystalline solid. It was filtered off, washed with n-hexane (3 × 20ml) and dried in vacuo for 3 hours to give 4.1 (0.1g, 85%), as shown by $^1$H and $^{31}$P NMR spectroscopy.

4.3.3 Preparation of bis(triphenylphosphine)$_2$-vinylphenyldiphenylphosphine palladium(0), Pd(PPh$_3$)$_2$(SP), 4.3

A solution of Pd(PPh$_3$)$_2$(C$_2$H$_4$) (4.0g, 6.07mmol) in toluene (100ml) at -70°C was added to a solution of SP (1.75g, 6.07mmol) in toluene (100ml) at -70°C. The colourless solution turned yellow instantly and evolution of a gas, presumed to be ethylene, was observed. After stirring the reaction mixture for 0.5 hour at -70°C, it was reduced to half its volume and on addition of n-hexane, a pale yellow compound precipitated. The product was filtered off at -70°C, washed with cold n-hexane (3 × 50ml) and dried in vacuo to give 4.3 (3.7g, 65%). The product seems to be thermally unstable, gradually darkening when stored at room temperature.

Found: C 71.98; H 5.32; P 10.01

C$_{56}$H$_{47}$P$_3$Pd requires: C 73.17; H 5.15; P 10.11

M.W. (toluene, 37°C) 503 (calc. 919).
4.3.4 Attempted preparation of bis(triphenylphosphine)\textsubscript{2}-vinylphenyldiphenylphosphine nickel(O), \textit{Ni(PPh\textsubscript{3})\textsubscript{2}(SP)}, 4.5

4.3.4.1 By reaction of \textit{Ni(PPh\textsubscript{3})\textsubscript{2}(C\textsubscript{2}H\textsubscript{4})} and SP

A solution of \textit{Ni(PPh\textsubscript{3})\textsubscript{2}(C\textsubscript{2}H\textsubscript{4})} (5.0g, 8.18mmol) in toluene (30ml) was added to a solution of SP (2.35g, 8.18mmol) in toluene (30ml). The initially yellow solution turned orange-red immediately, and a gas was evolved. The reaction mixture was stirred at room temperature for 0.5 hour then reduced to half its volume. Addition of n-hexane and cooling in dry ice-acetone bath, gave an orange solid. The product was filtered off, washed with n-hexane (3 \times 20ml) and dried in vacuo (6.1g). The product was characterised by \textit{\textsuperscript{1}H} and \textit{\textsuperscript{31}P} NMR spectroscopy as a mixture of \textit{Ni(PPh\textsubscript{3})\textsubscript{2}(SP)} (4.5), \textit{Ni(SP)\textsubscript{2}}, \textit{Ni(PPh\textsubscript{3})\textsubscript{3}}, \textit{Ni(PPh\textsubscript{3})\textsubscript{4}}, triphenylphosphine and \textit{o-vinylphenyldiphenylphosphine oxide} (see text).

\textbf{Found} \quad C 71.99; H 5.35; P 10.11; Ni 6.93

\textit{Ni(PPh\textsubscript{3})\textsubscript{2}(SP)}, \textit{C\textsubscript{56}H\textsubscript{47}P\textsubscript{3}Ni} requires: C 77.17; H 5.43; P 10.66; Ni 6.74

\textit{C\textsubscript{56}H\textsubscript{47}P\textsubscript{3}Ni + (CH\textsubscript{3}CH\textsubscript{2})\textsubscript{2}O} requires: C 76.20; H 6.07; P 9.82; Ni 6.21

(a trace of diethylether was visible in \textit{\textsuperscript{1}HNMR}).

4.3.4.2 By reaction of \textit{Ni(COD)\textsubscript{2}} with SP and triphenylphosphine

A solution of \textit{Ni(COD)\textsubscript{2}} (0.40g, 1.45mmol) in toluene (40ml) was added to a solution containing triphenylphosphine (0.76g, 2.90mmol) and SP (0.42g, 1.45mmol) in toluene (40ml). The resulting reaction mixture turned orange-red immediately and was stirred for 0.5 hour.
The reaction mixture was evaporated to dryness and dried in vacuo for 3 hours. The resulting orange solid was recrystallised from toluene-n-hexane. The product was filtered off, washed with n-hexane (3 x 20ml) and dried in vacuo (1.0g). The $^1$H and $^{31}$PNMR spectra indicate that this solid is a similar mixture to that obtained in section 4.3.4.1.

4.3.5 Reaction of bis(1,5-cyclooctadiene)platinum(O) with bis(diphenylphosphino)ethane and $o$-vinylphenyldiphenylphosphine

A solution of Pt(COD)$_2$ (0.073g, 0.179mmol) in toluene (20ml) was added to a solution of dppe (0.071g, 0.179mmol) and SP (0.051g, 0.179mmol) in toluene (20ml). The colourless solution turned yellow instantly. The reaction mixture was stirred for 0.5 hour and n-pentane was added to give a yellow precipitate. The product was filtered off, washed with ether (3 x 20ml) and dried in vacuo for 3 hours to give a 1:1 mixture of complexes, Pt(dppe)$_2$ and Pt(SP)$_2$, identified by their $^{31}$PNMR spectra.

4.3.6 Reaction of ethylene bis(dicyclohexylphosphino)ethane platinum(O) with $o$-vinylphenyldiphenylphosphine

Benzene (30ml) was added to the solid mixture of Pt(PC$_2$CH$_2$CH$_2$PC$_2$)(C$_2$H$_4$) (0.088g, 0.136mmol) and SP (0.058g, 0.200mmol). The reaction mixture immediately turned slightly yellow and it was stirred at room temperature for 3 hours. The volume of the reaction
mixture was reduced to half and addition of n-pentane gave an off-white solid. This solid was filtered off, washed with n-pentane (3 × 10ml) and dried in vacuo. It was characterised by $^1$H and $^{31}$P NMR spectroscopy as a mixture of starting materials (> 75%) and a small amount of unidentified products.
APPENDIX I
Cone angles of some tertiary phosphine ligands
(from reference 202)

\[ \begin{align*}
PR_3 & \quad \theta (\text{deg}) \\
\text{PMe}_3 & \quad 118 \pm 4 \\
\text{PET}_3 & \quad 132 \pm 4 \\
\text{P(CF}_3\text{)}_3 & \quad 137 \pm 2 \\
\text{P(}_{g}-\text{CH}_2=\text{CHC}_6\text{H}_4\text{PMe}_2\text{)} (\text{DMSP}) & \quad > 143^a \\
\text{PPh}_3 & \quad 145 \pm 2 \\
\text{P-i-Pr}_3 & \quad 160 \pm 10 \\
\text{P(}_{g}-\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2\text{)} (\text{SP}) & \quad > 161^a \\
\text{PCy}_3 & \quad 179 \pm 10 \\
\text{P-t-Bu}_3 & \quad 182 \pm 2 \\
\text{P(C}_5\text{F}_5\text{)}_3 & \quad 184 \pm 2 \\
\text{P(}_{g}-\text{C}_6\text{H}_4\text{CH}_3\text{)}_3 & \quad 194 \pm 6 \\
\end{align*} \]

\text{a: Calculated from cone angles of PPh}_3, \text{PMe}_3 \text{ and P(}_{g}-\text{C}_6\text{H}_4\text{CH}_3\text{)}_3 \text{ according to Tolman method}^{202}. 
REFERENCES

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   3240 (1972).
   51, 2562 (1978).
   (A)*, 190 (1968).
188 H.C. Clark, C.R. Jablonski, J. Halpern, A. Mantovani and T.A. Weil, 
   1332 (1975).


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225 M.A. Bennett and H. Neumann, Unpublished results.


271 The authentic \( \text{O-CH}_2=\text{CHC}_6\text{H}_4\text{POPh}_2 \) (SP oxide) was prepared by oxidation of \( \text{O-CH}_2\text{C}_6\text{H}_4\text{PPH}_2 \) with bromine and subsequent hydrolysis with \( \text{Na}_2\text{CO}_3 \). \(^{31}\text{PNMR} : \delta 29(\text{toluene}), \delta 31(\text{CH}_2\text{Cl}_2)\); \(^1\text{HNMR} : \delta 7.95(\text{d}, H^1), \delta 5.38(\text{d}, H^3), \delta 4.90(\text{d}, H^2), J(H^1H^2) = 11 \text{ Hz}, J(H^1H^3) = 17.5 \text{ Hz(d}_8\text{-toluene)}\) IR(KBr disk), \( \nu(P=0) = 1185 \text{ (s) cm}^{-1} \).


285 Dr N.K. Roberts, Private communication.

Addendum to Ph.D Thesis entitled "Olefinc Tertiary Phosphine Complexes of Nickel, Palladium and Platinum" by Chindarat Chiraratvatana

ERRATA

p.11 (-3)  
Li$_2$[Pt(CH$_3$)$_4$] is not the only platinum(II) alkyl compound not containing $\pi$-acid ligands. Other compounds of this type are Pt(CH$_3$)$_2$[(CH$_3$)$_2$NCH$_2$CH$_2$N(CH$_3$)$_2$] (H.C. Clark and L.E. Manzer, J. Organomet. Chem., 59, 411 (1973)) and Pt(CH$_3$I[(CH$_3$)$_2$NCH$_2$CH$_2$N(CH$_3$)$_2$] (J.R. Hall and G.A. Swile, J. Organomet. Chem., 76, 257 (1974)).

p.42 (+1 to +3 and Eq. 1.15) Change to

The reaction of [Pt(CH$_2$=CHCH$_2$CH$_2$PPh$_2$)Cl$_2$], 1.9 with methoxide ion gives a chelate $\sigma$-alkyl complex$^{154}$ that is believed to be the six-membered metallocyclic complex 1.10 (Eq. 1.15).$^{154a}$ [154a: R.N. Haszeldine, R.J. Lunt and R.V. Parish, J. Chem. Soc. (A), 3705 (1971)]
Change The $^{195}$Pt satellites may be broadened because the methine proton is also coupled to the quadrupolar $^{75}$As nucleus. The $^{195}$Pt satellites may be broadened because the $^{195}$Pt nucleus is interacting with the quadrupolar $^{75}$As nucleus.

The trans influence of olefins has previously been shown experimentally to be relatively low [see, for example, M.H. Chisholm and H.C. Clark, Inorg. Chem., 10, 2557 (1971)].

Delete "compound"

Delete "which"

... insertion of the olefinic moiety ... into the ...

... is polarised ...

... go through ...

... and Perkin-Elmer 683 spectrophotometers

For the purified mixture, found:

... to the phosphorus of the olefin-bonded SP ligand (Py).

... $\sigma$-alkyl complex ...

... of a nickel(II) ...

... on a Gallenkamp ...
The equilibration of the two triphenylphosphine ligands is probably by conformational "flipping" of the chelate ring (which involves a partial rotation of the olefin about the Pt-olefin bond) rather than dissociation of the Pt-olefin bond. The presence of $^{195}$Pt satellites for the olefinic protons at -50°C also supports this postulation.

... data were obtained ...

... was prepared as described in section 2.3.1.1 ...

... Tolman's method. 202

Delete references 73-75