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COMPLEXES OF NICKEL, PALLADIUM, PLATINUM, RHODIUM AND IRIDIUM CONTAINING CHELATING TERTIARY-SECONDARY DIPHOSPHINE LIGANDS

The Ohio State University

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Ph.D. 1982
COMPLEXES OF NICKEL, PALLADIUM, PLATINUM, RHODIUM AND IRIDIUM CONTAINING CHELATING TERTIARY-SECONDARY DIPHOSPHINE LIGANDS.

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Robert D. Waid, B.S., M.S.

* * * * *

The Ohio State University 1982

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ACKNOWLEDGEMENTS

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To Joann and Tippi
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PUBLICATIONS

"Controlled Syntheses and Structures of Bimetallic Complexes of Two
Bidentate Phosphine-Phosphido Ligands." Meek, D.W.; Waid, R.; Tau,
(1982).

"Synthesis and Investigation of Phosphine-Phosphide Bidentate Ligands
and Their Transition Metal Complexes." Waid, R.; Meek, D.W.; 11th
Central Regional Meeting of the American Chemical Society, 1979.
Abstract INOR #5.

FIELDS OF STUDY

Major Field: Inorganic Chemistry

Studies in Coordination Chemistry. Professor Devon W. Meek
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<td>Ph</td>
<td>(C_6H_5)</td>
</tr>
<tr>
<td>Me</td>
<td>(CH_3)</td>
</tr>
<tr>
<td>Et</td>
<td>(C_2H_5)</td>
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<tr>
<td>Cy</td>
<td>(C_6H_{11})</td>
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<tr>
<td>dppe</td>
<td>((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)</td>
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<tr>
<td>dppp</td>
<td>((C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2)</td>
</tr>
<tr>
<td>ttp</td>
<td>([((C_6H_5)_2PCH_2CH_2)_2PCl_3)</td>
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<td>eptp</td>
<td>((C_6H_5)_2PCH_2CH_2P(Ph)CH_2CH_2CH_2P(C_6H_5)_2)</td>
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<td>PPH</td>
<td>((C_6H_5)_2PCH_2CH_2CH_2P(H)C_6H_5)</td>
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<td>CyPPH</td>
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<td>Cyttp</td>
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<td>CyPPep</td>
<td>((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2)</td>
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<td>CyPPptp</td>
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<tr>
<td>dpet</td>
<td>((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)</td>
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<tr>
<td>COD</td>
<td>(1,5-C_6H_{12})</td>
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<td>PR₃</td>
<td>generalized tertiary phosphine</td>
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<tr>
<td>HPR₂</td>
<td>generalized secondary phosphine</td>
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INTRODUCTION

A. General

The chemistry of transition metal complexes containing tertiary organophosphine ligands has been a rewarding area of scientific investigation for many years. The enormous amount of research on tertiary phosphine complexes tends to obscure the closely related chemistry of transition metal complexes with secondary (R₂PH; R = alkyl, aryl) and primary (H₂PR) organophosphine ligands.

Studies of transition metal complexes containing ligated secondary phosphines have been carried out since 1959, shortly after high-yield syntheses of the secondary phosphines themselves were devised by Issleib and coworkers.¹ A feature of secondary phosphines not found in tertiary phosphines is facile heterolytic cleavage of the phosphorus-hydrogen bond,² which results in the formation of an organophosphide group (R₂P⁻). Coordination of the secondary phosphine group to a metal increases the acidity of the P-H proton, thereby facilitating the loss of H⁺ from the phosphino ligand and formation of the organophosphide.

B. Chemistry of Transition Metal Complexes Containing Secondary Phosphines.

Most of the investigations of complexes containing secondary phosphines have been carried out on phosphino-substituted metal carbonyl
compounds. Among those compounds most commonly employed are
Fe(CO)$_4$(HPPh$_2$)$_2$,$^3,^4$, cis-Mo(CO)$_4$(HPMe$_2$)$_2$,$^5,^6$, cis-Cr(CO)$_4$(HPPh$_3$)$_2$,$^7$ and W(CO)$_3$(HPPh$_2$)$_2$. In these compounds, the P-H moiety is quite
stable, especially when compared to complexes of the later transition
metals with secondary phosphines (vide infra). This stability is a
consequence of (1) the low oxidation state of the metal atom, which
limits the charge transfer from phosphorus to the metal atom and
limits polarization of the phosphorus-hydrogen bond, and (2) the
absence of halide or other negatively charged ligands (X$^-$) which would
facilitate decomposition of the complex via HX elimination reactions.

Numerous syntheses have been devised which take advantage of the
properties of the substituted carbonyl complexes. Typically, an
alkali-metal mono- or bis-organophosphido species is generated at
low temperature by the action of strong base on the ligated secondary
phosphine, as shown in Equations 1 and 2.

\[
\begin{align*}
&\text{cis-Mo(CO)$_4$(HPMe$_2$)$_2$} \quad \text{BuLi, THF} \quad \text{cis-Mo(CO)$_4$(LiPMe$_2$)$_2$} \\
&\quad \text{-78°C} \quad \text{[1]} \\
&\text{cis-Cr(CO)$_4$(HPPh$_3$)$_2$} \quad \text{BuLi, THF} \quad \text{cis-Cr(CO)$_4$(LiPPh$_2$)$_2$} \\
&\quad \text{-78°C} \quad \text{[2]}
\end{align*}
\]
These cis-organophosphido-complexes have often been useful as synthetic intermediates. Frequently the ultimate goal has been the synthesis of new chelating ligands in the coordination sphere of the metal atom. Some examples are presented in Equations 3, 4, 5, and 6.

\[
\begin{align*}
I + \text{Br}-(\text{CH}_2)_n\text{-Br} &\rightarrow (\text{CO})_4\text{Mo} \begin{array}{c}
\text{P} \\
\text{Me}_2
\end{array} \begin{array}{c}
\text{P} \\
\text{Me}_2
\end{array} (\text{CH}_2)_n \\
n = 2,3,4
\end{align*}
\]

\[
\begin{align*}
I + 2\text{MePCl}_2 &\rightarrow (\text{CO})_4\text{Mo} \begin{array}{c}
\text{P} \\
\text{Me}
\end{array} \begin{array}{c}
\text{P} \\
\text{Me}
\end{array} \\
\text{Me}_2
\end{align*}
\]

\[
\begin{align*}
\text{II} + \text{RC} = \text{CR} &\rightarrow (\text{CO})_4\text{Cr} \begin{array}{c}
\text{P} \\
\text{Ph}_2
\end{array} \begin{array}{c}
\text{R} \\
\text{R}
\end{array} \begin{array}{c}
\text{P} \\
\text{Ph}_2
\end{array} \\
\text{H}^+
\end{align*}
\]

Transition metal carbonyl complexes with secondary phosphine ligands have also recently been used in the synthesis of mixed-metal dimeric complexes in which ditertiary phosphines act as bridging groups, Equation 6.

\[
(\text{OC})_5\text{WPPh}_3\text{H} + (\text{OC})_5\text{MoPPh}_3\text{CH} = \text{CH}_2 \xrightarrow{\text{base}} (\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{Mo}(\text{CO})_5
\]
Finally, the organophosphido-carbonyl complexes were used in syntheses of bimetallic organophosphido-bridged compounds, as in Equations 7, 8, and 9.\textsuperscript{5,9,10}

\[
\text{I} + (\text{C}_2\text{Me}_3)\text{RhCl}_2 \rightarrow (\text{OC})_4\text{Mo} \xrightarrow{\text{P}} \text{Rh}(\text{C}_2\text{Me}_3) \quad [7]
\]

\[
\text{V}(\text{CO})_4(\text{FR}_2\text{H}) \xrightarrow{\text{hv}} (\text{CO})_4\text{V} \xrightarrow{\text{P}} (\text{CO})_4 \quad [8]
\]

\[
\text{Ni}(\text{Ph}_2\text{PH})(\text{CO})_3 + \text{FeCp}(\text{CO})_2\text{Cl} \rightarrow \text{CpFe}(\text{CO})_2\text{PPh}_2\text{Ni}(\text{CO})_3 \quad [9]
\]

Examples of complexes of secondary phosphines involving the later transition elements are much less plentiful, and their chemistry is much less developed, than in the compounds cited above. Specifically, complexes of d\textsuperscript{8} nickel, palladium, platinum, cobalt, rhodium, and iridium have received relatively little attention. This is due in part to the characteristics of the later transition metals. The positive charges of the d\textsuperscript{8} metal ions (+2 for Ni, Pd, and Pt; +1 for Co, Rh, and Ir) destabilize the phosphorus-hydrogen bond of a coordinated secondary phosphine, and the necessary presence of anionic ligands to balance charges permits elimination reactions to occur. Further, in 16-electron square-planar compounds, vacant coordination sites on either side of the plane (Figure 1) can accept electrons from
organophosphides bound to another metal atom. Hence, oligomerization frequently occurs as a side reaction in complexes of the later transition metals with secondary phosphine ligands.

In some cases, the products of elimination and oligomerization reactions are themselves interesting species, as in the reaction of PdCl₂ with diphenylphosphine.¹¹,¹²

\[
PdCl_2 + HPPH_2 \xrightarrow{EtOH} [PdCl_2(\mu-PPh_2)(HPPH_2)]_2
\]

[10]

The analogous phosphido-bridged complexes of Pt(II) have been synthesized, as well as monomers of formula PtCl₂(PR₃)(HPPH₂) and PdCl₂(HPR₂).¹³,¹⁶

However, in other cases, particularly those of nickel and rhodium halides¹⁵,¹⁶,¹⁷ poorly defined products are obtained when secondary
phosphines are used as ligands. The results obtained are often dependent on the ligand-to-metal ratio; for example, only reactions with a ligand:metal ratio of 3:1 or higher give well-defined compounds of Rh(I). Thus, RhCl(HPR₃)₃ and [Rh(HPR₃)₄]Cl (r = alkyl, aryl) are known. Reactions with fewer than three phosphines per rhodium atom typically yield uncharacterizable products.

In the later transition metals the oxidative addition of R₂PH to yield a :PR₂-M-H complex is a possible side reaction. Terminal organophosphido ligands are rare; thus, a metal-phosphido-hydrido compound formed via such an oxidative addition will almost certainly oligomerize. The oxidative addition of PH₃ to [Ir(dppe)₂] BPH₄, which gives stable [IrH(PH₃)(dppe)₂] BPH₄ has been observed. Oligomerization is prevented in this case by steric hindrance of the bulky phenyl groups on the diphosphine ligands as well as the coordinative saturation of the Ir(III) compound. Shunn et al. also observed oxidative addition of PH₃ to RhCl(PPh₃)₃; the resulting Rh(III) compound decomposed to an unspecified cluster species. A platinum-phosphido-hydrido compound arising from the oxidative addition of HPPH₂ to cis-PtCl₂(PhCN)₂ was proposed as an intermediate in a synthesis of the phosphido-bridged compound [PtCl(µ-PPh₃)(HPPH₂)]₂, but it was not actually observed.

C. Transition-Metal Complexes Containing Bridging Organophosphide Ligands.

Increasing research activity in the field of small transition metal clusters has led to renewed interest in bridging organophosphide
ligands. In these species the organophosphide behaves as a neutral three-electron donor bridging two metal atoms. Examples are also known in which a single phosphido group bridges more than two metal atoms.\textsuperscript{21,22} An important property of the organophosphide group is its ability to stabilize and accommodate a variety of metal-met interactions. For example, the diphenylphosphido group spans a metal-metal single bond in \textsuperscript{1}, two nonbonded metal atoms in \textsuperscript{2}, and a metal-metal double bond in \textsuperscript{3}. The diphenylphosphido group has been shown by X-ray crystallography to accommodate M-P-M' bond angles ranging from 67.4° to 105.5°.\textsuperscript{23}
Elimination reactions which involve secondary phosphines or their alkali metal salts provide efficient routes to many organophosphido-bridged transition metal complexes. Included among these elimination reactions are the base assisted eliminations of HCl in Equations 11 and 12, and the elimination of LiCl in Equations 13 and 14.26,27

\[
\text{[Equation 11]} \quad 2\text{PdCl}_2(\text{HPEt}_2)_2 \xrightarrow{\text{base}} [\text{PdCl}(\mu-\text{PEt}_2)(\text{HPEt}_2)]_2
\]

\[
\text{[Equation 12]} \quad [\text{Rh}(\mu-\text{Cl})(\text{CO})_3]_2 + \text{HPPh}_2 \xrightarrow{\text{base}} [\text{Rh}_3(\mu-\text{PPh}_2)_3(\text{CO})_3]
\]

\[
\text{[Equation 13]} \quad [\text{Rh}(\mu-\text{Cl})(\text{COD})]_2 + 2\text{LiPPh}_2 \rightarrow [\text{Rh}(\mu-\text{PPh}_2)(\text{COD})]_2
\]

\[
\text{[Equation 14]} \quad [\text{Rh}(\mu-\text{Cl})(\text{CO})_3]_2 + n\text{LiPPh}_2 \rightarrow [\text{Rh}_4(\mu-\text{PPh}_2)_3(\text{CO})_3]^{-}
\]

In some instances, primary and secondary phosphines may oxidatively add to metal clusters with P-H bond cleavage, producing clusters with organophosphido bridges.29

\[
\text{[Equation 15]} \quad \text{RPH}_2 + \text{Fe}_3(\text{CO})_{12} \rightarrow \quad (\text{carbonyls omitted for clarity})
\]
Numerous other routes to organophosphido-containing complexes exist, most of which are based on phosphorus-heteroatom or phosphorus-phosphorus bond cleavage. Among these reactions is thermal phosphorus-carbon bond cleavage, as shown in Equation 16^{29} and 17.^{30}

\[
\text{[PdCl(PPh}_3\text{)_3](BF}_4\text{)} \xrightarrow{\Delta \text{ sealed tube}} \text{[Pd}_3\text{(PPh}_3\text{)_2(PPh}_3\text{)_3]}(\text{BF}_4\text{})
\]

\[
\text{RhHCO(PPh}_3\text{)_2} \xrightarrow{120^\circ \text{C}} \text{[Rh}_3\text{(_μ-PPh}_2\text{)(CO)}_3\text{(PPh}_3\text{)_3]}
\]

Such thermal reactions are often of little synthetic utility because of generally low yields and unpredictable product composition. A recently developed method involves phosphorus-carbon bond cleavage in phosphino acetylens upon addition of the ligand to a transition metal dimer or cluster, as shown in Equation 18.^{32}

\[
\text{Fe}_2\text{(CO)}_9 + \text{Ph}_2\text{PC} = \text{CR} \rightarrow \text{(CO)}_3\text{Fe} - \text{Fe(CO)}_3
\]

Phosphorus-silicon bond cleavage has also been utilized (e.g., Equations 19 and 20).^{14,33}

\[
\text{[PtCl(μ-Cl)(PET}_3\text{)_2] + 2Me}_3\text{SiPPh}_2 \rightarrow \text{[PtCl(μ-PPh}_2\text{)(PET}_3\text{)_3] + 2Me}_3\text{SiCl}
\]
Halophosphines and biphosphines are important precursors to organophosphides. The biphosphine route is most useful when it is restricted to compounds which already possess a metal-metal bond.

\[(\text{Me}_3\text{Si})_2\text{P} + 2 (\text{CO})_3\text{MnBr} \rightarrow (\text{CO})_4\text{Mn}^\text{Br} \quad \text{Br} \quad \text{Mn}(\text{CO})_4 + \text{Me}_3\text{SiBr} \quad \text{P} \quad + 2\text{CO} \quad [20]\]

The most important characterization tool used in studies of organophosphido complexes has been X-ray crystallography. However, the presence of phosphorus-31 in these compounds also opens them to structural investigation via $^{31}\text{P}$ NMR spectroscopy.

D. Phosphorus-31 Nuclear Magnetic Resonance

Phosphorus-31 NMR spectroscopy has been used extensively for investigation of structure and bonding of phosphino complexes of transition metals. Phosphorus-31 is the only naturally occurring phosphorus isotope, and it possesses a nuclear spin of $\frac{1}{2}$. 
The three most important characteristics of a $^{31}$P NMR spectrum are the spectral pattern, the chemical shifts of phosphorus nuclei, and the coupling constants. The spectral pattern is itself a reflection of the latter two properties.

The chemical shift, $\delta$, of any given phosphorus nucleus is dependent upon several factors. One factor is the type of phosphorus substituent. In organophosphines, electron-withdrawing groups decrease the electronic shielding of the phosphorus atom and the phosphorus chemical shift is downfield relative to phosphorus atoms with electron-donor substituents. Thus, resonances of tri-alkyl phosphines are typically found upfield from those of tri-aryl phosphines, and secondary phosphine resonances occur at higher fields than do tertiary phosphine resonances. Coordination of a phosphine to a transition metal causes a downfield shift (increase) of the $\delta$ value; this change is known as the coordination chemical shift.\(^{36}\)

The bond angles about phosphorus also contribute to $\delta_P$, although the mechanism is not well understood. Bulky substituents on phosphorus that enlarge the C-P-C bond angles cause the chemical shifts to appear at low field, whereas compression or constraint of the bond angles results in a chemical shift change toward higher field.\(^{37}\)

In transition metal complexes of chelating phosphines, $A_R$, the chelate ring contribution to the chemical shift, is also important. In systems where the phosphorus atoms are contained within five-membered chelate rings, the phosphorus chemical shifts are further downfield by 3-33 ppm from those of non-chelating reference ligands.
with comparable donor groups. In four- and six-membered chelate ring systems, the magnitude of $\Delta R$ is much less than that of the five-membered ring, and any observed chemical shift change is generally upfield from that of the non-chelating reference ligand.$^{38}$

Organophosphides display a large chemical shift range as well. In compounds studied thus far by $^{31}$P NMR spectroscopy, the presence of a metal-metal bond causes the $^{31}$P resonance to appear several hundred ppm downfield of the $^{31}$P resonance of the same group spanning two metals without metal-metal bonds. Attempts have been made to relate these large downfield shifts to the bond angles about phosphorus or to a three-membered chelate ring effect.$^{39,40}$ Regardless of the cause, the large change in P when metal-metal bonding occurs is an important diagnostic feature of $^{31}$P NMR spectroscopy when applied to organophosphido compounds.

Phosphorus-phosphorus and phosphorus-metal (where applicable) coupling constants provide insight into structure and bonding in transition metal complexes containing phosphorus ligands. Phosphorus atoms that are not magnetically equivalent will exhibit phosphorus-phosphorus ($J_{P-P}$) coupling. In metal complexes, couplings between cis phosphorus atoms are typically smaller than couplings between phosphorus atoms that are mutually trans. In complexes of monophosphine ligands, the transmission of $J_{P-P}$ clearly can occur through the orbitals of the metal atom or through space. In complexes of chelating diphosphines, the coupling between nonequivalent
phosphorus atoms is apparently dependent upon both a metal orbital component and a contribution through the ligand backbone. These two components may be of the same or opposite sign and may therefore increase or decrease the phosphorus-phosphorus coupling compared to similarly substituted monophosphines. In ligands $R_2P(CH_2)_nPRR'$ where $n \geq 3$, the ligand backbone coupling contribution is commonly $\approx 0$, and in metal complexes of such ligands coupling is apparently transmitted solely via the metal orbitals. Thus, the phosphorus-phosphorus coupling values found for such chelate complexes are similar to those observed for complexes with monodentate phosphine ligands. Table 1 contains some representative $J_{p-p}$ and $J_{M-p}$ values for several transition metal-phosphine complexes.

One-bond metal phosphorus coupling constants ($J_{M-p}$) are important diagnostic features of the $^{31}P$ NMR spectrum whenever the metal atom has a nuclear spin. Two such metal isotopes are $^{103}$Rh (100% natural abundance; $I = \frac{1}{2}$) and $^{195}$Pt (33.7%; $I = \frac{3}{2}$). The magnitude of $J_{M-p}$ has long been thought to depend on the Fermi contact term, and to be directly proportional to the s-orbital character of the M-P bonding orbital. Recently, this assumption has been called into question for transition metal complexes; it has been postulated that the mutual polarizability term also present in the Fermi contact expression, not the s-orbital component, may be the dominant factor in determining the magnitude of $J_{M-p}$. The value of $J_{M-p}$ depends empirically on the hybridization of the metal atom and its charge; values of $J_{M-p}$ typically decrease with increasing coordination.
Table 1. Representative $^{31}$P NMR Data for Transition Metal Complexes Containing Phosphorus Ligands

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^2J_{P-P}$ (Hz)</th>
<th>$^3J_{M-P}$ (trans ligand)</th>
<th>ox. state</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdCl$_2$(PMe$_3$)$_2$</td>
<td>-8.0</td>
<td>-</td>
<td>cis</td>
<td>Pd(II) 40</td>
</tr>
<tr>
<td>[PdCl(PMe$_3$)$_3$]NO$_3$</td>
<td>-25</td>
<td>-</td>
<td>trans</td>
<td>Pd(II) 40</td>
</tr>
<tr>
<td>PtCl$_2$(PET$_3$)$_2$</td>
<td>-20</td>
<td>3520(C1); 2400(PET$_3$)</td>
<td>cis</td>
<td>Pt(II) 40,41</td>
</tr>
<tr>
<td>PtCl$_2$(PBU$_3$)$_2$</td>
<td>-10</td>
<td>3504(C1); 2386(PBU$_3$)</td>
<td>trans</td>
<td>Pt(II) 42</td>
</tr>
<tr>
<td>PtCl$_4$(PBU$_3$)$_2$</td>
<td></td>
<td>2065(C1); 1474(PBU$_3$)</td>
<td></td>
<td>Pt(IV) 42</td>
</tr>
<tr>
<td>PtClEt(dppe)</td>
<td>21</td>
<td>4418(C1); 1483(Et)</td>
<td></td>
<td>Pt(II) 43</td>
</tr>
<tr>
<td>PtClEt(dppe)</td>
<td>-2</td>
<td>4478(C1); 1558(Et)</td>
<td></td>
<td>Pt(II) 43</td>
</tr>
<tr>
<td>PtMe$_3$(I)(dppe)</td>
<td></td>
<td>1039(Me)</td>
<td></td>
<td>Pt(IV) 44</td>
</tr>
<tr>
<td>RhCl(PPh$_3$)$_3$</td>
<td>38</td>
<td>189(C1); 142(PPh$_3$)</td>
<td>cis</td>
<td>Rh(I) 45</td>
</tr>
<tr>
<td>RhClCO(dppe)</td>
<td>34</td>
<td>158(C1); 124(CO)</td>
<td>trans</td>
<td>Rh(I) 46</td>
</tr>
<tr>
<td>RhCl$_3$(PBU$_3$)$_3$</td>
<td>21 + 3</td>
<td>112.5(C1); 83.6(PBU$_3$)</td>
<td></td>
<td>Rh(III) 42</td>
</tr>
</tbody>
</table>
number and increasing positive charge on the metal. Competition between phosphorus and other ligands (both cis and trans) for metal orbital overlap leads to variations in $J_{M-P}$. For example, in square-planar cis and trans- PtCl$_2$(PEt$_3$)$_2$, the respective $J_{M-P}$ values of 3520 and 2400 Hz are consistent with triethylphosphine being a stronger trans- influencing ligand than chloride; bond distance data also support this conclusion.$^{48}$

D. Platinum-195 Nuclear Magnetic Resonance

Direct and indirect measurement of the NMR spectra of transition metal nuclei is becoming increasingly common. Platinum-195 NMR spectroscopy has been shown to be extremely sensitive to the oxidation state of the metal, and to the number and mode of bonding of coordinated ligands. Like most heavy nuclei, the platinum-195 nucleus exhibits a large chemical shift range (over 13,000 ppm).$^{49}$

The sensitivity of the chemical shifts to temperature, solvent, and concentration sometimes makes comparison of data from different sources difficult. Thus, platinum-195 chemical shift data are most useful when spectra of similar compounds are compared and the experimental conditions under which the spectra are collected remain constant. There is as yet no universally accepted method of referencing $^{195}$Pt spectra, since the large sweep widths required for $^{195}$Pt NMR effectively preclude the use of a single standard. Some of the most commonly used reference compounds and their relative chemical shifts are shown in Figure 2;$^{50}$ in Figure 2 cis-PtCl$_2$(SMe$_2$)$_2$ is given the arbitrary value of 0 ppm.$^{51}$
The distribution of $^{195}$Pt nuclei in dimeric compounds and in multinuclear platinum clusters gives rise to different patterns in the $^{195}$Pt NMR spectrum corresponding to different mixtures of isotopomers. Such isotopomer distributions have been utilized in NMR investigations of platinum cluster compounds.$^{52}$

F. Tertiary-Secondary Chelating Diphosphine Ligands

The ligand PPH, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P(H)}\text{C}_6\text{H}_5$, was originally synthesized by Tau as an intermediate to substituted diphosphine ligands such as ppol, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P(}\text{C}_6\text{H}_5)(\text{CH}_2\text{CH}_3\text{CH}==\text{CH}_2)$. It was recognized that PPH itself possessed useful properties as a ligand. Chelating diphosphines with dissimilar phosphorus atoms can provide much useful $^{31}$P NMR spectroscopic data. The chelation of the ligand
to suitable metals followed by deprotonation or substitution at the
coordinated secondary phosphine seemed a promising synthetic approach
to new transition metal complexes. The generation of organophosphido-
bridged compounds containing a unique chelating-bridging ligand was
accomplished via the following reaction.

\[
\text{Pt(COD)(CH}_3\text{)}_2 + \text{PPH} \xrightarrow{\Delta} \text{[Pt(\mu-PP)(CH}_3\text{)]}_2
\]

[23]

Very recently, an iridium cluster compound, 4, also containing a
chelating-bridging ligand, has been synthesized, possibly via depro-
tonation of \( \text{Ph}_2\text{PCH=CHPH} \) present as an impurity in the \( \text{cis-} \)
\( \text{Ph}_2\text{PCH=CHPPH}_2 \) ligand used.\(^{54}\)

Thus, the tertiary-secondary diphasphine ligand \( \text{PPH} \) and its
analogue \( \text{CyPPH} \) seemed to be promising starting materials with which to extend
the known chemistry of secondary phosphine ligands to the later transition
metals.
Statement of Research Problem

The objectives of the present research are:

A. To synthesize d⁶-transition metal complexes containing tertiary-secondary diphosphine ligands.

B. To investigate the ³¹P NMR spectral characteristics of transition metal complexes of tertiary-secondary diphosphine ligands.

C. To investigate the ¹⁹⁵Pt NMR spectral characteristics of platinum-containing compounds containing phosphorus ligands.

D. To examine reactions of the coordinated P-H moiety.
A. Reagents and Chemicals

The chemicals used in this research were reagent grade and were used without further purification unless otherwise stated. Diphenylphosphine, phenylphosphine, and dicyclohexylphosphine were obtained from Pressure Chemical Company, Pittsburgh, Pennsylvania. Allyldiphenylphosphine and vinylidiphenylphosphine were purchased from Strem Chemical Company, Newburyport, Massachusetts. Triphenylphosphine, 1,3-dichloropropane and 1,8-dimethylaminonaphthalene were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. The diphosphine ligand 1-diphenylphosphino-2-phenylethylphosphinoethane (dpet) was supplied by Professor S. O. Grim, University of Maryland, College Park, Maryland. The tertiary-secondary diphosphine 1-diphenylphosphino-3-phenylphosphinopropane (PPH) was prepared by Uriarte's modification\textsuperscript{33} of Tau's method. The reagent methylolithium was obtained as a 1.2 M solution in diethyl ether from Alfa Products, Danvers, Massachusetts.

The transition metal salts sodium tetrachloropalladate (Na\textsubscript{2}PdCl\textsubscript{4}), rhodium trichloride trihydrate (RhCl\textsubscript{3}·3H\textsubscript{2}O), and iridium trichloride hydrate (IrCl\textsubscript{3}·xH\textsubscript{2}O) were obtained from Engelhard Industries, Newark, New Jersey. Potassium tetrachloroplatinate (K\textsubscript{2}PtCl\textsubscript{4}) was prepared
from platinum metal or from recycled platinum-containing laboratory wastes. The aforementioned salts were converted to other starting materials by established procedures.\textsuperscript{56,57} The nickel compounds \( \text{NiCl}_2(\text{glyme}) \) and \( \text{Ni(BF}_4)_2\cdot6\text{H}_2\text{O} \) were purchased from Alfa Inorganics, Danvers, Massachusetts. Other reagents were prepared by literature methods and are referenced where appropriate.

All solvents were reagent grade and were distilled under \( \text{N}_2 \) from appropriate drying agents,\textsuperscript{58} except for absolute ethanol, anhydrous diethyl ether, and hexane which were used as received.

B. Instrumentation

Infrared spectra were recorded on either a Perkin-Elmer 337 or a Perkin-Elmer 283B grating spectrophotometer from 4000 to 400 (P.E. 337) or 200 (P.E. 283B) \( \text{cm}^{-1} \). The samples were examined as pressed KBr pellets or Nujol mulls between KBr plates. Spectra were calibrated against sharp peaks (1601.4 and 1028.0 \( \text{cm}^{-1} \)) of polystyrene film.

Continuous-wave 60-MHz proton NMR spectra were collected on a Varian EM-360 spectrometer and Fourier-mode proton spectra were obtained on either a Bruker HX-90 spectrometer operating at 90 MHz or a Bruker WM-300 at 300 MHz. Spectra were obtained using deuterated solvents, and they were standardized against either internal TMS (\( \delta = 0 \text{ ppm} \)) or against residual solvent proton resonances. All reported \( ^1\text{H} \) chemical shifts are given in ppm relative to TMS.

Phosphorus-31 NMR spectra were run in 10 mm tubes using non-deuterated solvents on the Bruker HX-90 operating at 36.43 MHz in
the Fourier mode. Spectra were calibrated through the use of coaxial insert tubes which contained trimethylphosphate (δ = 58.09 Hz relative to 85% H₃PO₄) as well as deuterated acetone or deuterated toluene. The insert tube remained in the sample tube throughout the data collection period. The accuracy of the ³¹P NMR data is ± 0.1 ppm, with variations due mainly to solvent and concentration effects, as well as mechanical instabilities of the spectrometer. Spectra were recorded both in the ¹H-coupled and broadband-noise ¹H-decoupled modes. Computer simulation of experimental ³¹P NMR spectra was performed with the ITRCAL program provided by the Nicolet Instrument Corporation or by the PANIC program provided by Bruker Instrument Corp. Both PANIC and ITRCAL are adaptations of the LAOCOON III program.⁵⁹

Broadband-noise ¹H-decoupled ¹⁹⁵Pt NMR spectra were obtained at 64.30 MHz on a Bruker WM-300 spectrometer equipped with an Aspect 2000 data system. Spectra were referenced to an external saturated aqueous solution of K₂PtCl₄ (± 1927 ppm relative to cis-PtCl₂(SCH₃)₂).⁶⁰ Chemical shifts thus determined are reproducible to ± 2.0 ppm, and may be converted to the other commonly used reference conventions for ¹⁹⁵Pt NMR spectroscopy.⁵⁰ Non-deuterated solvents and 10 mm sample tubes were employed in the ¹⁹⁵Pt NMR work.

Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona. In the presence of heavy metals per-cent carbon is sometimes decreased by the formation of metal carbides during analysis.⁶¹
C. General Experimental Procedures

All reactions were carried out under an atmosphere of high-purity nitrogen using standard Schlenk techniques. Solutions of air-sensitive reagents were transferred between reaction vessels using syringes flushed with nitrogen, stainless steel needles, or a glass transfer tube equipped with a Teflon stopcock. Air-sensitive solids were handled and transferred in either a glove bag or a Vacuum Atmospheres HE43 dry box equipped with an MO-40 catalyst system. Solvents were purged with nitrogen for 30 minutes immediately prior to use.

D. \((\text{C}_6\text{H}_{11})_2\text{PCH}_2\text{CH}_2\text{P}(\text{H})\text{C}_6\text{H}_5, \text{CyPPH}\)

To a Pyrex Schlenk flask containing 25.0 g (0.126 mol) of \((\text{C}_6\text{H}_{11})_2\text{PH}\) dissolved in 300 ml of THF and cooled to 0°C was added 155 ml of a 1.2 M (1.1 equiv.) methylolithium-diethyl ether solution. The clear solution became dark red immediately and evolved a large quantity of methane gas. A finely divided yellow suspension of LiPCy₂ appeared in the reaction vessel as it was allowed to warm to room temperature. This suspension was slowly transferred via a stopcock-equipped glass tube to a second flask containing a solution of 100 g of 1,3 dichloropropane (0.89 mol) in 200 ml of diethyl ether. The solution in the second flask was stirred vigorously during the addition. The first reaction flask was rinsed with 100 ml of diethyl ether after the transfer was completed, and this rinse solution was also added to the contents of the second flask.

After the solution was stirred overnight, the reaction solvents were evaporated under reduced pressure to give a cloudy oil which was
treated with 60 ml of ethanol and 150 ml of water before being extracted three times with 150 ml portions of diethyl ether. The extracts were transferred to a flask containing MgSO₄ and charcoal and allowed to stand overnight. This solution was then filtered and transferred to a clean flask; the solvent was then evaporated at 40°C to yield 29.4 g of the nonvolatile yellowish oil (C₆H₁₄)₂PCH₂CH₂-CH₂Cl. The yield was 84.9% based on (C₆H₁₄)₂PH.

A solution consisting of 22.6 g of (C₆H₁₄)₂PCH₂CH₂CH₂Cl dissolved in 100 ml of toluene was added dropwise from a pressure-equalizing funnel to a mechanically stirred solution of liquid ammonia at -78°C containing 2.0 g of Na metal, 9.5 g of phenylphosphine, and 100 ml of diethyl ether. After this addition was complete, the ammonia was allowed to evaporate overnight. The residue in the flask was treated with 200 ml of a saturated aqueous solution of NH₄Cl. The organic portion of the resulting two-phase system was extracted with diethyl ether as before, dried over MgSO₄, and isolated by removal of all volatile materials at 50°C and 0.1 torr pressure. The diphosphine CyPPH prepared in this manner was generally pure enough for use as a ligand, but purer material could be obtained by fractional distillation on a Kugelrohr apparatus. The fraction collected at 130-160°C (0.1 torr) was identified as CyPPH on the basis of its infrared, ¹H NMR and ³¹P NMR spectra. (See the Results and Discussion section) Yield: 38.54 g (65%, based on (C₆H₁₄)₂PH).
E. Complexes of Nickel(II).

1. \(\text{NiCl}_2(\text{PPH})\)

To a solution of 0.434 g (1.98 mmol) of \(\text{NiCl}_2(\text{glyme})\) in 25 ml of ethanol was added 0.5 ml of 12 M HCl and 1.8 ml of a benzene solution 0.895 M in PPH. Upon addition of the phosphine ligand the solution changed color from yellow-green to deep red. The solution was stirred for one hour, reduced to approximately 1-2 ml in vacuo, and treated with 40 ml of diethyl ether to yield a finely divided precipitate; this precipitate was collected on a Schlenk filter and washed with 20 ml of diethyl ether. The red complex was recrystallized from THF. Yield: 0.47 g (63%)

Analysis for \(\text{C}_{21}\text{H}_{22}\text{Cl}_2\text{NiP}_2\):

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
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<tr>
<td>H</td>
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<td>12.95</td>
</tr>
<tr>
<td>Cl</td>
<td>15.20</td>
<td>15.06</td>
</tr>
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</table>

2. \([\text{Ni(PPH)}_2][\text{BF}_4]\)

A solution of 0.350 g (1.112 mmol) of \(\text{Ni(BF}_4)_2\cdot6\text{H}_2\text{O}\) in 20 ml of THF was treated with 0.2 ml of \(\text{HBF}_4\cdot\text{Et}_2\text{O}\) and 1.2 ml of a 0.895 M benzene solution of PPH (2 equiv.). A finely divided yellow solid precipitated immediately from the solution. The product was collected on a Schlenk frit, washed with 2 x 5 ml of THF, and dried in vacuo. Yield: 0.730 g (71%)
Analysis for $C_4H_4B_2FeNiP_4$:

<table>
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<td>Found</td>
<td>55.62</td>
<td>5.12</td>
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F. Complexes of Palladium (II)

1. $[PdCl(\mu-PP)]_2$

Method A

A suspension of 0.180 g (0.62 mmol) of $Na_2PdCl_4$ in 25 ml of ethanol was treated with 1.5 ml of 0.41 M PPH (0.62 mmol) in toluene. The resulting yellow suspension was refluxed for 30 minutes. The solvent was then evaporated, and the solid residue was extracted with 3 x 30 ml of $H_2O$. The residue was then dissolved in 60 ml of hot acetonitrile. Yellow microcrystals then spontaneously precipitated from the hot solution and were collected on a frit. The complex was recrystallized from benzene and ethanol. Yield: 0.373 g (78%); M.P. 220°C (dec.)

Analysis for $C_4H_4Cl_2Pd$:

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<td>Found</td>
<td>51.50</td>
<td>4.57</td>
<td>8.11</td>
<td>13.94</td>
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</table>

Method B.

A solution of $PdCl_2(COD)$ (0.200 g, 0.70 mmol) in 20 ml of dichloromethane was treated with one equivalent of the PPH-benzene solution. A transient color change from yellow to red occurred immediately; precipitation of a yellow material then occurred.
The volume of the resulting suspension was reduced to about 2 ml in a stream of N₂, and additional solid was precipitated by the addition of 40 ml of diethyl ether. The yellow solid was collected on a frit, washed with 2 x 5 ml of diethyl ether, and dried in vacuo. The compound was formulated as [PdCl(μ-PP)]₂ on the basis of its ³¹P{¹H} NMR spectrum. (See the Results and Discussion section) Yield: 0.39 g (82%).

2. [PdCl(μ-CyPP)]₂

Substitution of 1 equivalent of CyPPH ligand solution for the ligand PPH in Method A in the preceding preparation gave [PdCl(μ-CyPP)]₂ in 68% yield. The compound was identified primarily by comparison of its ³¹P{¹H} NMR spectrum with that of [PdCl(μ-PP)]₂. M.P. 220°C (dec.)

3. PdCl₂(CyPPH)

A suspension of 0.883 g (3.0 mmol) of Na₂PdCl₄ in 25 ml of benzene was treated with 1 equivalent of a stock solution of CyPPH in benzene. The reaction mixture turned from red to bright yellow on heating to reflux temperature. After the mixture was refluxed for 90 minutes, all of the benzene was removed under reduced pressure, and the residue was extracted with 3 x 10 ml of CH₂Cl₂. The dichloromethane extract was reduced in volume on a rotary evaporator to about 5 ml; then the extract was treated with 50 ml of diethyl ether to give a yellow precipitate. The precipitate was collected on a frit and washed with 2 x 5 ml of acetone. The compound was formulated as PdCl₂(CyPPH) on the basis of its ³¹P{¹H} NMR spectrum and infrared spectrum. (See
the Results and Discussion Section). Yield: 0.50 g (33%); M.P. 157°C (dec.)

4. Conversion of PdCl₂(CyPPH) to [PdCl₂(μ-CyPP)]₂

A solution of 0.060 g of PdCl₂(CyPPH) in 1.8 ml of dichloromethane in a 10 mm NMR tube was treated with 1.1 equivalents of 1,8-dimethylaminonapthalene, a non-coordinating amine base. Changes in the ³¹P{¹H} NMR spectrum of this solution after 12 hours indicated that the starting material was converted quantitatively to [PdCl₂(μ-CyPP)]₂. (See the Results and Discussion section).

5. [Pd(PPH₃)₂][BF₄]₂

A solution of 0.402 g of [Pd(CH₃CN)₄][BF₄]₂ dissolved in 20 ml of acetonitrile was treated with 2 equivalents of PPH ligand in benzene. A white precipitate appeared after one hour; it was collected on a frit and washed with 3 x 5 ml of benzene. Yield: 0.7478 g (81%)

Analysis for C₄₂H₄₄B₂F₄P₄Pd:

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<td>Found 52.33</td>
<td>4.50</td>
<td>14.22</td>
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6. [Pd(CyPPH)₂][BF₄]₂

Two equivalents of CyPPH were added to an acetonitrile solution of [Pd(CH₃CN)₄](BF₄)₂ (0.2189 g, 0.49 mmol). When the resulting solution was heated to 60°C a white microcrystalline solid precipitated. This white solid was collected on a Schlenk frit and recrystallized from THF and acetone. Yield: 0.54 g (76%).
Analysis for $C_{42}H_{60}B_{2}F_{6}P_{4}Pd$:

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<td>Found 50.58</td>
<td>7.04</td>
<td>13.27</td>
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G. Complexes of Platinum (II)

1. PtCl$_2$(PPH)

A slurry of 2.230 g (0.62 mmol) of PtCl$_2$(COD) in 20 ml of benzene was treated with 1.5 ml of a toluene solution of PPH (0.41 M, 0.62 mmol). Addition of the diphosphine caused the disappearance of the solid starting material and rapid deposition of PtCl$_2$(PPH) as a finely divided white solid. Additional product was obtained by reduction of the solvent volume to 1-2 ml in a stream of N$_2$ and addition of 40 ml of diethyl ether. The product was collected on a filter and washed with 2 x 10 ml of diethyl ether. Crystals of PtCl$_2$(PPH) were obtained by recrystallization from CH$_3$NO$_2$. Yield: 0.31 g (83%); M.P. 220°C (dec.)

Analysis for $C_{43}H_{62}Cl_{2}P_{2}Pt$:

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<th>%P</th>
<th>%Cl</th>
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<td>Found 41.94</td>
<td>3.73</td>
<td>10.61</td>
<td>11.84</td>
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2. PtCl$_2$(CyPPH)

Substitution of CyPPH for PPH in the preceding reaction yields PtCl$_2$(CyPPH) in 86% yield based on PtCl$_2$(COD).
Analysis for C₃₂H₆₄Cl₂P₂Pt:

<table>
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<td>Found 41.36</td>
<td>5.71</td>
<td>11.29</td>
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</table>

3. [PtCl(μ-PP)]₂

Method A

A suspension of 0.374 g (1.0 mmol) of PtCl₂(COD) in 10 ml of benzene was treated with one equivalent of PPH and refluxed for 90 minutes. The resulting white suspension was allowed to cool to room temperature; addition of 40 ml of diethyl ether followed by filtration yielded 0.487 g of the title complex (86%). The complex was recrystallized from CH₃NO₂. M.P. > 250° (dec.)

Analysis for C₄₅Cl₂P₂Pt₂:

<table>
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<tr>
<td>Found 44.67</td>
<td>3.50</td>
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<td>6.51</td>
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</table>

Method B

A dichloromethane solution of [PtCl(C₃H₅)]₄ (0.277 g, 1.0 mmol of Pt) was treated with 1.0 mmol of PPH. The resulting dark yellow solution was stirred for two hours. Sufficient ice-cold hexane was added to cause the precipitation of a yellow-white powder, which was collected on a filter. The powder was redissolved in dichloromethane; the resulting solution was then filtered through silica gel.
A colorless complex was precipitated from the dichloromethane solution by the addition of hexane. The $^{31}$P($^1$H) NMR spectrum of this material was identical to that of $[\text{PtCl(μ-PP)}]_2$ prepared from PtCl$_2$(COD).

Yield: 0.33 g (56%); M.P. > 250°C (dec.)

Method C

A suspension of PtCl$_2$(PPH) (0.30 g, 0.50 mmol) in 20 ml of THF was treated with 0.5 ml of NEt$_3$. Addition of the amine base caused part of the suspended solid to dissolve. After the mixture was stirred for 12 hours, a large quantity of white solid was isolated on a frit and washed with 3 x 5 ml of absolute ethanol. The $^{31}$P($^1$H) NMR spectrum of the compound revealed that it was a mixture of two geometrical isomers of $[\text{PtCl(μ-PP)}]_2$. Yield: 0.27 g (90%); M.P. > 250°C (dec.).

4. $[\text{PtCl(μ-CyPP)}]_2$

Substitution of CyPPH for PPH in Method 3A above produced $[\text{PtCl(μ-CyPP)}]$ in 83% yield based on PtCl$_2$(COD). This compound was also prepared according to Methods 3B and 3C. Preparation of the complex according to Method 3C produced a mixture of two geometrical isomers of $[\text{PtCl(μ-CyPP)}]_2$.

Analysis for $\text{C}_4\text{H}_{68}\text{Cl}_2\text{P}_2\text{Pt}$:

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<tr>
<td>Calcd.</td>
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<td>10.72</td>
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<td>Found</td>
<td>43.46</td>
<td>5.76</td>
<td>10.51</td>
<td>6.12</td>
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</table>
5. Separation of the Geometrical Isomers of [PtCl(μ-CyPP)]₂

Treatment of 0.60 g (1.0 mmol) of PtCl₂(CyPPH) suspended in 10 ml of THF with 0.5 ml of triethylamine followed by work-up according to Method 3C yielded 0.51 g of an approximately 1:1 ratio (determined by ³¹P NMR spectroscopy) of two isomers of [PtCl(μ-CyPP)]₂. This isomeric mixture was dissolved in 50 ml of dichloromethane; the volume of the resulting solution was then reduced by rotary evaporation to about 15 ml. The addition of 40 ml of diethyl ether to this solution caused the precipitation of 0.25 g of a white solid which was collected on a frit. This precipitate was recrystallized from dichloromethane and acetone. Investigation of this solid by ³¹P and ¹H NMR spectroscopy revealed that the compound was the β isomer of [PtCl(μ-CyPP)]₂. (See the Results and Discussion Section). Concentration of the filtrate and treatment of it with 60 ml of additional ether yielded 0.22 g of the α isomer of [PtCl(μ-CyPP)]₂ which exhibits a ³¹P(¹H) spectrum identical to that of [PtCl(μ-CyPP)]₂ prepared via Methods 3A and 3B.

6. PtCl₂(PPH) + Pt(PPH₃)₃

To a suspension of PtCl₂(PPH) (0.250 g, 0.42 mmol) in 15.0 ml of THF was added 0.407 g (0.41 mmol) of solid Pt(PPH₃)₃. The reaction mixture was refluxed for 90 minutes and allowed to cool; it was concentrated to about 2.0 ml and treated with 25.0 ml of diethyl ether. A fine white precipitate appeared and it was isolated by filtration. This material, which proved to be a mixture of compounds, was examined by infrared, ¹H NMR, and ³¹P NMR spectroscopy, and its characterization is included in the Results and Discussion section.
7. \( \text{PtCl}_2(\text{PPH}) + \text{HgCl}(\text{CH}_3) \)

In a Schlenk flask were combined 0.041 g of \( \text{HgCl}(\text{CH}_3) \) (0.163 mmol) and 0.100 g (0.167 mmol) of \( \text{PtCl}_2(\text{PPH}) \). Tetrahydrofuran (5.0 ml) was added, and the resulting suspension was refluxed for 30 minutes. All solvent was removed, and the resulting solid was dissolved in DMSO and was examined by \( ^{31} \text{P} \) NMR spectroscopy. The \( ^{31} \text{P} \) NMR spectrum revealed only the presence of the starting material \( \text{PtCl}_2(\text{PPH}) \).

8. \([\text{PtCl}(\text{ttp})]\text{Cl}\)

To a suspension of 0.278 g (0.46 mmol) of \( \text{PtCl}_2(\text{PPH}) \) in 20 ml of THF was added with vigorous stirring 1.0 ml of a diethyl ether solution 0.53 M in \( (\text{C}_6\text{H}_3)\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl} \), followed immediately by 1.0 ml of triethylamine. All remaining solids dissolved, and a white precipitate began to appear after an hour. After the suspension was stirred overnight, the white solid was collected on a filter and identified as \([\text{PtCl}(\text{ttp})]\text{Cl}\) after comparison of its \( ^{31} \text{P}({^1} \text{H}) \) NMR data with those of an authentic sample of \([\text{PtCl}(\text{ttp})]\text{AsF}_4\).

The \( ^{31} \text{P}({^1} \text{H}) \) NMR spectrum of \([\text{PtCl}(\text{Ph}_3\text{P}^\text{\alpha}_\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{P}^\text{\alpha}_\text{Ph})\text{Cl}\) :

\[
\delta \cdot \text{P}_\alpha = -3.94 \text{ ppm}; J_{\text{P}_\alpha-\text{P}_B} = 26,47 \text{ Hz}; J_{\text{P}_B-\text{Pt}} = 3081 \text{ Hz}
\]

\[
\delta \cdot \text{P}_B = -20.65 \text{ ppm}; J_{\text{P}_B-\text{Pt}} = 2220 \text{ Hz}
\]

9. \([\text{PtCl}(\text{CyPtt})]\text{AsF}_4\)

Addition of 1 equivalent of \( (\text{C}_6\text{H}_{11})_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl} \) dissolved in toluene to a suspension of 0.30 g (0.50 mmol) of \( \text{PtCl}_2(\text{PPH}) \) in 20 ml of absolute ethanol caused all of the solids in the flask to dissolve.
The resulting solution was treated with 0.5 ml of triethylamine and
stirred for eight hours. Removal of solvent under reduced pressure
(vacuum pump) followed by treatment with diethyl ether resulted in the
precipitation of [PtCl(CyPPtp)]Cl. The complex was collected on a
filter and washed with 2 x 5 ml of water and 2 x 10 ml of diethyl
ether. The compound was treated with one equivalent of NaAsF₆ in
boiling ethanol to yield the title complex, [PtCl(CyPPtp)]AsF₆ in
80% yield. The elemental analysis data for this compound are included
in Table 2.

10. [PtCl(Cyttp)]AsF₆

Substitution of PtCl₂(CyPPH) for PtCl₂(PPH) in preparation 9 above
resulted in the isolation of [PtCl(Cyttp)]AsF₆. Elemental analysis
data for this compound are included in Table 2.

11. [PtCl(eptp)]AsF₆

A suspension of 0.30 g (0.50 mmol) of PtCl₂(PPH) in 20 ml of ethanol
was treated with one equivalent of neat vinylidiphenylphosphine. The
addition of the vinylidiphenylphosphine caused all of the solid material
in the flask to dissolve. After the solution was stirred for 12 hours,
a white solid precipitate was obtained by the reduction of the solvent
volume followed by treatment with diethyl ether. The precipitate was
isolated by filtration and characterized as [PtCl(eptp)]Cl by comparision
of its ³¹P(H) NMR spectrum with that of an authentic sample.³³ The
compound was then treated with NaAsF₆ in boiling ethanol to yield the
title compound, [PtCl(eptp)]AsF₆, in about 77% yield. Elemental analy-
sis data for this compound are included in Table 2.
12. \([\text{PtCl(CyPPep)}]\text{AsF}_6\)

Substitution of \(\text{PtCl}_2(\text{CyPPH})\) for \(\text{PtCl}_2(\text{PPH})\) in procedure 11 above resulted in the synthesis of \([\text{PtCl(CyPPeP)}]\text{AsF}_6\). Elemental analysis data for this compound are included in Table 2.

Table 2 Elemental Analyses of Platinum-Triphosphine Complexes

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</thead>
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<tr>
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<td>% C</td>
<td>% H</td>
</tr>
<tr>
<td>([\text{PtCl(eptp)}]\text{AsF}_6)</td>
<td>43.42(42.52)</td>
<td>3.64(3.77)</td>
</tr>
<tr>
<td>([\text{PtCl(Cytpp)}]\text{AsF}_6)</td>
<td>42.97(42.78)</td>
<td>6.11(6.32)</td>
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<tr>
<td>([\text{PtCl(CyPtp)}]\text{AsF}_6)</td>
<td>47.37(47.07)</td>
<td>6.73(7.00)</td>
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<tr>
<td>([\text{PtCl(CyPPep)}]\text{AsF}_6)</td>
<td>42.89(42.60)</td>
<td>4.83(5.00)</td>
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13. \([\text{Pt(PPH)}_2]\text{AsF}_6\)_2

A suspension of 0.188 g (0.5 mmol) of \(\text{PtCl}_2(\text{COD})\) in 20 ml of THF and 3.0 ml of \(\text{NEt}_3\) was treated with 0.30 g (0.5 ml) of \(\text{PtCl}_2(\text{PPH})\) which was added as a solid in small increments. After each addition, a transient yellow color appeared. A colorless precipitate appeared after the last addition was made. The resulting white suspension was stirred for 30 minutes; the solvent was then evaporated in a stream of \(\text{N}_2\) and 10 ml of ethanol was added. The product was collected on a filter and characterized by infrared, \(^1\text{H NMR}\) and \(^{31}\text{P NMR}\) spectroscopy. (See the Results and Discussion Section)

14. \([\text{Pt(PPH)}_2]\text{[AsF}_6\text{]}_2\)

A suspension of 0.187 g (0.50 mmol) of \(\text{PtCl}_2(\text{COD})\) in 20 ml of ethanol was treated with two equivalents of \(\text{PPH}\)-benzene stock solution.
The resulting clear solution was heated under reflux for two hours. All of the solvents were removed under reduced pressure, and the remaining white residue was dissolved in a minimum amount of dichloromethane. The addition of 40 ml of diethyl ether caused the precipitation of the microcrystalline white solid, \([\text{Pt}(\text{PPH})_2]\text{Cl}_2\). Following the examination of this complex by \(^{31}\text{P}\) NMR spectroscopy in ethanol solution, the complex was isolated as \([\text{Pt}(\text{PPH})_2][\text{AsF}_6]_2\) by treatment of the solution with NaAsF\(_6\). Yield: 0.32 g (60%)

Analysis for C\(_{42}\)H\(_{44}\)As\(_2\)F\(_{12}\)P\(_4\)Pt:

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<tr>
<td>Found:</td>
<td>39.98</td>
<td>3.75</td>
<td>17.61</td>
</tr>
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15. \([\text{Pt}(\text{CyPPH})_2][\text{AsF}_6]_2\)

A suspension of 0.278 g (0.74 mmol) of PtCl\(_4\)(COD) in 10 ml of benzene was treated with two equivalents of CyPPH. All of the suspended solids dissolved immediately; moments later, a creamy white solid precipitated from the solution. The benzene was removed under reduced pressure, and the remaining white residue was redissolved in a minimum amount of ethanol, and reprecipitated as white microcrystals by the addition of 40 ml of diethyl ether. The product, \([\text{Pt}(\text{CyPPH})_2]\text{Cl}_2\), was collected on a frit and washed with additional ether. The title complex was prepared by the metathesis of \([\text{Pt}(\text{CyPPH})_2]\text{Cl}_2\) with NaAsF\(_6\) in ethanol. Yield: 0.67 g (62%)
Analysis for C_{22}H_{40}As_{2}F_{12}P_{4}Pt:

<table>
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<tr>
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<tr>
<td>Found:</td>
<td>39.78</td>
<td>5.42</td>
<td>17.47</td>
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</table>

16. Pt(CH_{3})_{2}(CyPPH)

A solution of 0.330 g (1.00 mmol) of Pt(CH_{3})_{2}(COD) in 20 ml of THF was treated with one equivalent of CyPPH-benzene solution. The resulting solution was stirred for three hours; the volume of solution was then reduced to about 2 ml in a stream of N_{2}. The addition of 20 ml of diethyl ether caused the precipitation of a white solid which was collected on a frit, washed with 2 x 5 ml of ethanol, and dried overnight in vacuo. The complex was recrystallized from THF and ethanol. Yield: 0.37 g (54%)

Analysis for C_{22}H_{40}P_{4}Pt:

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<td>6.98</td>
<td>10.80</td>
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<tr>
<td>Found</td>
<td>47.80</td>
<td>6.89</td>
<td>12.32</td>
</tr>
</tbody>
</table>

17. Pt(CH_{3})_{2}(PPH)

Substitution of PPH for CyPPH in the preceding synthesis gave Pt(CH_{3})_{2}(PPH) in approximately 60% yield.

Analysis for C_{22}H_{40}P_{4}Pt:

<table>
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<th>C</th>
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<tr>
<td>Calcd.</td>
<td>49.20</td>
<td>4.03</td>
<td>11.03</td>
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<tr>
<td>Found</td>
<td>47.40</td>
<td>4.79</td>
<td>11.45</td>
</tr>
</tbody>
</table>
18. PtCl₂(dppt)

A suspension of PtCl₂(COD) (0.2823 g, 0.75 mmol) in 15 ml of ethanol was treated with 7.0 ml of a 0.106 M benzene solution of Ph₃PCH₂CH₂P(Et)Ph. The solution was heated under reflux for 30 minutes. The ethanol was evaporated and the residue redissolved in the minimum amount of dichloromethane. The addition of 40 ml of diethyl ether resulted in the precipitation of a white solid, which was collected on a filter frit and washed with 2 x 10 ml of diethyl ether. Yield: 0.56 g (91%)

Analysis for C₃₉H₂₄Cl₂P₂Pt:

<table>
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<tr>
<th></th>
<th>% C</th>
<th></th>
<th>% H</th>
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<th>% Cl</th>
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<td>3.92</td>
<td>11.50</td>
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<tr>
<td>Found</td>
<td>42.69</td>
<td>3.89</td>
<td>11.56</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

19. Pt(PPh₃)₄ + PPH

To a solution of 0.8173 g (0.70 mmol) of Pt(PPh₃)₄ in 12.0 ml of benzene was added one equivalent of a benzene solution of PPH. The addition of the diphosphine ligand caused the solution to change in color from yellow to clear red over a 15 minute period. After three hours the volume of the solution was reduced to about 3 ml in vacuo, addition of ice-cold hexane (~40 ml) caused the precipitation of a large quantity of a flocculent orange solid. This solid was isolated by filtration, washed with 2 x 5 ml of hexane, and dried in vacuo.

Similar procedures were used in the reaction of Pt(PPh₃)₃ and Pt(C₂H₄)₂(PPh₃) with CyPPH and PPH. (See the Results and Discussion section).
29. Attempted Reduction of [PtCl(μ-CyPP)]₂ with NaBH₄

Solid [PtCl(μ-CyPP)]₂ (0.1459 g, 0.126 mmol) and NaBH₄ (0.0098 g, 0.26 mmol) were combined in a Schlenk flask fitted with a reflux condenser. Ethanol (15 ml) was added and the resulting solution was heated under reflux for 45 minutes. Evaporation of all of the solvent left a red oily residue. Attempts to obtain a solid precipitate were not successful. (See the Results and Discussion section.)

H. Complexes of Rhodium

1. Attempted Preparation of [Rh(μ-Cl)(PPH)]₂

A solution of 0.162 g of [Rh(μ-Cl)(COD)]₂ in 20 ml of benzene was treated with 0.93 ml of a 0.70 M solution of PPH in benzene. The solution turned nearly black in color. The solution was stirred for three hours, the volume reduced to about 5 ml, and the resulting solution was treated with 30 ml of diethyl ether. A small quantity of purple solid was isolated by filtration. This material failed to give an observable signal in its ³¹P(¹H) NMR spectrum. Similar results were obtained when the reaction was carried out in THF, dichloromethane, and toluene.

2. ¹/₄ [Rh(μ-Cl)(COD)]₂ + PPH (-78°)

A 10 mm NMR tube was placed in a Schlenk tube which was cooled to -78°C by dry ice. To the NMR tube were added 0.0585 g (0.24 mmol) of [Rh(μ-Cl)(COD)]₂, 0.5 ml d₆-acetone, and one equivalent of a toluene stock solution of PPH (2.0 ml). The NMR tube containing this solution
was then placed in the pre-cooled (193°C) probe of the Bruker HX-90, and \(^{31}\)P\([\text{^1}H]\) NMR spectra of the solution mixture were collected at 10° intervals in the temperature range from 193–293°C. A similar series of \(^1\)H NMR spectra was also obtained employing a 5 mm NMR tube and d\(_6\)-toluene as the only solvent. These spectra are interpreted in the Results and Discussion section.

3. RhCl(CyPPH)(PPh\(_3\))

A solution of 0.238 g (0.47 mmol) of RhCl(COD)(PPh\(_3\)) in 10 ml of THF was treated with one equivalent of a toluene stock solution of CyPPH. Reduction of the solution volume to 2 ml in a stream of \(\text{N}_2\) followed by the addition of 30 ml of diethyl ether resulted in the precipitation of a yellow powder which was collected on a Schlenk frit and washed with 2 x 5 ml of diethyl ether. Yield: 0.264 g (72%)

Analysis for C\(_{29}\)H\(_{49}\)ClP\(_3\)Rh:

<table>
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<th>%C</th>
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<td>Found 61.41 8.17</td>
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4. [Rh(COD)(PPH)]AsF\(_6\)

A two-phase reaction mixture consisting of a solution of 0.2321 g of [Rh(μ-Cl)(COD)]\(_2\) (0.94 mmol of Rh) in 10 ml of dichloromethane (lower layer) and a solution of 0.31 g (1.1 equivalents) of NaAsF\(_6\), 0.1 ml HASF\(_6\), and 10 ml of water (top layer) was stirred vigorously while one equivalent of PPH-benzene stock solution was added. Addition of the diphosphine caused the reaction mixture to turn red.
The reaction mixture was stirred for two hours; the layers were then allowed to separate and the dichloromethane layer was transferred to a second flask via a syringe. The aqueous layer was washed with 2 x 10 ml of additional dichloromethane and these washings were also transferred. The volume of the red solution was reduced in a stream of N₂ to about 2 ml. Treatment of the solution with 40 ml of diethyl ether initially caused the formation of a red oil which was converted to a yellow precipitate as the mixture was stirred for several hours. The yellow precipitate was collected on a frit and dried in vacuo for eight hours. The product was recrystallized from acetone and diethyl ether, and characterized by infrared, ³¹P NMR, and ¹H NMR spectroscopy. (See the Results and Discussion section) Yield: 0.53 g (77%); M.P. 189°C (dec.)

5. \([\text{Rh(COD)}(\text{CyPPH})]\text{AsF}_4\)

Substitution of CyPPH for PPH in the preceding preparation gives \([\text{Rh(CyPPH)(COD)}]\text{AsF}_4\) in 70% yield.

6. \([\text{Rh(CyPPH)}_2]\text{AsF}_4\)

A solution of 0.116 g of \([\text{Rh(μ-Cl)(COD)}]\text{AsF}_4\) (0.47 mmol of Rh) was treated with two equivalents of a toluene stock solution of CyPPH. A yellow precipitate rapidly appeared. The volume of the solution was reduced in a stream of N₂ to about 2 ml, then 30 ml of diethyl ether was added to the solution. A large quantity of microcrystalline yellow \([\text{Rh(CyPPH)}_2]\text{Cl}\) was collected on a frit and washed with additional ether. Treatment of an ethanol solution of the yellow
complex with a slight excess of NaAsF₆ gave the title compound in 66% overall yield. M.P. 200°C (dec.)

Analysis for C₄₂H₄₈AsF₆P₄Rh:

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<td>Found</td>
<td>50.87</td>
<td>6.71</td>
<td>11.76</td>
</tr>
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</table>

7. [Rh(PPH)₂]AsF₆

Substitution of PPH for CyPPH in the procedure used to prepare [Rh(CyPPH)₂]AsF₆ above gave [Rh(PPH)₂]Cl and [Rh(PPH)₂]AsF₆. The title complex was characterized by $^3$P NMR spectroscopy and its infrared spectrum. M.P. 200°C (dec.)

8. [RhCO(PPH)₂]AsF₆

Carbon monoxide was bubbled through a dichloromethane solution of [Rh(PPH)₂]AsF₆. Changes in the $^3$P{¹H} NMR spectrum and infrared spectrum of this compound indicated that the formation of a carbonyl adduct had occurred. $ν_{CO} = 2030 \text{ cm}^{-1}$

9. [RhCO(CyPPH)₂]AsF₆

Carbon monoxide was bubbled through an ethanol solution of [Rh(CyPPH)₂]AsF₆. Changes in the $^3$P{¹H} and infrared spectrum of the complex indicated that a carbonyl adduct was formed. $ν_{CO} = 1940 \text{ cm}^{-1}$

10. RhCl₂(CH₂CH₂CH₂PCy₂)(CyPPH)

A solution of 0.172 g (0.70 mmol of Rh) of [Rh(µ-Cl)(COD)]₂ in 10 ml of toluene was treated with 0.67 ml of a toluene solution of
Cy$_2$PCH$_2$CH$_2$CH$_2$Cl (1.06 M, 0.70 mmol). The resulting solution was gold in color. The reaction mixture was cooled to -78°C and treated with one equivalent of CyPPH ligand. The solution was allowed to warm to room temperature over a two hour period. The toluene was evaporated under reduced pressure (vacuum pump); the residue was then redissolved in 15 ml of ethanol. A white precipitate appeared after approximately thirty minutes. The material was isolated by filtration and washed with 10 ml of ethanol. Yield: 0.45 (84%); M.P. 189° (dec.)

Analysis for C$_{16}$H$_{23}$Cl$_3$P$_3$Rh:

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<td>Found 55.88</td>
<td>8.41</td>
<td>10.00</td>
<td>12.92</td>
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</table>

11. RhCl$_2$(CH$_2$CH$_2$CH$_2$PCy$_2$)(PPH)

Substitution of PPH for CyPPH in the preceding reaction yields RhCl$_2$(CH$_2$CH$_2$CH$_2$PCy$_2$)(PPH) in 86% yield. The complex was characterized by infrared, $^{31}$P NMR, and $^1$H NMR spectroscopy. M.P. 190°C (dec.)

Analysis for C$_{36}$H$_{30}$Cl$_2$P$_3$Rh:

<table>
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<td>Found 57.47</td>
<td>6.75</td>
<td>12.56</td>
<td>9.23</td>
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</table>

12. RhCl(Cyttp)

A solution of 0.172 g (0.70 mmol of Rh) of [Rh(μ-Cl)(COD)$_2$ in
10 ml of toluene was treated with 0.67 ml of a 1.06 M solution of ClCH$_2$CH$_2$CH$_2$PCy$_2$. The resulting gold solution was cooled to -78° and treated with one equivalent of a toluene stock solution of CyPPH. Triethylamine (0.5 ml) was then added; the solution was stirred for two hours at -78° and was then allowed to warm slowly to room temperature. The solvent was evaporated under reduced pressure to 1-2 ml, then 20 ml of ethanol was added to give a gold precipitate which was collected on a frit and washed with 2 x 5 ml of EtOH. The $^{31}$P($^1$H) spectrum (toluene) and infrared spectrum of this compound were identical to those of an authentic sample of RhCl(Cyttp). Yield: 0.39 g (77%)

The $^{31}$P($^1$H) NMR spectrum of RhCl(Cyttp):

\[
\text{RhCl}[\text{Cy}_3\text{P}{_A}\text{CH}_2\text{CH}_2\text{CH}_2\text{P}{_B}\text{Ph}] \\
\delta P_A = 9.2 \text{ ppm}; ^{3}J_{\text{Rh-P}_A} = 126 \text{ Hz} \\
\delta P_B = 20.6 \text{ ppm}; ^{3}J_{\text{Rh-P}_B} = 174 \text{ Hz} \\
^{3}J_{\text{P}_A-\text{P}_B} = 49.0 \text{ Hz}
\]
Compounds of Iridium (I)

1. IrCl(COD)(CyPPH)

A solution of 0.3312 g of [Ir(μ-Cl)(COD)]₂ (0.986 mmol of Ir) dissolved in 20 ml of toluene was treated with 2.0 ml of a 0.472 M standard toluene solution of CyPPH; the addition resulted in the solution changing color from red to yellow. The solution was stirred for 90 minutes, the solvent removed under reduced pressure (vacuum pump), and then 40 ml diethyl ether was added. The resulting yellow precipitate was collected on a Schlenk frit, washed with 2 x 5 ml of additional ether, and dried in vacuo. Yield: 0.54 g (80%); M.P. 156°C (dec.)

Analysis for C₂₉H₄₆ClIrP₂:

<table>
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</tr>
<tr>
<td>Found 50.11</td>
<td>6.31</td>
<td>5.34</td>
</tr>
</tbody>
</table>

2. IrCl(COD)(PPH)

Substitution of PPH for CyPPH in the preparation of IrCl(COD)(CyPPH) (above) gives IrCl(COD)(PPH) in 80% yield. The complex was characterized on the basis of ³¹P NMR, ¹H NMR, and infrared spectroscopy M.P. 150°C (dec.)

3. [Ir(COD)(CyPPH)]AsF₆

A two-phase system consisting of 15 ml of a dichloromethane solution of [Ir(μ-Cl)(COD)]₂ (0.317 g, 0.94 mmol of Ir) and 15 ml of an aqueous solution of 0.220 g (1.04 mmol) of NaAsF₆ was stirred
vigorously and treated with one equivalent of a toluene solution of CyPPH. After two hours, the layers were allowed to separate, and the dichloromethane layer was transferred to a second flask along with two 10 ml dichloromethane washings of the aqueous layer. The dichloromethane solution volume was reduced to 1-2 ml and a red solid precipitated by the addition of 40 ml of diethyl ether. The air sensitive solid was isolated by filtration, washed with 2 x 10 ml of additional ether, and dried in vacuo. Yield: 0.68 g (87%)

Analysis for C_{29}H_{44}AsF_6IrP_2:

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<th>%C</th>
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</tr>
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<td>Calcd. 41.68</td>
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<td>7.40</td>
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<td>7.62</td>
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Results and Discussion

A. The Diphosphine Ligand \((\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_3\text{P}(\text{H})(\text{C}_6\text{H}_3)\), CyPPH.

The reaction scheme used in the preparation of CyPPH is shown below in equations 24 through 27. The intermediate \(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}\) was prepared by a modification of Mazanec’s method used in the preparation of the tridentate Cyttp.\(^{a2}\) A coupling reaction between \(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}\) and NaHPPH\(_2\) was used to produce CyPPH in a manner exactly analogous to that used by Tau\(^{a3}\) to prepare \((\text{C}_6\text{H}_3)_2\text{P}(\text{CH}_2)_3\text{P}(\text{H})\text{C}_6\text{H}_3\), PPH, the other chelating tertiary-secondary diphosphine used in the present study.

\[
\text{Cy}_2\text{P} + \text{nBuLi} \xrightarrow{\text{THF}} \text{Cy}_2\text{PLi} + \text{BuH} \quad [24]
\]

\[
\text{Cy}_2\text{PLi} + \text{xS} \text{Cl}(\text{CH}_2)_3\text{Cl} \rightarrow \text{Cy}_2\text{P}(\text{CH}_2)_3\text{Cl} + \text{LiCl} \quad [25]
\]

\[
\text{H}_2\text{PPH} + \text{Na} \xrightarrow{\text{lig. NH}_3} \text{NaHPPH} + \frac{1}{2} \text{H}_2 \quad [26]
\]

\[
\text{Cy}_2\text{P}(\text{CH}_2)_3\text{Cl} + \text{NaHPPH} \rightarrow \text{Cy}_2\text{P}(\text{CH}_2)_3\text{P}(\text{H})\text{Ph} + \text{NaCl} \quad [27]
\]

The aforementioned modification to the synthesis of \(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}\) is the use of THF as solvent in Equation 24, rather than diethyl ether which was used in the original preparation. When the author used THF instead of diethyl ether the yield of the initial step was increased from 75% to 85%. An important factor in the yield of product is the smoothness and completeness of the transfer of the
dicyclohexylphosphide slurry to the reaction mixture containing 1,3-dichloropropane (Equation 25). A smooth transfer over several hours of small amounts of phosphide solution insures that formation of the diphosphine \( \text{Cy}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P} \text{Cy}_2 \) is minimized. The superior coordination and solvent properties of THF versus diethyl ether resulted in well-regulated and quantitative transfer of LiPCy₂.

The infrared and \(^1\text{H} \) NMR spectra of CyPPH are shown in Figures 3 and 4. Absorptions in the infrared spectrum of the neat ligand at 3060 (aromatic C-H, stretching), 2850 (aliphatic C-H stretching) and 740 cm\(^{-1}\) (out of plane C-H bending) are assigned to the phosphorus substituent groups. The strong band at 2280 cm\(^{-1}\) represents the P-H stretching vibration of the secondary phosphine group.\(^{63}\)

The \(^1\text{H} \) NMR spectrum of CyPPH in C\(_6\)D\(_6\) shows the expected ratio of aromatic:aliphatic protons of 1:5.4. Absorptions due to the protons of the trimethylene linkage are masked by the absorptions of cyclohexyl group protons in the region from 0.7 \( \delta \) to 2.1 \( \delta \). The weak resonances appearing at 2.4 \( \delta \) and 5.8 \( \delta \) are due to the proton of the secondary phosphine moiety; this \(^1\text{H} \) resonance is centered at 4.1 \( \delta \) and split by \(^{31}\text{P}(^1J_{\text{P-H}} \approx 204 \text{ Hz})\).

The \(^{31}\text{P}(^1\text{H}) \) spectrum of CyPPH in C\(_6\)H\(_6\) and the \(^1\text{H}-\)coupled spectrum are shown in Figure 5. The singlets at -7.72 and -54.0 ppm relative to 85\% \( \text{H}_3\text{PO}_4 \) are assignable to the \( \text{Cy}_2\text{P} \) - and \(-\text{P(H)Ph} \) groups respectively. The definitive assignment is made by the \(^1\text{H} \) coupled spectrum which exhibits a doublet centered at -54.0 ppm with \(^1J_{\text{P-H}} = 204.5 \text{ Hz} \). The P-H coupling constant and the chemical shift of the
Figure 3. The Infrared Spectrum of CyPPH (Neat)
Figure 4. The 60-MHz $^1$H NMR Spectrum of CyPPH in C$_6$D$_6$. 
Figure 5. The $^{31}$P NMR Spectrum of CyPPH in C$_6$H$_6$
Top: $^1$H-coupled Spectrum
Bottom: $^1$H-Decoupled Spectrum
-P(H)Ph unit are virtually identical to the corresponding values of PPH. Appendix A contains infrared, $^{31}P$, and $^1H$ NMR spectral data for PPH.

The chemical shift of the Cy$_2$P- unit, at -7.72 ppm, is considerably downfield from the Ph$_2$P- unit of PPH, which has a chemical shift of -18.0 ppm. In general, alkyl phosphines are more basic and occur at higher field than aryl phosphines. It has been observed, however, that increased steric crowding of substituents around phosphorus shifts the $^{31}P$ signal to lower field. For example, $\delta P(t$-Bu)$_3 = 61.9$ ppm, but $\delta P(i$-Bu)$_3 = -40$ ppm. This shift has been attributed to increased C-P-C bond angles. Phosphines with cyclohexyl substituents experience steric crowding; Mazanec observed that the chemical shift of Cy$_2$P- was downfield from the corresponding Ph$_2$P- resonance when he compared the $^{31}P$ spectra of Cyttp and ttp.

The principal impetus for synthesizing CyPPH was the need to enhance the solubility of some of the metal complexes under study. The earliest results from this Author's dissertation study with PPH showed that complexes formed between PPH and simple metal salts (e.g. the chlorides of Ni(II), Pd(II), and Pt(II)) were often only sparingly soluble in common organic solvents. Enhancement of product solubility therefore received a high priority due to the importance of $^{31}P$ NMR spectroscopy in the determination of the structure and mode of bonding of these complexes. Increased solubility of CyPPH complexes is shown by a comparison of the Pt(II) species PtCl$_2$(PPH) and PtCl$_2$(CyPPH). The former is reasonably soluble only in DMSO or hot
nitromethane, whereas the latter is also very soluble in dichloromethane; it is even moderately soluble in benzene. Very few differences in other properties of the two ligands have been noted; these are described herein where appropriate.

**B. Complexes of Nickel (II)**

Our first systematic investigation of the chemistry of transition-metal complexes of PPH was undertaken with Ni(II) salts. The reaction of one equivalent of PPH with NiCl$_2$(glyme) in ethanol produces only a red oil. However, if the reaction mixture is acidified with a large excess of aqueous HCl, prior to addition of the phosphine, a red solid powder can be isolated. The infrared spectrum (Nujol) of this "NiCl$_2$(PPH)", Figure 6, shows absorptions at 3060, 1100, 910, 740, and 695 cm$^{-1}$ which are attributable to PPH (see Appendix A). A band at 2390 cm$^{-1}$ indicates the presence of P-H; however, in the complex this band is much weaker relative to other ligand absorptions than that observed in the free ligand. The $^1$H NMR spectrum of "NiCl$_2$(PPH)" (d$_6$-DMSO) shows a broad resonance centered at 7.2 $\delta$ and a low broad resonance in the aliphatic region, consistent with the $^1$H NMR spectrum of the diphosphine ligand.

Despite the infrared and $^1$H NMR data and the elemental analysis, the $^{31}$P($^1$H) NMR of "NiCl$_2$(PPH)" reveals it to be a complex mixture of products. Normally a square-planar complex of formula NiCl$_2$-(diphosphine) with dissimilar phosphines shows only a simple 'four-line AB pattern in its $^{31}$P($^1$H) spectrum. The complexity of the experimental spectrum most probably indicates partial dimer or cluster
Figure 6. The Infrared Spectrum of NiCl$_2$(PPH) (Nujol mull)
formation, probably through elimination of HCl as observed by Hayter in the decomposition of [NiCl₂(HF(C₆H₅)₂)₂]₁³. Few well-characterized nickel halide complexes containing fewer than three secondary monophosphine groups are known, and they must be stabilized either by bulky phosphines as in [NiX₂(HP(C₆H₅)₂)₂], or by iodide rather than chloride as in [NiI₂(HPC₆H₅)₂]₂. Although separation of the product mixture was attempted by chromatography on alumina, it was unsuccessful due to the decomposition of the products while on the column.

Treatment of Ni(BF₄)₂•6H₂O with two equivalents of PPH results in the precipitation of a yellow solid which analyzes for [Ni(PPH)₂]⁻BF₄. The infrared spectrum (Nujol) of the complex exhibits ligand absorptions at 3060, 740, and 695 cm⁻¹, as well as a very strong broad peak at 1040 cm⁻¹ due to the BF₄⁻ anion. As in the case of NiCl₂(PPH)², the P-H absorbance at 2380 cm⁻¹ is much less intense than that of the free ligand. The \(^{1}H\) NMR spectrum in d₆-DMSO shows proton resonances at 7.2 \(\delta\) (aromatic) and low, broad resonances from approximately 1.0 to 2.3 \(\delta\) (aliphatic). However, as in the case of NiCl₂(PPH), the \(^{31}P(\text{¹H})\) NMR spectrum provided insufficient information about the structure of this complex to characterize it adequately.

C. Complexes of Palladium (II) with PPH and CyPPH

The reactions of PPH and CyPPH with nickel(II) provided incentives to expand this study to other d⁸ transition metals, particularly palladium(II) and platinum (II). In contrast to nickel(II), the stereochemistry about palladium(II) and platinum(II) is essentially fixed as
planar and four-coordinate and not influenced by the steric and electronic effects of coordinated ligands. Several complexes of palladium(II) and platinum(II) with secondary phosphines and phosphido bridges were known at the time this investigation was begun, and their syntheses and characterization were generally more straightforward than those of the nickel(II) analogues.

The treatment of Na₂PdCl₄ with one equivalent of PPH at room temperature results in the rapid deposition of a finely divided yellow solid. The infrared spectrum of the solid exhibits the absorption bands of PPH, including a weak band at 2360 cm⁻¹ which may be assigned to a P-H stretching vibration. This yellow material is insoluble in common organic solvents, but soluble derivatives may be prepared (Equation 28).

$$\text{Precipitate + PR}_3 \xrightarrow{\text{EtOH}} \text{NaAsF}_6 \rightarrow \text{[PdCl}(\text{PPH})(\text{PR}_3)]\text{AsF}_6$$

$$\text{[Pd(PPH)]}_2[\text{AsF}_6]_2$$

$$\text{PR}_3 = \text{tertiary phosphine}$$

Two compounds result from derivitization of the precipitate, and both are soluble enough in nitromethane to be identified by $^{31}\text{P}({}^{1}\text{H})$ NMR spectroscopy. These two soluble species, [PdCl(PR₃)(PPH)]⁻AsF₆ (PR₃ = P(C₆H₅)₂(C₆H₅)₂), and [Pd(PPH)₂][AsF₆]₂ are derived from, respectively, PdCl₂(PPH) and [Pd(PPH)₂][PdCl₄]; therefore the initial insoluble precipitate consists of a mixture of the latter two compounds. Replacement of a halogen by a tertiary phosphine (PR₃) in a complex of formula PdCl₂(PR₃)₂ to produce the ionic species [PdCl(PR₃)₃]^⁺Cl⁻
is a known reaction.\textsuperscript{67} Insoluble Magnus-type salts \[\text{Pd}(\text{L-L})_2][\text{PdCl}_4]\], which are often formed from reactions of bidentate ligands with \(\text{Na}_2\text{PdCl}_4\), have been solubilized by the replacement of \(\text{PdCl}_4\) with other anions.\textsuperscript{68}

The \(^{31}\text{P}(^1\text{H})\) NMR spectrum (\(\text{CH}_3\text{NO}_2\)) of the derivative mixture displays a distinct ABX spectral pattern attributable to \[\text{PdCl}(\text{PR}_3)(\text{PPH})_2\] - \(\text{AsF}_6\) and an \(A_2B_2\) pattern assigned to \(\text{Pd}(\text{PPH})_2[\text{AsF}_6]\). The \(^{31}\text{P}(^1\text{H})\) spectral parameters of \[\text{Pd}(\text{PPH})_2[\text{AsF}_6]\] are identical to those of \[\text{Pd}(\text{PPH})_2[\text{BF}_4]\] (vide infra) prepared by another method during this study. The \(^{31}\text{P}(^1\text{H})\) spectral parameters of \[\text{PdCl}(\text{PR}_3)(\text{PPH})][\text{AsF}_6]\] are collected in Table 3.

The high-field signal (\(-6.94\) ppm) has been assigned to the secondary phosphine group (\(P^\text{x}\)). The \(^{31}\text{P}(^1\text{H})\) NMR spectrum of this compound in itself does not provide sufficient information to assign the chemical shifts of \(P^A\) and \(P^B\) unambiguously to the two remaining phosphorus nuclei.

Table 3. The \(^{31}\text{P}(^1\text{H})\) Spectral Parameters of \[\text{PdCl}(\text{PR}_3)(\text{PPH})][\text{AsF}_6]\]

<table>
<thead>
<tr>
<th>(\delta P^A)</th>
<th>(\delta P^B)</th>
<th>(\delta P^X)</th>
<th>(^2J^A)</th>
<th>(^2J^AX)</th>
<th>(^2J^BX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.1</td>
<td>1.97</td>
<td>-6.94</td>
<td>416</td>
<td>13.4</td>
<td>39.1</td>
</tr>
</tbody>
</table>

\(\text{PR}_3 = \text{P}(\text{C}_9\text{H}_5)(\text{C}_6\text{H}_5)_2\)

\(\text{a. Chemical shifts are in ppm relative to } 85\% \text{H}_3\text{PO}_4, \text{ upfield shifts are negative.}\)

\(\text{b. Coupling constants are in Hz.}\)
Figure 7. The $^{31}\text{P}[^1\text{H}]$ NMR Spectrum of PdCl$_2$(CyPPH) in CH$_2$Cl$_2$
The magnitude of \(^2J_{AB}\) (416 Hz) clearly indicates that \(P_A\) and \(P_B\) are mutually trans. The cis coupling constants \(^2J_{AX}\) and \(^2J_{BX}\) are within the range found for similar compounds; for example, the \(^2J_{P-P}\) cis coupling in \([\text{PdCl}(\text{PMe}_3)_3]\text{NO}_3\) is equal to 25 Hz.\(^9\) The structural assignment in Table 3 would not be affected by a reversal of the A and B spin labels.

Although \(\text{PdCl}_2(\text{PPH})\) was not characterized directly, \(\text{PdCl}_2(\text{CyPPH})\) was also prepared and it had sufficient solubility in \(\text{CH}_2\text{Cl}_2\) to be investigated by \(^{31}\text{P}\) NMR spectroscopy. The \(^{31}\text{P}^{1\text{H}}\) NMR spectrum of this compound is shown in Figure 7. This spectrum consists of the simple four-line AB pattern expected for a palladium compound containing dissimilar phosphines in a cis orientation. The doublet downfield from the standard (\(\delta = 31.1\) ppm) is assigned to the Cy,P-group while the high-field doublet at \(\delta = 14.1\) ppm is assigned to the more electron-rich secondary phosphino group. The magnitude of the phosphorus-phosphorus coupling constant (7.3 Hz) is very close to the values typical of cis-phosphine couplings in compounds like cis-\(\text{PdCl}_2(\text{PMe}_3)_2\), which has a \(^2J_{P-P}\) of 8.0 Hz. Direct observation of AB spectra cannot provide information about the absolute sign of the coupling constant; however, the absolute signs of cis-couplings in \(\text{PdCl}_2(\text{PMe}_3)_2\) and related species (determined indirectly) have been found to be negative.\(^{10}\)

**D. Organophosphido Complexes of Palladium(II)**

The yellow precipitate which results from the treatment of \(\text{Na}_2\text{PdCl}_4\) with PPH is soluble in hot acetonitrile; however, a yellow
microcrystalline material spontaneously precipitates from the hot solution after only a few minutes. The infrared spectrum of this compound, Figure 8, exhibits the characteristic bands of PPH (e.g. 3080, 1100, and 690 cm\(^{-1}\)) but no absorption attributable to \(\nu_{\text{P-H}}\) in the vicinity of 2360 cm\(^{-1}\), even in very concentrated mulls. There are no infrared bands in the region for coordinated CmN absorbances (2300 - 2200 cm\(^{-1}\)) which would suggest formation of an acetonitrile complex.\(^6\)

The experimental (C\(_6\)H\(_6\)) and simulated \(^{31}\)P\(^{1}\)H NMR spectrum of this microcrystalline precipitate from acetonitrile are presented in Figure 9. On the basis of the \(^{31}\)P spectrum and infrared evidence (i.e., disappearance of \(\nu_{\text{P-H}}\)) this compound is formulated as [PdCl(\(\mu\)-PP)]\(_2\), where the "\(\mu\)-PP" designation is used to indicate the presence of deprotonated PPH acting simultaneously as a chelating ligand toward one metal atom and as a bridging ligand between two atoms, as illustrated in Figure 10, below.

![Figure 10](image)

*Figure 10. The Chelating-Bridging Bonding Mode of "\(\mu\)-PP" in [PdCl(\(\mu\)-PP)]\(_2\): Assignment of the NMR Spin Labels AA'XX'.
Figure 8. The Infrared Spectrum of [PdCl(μ-PP)]_2 (Nujol mull).
Figure 9. The Computer-Simulated (Top) and Experimental (Bottom) \(^{31}\text{P}[^{1}\text{H}]\) NMR Spectra of [PdCl(µ-PP)]$_2$ in C$_6$H$_6$. 
Figure 11. The $^{31}$P{'H} NMR Spectrum of [PdCl(μ-CyPP)]$_2$ in CH$_2$Cl$_2$. * denotes a minor isomer.
Treatment of an NMR sample of PdCl₂(CyPPH) in situ with a slight excess of the non-coordinating amine base 1,8-dimethylamino-naphthalene at room temperature produced the $^{31}$P($^1$H) NMR spectrum reproduced in Figure 11. Comparison of this spectral pattern with that of [PdCl(μ-PP)]₂ indicates that dimerization of PdCl₂(CyPPH) has occurred through elimination of HCl (Equation 29), and that the structures of the two dimers are similar.

$$2 \text{PdCl}_2(\text{CyPPH}) + 2\text{B} : \longrightarrow [\text{PdCl(μ-CyPP)}]_2 + 2\text{B}_2\text{HCl} \quad [29]$$

The $^{31}$P($^1$H) NMR spectra of [PdCl(μ-PP)]₂ and [PdCl(μ-CyPP)]₂ both exhibit the main features of an AA'XX' spin system, and the spin assignments are as shown in Figure 9. However, the spectra are deceptively simple as all of the expected transitions are not resolved.

For example, in the case of [PdCl(μ-PP)]₂, each of the large multiplets centered at -14.5 and -146.9 ppm should contain 10 lines as (e.g., Figure 12), rather than the six lines actually resolved.

Figure 12. An Idealized AA' Portion of An AA'XX Spectrum.
(Reference 69)
This degeneracy of inner and outer lines was found to be field invariant, as the transitions were not resolved in a $^{31}$P spectrum collected at 121.4 MHz. The practical effect of the loss of this additional coupling data is to make the calculation of an exact value of the $J_{AA'}$ coupling impossible, but a satisfactory computer simulation was obtained when 0 Hz was used as the value of the $J_{AA'}$ parameter.

While dimeric complexes of the type $[\text{PdCl}(\mu-\text{PR}_2)(\text{PR}_3)]_2$ ($R = \text{aryl, alkyl}$) were known at the onset of this work, their $^{31}$P NMR spectra had not been examined. A publication containing the $^{31}$P NMR parameters for five dimeric palladium(II) compounds of this type has recently appeared, and these literature data along with those of $[\text{PdCl}(\mu-\text{PP})]_2$ and $[\text{PdCl}(\mu-\text{CyPP})]_2$ are given for comparison in Table 4.

As may be seen from the table, the $J_{AA'}$ values for the $[\text{PdCl}(\mu-\text{PR}_2)(\text{PR}_3)]_2$ species, though small, could be calculated for all but two cases, i.e., the chemical shift differences of the two ab subspectra in each large multiplet were detectable. The apparent equivalence of the AA' nuclei (no measureable $J_{AA'}$) in $[\text{PdCl}(\mu-\text{PP})]_2$ and $[\text{PdCl}(\mu-\text{CyPP})]_2$ may result from the AA' nuclei being in rigid chelate rings. Alternatively, the chelating ligands may not achieve ideal bond angles about palladium(II), which would reduce the already weak $J_{AA'}$ coupling because of poor phosphorus-metal orbital overlap. Structural data for $\text{PdCl}_2(dppp)^+$ ($dppp = \text{Ph}_2P(CH_2)_2P\text{Ph}_2$) reveal that the P-M-P bond angle in that compound is 90°, the theoretical
Table 4. $^{31}$P{$^1$H} Data for Phosphido-Bridged Compounds of Palladium(II).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_A$</th>
<th>$\delta_X$</th>
<th>$J_{AA}$</th>
<th>$J_{AX}$</th>
<th>$J_{XX}$</th>
<th>$J_{AX}'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PdCl($\mu$-PP)]$_2$</td>
<td>-14.5</td>
<td>-146.9</td>
<td>-10.4</td>
<td>-246</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>[PdCl($\mu$-CyPP)]$_2$</td>
<td>0.0</td>
<td>-126.8</td>
<td>2.3</td>
<td>-235</td>
<td>411'</td>
<td></td>
</tr>
<tr>
<td>[PdCl($\mu$-CyPP)]$_2$</td>
<td>-3.1</td>
<td>-168</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>[PdCl($\mu$-PPh$_2$)(PEt$_3$)]$_2$</td>
<td>14.5</td>
<td>-127.9</td>
<td>2.9</td>
<td>31.9</td>
<td>-290</td>
<td>405.9</td>
</tr>
<tr>
<td>[PdCl($\mu$-PPh$_2$)(PHPH$_2$)]$_2$</td>
<td>-3.1</td>
<td>-132.9</td>
<td>0.2</td>
<td>20.9</td>
<td>-261</td>
<td>423.1</td>
</tr>
<tr>
<td>[PdCl($\mu$-PMe$_2$)(PHMe$_2$)]$_2$</td>
<td>-54.3</td>
<td>-180.7</td>
<td>-0.4</td>
<td>24.1</td>
<td>-310</td>
<td>442.9</td>
</tr>
<tr>
<td>[PdCl($\mu$-PMe$_2$)(PEt$_3$)]$_2$</td>
<td>14.3</td>
<td>-182.1</td>
<td>9.3</td>
<td>31.7</td>
<td>-344</td>
<td>408.4</td>
</tr>
<tr>
<td>[PdCl($\mu$-PMe$_2$)(PHPH$_2$)]$_2$</td>
<td>15.7</td>
<td>-174.4</td>
<td>+12.7</td>
<td>23.5</td>
<td>-341</td>
<td>373.6</td>
</tr>
</tbody>
</table>

- a. ppm, positive values are downfield from H$_3$PO$_4$
- b. coupling constants in Hz
- c. Reference 70
- d. Reference 28 gives slightly different data for this compound
- e. $J_{AA}'$ splitting not resolved
ideal value. However, the structural data also reveal that the di-phosphine ligand experiences a very poor fit about the palladium atom. Unfortunately, there are no structural data available for dimeric palladium complexes containing the chelating-bridging di-phosphine ligand. In the case of $[\text{Pt(CH}_3)(\mu-\text{PP})]_2$\[^7\text{5}\], the only $\mu$-PP complex studied by X-ray crystallography, the corresponding P-M-P bond angle is 95.9°, which is quite close to the 96.3° value found for $\text{PtCl}_2(\text{PMe}_3)_2$.\[^7\text{2}\] This indicates that involvement of the chelated diphosphine in a bridging linkage in itself does not cause great distortion of the remaining bond angles about the metal atom.

Another parameter which tends to differentiate between the chelate-containing dimers and the other tabulated compounds is the magnitude of $^3J_{AX}$, the cis phosphorus-phosphorus coupling constant between a terminal phosphine and the phosphido bridge connected to it via a trimethylene chain. In $[\text{PdCl(}\mu-\text{PP})]_2$, this $^3J_{AX}$ value (10 Hz) is comparable to cis phosphorus-phosphorus coupling constants in cis $\text{PdCl}_2(\text{PMe}_3)_2$ (8.0 Hz) and $\text{PdCl}_2(\text{CyPPH})$ (7.3 Hz). However, in the compounds of general formula $[\text{PdCl}(\mu-\text{PR}_2)(\text{PR}_3)]_2$ the corresponding cis coupling constants are all greater than 20 Hz.

The $^2J_{P-P}$ coupling constant for $[\text{PdCl}(\mu-\text{PMe}_2)(\text{PHMe}_2)]_2$, for example (24.1 Hz), is almost identical to that of $[\text{PdCl(}\text{PMe}_3)_3]\text{NO}_3$ (25.0 Hz), which has a similar coordination environment (i.e., three phosphines and one chloride coordinated to palladium). With respect to this cis coupling parameter the $[\text{PdCl}(\mu-\text{PR}_2)(\text{PR}_3)]_2$ complexes therefore resemble monomeric $[\text{PdX(}\text{PR}_3)_3]\text{Y}$ more closely than do
[PdCl(μ-PP)]₂ and [PdCl(μ-CyPP)]₂. However, the signs of cis $^{2}J_{P-P}$ in monomeric complexes of Pd(II) have been negative,$^{40}$ whereas the best computer simulations of the $^{31}P$ NMR spectra of all of the dimeric compounds required a positive value be given to this coupling.

A possible explanation for the smaller magnitude of cis $^{2}J_{AX}$ in [PdCl(μ-PP)]₂ and [PdCl(μ-CyPP)]₂ relative to the other dimeric compounds may be attributed to the transmission mechanism of phosphorus-phosphorus couplings. Grim$^{73}$ suggested that the magnitude of phosphorus-phosphorus coupling in a chelate ring can be factored into a sum of two contributions (Equation 30) where $^{B}J_{P-P}$ is a contribution to the coupling through the carbon backbone and $^{M}J_{P-P}$ is a contribution through the metal d orbitals. Although the $^{J}_{P-P}$ coupling in free PPH is $\sim 0$, it is possible that chelation locks the ligand backbone into a rigid conformation that permits transmission of a small $^{J}_{P-P}$ coupling. If the metal orbital and backbone contributions are of opposite sign, the magnitude of the $^{2}J_{P-P}$ coupling would be reduced. Small couplings between phosphorus atoms exclusively through trimethylene and tetramethylene carbon chains have been reported.$^{74,75}$ In both of these cases it was speculated that the ligand systems were sufficiently rigid to allow this coupling ($< 5$ Hz) to be transmitted through the P-C-C-C-P linkage.

A more qualitative rationale assumes that the steric restriction of the chelate ring about palladium lowers the cis coupling
as a result of poor ligand-metal interaction, with no significant transmission of coupling through the ligand carbon skeleton. In any event, the chelating nature of the ligand seems to have significant impact on the $^{31}\text{P}$ NMR spectrum of the dimeric compounds.

A final major difference between the two classes of dimeric compounds is seen in the chemical shifts of the terminal tertiary phosphines. Again citing $[\text{PdCl}(\mu-\text{PP})]_2$, the $\delta_A$ of 14.5 ppm is considerably upfield from that of $[\text{PdCl}(\mu-\text{PPh}_2)(\text{HPPh}_2)]_2$, with $\delta_A = -3.1$ ppm. The corresponding free ligand values are $\delta = -18.7$ ppm (PPH) and $\delta = -41$ ppm for PPh$_2$H. The chemical shifts of the terminal groups of the $[\text{PdCl}(\mu-\text{PR})_2(\text{PR}_3)]_2$ compounds have been assigned unequivocally to the lowfield multiplet, and this assignment should also hold for $[\text{PdCl}(\mu-\text{PP})]_2$; the observed anomaly is therefore not due to a misassignment of $^{31}\text{P}$ resonances.

Such a reversal of chemical shift order on coordination is not explainable by any known chelate ring effect. The differing trans influences of the bridging groups $\mu$-PPh$_2$ and $\mu$-PPh(alkyl) are probably not responsible for this chemical shift reversal either, since the substitution of $\mu$-PMe$_2$ for $\mu$-PPh$_2$ in $[\text{Pd}(\mu-\text{PPh}_2)(\text{PET})_3]_2$ did not significantly change the chemical shift of the PET$_3$ group trans to the phosphido ligand (See Table 4). Constraints imposed on the phosphorus atoms by the chelate ring again may be the most significant factor. Chelation by the ligand to one metal might allow the orbitals of the $\mu$-PPh(alkyl)$^-$ group to overlap more efficiently with d-orbitals of a second metal atom, enhancing the trans influence
of the bridging group and thereby causing the resonance of the trans terminal phosphine to move upfield. If this is the cause of the upfield shifts of the Cy₂P⁻ and Ph₂P⁻ moieties, however, it is not reflected in an unusually high $^2J_{AX}$ (trans) coupling constant. The trans-coupling constants of the chelate-containing compounds are very similar to those of the analogous [PdCl(μ-PR₃)(PR₃)]₂ compounds, and also similar to the trans coupling constant (461 Hz) of [PdCl(PMe₃)₃]NO₂.⁶⁰

The cis-phosphide-phosphide ($^3J_{XX}$) coupling constants in all cases are far larger than common cis-phosphine-phosphine coupling constants (vide supra). Although the data base is very small, again it is the complexes of the chelating ligand which exhibit anomalous behavior, with the lowest coupling between bridgehead phosphorus atoms. The expected order of decreasing basicity for the phosphide ligands is μ-PMe₂ > μ-PPh(alkyl) > μ-PPh₂, based on analogy with comparable phosphines and on the ability of aryl groups to delocalize charge. The steric requirements of the ligands likewise increase in the order μ-PMe₂ < μ-PPh(alkyl) < μ-PPh₂. Kreter²⁸ proposed that the unusually high cis coupling between the phosphide phosphorus nuclei in compounds of this class resulted in part from interaction through space of phosphorus 3s and 3p orbitals. Low steric demands by substituent groups on phosphorus would allow the phosphido nuclei to approach more closely, presumably increasing this coupling through
space. On the basis of Kreter's suggestion, the fact that the \( \mu\text{-PPh(alkyl)} \) groups of \([\text{PdCl(\mu-PP)}]_2\) and \([\text{PdCl(\mu-CyPP)}]_2\) exhibit a lower \( ^2J_{XX} \) value than those of \([\text{PdCl(\mu-PR_2)(PR_3)}]_2\) implies that the bridging PPh(alkyl) group may be constrained. However, without more structural data on the dimeric compounds the exact causes of many of the differences in the NMR spectra of the two types of phosphido-bridged compounds remain speculative.

Excluding the differences in the \( ^{31}\text{P} \) NMR parameters, the compounds \([\text{PdCl(\mu-PP)}]_2\) and \([\text{PdCl(\mu-CyPP)}]_2\) share the gross structural features of the \([\text{PdCl(\mu-PR_2)(PR_3)}]_2\) compounds. The high-field chemical shift of the phosphido-phosphorus atoms indicates that there is no Pd-Pd bond. A large number of examples now exist which indicate that the presence of a metal-metal bond in phosphido-bridged dimers and clusters causes the phosphido-phosphorus chemical shifts to appear up to 400 ppm downfield from the chemical shifts of the same groups spanning non-bonded metals.\(^{28,32}\) Further, the X-ray structures of the isoelectronic compounds \([\text{PtCH_3(\mu-PP)}]_2\)\(^{27}\) and \([\text{PtCl(\mu-PPh_2)-(HPPh_2)}]_2\)\(^{25}\) indicate that there is no M-M bonding in those cases.

The \( ^{31}\text{P}[^1\text{H}] \) NMR spectrum of \([\text{PdCl(\mu-CyPP)}]_2\) in Figure 11 shows a set of eight extra lines (marked by asterisks in the figure) with spacings and intensities which resemble the major transitions of an AA'XX' spin system. The chemical shifts of these two four-line groupings are also included in Table 4. This compound is not likely to be an amine-substituted derivative of \([\text{PdCl(\mu-CyPP)}]_2\) because 1,8-dimethylamino-naphthalene is sterically hindered and generally
does not function as a ligand. Further, replacement of a terminal chloride by an amine (p-toluidine) has not previously been observed in this type of compound, even under forcing conditions. The presence of four different groups bonded to each of the bridging phosphorus atoms results in the formation of geometrical isomers with different $^{31}$P NMR spectra. A more detailed examination of geometrical isomerism was carried out on analogous platinum(II) systems and a detailed discussion of the results will be presented in the appropriate section of the Dissertation.

The syntheses of $[\text{PdCl}(\mu-\text{PP})]_2$ and $[\text{PdCl}(\mu-\text{CyPP})]_2$ from Na$_2$PdCl$_4$ resemble syntheses of $[\text{PdCl}(\mu-\text{PR})_2(\text{HPR})_2]_2$ (R = phenyl, ethyl) from Na$_2$PdCl$_4$ performed by Isslèib and Hayter. Hayter and Humiec isolated PdCl$_2$(HP(Et)Ph)$_2$ and PdCl$_2$(HPEt)$_2$ and converted them to the corresponding phosphido-bridged dimers by the action of amine bases. However, they found that dimerization of PdCl$_2$(HPPh)$_2$ to $[\text{PdCl}(\mu-\text{PPh})_2(\text{HPPh})_2]_2$ was spontaneous and could not be prevented, even by addition of excess HCl. Thus, the coordinated diphosphines CyPPH and PPH resemble coordinated HPEt$_2$ and HP(Et)Ph in their acidity.

When PdCl$_2$(COD) is treated with PPH at room temperature in dichloromethane, only dimeric $[\text{PdCl}(\mu-\text{PP})]_2$ results. This contrasts with reactions of CyPPH and PPH with Na$_2$PdCl$_4$, in which formation of monomeric products is favored. Thus, the acidity of the secondary phosphino group is not the only factor which determines whether HCl elimination reactions occur in PPH complexes. Another factor which
could influence these reactions is the heat of solvation of HCl in the reaction solvent; a high heat of solvation would provide the driving force for the dimerization reaction. However, the heat of solvation of HCl is higher in alcohols than in chlorinated hydrocarbons.

The dimerization reaction may occur via the route of Equation (31):

\[
\text{(COD)Pd} \text{Cl} \quad + \quad \text{Ph} \text{Ph} \quad \text{Ph} \quad \text{Ph} \text{Cl} \quad \rightarrow \quad \text{(COD)Pd} \text{Cl} \quad + \quad \text{HCl}
\]

Since the COD-Pd bonding interaction is quite strong, \(^{56}\)Cl\(^-\) and not the diolefin may be displaced by the first end (probably the secondary end) of the chelating diphosphine to become coordinated. The newly generated anionic chloride may then assist in the removal of H\(^+\) from the acidic secondary phosphino group. The diolefin is eliminated during the subsequent dimerization reaction. In contrast, the reaction of PPH with Na\(_2\)PdCl\(_4\) produces only neutral species, (Equation (32)); consequently HCl elimination cannot occur.

\[
\text{Na}_2\text{PdCl}_4 \quad + \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{NaCl}_2\text{Pd} \quad + \quad \text{NaCl}
\]

Similar results with rhodium-diolefin compounds will be discussed later in the dissertation.

The compounds [Pd(PPH)\(_2\)] [BF\(_4\)] \(_2\) and [Pd(CyPPH)\(_2\)] [BF\(_4\)] \(_2\) were also synthesized. Treatment of [Pd(CH\(_3\)CN)\(_4\)] [BF\(_4\)] \(_2\) with two equivalents of
PPH yields an air-stable white complex. The infrared spectrum of this material after recrystallization from dichloromethane displays the characteristic absorbances of the PPH ligand including the P–H stretching vibration at 2350 cm\(^{-1}\). A very strong, broad absorbance centered at 1060 cm\(^{-1}\) is attributed to the BF\(_4^-\) anion.

The \(^{31}\)P\({}^1\)H NMR spectrum of the white compound along with a computer simulation comprises Figure 13. The main features of the experimental spectrum are a pair of resonances centered at -0.3 ppm and -25.26 ppm. These resonances appear to be triplets, but additional splitting of the central peak of each indicates that the spectrum is actually more complex, and appears as a doublet of triplets because of deceptive simplicity. The simulated spectrum was generated assuming an \(A_2B_2\) spin system. The proposed structure of this complex is shown in Figure 13 and the NMR parameters arising from the computer simulation are presented in Table 5.

<table>
<thead>
<tr>
<th>(\delta P_{1,3}) (ppm)</th>
<th>(\delta P_{2,4}) (ppm)</th>
<th>(^2J_{P_1-P_3}) (Hz)</th>
<th>(^2J_{P_2-P_4}) (Hz)</th>
<th>(^3J_{P_1-P_3}) (Hz)</th>
<th>(^3J_{P_1-P_2}) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.32</td>
<td>-25.25</td>
<td>400</td>
<td>400</td>
<td>45.65</td>
<td>20.53</td>
</tr>
</tbody>
</table>

Table 5. Iterated Phosphorus-31 NMR Parameters for [Pd(PPH)\(_2\)][BF\(_4\)]\(_2\)
Figure 13. The Computer Simulated (Top) and Experimental (Bottom) $^{31}$P$^{[	ext{3H}]}$ NMR Spectra of [Pd(PPH)$_2$][BF$_4$]$_2$ in CH$_3$NO$_2$. 
The analogous CyPPH complex, [Pd(CyPPH)₂][BF₄]₂, was also prepared from [Pd(CH₃CN)₄][BF₄]₂. Slightly more forcing reaction conditions (60°C) were necessary to form this complex, probably because more energy was required to overcome the steric crowding of the cyclohexyl groups. As in the ³¹P{¹H} NMR spectrum of the PPH species, two large triplets are a manifestation of a deceptively simple A₂B₂ spin pattern in the ³¹P spectrum of [Pd(CyPPH)₂][BF₄]₂. Unfortunately, the inner lines of the spectrum are not resolved as they were in the PPH derivative. Thus, the only coupling information that can be determined is the average value of the cis ²J_P-P coupling between the two types of phosphorus nuclei (i.e. tertiary and secondary).

In both [Pd(PPH)₂][BF₄]₂ and [Pd(CyPPH)₂][BF₄]₂ a smaller set of resonances due to a minor constituent appears. The spectrum of the CyPPH compound shows this most clearly, exhibiting smaller "triplets" contained within the large triplet resonances. The ³¹P{¹H} NMR data of the major and minor isomers of [Pd(CyPPH)₂][BF₄]₂ are given in Table 6.

Table 6. ³¹P{¹H} NMR Data of Major and Minor Isomers

<table>
<thead>
<tr>
<th></th>
<th>δP₁,₂ᵃ</th>
<th>δP₀,₄</th>
<th>J_P₁₋₂ = J_P₀₋₄ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(CyPPH)₂][BF₄]₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(major)</td>
<td>9.32</td>
<td>-33.7</td>
<td>32.5</td>
</tr>
<tr>
<td>[Pd(CyPPH)₂][BF₄]₂</td>
<td>8.89</td>
<td>-32.3</td>
<td>31.5</td>
</tr>
<tr>
<td>(minor)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Chemical shifts relative to 85% H₃PO₄
b. Coupling Constants are in Hz.
The presence of two chiral phosphorus atoms in the complex cation leads to the formulation of the three possible stereoisomers as depicted below in Figure 14.

Figure 14. Stereoisomerism in [Pd(PPH$_2$)$_2$]$^{2+}$ and [Pd(CyPPH)$_2$]$^{2+}$ cations.

Isomers A and B are enantiomers and are diastereomers of C. The presence of diastereomers has previously been shown to cause multiple resonances to appear in the $^{31}$P NMR spectrum of samples with chiral centers at phosphorus. The difference in chemical shifts of the resonances of the tertiary phosphines in the two isomers, 0.43 ppm, is less than the difference in the resonances of the secondary phosphines, 1.4 ppm. This is an indication that the difference between the two isomers arises from differences at the coordinated secondary
(chiral) phosphine. Examination of the $^{31}\text{P}[^1\text{H}]$ NMR spectrum of a mixture of the diastereomers of PtMe$_2$(P-P*) (P-P* is the chiral ligand 2-diphenylphosphinoethylneomethylphenylphosphine) showed that the resonances of the phosphorus donors bearing the chiral substituents in the two diastereomers were separated by 4.5 ppm, whereas the resonances of the achiral phosphorus atoms were separated by only ~1 ppm.$^5$

The major product is probably diastereomer C (Figure 16) since its formation causes less steric interaction between phosphorus substituents on the same side of the plane of the complex. However, no attempt was made to separate the components of the isomer mixture, and no absolute structural determination was attempted.

E. Complexes of PPH and CyPPH with Platinum(II)

The work of Chatt and Davidson included the synthesis of the first monomeric secondary phosphine complexes of divalent platinum, cis-PtCl$_2$(HPPH$_2$)(PET$_3$), and the first dimeric complex of platinum with organophosphido bridging ligands. The monomer was synthesized according to Equation 33:$^{13}$

$$\frac{1}{2} [\text{PtCl}(_2\text{H})\text{PET}_3]_2 + \text{HPPH}_2 \rightarrow \text{cis-PtCl}_2(\text{HPPH}_2)(\text{PET}_3) \quad [33]$$

Treatment of this monomer with base (NaOEt) gave the dimer [PtCl(μ-PPh$_2$)(PET$_3$)]$_2$, a compound analogous to the dimeric palladium species [Pd(μ-PR$_3$)(PR$_3$)]$_2$ discussed in the preceding section.
A different route to similar platinum complexes of PPH and CyPPH was necessary for this study. Cleavage of the halide bridge of 
\[\text{[PtCl(μ-Cl)(PET₃)]}_₂\] with the bidentates might have produced a mixture of products, which would have required separation (Equation 34) as well as competition by PET₃ for coordination sites on platinum.

\[
\begin{align*}
\text{Et}_2\text{P} & \quad \text{Pt} \quad \text{Cl} \quad \text{Pt} \quad \text{Cl} \quad + \quad \text{PPH} \\
\text{Cl} & \quad \text{Cl} & \quad \text{PET}_3 & \\
\text{[} \text{R}_2\text{P} & \quad \text{P(H)}\text{PH} & \text{]} & \quad \text{CL} & \quad \text{[} \text{R}_2\text{P} & \quad \text{P(H)}\text{PH} & \text{]} & \quad \text{Cl} \\
\text{Cl} & \quad \text{PET}_3 & \quad & \quad \text{Et}_3\text{P} & \quad \text{Cl} & \quad \text{[} \text{R}_2\text{P} & \quad \text{P(H)}\text{(Ph)} & \text{]} & \quad \text{Cl} & \quad \text{[} \text{R}_2\text{P} & \quad \text{P(H)}\text{(Ph)} & \text{]} & \quad \text{Cl}_2 \\
\end{align*}
\]

[34]

The most desirable compound has the formula PtCl₂(PPH). Replacement of chloride ions from this compound could allow further substitution in the coordination sphere of the platinum atom; this was expected to be particularly useful in dimerization reactions and syntheses involving the P-H function. The \(^{31}\text{P}\) and \(^1\text{H}\) NMR spectra of the resulting complexes would also be simplified by the presence of only two ligand phosphorus atoms per metal atom.
In the first synthesis of PtCl$_2$(PPH) attempted, treatment of ethanolic K$_2$PtCl$_4$ with one equivalent of PPH stock solution gave a pink precipitate. The infrared spectrum of this material shows absorbances typical of PPH including a broad, weak band at 2350 cm$^{-1}$, arising from coordinated P–H. The insolubility of the product precluded characterization by NMR spectroscopy. It is a tendency of PtX$_4^{2-}$ salts to form insoluble Magnus-type salts of general formula [Pt(LLL)$_2$][PtX$_4$] with bidentate ligands, and this is believed to have been the result of this experiment. Conversion of this compound to PtCl$_2$(PPH) by refluxing it in high-boiling solvents (e.g., DMF) was not attempted because of the probable thermal sensitivity of the P–H moiety. The infrared spectrum of [Pt(PPH)$_2$]Cl$_2$ which was later prepared and characterized is similar to that of this supposed Magnus salt.

The displacement of the coordinated diolefin from PtCl$_2$(COD) by PPH at room temperature in benzene, ethanol or THF yielded the desired complex PtCl$_2$(PPH). The infrared spectrum of this compound (KBr, Figure 15), displays the characteristic pattern of PPH with the exception that no $\nu_{P-H}$ is observable in the region 2200–2400 cm$^{-1}$. It was hoped that the P–H stretching vibration would be a valuable source of structural information; however, in this and many subsequent spectra of PPH complexes the P–H absorbance was weak or unobservable.

Although the 90 MHz $^1$H NMR spectrum of this compound included the normal ligand resonances, the resonance of the proton directly bound
Figure 15. The Infrared Spectrum of PtCl$_2$(PPH) (KBr pellet).
to phosphorus was not identifiable. Other workers have reported similar difficulties in making direct observation of phosphorus-bound protons in the $^1$H NMR spectra of transition metal complexes of secondary phosphines. The polarization of the P-H bond on coordination of the secondary phosphine to the metal ion deshields this proton, shifting its resonance to lower field from the free ligand chemical shift value of 4.1 $\delta$. Pidcock gives a value of 6.26 $\delta$ for the chemical shift of the P-H proton in the similar complex cis-PtCl$_2$(PPr$_3^\text{N}$(HPPh)$_2$); in the PPH compound this proton resonance may be obscured by other proton resonances of the ligand. Additional splitting of this resonance by the tertiary phosphine of the ligand ($^3J_{P-H}$) and the 33.7% abundant $^{195}$Pt($I = \frac{3}{2}$) contribute to the difficulty in making the assignment on the coordinated diphosphine.

Consequently, $^{31}$P NMR spectroscopy was used to determine whether the product was a monomer or a dimer. The $^{31}$P($^1$H) NMR parameters of well-known PtCl$_2$(dppp), PtCl$_2$(PPH), and PtCl$_2$(CyPPH) (which is obtained under the same reaction conditions as PtCl$_2$(PPH)) are summarized in Table 7. The $^1$H-decoupled and $^1$H-coupled $^{31}$P NMR spectra (CH$_2$Cl$_2$) of PtCl$_2$(CyPPH) comprise Figures 16 and 17, respectively. The $^{31}$P($^1$H) NMR spectra of both PtCl$_2$(PPH) and PtCl$_2$(CyPPH) consist of first-order AB spectra (the four large transitions) and eight smaller transitions due to the large coupling of each phosphorus nucleus with the 33.7% abundant platinum-195 ($I = \frac{3}{2}$). The small coupling in the doublets is the $^2J_{P-P}$ cis coupling between the dissimilar phosphorus atoms of the coordinated ligands. When the
Figure 16. The $^{31}$P-$^1$H NMR Spectrum of PtCl$_2$(CyPPH) in CH$_2$Cl$_2$. 
Figure 17. The $^1H$-Coupled $^{31}P$ NMR Spectrum of PtCl$_2$(CyPPH) at Room Temperature in CH$_2$Cl$_2$. 

$^{1}J_{P-H} = 460$ Hz

(MeO)$_3$P=0 (Std.)
Table 7. $^3$P($^1$H) NMR Data for PtX$_2$(L-L') Compounds and Corresponding PtX$_2$(dppp) Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_{P_1}$</th>
<th>$\delta_{P_2}$</th>
<th>$^3J_{P_1-P_2}$</th>
<th>$^1J_{^1H}$</th>
<th>$^1J_{Pt-P_2}$</th>
<th>$^1J_{P-H}$</th>
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<tbody>
<tr>
<td>PtCl$_2$(PPH)</td>
<td>-5.74</td>
<td>-28.85</td>
<td>24.42</td>
<td>3403</td>
<td>3256</td>
<td>460 ± 10</td>
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<tr>
<td>PtCl$_2$(CyPPH)</td>
<td>+7.54</td>
<td>-28.83</td>
<td>19.69</td>
<td>3303</td>
<td>3390</td>
<td>430 ± 10</td>
</tr>
<tr>
<td>PtCl$_2$(dppp)$^d$</td>
<td>-5.6</td>
<td>—</td>
<td>—</td>
<td>3408</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pt(CH$_3$)$_2$(PPH)</td>
<td>+3.28</td>
<td>-18.05</td>
<td>17.7</td>
<td>1805</td>
<td>1654</td>
<td>—</td>
</tr>
<tr>
<td>Pt(CH$_3$)$_2$(CyPPH)</td>
<td>+4.64</td>
<td>-17.33</td>
<td>18.7</td>
<td>1773</td>
<td>1748</td>
<td>—</td>
</tr>
<tr>
<td>Pt(CH$_3$)$_2$(dppp)$^e$</td>
<td>+3.2</td>
<td>—</td>
<td>—</td>
<td>1790 ± 10</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

a.) ppm, negative values are upfield from 85% H$_3$PO$_4$
b.) coupling values are in Hz
c.) values obtained from satellite spectra
d.) reference 43
e.) reference 80
f.) $P_1$ is a tertiary phosphine, $P_2$ is a secondary phosphine

broadband $^1$H decoupling is eliminated, the doublet at high field and its satellite spectra are further split by over 400 Hz; this indicates that the high field resonance centered at -28.8 ppm is that of the secondary phosphino group.

The large increase of $^1J_{P-H}$ on coordination of the secondary phosphino residue (204 Hz in free ligand vs 460 Hz in coordinated PPH) has been observed previously in the $^1$H NMR spectra of other transition metal complexes. In substituted metal carbonyl compounds of secondary phosphines the $^1J_{P-H}$ values are typically 300-320 Hz.$^3$,$^6$
An example of the magnitude of this coupling in platinum(II) complexes is the $^{1}J_{P-H}$ value (393 Hz) of cis-PtCl$_2$(HPPh)$_2$(PPH)$_3$. The increase in $^{1}J_{P-H}$ coincident with the polarization of the P-H bond is due to the increased s orbital character of the P-H bonding orbital when the phosphino moiety is coordinated. The Fermi-contact term, which is the dominant factor determining the magnitude of one-bond coupling to phosphorus is a function of the s orbital character of the P-H bond. The s character of the P-H bond increases upon coordination of the phosphine to the metal, due to the increase of s character in the rehybridized sp$^3$ orbitals of the coordinated phosphorus atom. The same effect is seen in the $^{1}J_{P-H}$ coupling constants of PH$_3$ (182 Hz) and PH$_4^+$ (547 Hz).

As expected, the $^{31}P$ spectral data of PtCl$_2$(PH) and PtCl$_2$(CyPPH) are very similar. The considerable difference (13.3 ppm) between the chemical shift of the Cy$_2$P- group and -PPh$_2$ group in the respective complexes again reflects the C-P-C bond angle strain in the Cy$_2$P- group; this effect is also observed in the free ligands. From a comparison of the $\delta P_2$ (secondary phosphino) values of PtCl$_2$(PPH) and PtCl$_2$(CyPPH) it is clear that the cis- influence is insignificant in determining the chemical shift of P$_2$ in these complexes, but it does have some effect on $^{1}J_{M-P_2}$. Comparison of $\delta P_1$ between PtCl$_2$- (dppp) and PtCl$_2$(PPH) also indicates that differing cis phosphino groups (i.e. -PPh$_2$ and -P(H)Ph) have a negligible effect on the chemical shift of these tertiary phosphine nuclei. The $^{1}J_{Pt-P}$ coupling constants obtained from the satellite spectra are in the
range reported for tertiary phosphines trans to chloride in platinum(II) complexes. Literature examples include the compounds PtCl₂(PMePh₂)₂ with a corresponding \(^4J_{Pt-P}\) value of 3549 Hz,\(^8\) PtCl₂(dppp) with a \(^2J_{Pt-P}\) of 3408 Hz,\(^4\) and cis-PtCl₂(HPPh₃)(PPh₃) with coupling constants of 3572 Hz (Pt-P(H)Ph₂) and 3582 Hz (Pt-PPh₃).\(^1\)

The complexes Pt(CH₃)₂(PPh) and Pt(CH₃)₂(CyPPH) were synthesized by adding one equivalent of the appropriate ligand to Pt(CH₃)₂(COD) in THF at room temperature. Unlike previously synthesized platinum(II)-methyl complexes of di-tertiary and tri-tertiary phosphines, these complexes are unstable in refluxing benzene or toluene, formally eliminating methane to give dimeric phosphido-bridged [Pt(CH₃)(μ-PP)]₂ and [Pt(CH₃)(μ-CyPP)]₂. The \(^31P(\text{^1H})\) NMR spectral data of Pt(CH₃)₂(PPh), Pt(CH₃)₂(CyPPH), and Pt(CH₃)₂(dppp)\(^9\) are also included in Table 7.

The spectra of Pt(CH₃)₂(PPh) and Pt(CH₃)₂(CyPPH) consist of a first-order, four-line AB pattern resembling that of the spectra of the analogous chloro compounds. The major transitions are again accompanied by satellite spectra due to coupling of \(^{195}Pt\) (I = \(\frac{3}{2}\)) to each of the two types of phosphorus nuclei. The magnitude of this \(^1J_{Pt-P}\) coupling is a valuable diagnostic tool, in these cases indicating that the diphosphines are trans to methyl groups. For comparison, in addition to the tabulated value of \(^1J_{Pt-P}\) for Pt(CH₃)₂(dppp) (1790 Hz), similar \(^1J_{M-P}\) values include those of Pt(CH₃)₂(FEt₃)₂ (1856 Hz)\(^2\) and Pt(CH₃)Cl(dppp) (P-trans to CH₃),
In general, strong trans-influence ligands (e.g., CH₃, R₃P) are known to reduce the \(^{1}J_{M-P}\) coupling constants relative to those of the analogous chloro compounds.\(^{62}\)

Examination of the other spectral data again shows very good agreement between the chemical shifts of Ph₂P- groups in Pt(CH₃)₂-(PPH) and Pt(CH₃)₂(dppp). The large chemical shift differences between the Cy₂P and PPh₂ group observed in the PtCl₂(ligand) compounds (vide supra) has virtually disappeared; in Pt(CH₃)₂(CyPPH) and Pt(CH₃)₂(PPH) \(\delta_{P_{Cy}} = 4.64\) ppm and \(\delta_{P_{Ph}} = 3.28\) ppm. The decrease in the \(^{2}J_{P-P\text{cis}}\) coupling constant from PtCl₂(ligand) to Pt(CH₃)₂(ligand) seems to follow a trend observed in Pt(II) complexes as halide ions are replaced by stronger ligands. Data available for Pt(CH₃)₂(R₂P(CH₂)₃PR') compounds are in good agreement with the observed coupling constants of Pt(CH₃)₂(PPH) and Pt(CH₃)₂-(CyPPH). Examples include Pt(CH₃)₂(ppol) \(^{2}J_{P-P} = 18.0\) Hz, Pt(CH₃)₂(η²-ttp) \(^{2}J_{P-P} = 18.0\) Hz, Pt(CH₃)₂(η²-Cyttpp) \(^{2}J_{P-P} = 19.0\) Hz,\(^{74}\) and PtClEt(dppp), \(^{2}J_{P-P} = 20.6\) Hz.\(^{43}\)

If two equivalents of PPH or CyPPH are added to PtCl₂(COD) in refluxing ethanol, [Pt(PPH)₂]Cl₂ and [Pt(CyPPH)₂]Cl₂ are formed. They may be converted by metathesis with NaAsF₆ to [Pt(PPH)₂][AsF₆]₂ and [Pt(CyPPH)₂][AsF₆]₂, respectively. The \(^{31}P\) \(^{1}H\) and \(^{1}H\)-coupled spectra of [Pt(CyPPH)₂][AsF₆]₂ are shown in Figure 18; the NMR data for both the bis-PPH and bis-CyPPH compounds comprise Table 8.
Figure 18. The $^{31}$P NMR Spectrum of [Pt(CyPH)$_3$]Cl$_2$ in EtOH.
Top: $^1$H-Coupled Spectrum
Bottom: $^1$H Decoupled Spectrum
Table 8. Phosphorus-31 NMR Data for [Pt(PPH)$_2$]Cl$_2$ and Pt(CyPPH) Cl$_2$.

<table>
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<tr>
<th></th>
<th>$P_1$</th>
<th>$P_2$</th>
<th>$J_{P_1-P_2}$</th>
<th>$J_{Pt-P_1}$</th>
<th>$J_{Pt-P_2}$</th>
<th>$J_{P_2-H}$</th>
<th>$J_{P_2-H}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pt(PPH)$_2$]Cl$_2$</td>
<td>-9.92</td>
<td>-30.6</td>
<td>31.0</td>
<td>1884</td>
<td>2229</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>[Pt(CyPPH)$_2$]Cl$_2$</td>
<td>-1.81</td>
<td>-28.9</td>
<td>28.6</td>
<td>2081</td>
<td>2264</td>
<td>305</td>
<td>5-10</td>
</tr>
</tbody>
</table>

a.) chemical shifts relative to 85% H$_3$PO$_4$

b.) coupling constants are in Hz.

Both of the compounds exhibit deceptively simple $A_2B_2$ patterns in their $^{31}$P NMR spectra; both spectra appear to be composed of a pair of triplets and the satellite spectra due to $^{31}$P-$^{19}$Pt coupling. Thus, the only phosphorus-phosphorus coupling information that is available directly from these spectra are the average cis-couplings between the tertiary and secondary phosphino groups. The geometry of the complexes is shown in Figure 1A; the magnetic pseudo-equivalence of the mutually trans- phosphine groups which eliminate their trans coupling is similarly observed in ttp compounds of platinum$^{33}$ and rhodium.$^{33}$

When broadband $^1$H decoupling is eliminated, the secondary phosphino resonance (-28.9 ppm) is split into a pattern with spacings and intensities that resemble the AA' portion of an AA'XX' spin system. The XX' portion consists of the phosphorus-bound proton resonances. The $J_{P-H}$ coupling is approximately 305 Hz for [Pt(CyPPH)$_2$]Cl$_2$ and the $J_{P-H}$ coupling value is between 5 and 10 Hz. This value of $J_{P-H}$ confirms the trans-configuration of the secondary phosphines; a typical $J_{P-H}$ (for Pt(CH$_3$)$_2$(dppp); trans P-Pt-C-H) has a magnitude of 7.5 Hz.$^{44}$
A small pseudo-triplet in the $^{31}P\{^1H\}$ NMR spectrum of each compound, visible in Figure 18, just to the left of the -28.9 ppm triplet, is assigned to a small quantity of a second diastereomer of [Pt(CyPPH)$_2$]Cl$_2$. Such isomerism was observed in the analogous palladium compounds in the preceding section.

Both PtCl$_2$(PPH) and PtCl$_2$(CyPPH) were used as starting materials for investigations of the chemistry of coordinated secondary phosphines. Platinum(II) complexes of new tridentate chelating ligands were synthesized from these two complexes. The preparation of unsymmetrical organophosphido bridged species was attempted using PtCl$_2$(PPH) and PtCl$_2$(CyPPH). Additionally, the symmetrical organophosphide-bridged dimers [PtCl(μ-PP)$_2$] and [PtCl(μ-CyPP)$_2$] were synthesized from PtCl$_2$(PPH) and PtCl$_2$(CyPPH).

F. Triphosphine Complexes of Platinum(II)

Chelating triphosphine ligand complexes of platinum(II) have previously been synthesized by the reactions shown: $^{33}$

\[
\begin{align*}
\text{PtCl}_2(\text{COD}) + \text{P}^-\text{P}^-\text{P}^- & \overset{\Delta}{\longrightarrow} \text{Cl} \begin{bmatrix} \text{P}^- \text{P}^-\text{Pt}^-\text{P}^- \end{bmatrix} + \text{Cl}^- \\
\text{K}_2\text{PtCl}_4 + \text{P}^-\text{P}^-\text{P}^- & \rightarrow \text{I}^- + 2\text{KCl}.
\end{align*}
\]

Synthesis of the free multidentate ligands is usually carried out via coupling reactions between alkali-metal organo-phosphides (LiPR$_3$) and
alkyl halides or by additions of the P-H function of a secondary phosphine across a vinyl or allyl substituent of a substituted phosphine or other donor atom: 

\[ \text{Li}_2\text{PPh} + 2\text{Cl(CH}_2)_3\text{PPh}_2 \rightarrow \text{ttp} + 2\text{LiCl} \]  

\[ \text{Ph}_2\text{PH} + \text{PPh}_2 \xrightarrow{\text{base catalyst}} \text{Ph}_2\text{P} \equiv \text{PPh}_2 \]  

\[ \text{Ph}_2\text{P} \equiv \text{P(H)Ph} + \text{NH}_2 \xrightarrow{\text{hv}} \text{Ph}_2\text{P} \equiv \text{P} \equiv \text{NH}_2 \]  

The synthesis of triphosphine ligands in the metal coordination sphere is described in the present work, starting from complexes containing the PPH ligand. Because of the increase in acidity of the coordinated P-H moiety relative to that of the P-H group of uncomplexed secondary phosphine, the coupling and addition reactions to a substituted monophosphine proceeded rapidly and under more mild conditions than those required for syntheses of the uncomplexed ligands. The availability of both PtCl\(_2\)(CyPPH) and PtCl\(_2\)(PPH) permitted the synthesis of new complexes with different substituents on the terminal or "wing" phosphorus atoms. For example, the new compounds [PtCl(Cy\(_2\)(CH\(_2\))\(_3\)PPh(CH\(_2\))\(_3\)PPh]Cl and [PtCl(Cy\(_2\)P(CH\(_2\))\(_3\)PPh(CH\(_2\))\(_2\)PPh\(_2\)]Cl were prepared during this research study.

The initial reaction was the conversion of PtCl\(_2\)(PPH) to the known complex PtCl(egtp) Cl by (1) addition of vinyldiphenylphosphine to a suspension of the PPH compound, followed by (2) addition of P-H across the C=C bond of vinyldiphenylphosphine. The
conditions employed were similar to those used by Carty for the in situ synthesis of unsaturated bidentate phosphines on palladium (II) complexes. A catalytic amount of triethylamine was employed as the catalyst in a THF suspension of the metal complex. The entire reaction required only about 30 minutes at room temperature. The reaction is summarized below in Equation 40.

\[
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{P} \quad \text{P} \quad \text{Ph} \\
\text{Pt} & \quad \text{Cl} \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
+ & \quad \text{PPh}_2 \\
\rightarrow & \quad \text{Ph}_2\text{P} & \quad \text{P} \quad \text{P} \quad \text{P} \quad \text{Ph} \\
\text{Pt} & \quad \text{Cl} \quad \text{Cl} \\
+ & \quad \text{PPh}_2
\end{align*}
\]

The \( ^{31}\text{P}\{^1\text{H}\} \) NMR spectrum (CH\(_2\text{Cl}_2\)) of the reaction product is reproduced in Figure 19. The \( ^{31}\text{P} \) NMR parameters for this material, those of the authentic [PtCl(eptp)]AsF\(_6\), and those of the analogous new complex [PtCl(CyPPh)]Cl, which was synthesized from PtCl\(_2\)(CyPPH) and vinylidiphenylphosphine, are summarized in Table 9. The only platinum-phosphine complex detectable in the reaction mixture by \( ^{31}\text{P}\{^1\text{H}\} \) NMR is the desired [PtCl(eptp)]Cl. Inspection of the \( ^{31}\text{P}\{^1\text{H}\} \) NMR data in Table 9 reveals the excellent agreement between the spectrum of the experimental complex and the authentic sample prepared by Tau from PtCl\(_2\)(COD) and free eptp.

The \( ^{31}\text{P} \) \(^1\text{H} \) NMR spectrum of [PtCl(eptp)]Cl consists of an ABM spectral pattern for the main phosphorus resonances accompanied by satellite spectra arising from the isotopomer containing \(^{195}\text{Pt} \). The spin-label assignment is shown in Figure 20.
Figure 19. The $^{31}\text{P}^{'\text{H}}$ NMR Spectrum of [PtCl(epE)]Cl in CH$_2$Cl$_2$. 
Table 9. $^{31}$P($^1$H) Spectral Parameters for Three Pt(II)-
Triphosphine Complexes

<table>
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<tr>
<th></th>
<th>$\delta_{PA}$</th>
<th>$\delta_{PM}$</th>
<th>$\delta_{PB}$</th>
<th>$^1J_{PA-PM}$</th>
<th>$^2J_{PA-PB}$</th>
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<tr>
<td>[PtCl(eptp)]AsF$_6$</td>
<td>50.6</td>
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<td>376</td>
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<td>[PtCl(eptp)]Cl</td>
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<td>26.6</td>
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<tr>
<td>[PtCl(CyPpep)]Cl</td>
<td>49.5</td>
<td>33.2</td>
<td>9.12</td>
<td>5.0</td>
<td>349</td>
<td>23.6</td>
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$^1J_{Pt-P_A}$ $^1J_{Pt-P_M}$ $^1J_{Pt-P_B}$

<table>
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<tr>
<th></th>
<th>$^1J_{Pt-P_A}$</th>
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<td>[PtCl(eptp)]AsF$_6$</td>
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<td>3118</td>
<td>2246</td>
</tr>
<tr>
<td>[PtCl(eptp)]Cl</td>
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<td>2241</td>
</tr>
<tr>
<td>[PtCl(CyPpep)]Cl</td>
<td>2260</td>
<td>3140</td>
<td>2219</td>
</tr>
</tbody>
</table>

a. Reference 55

Figure 20. Spin Label Assignment for [PtCl(eptp)]Cl and [PtCl(CyPpep)]Cl (when B = Cy$_2$P)
The best indications that P-H addition across the C=C bond has occurred in the reaction are the chemical shifts of the phosphorus nuclei labelled $P_A$ and $P_B$. Involvement of phosphorus in five-membered chelate rings causes a shift of the $^{31}$P NMR resonances to lower field by significant amounts, compared to comparable, non-chelating phosphines in similar environments. Comparison of the chemical shifts for $P_A$ and $P_M$ in the complexes in Table 9 with the corresponding data for complexes not containing phosphorus in a five-membered chelate ring (vide infra) reveals that ring closure has occurred. The $^2J_{AB}$ values in these compounds (approximately 6 Hz) are also typical of platinum-coordinated cis-phosphines connected by a $-\text{CH}_2\text{CH}_2-$ linkage, as for example PtClEt(dppe) ($J_{P-P} < 2$ Hz). Coupling occurs both through the metal d orbitals and through the ligand backbone; the signs of the couplings are opposite and they tend to cancel one another. In contrast, the couplings between the ligand phosphorus atoms connected via $-\text{CH}_2\text{CH}_2\text{CH}_2-$ linkages are in the normal range (~20-25) for platinum (II) complexes. Additional evidence for the formation of [PtCl(eptp)]Cl is found in the infrared spectrum (Nujol, Figure 21) of the compound following metathesis with NaAsF$_6$ (Experimental Section); the spectrum exhibits typical ligand absorbances but no absorbance corresponding to a vinyl group (1590 cm$^{-1}$ in free vinylidiphenylphosphine) is evident.

During the synthesis of [PtCl(CyPPh)]Cl an attempt was made to observe the probable intermediate compound [PtCl(CyPH)](P(C$_2$H$_5$)$_2$- (C$_6$H$_5$)$_2$)]Cl by $^{31}$P NMR spectroscopy. The reaction was carried out
Figure 21. The Infrared Spectrum of $[\text{PtCl}(\text{eptp})]\text{AsF}_5$ (Nujol mull).
Figure 22. The $^{31}\text{P}^{[1}\text{H}]$ NMR Spectrum of $[\text{PtCl}(\text{CyPPh})]\text{Cl}$ in CH$_2$Cl$_2$. 
in ethanol, in which both the expected intermediate and product were soluble. No additional base was added to the reaction mixture. The $^{31}$P-$^1$H NMR spectrum of the reaction mixture, shown in Figure 22, reveals that ring closure occurred after approximately twelve hours at room temperature despite the absence of an added basic catalyst. As in the case of [PtCl(eptp)]Cl, the low field chemical shifts of phosphorus nuclei $P_A$ and $P_B$ and $^2J_{A-B}$ indicate that these nuclei are involved in a five-membered chelate ring. The 60 MHz $^1$H NMR of [PtCl(CyPPh)]AsF$_6$ (CDCl$_3$) shows the proper ratio of phenyl:aliphatic protons of ~2.1:1, and is free of proton resonances in the region 5.4 to 7.0 $\delta$ where free vinylidiphenylphosphine displays a complex pattern of resonances due to the vinyl group protons. Apparently the alcohol solvent is sufficiently basic to generate the phosphido nucleophile which then attacks the activated terminal carbon of the vinyl group.

The synthesis of a triphosphine-Pt(II) complex was attempted by combining PtCl$_2$(CyPPH) with allyldiphenylphosphine in ethanol. The objective of the experiment was the addition of the P-H moiety across the C=C bond of the allyl substituent of the monophosphine. However, in the absence of additional base, ring closure did not occur. The product of the reaction was exclusively [PtCl$\{P(C_3H_5)(C_6H$_5$)$_2$\}$-$(CyPPH)]Cl. The structure of the compound is confirmed by its $^{31}$P NMR spectrum; the $^{31}$P-$^1$H NMR spectrum (CH$_2$Cl$_2$) is presented in Figure 23.

The $^{31}$P-$^1$H NMR spectrum of [PtCl(allyl)$PPh_2$)(CyPPH)]Cl consists of an ABM pattern accompanied by satellite spectra caused by coupling
Figure 23. The $^{31}\text{P}$/$^1\text{H}$ NMR Spectrum of $[\text{PtCl}\{\text{P(C}_3\text{H}_5)\{\text{C}_6\text{H}_5\}_2\}(\text{CyPPH})]\text{Cl}$ in $\text{CH}_2\text{Cl}_2$
of the phosphorus nuclei to $^{31}\text{P}$. The AB portion of the spectrum is a pattern of four doublets denoted by the letters A and B in Figure 23. The doublet splitting of the basic four-line AB pattern results from $^{2}J_{\text{P-P}}$ cis coupling (20.7 Hz, 23.6 Hz) from phosphorus M. In turn, the resonance of the nucleus is split into a doublet of doublets; however, the overlap of the inner two lines of the doublets causes the resonance to appear as a 1:2:1 triplet in the $^{31}\text{P}$ spectrum. The appearance of the triplet is an indication that the two cis couplings $^{2}J_{\text{BM}}$ and $^{2}J_{\text{AM}}$ are of equal sign. This is consistent with Tau's earlier observations on this type of complex. The strong coupling of nuclei A and B combined with the small difference in their chemical shifts results in the weakened outer transition A and B in Figure 23. Theoretical AB spectra are shown in Figure 24. The ratio of $J/\nu_{o}$ in the AB portion of the $^{31}\text{P}$ NMR spectrum of $[\text{PtCl} \{\text{P} \{\text{C}_{8}\text{H}_{8}\} \{\text{C}_{8}\text{H}_{8}\}_{2}\} \{\text{CyPPH}\}]\text{Cl}$ which determines the relative intensities of the inner and outer lines of the AB pattern is equal to ~0.46.

Table 10. $^{31}\text{P} \{^{1}\text{H}\}$ Spectral Parameters for $[\text{PtCl} \{\text{P} \{\text{C}_{8}\text{H}_{8}\} \{\text{C}_{8}\text{H}_{8}\}_{2}\} \{\text{CyPPH}\}]\text{Cl}$

<table>
<thead>
<tr>
<th>$\delta_{\text{P}}$</th>
<th>$\delta_{\text{P}}$</th>
<th>$\delta_{\text{P}}$</th>
<th>$^{1}J_{\text{P-P}}$</th>
<th>$^{2}J_{\text{P-P}}$</th>
<th>$^{2}J_{\text{P-P}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{1}\text{J}_{\text{P-P}}$</td>
<td>13.7</td>
<td>-24.6</td>
<td>9.3</td>
<td>20.7</td>
<td>363</td>
</tr>
</tbody>
</table>

$^{1}\text{J}_{\text{Pt-P}}$ | $^{1}\text{J}_{\text{Pt-P}}$ | $^{1}\text{J}_{\text{Pt-P}}$

| $^{1}\text{J}_{\text{Pt-P}}$ | 2177 | 3279 | 2136 |
Figure 24. Theoretical AB NMR Spectra as a Function of J/\nu_{66} (Reference 69)
The satellite spectra arising from the coupling of $P_A$ and $P_B$ are easily assigned. The accidental overlap of the central lines of the satellite spectra downfield of the main AB resonance results from the slightly different $^1J_{Pt-P}$ coupling constants between phosphorus nuclei A and B. Consistent with this interpretation, the doublets of the upfield satellite resonance are separated farther from each other than are the corresponding peaks of the main AB resonance. The weak outer transitions $A_1$ and $B_2$ are not resolved in the satellite spectrum.

An absolutely unequivocal assignment of resonances A and B is not possible in this spectrum without additional information. The assignments of A and B in the Table 10 were made by comparison of the $^3P$ NMR spectral parameters of PtCl$_2$(CyPPH) and PtCl$_2$(PPH) with those of [PtCl{P(C$_3$H$_5$)(C$_6$H$_5$)$_2$}(CyPPH)]Cl and are primarily based on the magnitude of the cis $^2J_{P-P}$ coupling between the phosphorus atoms of [PtCl{P(C$_3$H$_5$)(C$_6$H$_5$)$_2$}(CyPPH)]Cl. Also, the previously noted low-field chemical shift of the Cy$_2$P- resonance in the free and complexed diphosphine ligand relative to coordinated Ph$_2$P- groups is consistent with the chosen spectral assignments.

In contrast to the reaction between PtCl$_2$(CyPPH) and vinylidiphenylphosphine, chelate ring closure did not occur after coordination of allyldiphenylphosphine to PtCl$_2$(CyPPH). The existence of the P-H bond in [PtCl{P(C$_3$H$_5$)(C$_6$H$_5$)$_2$}(CyPPH)]Cl was confirmed by the proton-coupled $^3P$ NMR spectrum of this complex. The observed $^1J_{P-H}$ coupling of $\sim$430 Hz is comparable to the $^1J_{P-H}$ coupling in PtCl$_2$(CyPPH). The
spectrum of [PtCl\{P(C_3H_5)(C_6H_5)_2\}(CyPPH)]Cl was collected using CH_3OD as solvent in order to determine whether or not the P-H proton exchanges with deuterium in the alcohols. Figure 25, the ^{31}p[^{1}H]\ NMR spectrum (CH_3OD), shows that this exchange takes place.

The pseudo-triplet originally present in the spectrum of [PtCl\{P(C_3H_5)(C_6H_5)_2\}(CyPPH)]Cl at -24.1 ppm is split into three triplets of 1:1:1 intensity by D(I=1). The value of J_{P-D} is equal to 67 Hz; the ratio J_{P-H}/J_{P-D} is therefore very close to the ratio \gamma_H/\gamma_D of 6.51. The isotopic chemical shift \Delta\delta_{PD} calculated from the spectrum is 0.7 ppm, approximately equal to isotopic NMR shifts determined for other four-coordinate phosphorus atoms. Although exchange of deuterium for H has been observed previously for phenyl and diphenylphosphines in CD_3OD, we believe this to be the first observation of such an exchange in a transition metal complex of a secondary phosphine under mild conditions. It has been reported that the protons of Fe(CO)_4(HPPh_2)_2 do not exchange with D_2O. Proton exchange is reported for M(CO)_4(PH_3)_2 and M(CO)_3(PH_3)_2 (M = Cr, Mo, W) when the complexes are passed through acidic alumina which has been deactivated by D_2O, or in the presence of a strong base.

From the NMR evidence, the ring closure reaction which produces [PtCl(CyPPe)]Cl in EtOH may be classified as a base-catalyzed addition of P-H across a C=C bond. The thermodynamic stability of the five-membered chelate ring on platinum(II) and the template effect of the metal atom in keeping the reactant in proximity probably contribute to the rapidity and quantitative yield of the vinyl addition.
Figure 25. The $^{31}$P{$^{1}$H} NMR Spectrum of $\text{[PtCl}_2\text{P}((\text{C}_3\text{H}_5)\text{H}_3)\text{H}_2\text{CyPPH})\text{Cl}$ in CH$_3$OD.
reaction. In contrast, all of the attempts to form a six-membered chelate ring by the analogous addition of P–H across the allyl moiety of coordinated allyldiphenylphosphine by the base-catalyzed route were unsuccessful. The use of a stronger base catalyst (NEt₃) in the reaction gave a complex mixture of starting material and products. This result is similar to that found when the base-catalyzed addition of P–H across allyl groups is carried out on uncomplexed phosphines.®®®®

Ring closure via free-radical addition of P–H across the allyl group in this compound was also attempted. Photolysis of [PtCl((allyl)PPh₂)–(CyPPH)]Cl in THF, toluene, and dichloromethane at 350 nm (Pyrex filter) alone and in the presence of the radical initiator AIBN did not produce the desired compound [PtCl(CyPPh₃)]Cl. Authentic [PtCl(CyPPh₃)]Cl was prepared via a different route.

The alkylhalide–organophosphide coupling reaction (Equation 35) was adapted successfully to the PtCl₂(PPh) and PtCl₂(CyPPH) complexes. The known complex [PtCl(ttp)]Cl and the new complexes [PtCl(Cyttp)Cl] and [PtCl(CyPPh₃)]Cl were synthesized by the reaction of PtCl₂(PPh) and PtCl₂(CyPPH) with either Cl(CH₃)₃PPh₂ or Cl(CH₃)₃PCy₂ in THF or ethanol in the presence of a stoichiometric quantity of triethylamine.

The reactions were monitored by observing the disappearance of the triplet ¹H resonance of the ~CH₃Cl group of the monophosphine (δ = 3.5 ppm). The 60-MHz ¹H NMR spectrum (CDCl₃) of [PtCl(CyPPh₃)]Cl formed from PtCl₂(PPh) and Cl(CH₃)₃PCy₂ is given in Figure 26. The phenyl:aliphatic ratio is approximately correct for [PtCl(CyPPh₃)]Cl. A small amount of HNEt₃Cl (δ 3.2, q, δ 1.5, t)°°°° was present in this
Figure 26. The $^1$H NMR Spectrum of [PtCl(CyPPtp)]Cl in CDCl$_3$.
sample, and it was removed later by recrystallization from ethanol. The appearance of HNEt$_3$Cl in the $^1$H NMR spectrum serves as an additional confirmation of the coupling reaction. The $^{31}$P NMR spectral data for authentic [PtCl(ttp)]AsF$_5$ and for three other triphosphate complexes synthesized from either PtCl$_2$(PPH) or PtCl$_2$(CyPPH) via the coupling reaction are presented in Table 11.

The $^{31}$P($^1$H) NMR spectra of [PtCl(Cyttp)]Cl (Figure 27) and [PtCl(ttp)]Cl consist of A$_2$B spin systems (two equivalent P, one non-equivalent P) which are composed of a downfield doublet due to the "wing" phosphorus atoms (P$_1$ and P$_3$) and an upfield triplet representing the central PPh unit. The doublet and triplet splittings are equivalent and represent the $^2$J$_{P-P}$ coupling (cis) of the wing phosphorus atoms to the central phosphorus atom. The degeneracy of the A$_2$B spectral pattern is eliminated in the spectrum of [PtCl(CyPPtp)]Cl. The pattern of the main resonances in this spectrum (Figure 28) is an ABM pattern with the AB portion strongly coupled. The spectrum of [PtCl(CyPPtp)]Cl is therefore very similar to that of [PtCl{P(C$_3$H$_5$)(C$_6$H$_5$)$_2$}(CyPPH)]Cl (vide supra).

In this spectrum the outer transitions A$_1$ and B$_2$ are more clearly resolved than in the spectrum of the allyldiphenylphosphine compound. An unambiguous assignment of A and B (i.e. P$_1$ and P$_3$) is not possible strictly from the $^{31}$P spectrum; however, on the basis of the NMR chemical shift data for the other triphosphate complexes the
Table 11. $^{31}$P Spectral Data for Pt(II) Triphosphine Complexes Prepared from the
Coupling Reaction.

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{P_1}$</th>
<th>$\delta_{P_2}$</th>
<th>$\delta_{P_3}$</th>
<th>$^2J_{P_1-P_2}$</th>
<th>$^2J_{P_2-P_3}$</th>
<th>$^1J_{Pt-P_1}$</th>
<th>$^1J_{Pt-P_2}$</th>
<th>$^1J_{Pt-P_3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PtCl(ttp)]Cl$^{a,b}$</td>
<td>-3.7</td>
<td>-20.7</td>
<td>-3.7</td>
<td>27</td>
<td></td>
<td>2229</td>
<td>3134</td>
<td></td>
</tr>
<tr>
<td>[PtCl(ttp)]Cl$^b$</td>
<td>-3.9</td>
<td>-20.6</td>
<td>-3.9</td>
<td>26.5</td>
<td></td>
<td>2221</td>
<td>3076</td>
<td></td>
</tr>
<tr>
<td>[PtCl(Cytpp)]Cl$^b$</td>
<td>-4.0</td>
<td>-20.4</td>
<td>-4.0</td>
<td>23.6</td>
<td></td>
<td>2152</td>
<td>3236</td>
<td></td>
</tr>
<tr>
<td>[PtCl(CyPtp)]Cl$^c$</td>
<td>-3.10</td>
<td>-16.3</td>
<td>4.85</td>
<td>25.6</td>
<td>23.63</td>
<td>344</td>
<td>2110</td>
<td>3158</td>
</tr>
</tbody>
</table>

a. reference 53, solvents CH$_3$NO$_2$ and CD$_3$NO$_2$.
b. $P_1$ and $P_3$ are equivalent
c. $P_1$, R=Ph; $P_3$, R=Cy
Figure 27. The $^{31}\text{P}{}^1\text{H}$ NMR Spectrum of [PtCl(Cyttp)]Cl in CH$_2$Cl$_2$. 

\[ [\text{PtCl}(\text{Cy}_2\text{P} - \text{P} - \text{PCy}_2)]\text{Cl} \]
Figure 28. The $^3$P$^+_1$H NMR Spectrum of [PtCl(CyPtp)]Cl in CH$_2$Cl$_2$. 
assignment of the resonance at -3.10 ppm to the PPh₂ group is probably correct. The resonance of the Cy₂P- group would then be the one centered at 4.9 ppm; this assignment remains consistent with the previous observations of Cy₂P- resonances being upfield from the Ph₂P- resonances in similar environments.

The reason for the chemical shift anomaly of P₂ in [PtCl-(CyPPh₂tp)]Cl (-16.3 ppm) compared to the chemical shifts of identical groups in the other complexes in Table II (all occur at approximately -20.5 ppm) is not obvious. In the absence of other reasonable explanations, a C-P-C bond angle strain argument for P₂ may be invoked for this complex. The bending of the phenyl substituents on the central phosphorus atom away from the bulky cyclohexyl groups on one side of the complex would open the C-P-C bond angle ϕ about P₂, (see Figure 29) perhaps causing a small decrease in the chemical shift

![Figure 29. Sterically Induced Bond Angle Distortion in [PtCl(CyPPh₂tp)]Cl](image-url)
of $P_2$. The anomaly does not appear in the PPh$_2$ resonance of
[PtCl(Cyttp)]Cl since the steric interactions to either side of the
PPH moiety are equal; thus, no net distortion occurs. Structural
data on [PtCl(CyPPtp)]Cl may be necessary for this hypothesis to be
tested.

The coupling constant $^2J_{P_1-P_2}$ of [PtCl(CyPPtp)]Cl which is un-
observable in the ttp and Cyttp complexes due to the equivalence of
the "wing" phosphines is equal to 344 Hz and is comparable to the
trans coupling seen in [PtCl(eptp)]Cl (374 Hz) and [PtCl(CyPPep)]Cl
(349 Hz).

G. $^{195}$Pt-{H} NMR Spectra of Monomeric Complexes

The purchase of the 300 MHz NMR instrument made $^{195}$Pt-{H} FT NMR
spectroscopy available for examination of the effects of the various
phosphino ligands on the chemical shift of the platinum nucleus. The
$^{195}$Pt NMR data for a number of mono-, di-, and tri-phosphine com-
plexes of platinum (II) are given in Table 12.

The shielding term, $\sigma$, for heavy nuclei such as $^{195}$Pt is gener-
ally considered to be a sum of a diamagnetic contribution, $\sigma_d$, and a
paramagnetic contribution, $\sigma_p$. For $^{195}$Pt the paramagnetic term is
by far the larger of the two; therefore discussions of $^{195}$Pt chemical
shifts generally only consider the $\sigma_p$ term. The paramagnetic term is
inversely related to the cube of the average radius of the platinum
5d and 6s orbitals and to the energy difference between the ground and
excited states of the 5d and 6s electrons. The paramagnetic term is
directly proportional to the degree of asymmetry of the valence electron
Table 12. \textsuperscript{195}Pt NMR Data for Platinum (II) Monomeric Complexes

<table>
<thead>
<tr>
<th></th>
<th>( \delta_{\text{Pt}} )</th>
<th>( ^{1}J_{\text{Pt-P}} )</th>
<th>( ^{1}J_{\text{Pt-P}} )</th>
<th>( ^{1}J_{\text{Pt-P}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. \textit{cis-PtCl}_2(PMe_2Ph)\textsubscript{2} \textsuperscript{b,c}</td>
<td>-853</td>
<td>3548</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2. \textit{cis-PtCl}_2(PMePh)\textsubscript{2} \textsuperscript{b,c}</td>
<td>-886</td>
<td>3622</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3. \textit{cis-PtCl}_2(PBu_2^n)\textsubscript{2} \textsuperscript{b,c}</td>
<td>-888</td>
<td>3435</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4. \textit{cis-PtCl}_2(PEt_3)\textsubscript{2} \textsuperscript{b,c}</td>
<td>-932</td>
<td>3560</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>5. PtCl\textsubscript{2}(PPH)</td>
<td>-955</td>
<td>3403</td>
<td>3256</td>
<td>—</td>
</tr>
<tr>
<td>6. PtCl\textsubscript{2}(dppp) \textsuperscript{c}</td>
<td>-963</td>
<td>3410</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>7. PtCl\textsubscript{2}(CyPPH)</td>
<td>-993</td>
<td>3303</td>
<td>3390</td>
<td>—</td>
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<tr>
<td>8. PtCl\textsubscript{2}(dppt)</td>
<td>-1062</td>
<td>3557</td>
<td>3662</td>
<td>—</td>
</tr>
<tr>
<td>9. \textit{[PtCl}(Cyttp)\textsubscript{]}Cl \textsuperscript{d}</td>
<td>-1185</td>
<td>2152</td>
<td>3236</td>
<td>—</td>
</tr>
<tr>
<td>10. \textit{[PtCl}(CyPPTp)\textsubscript{]}Cl</td>
<td>-1234</td>
<td>2110</td>
<td>3158</td>
<td>2164</td>
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<tr>
<td>11. \textit{[PtCl}(ttpp)\textsubscript{]}Cl \textsuperscript{d}</td>
<td>-1240</td>
<td>2221</td>
<td>3076</td>
<td>—</td>
</tr>
<tr>
<td>12. \textit{[PtCl}(CyPpPep)\textsubscript{]}Cl</td>
<td>-1295</td>
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<td>3140</td>
<td>2219</td>
</tr>
<tr>
<td>13. \textit{[PtCl}(eptp)\textsubscript{]}Cl</td>
<td>-1325</td>
<td>2347</td>
<td>3066</td>
<td>2241</td>
</tr>
</tbody>
</table>

\( \delta \) is given ppm relative to \textit{cis-PtCl}_2(SMe)\textsubscript{2} at 0 ppm, negative values are upfield from the standard.

b) Data from reference 51

c) \( P_1, P_2 \) are equivalent, no \( P_3 \)

d) \( P_1, P_3 \) are equivalent
distribution about the platinum nucleus. The explanation and definition of simple trends in the chemical shifts of $^{195}$Pt are made extremely difficult by the complex interactions of these three quantities. Empirical trends which have emerged and seem to hold for a fairly broad range of complexes include the following: (a) replacement of an alkyl group by an aryl group on a coordinated phosphorus or arsenic causes increased shielding of platinum and an increase in its chemical shift; (b) a decrease in the electronegativity of the ligands bonded to platinum causes increased shielding of platinum; (c) increased covalent bonding between a platinum atom and its ligands withdraws electron density from the metal leading to more positive (i.e., down-field) chemical shifts. Covalency increases as ligand polarizability or $\pi$-acceptor character increases.

Concentration, solvent, and temperature effects on the chemical shifts have been minimized in the present study by the use of the minimum number of solvents and approximately equal concentrations of the platinum(II) complexes. Therefore, the chemical-shift data of complexes 5-13 (this work) should be consistent. Examination of the chemical-shift data for complexes 1-8 (i.e. PtCl$_2$(L-L) and cis-PtCl$_2$L$_2$) indicates general agreement with observation (a) above. In this series of complexes, the effects of (b) and (c) are minimized by the appearance of chloride in all of the compounds. The chemical shift ordering of PtCl$_2$(PPH) and PtCl$_2$(CyPPH) is reversed from that expected from condition (a). Increasing ligand bulkiness normally has had the effect of decreasing the shielding of platinum, possibly by
distorting the bond angles about platinum. A decrease in the chemical shift of $^{195}$Pt has been noted on substitution of PCy$_3$ for PPr$_3$ in a series of Pt(0) compounds.$^{32}$ The large disparity in size between the Cy$_2$P- and -P(H)Ph groups of CyPPH may be influencing the chemical shift by contributing to the asymmetry of the electron distribution around platinum. It is interesting that the more symmetrical platinum(II) triphosphines (Compounds 9-13) all obey the general trend (a) above. Deviations from (a) have previously been noted in complexes with ligands of widely differing sizes.$^{31}$

The chemical shift of PtCl$_2$(dpet) (-1062 ppm) is upfield from those of PtCl$_2$(PPh), PtCl$_2$(CyPPH), and PtCl$_2$(dppp). The major difference between PtCl$_2$(dpet) and the latter three compounds is the inclusion of platinum in a five-membered chelate ring in PtCl$_2$(dpet) as opposed to six-membered chelate rings in other compounds. A five-membered chelate ring effect (i.e., a shift of platinum chemical shift to higher field) also has been observed in platinum(II)-cycloalkane, platinum(II)-thiolato, and platinum(IV)-phosphino complexes.$^{92}$ In the case of platinum(II)-phosphino complexes, a small effect has previously been observed between Pt(CH$_3$)$_2$(dppp) and Pt(CH$_3$)$_2$(dppe). However, the authors of that paper did not believe that the effect (14 ppm) was significant when compared to the huge range of $^{195}$Pt chemical shifts.

Involvement of a phosphorus atom in a five-membered ring causes the $^{31}$P resonance to appear downfield (20-30 ppm) from that of
similarly substituted non-chelating phosphines. It is interesting
that these low-field $^{31}$P chemical shifts are apparently concomitant
with high-field shifts in the $^{195}$Pt spectra. The $^{195}$Pt{$^1$H} spectrum
of PtCl$_2$(CyPPH) appears in Figure 30. The presence of two dissimilar
phosphines splits the $^{195}$Pt resonance into a doublet of doublets.
Attempts to obtain the $^1$H-coupled spectrum were unsuccessful, due to
the decrease in signal-to-noise ratio which occurs when decoupling
is eliminated.

As previously stated, the platinum(II)-triphosphine complexes
obey empirical observation (a); the chemical shifts of the platinum
atoms bearing alkyl-substituted phosphines appear at lower field than
do the aryl-substituted analogs. The large upfield shift of the $^{195}$Pt
resonance of the triphosphine complexes relative to the diphosphine
complexes has been rationalized as a consequence of a decrease in the
transition energies between the ground and excited states of the
platinum 5d and 6s electrons on formation of the cationic complexes. $^{31}$

Once again, the platinum nuclei involved in five-membered chelate
rings (ligands eptp and CyPPep) appear at higher field than do the
platinum nuclei involved in six-membered rings with identical substitu-
tuent groups on the ligating phosphorus atoms.

The $^{195}$Pt{$^1$H} NMR spectra of [PtCl(Cyttp)]Cl and [PtCl(CyPPep)]Cl
are presented in Figures 31 and 32, respectively. The $^{195}$Pt NMR
spectrum of the Cytttp compound is easily analyzed as the X portion
of an $A_2B_2$ spin system; the $A_2$ nuclei consist of two equivalent
Figure 30. The $^{195}$Pt$^{1}$H NMR Spectrum of [PtCl$_2$(CyPPH)] in DMSO.
Figure 31. The $^{195}\text{Pt}^{1}{\text{H}}$ NMR Spectrum of [PtCl(Cyttp)]Cl in CH$_2$Cl$_2$. 
Figure 32. The $^{195}$Pt$^{1}$H NMR Spectrum of [PtCl(CyPPep)]Cl in CH$_2$Cl$_2$. 
Cy$_2$P- groups and the B portion consists of the central -PPh unit. The $^{195}$Pt NMR spectrum of PtCl(CyPpep)Cl comprises the X portion of an ABMX pattern. In both cases the $^1J_{Pt-P}$ coupling data are easily extracted by a direct measurement of the line splittings.

H. Complexes of Platinum(II) Containing Organophosphido-Bridges

The dimeric complexes $[\text{PtCl}(\mu-PP)]_2$ and $[\text{PtCl}(\mu-CyPP)]_2$, which have bidentate ligands functioning in the chelating-bridging mode, were synthesized by the following routes:

$$2 \text{PtCl}_2(\text{COD}) + 2\text{PPH} \xrightarrow{\Delta, 1.5 \text{ hr}} [\text{PtCl}(\mu-\text{PP})]_2 \quad [41]$$

$$2 \text{PtCl}_2(\text{PPH}) + \text{BASE} \xrightarrow{\text{THF}} [\text{PtCl}(\mu-\text{PP})]_2 \quad [42]$$

$$[\text{PtCl}(\text{C}_3\text{H}_5)]_4 + 4 \text{PPH} \xrightarrow{\text{CH}_2\text{Cl}_2, \text{RT}} [\text{PtCl}(\mu-\text{PP})]_2 \quad [43]$$

Variations of each of these three reactions have been used previously to synthesize organophosphido-bridged compounds from compounds containing monodentate secondary phosphines.$^{20,13,92}$

As previously stated, examination of the reaction products by $^{31}\text{P}[^1\text{H}]$ NMR was the most convenient spectroscopic method of distinguishing the dimeric species from the monomers. The $^{31}\text{P}[^1\text{H}]$ NMR spectrum ($\text{CH}_2\text{Cl}_2$) of $[\text{PtCl}(\mu-\text{CyPP})]_2$ is presented in Figure 33. This spectrum consists of two large ten-line multiplets (AA'XX' spin system) centered at -2.68 and -142.6 ppm arising from phosphorus-phosphorus coupling and a subspectrum (AA'MM'X) resulting from the coupling of
Figure 33. The $^{31}$P$[^1]$H NMR Spectrum of [PtCl($\mu$-CyPP)$_2$]$_2$ in CH$_2$Cl$_2$. 
the phosphorus atoms to the $^{31}\text{P}$ nuclei. The spectrum of
$[\text{PtCl}(\mu-\text{CyPP})]_2$ and $[\text{PtCl}(\mu-\text{PP})]_2$ therefore strongly resemble those of several known platinum(II)-organophosphido bridged dimers of similar structure.

The $^{31}\text{P}({}^1\text{H})$ NMR spectral data for the AA'XX' portion of the spectra of some of the literature compounds and the complexes $[\text{PtCl}(\mu-\text{PP})]_2$, $[\text{PtCl}(\mu-\text{CyPP})]_2$, $[\text{PtCH}_3(\mu-\text{PP})]_2$, and $[\text{Pt}(\text{CH}_3)(\mu-\text{CyPP})]_2$ comprise Table 13. The AA'XX' spin labels of the main (ten-line) multiplets of these complexes are assigned according to the diagram (Figure 34).

Figure 34. NMR Spin Label Assignments for Platinum(II) Dimers.
Table 13. The $^{31}$P($^1$H) NMR Spectral Data for Organophosphido-Bridged Complexes of Platinum(II). (Excludes $^{195}$Pt–P Coupling Data)

<table>
<thead>
<tr>
<th></th>
<th>$\delta_X$</th>
<th>$\delta_A$</th>
<th>$^2J_A'X$</th>
<th>$^2J_A$</th>
<th>$^2J_{XX}'$</th>
<th>$^2J_{AA}'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>[PtCl($\mu$-PPh$_2$)(PET$_3$)$_2$]$_2$</td>
<td>14.4</td>
<td>-136.2</td>
<td>4.5</td>
<td>374.3</td>
<td>9.5</td>
</tr>
<tr>
<td>2)</td>
<td>[PtCl($\mu$-PPh$_2$)(HPPH$_2$)]$_2$</td>
<td>-2.4</td>
<td>-139.2</td>
<td>-1.0</td>
<td>395.4</td>
<td>7.6</td>
</tr>
<tr>
<td>3)</td>
<td>[PtCl($\mu$-PPh$_2$)(PM$_2$PPh)]$_2$</td>
<td>-6.5</td>
<td>-138</td>
<td>-8.2</td>
<td>389.9</td>
<td>5.7</td>
</tr>
<tr>
<td>4)</td>
<td>[PtCl($\mu$-PP)]$_2$</td>
<td>-5.8</td>
<td>-144.6</td>
<td>-4.4</td>
<td>382</td>
<td>5.1</td>
</tr>
<tr>
<td>5)</td>
<td>[PtCl($\mu$-CyPP)]$_2$</td>
<td>-2.68</td>
<td>-142.6</td>
<td>-3.0</td>
<td>364</td>
<td>4.0</td>
</tr>
<tr>
<td>6)</td>
<td>[Pt(CH$_3$)($\mu$-PP)]$_2$</td>
<td>+2.27</td>
<td>-155.0</td>
<td>-23.0</td>
<td>337</td>
<td>7.3</td>
</tr>
<tr>
<td>7)</td>
<td>[Pt(CH$_3$)($\mu$-CyPP)]$_2$</td>
<td>+2.5</td>
<td>-154.9</td>
<td>-19.5</td>
<td>325</td>
<td>6.5</td>
</tr>
</tbody>
</table>

a) Chemical shifts are in ppm relative to 85% H$_3$PO$_4$; negative values are upfield of standard
b) Coupling constants are in Hz.
c) Reference 70, also references 28, 14
d) Reference 14
The chemical shifts of phosphorus and phosphorus–phosphorus coupling constants of the tabulated compounds show close agreement between the complexes containing the chelating-bridging diphosphine ligands and those with monophosphino and monophosphido ligands. For example, the $\delta$ values (terminal phosphino groups) are reasonably similar between [PtCl($\mu$-PPh$_2$)(PMe$_2$Ph)$_2$] and [PtCl($\mu$-PP)$_2$]. As has been previously observed during this work, the resonance of the Cy$_2$P-groups of [PtCl($\mu$-CyPP)$_2$] (-2.68 ppm) is downfield from that of the corresponding Ph$_2$P- unit of [PtCl($\mu$-PP)$_2$] (-5.8 ppm). An exception to this is seen when the Cy$_2$P- and -PPh$_2$ chemical shifts are compared in the compounds [Pt(CH$_3$)($\mu$-PP)$_2$] and [Pt(CH$_3$)($\mu$-CyPP)$_2$]. In these two compounds the chemical shifts are virtually identical. It has been our general observation throughout this study, however, that when chloride trans to PCy$_2$ or PPh$_2$ is replaced by stronger ligands (methyl) the chemical shift difference between Cy$_2$P- and Ph$_2$P- in analogous complexes of CyPPH and PPH decreases.

The values of the chemical shifts of the phosphido nuclei ($\delta^1_A$) in [PtCl($\mu$-PP)$_2$] and [PtCl($\mu$-CyPP)$_2$] indicate slightly greater shielding of the phosphido phosphorus atoms of these compounds relative to the phosphido bridges of the [PtCl($\mu$-PPh$_2$)(PR$_3$)$_2$] compounds. This is probably due to the greater basicity of the $\mu$-PPh(alkyl) moiety as opposed to the $\mu$-PPh$_2$ group. The increase in shielding experienced by the (alkyl)PPh group when Cl is replaced by CH$_3$ in [PtCl($\mu$-PP)$_2$] and [PtCl($\mu$-CyPP)$_2$] is believed to be a consequence of the high trans-influence of the methyl group which causes the phosphorus resonance to appear at higher field.$^{32}$
The corresponding coupling constants of all of the tabulated compounds are similar in magnitude in the series of chloro complexes (compounds 1-5). Assignment of the signs of the coupling constants depends on a computer simulation of the $^{31}$P-$^1$H NMR spectrum. Published data in two articles concerning $[\text{PtCl}(\mu-\text{PPh}_2)(\text{PEt}_3)]_2$ differ in the signs of the $^2J_{AA}$ and $^4J_{XX}$ coupling constants. Solution of an AA'XX' spectrum will not give the signs of these constants directly, nor will it provide the signs of the two coupling constants relative to each other. Analysis of an AA'XX' spectrum will provide the relative signs of the coupling constants $^2J_{AX}$ and $^2J_{A'X'}$, however. The author has chosen to treat the $^2J_{AX}$ coupling (trans phosphine-phosphide coupling) as large and positive, in accord with the work of Dixon et al. and in agreement with sign of trans-couplings previously determined for phosphino ligands on platinum-(II).

Platinum-phosphorus coupling constants for $[\text{PtCl}(\mu-\text{PP})]_2$, $[\text{Pt}(\text{CH}_3)(\mu-\text{PP})]_2$, and $[\text{PtCl}(\mu-\text{PPh}_2)(\text{HPh})_2]_2$ are compiled in Table 14. The methodology by which the complex AA'MM'X spectra of the isotopomer containing $^{195}$Pt is analyzed is now well-documented and will not be repeated here. Only the isotopomer containing a single $^{195}$Pt atom (44.8% of total concentration) gives a satellite spectrum sufficiently intense to be solved. Figure 35 displays the spin-labelling convention for these spectra.
Table 14. Platinum-Phosphorus Coupling Constants for Three Phosphido-Bridged Dimeric Compounds (J values in Hz).

<table>
<thead>
<tr>
<th>Compound</th>
<th>${^1J}_{M-X}$</th>
<th>${^3J}_{M-X'}$</th>
<th>${^1J}_{M-A}$</th>
<th>${^1J}_{M-A'}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{PtCl}(\mu-\text{PPh}_2)\text{HPPh}]_2$</td>
<td>2184</td>
<td>29.2</td>
<td>2364</td>
<td>1991</td>
</tr>
<tr>
<td>$[\text{Pt}(\text{CH}_3)(\mu-\text{PP})]_2$</td>
<td>2200</td>
<td>15.0</td>
<td>1089</td>
<td>1965</td>
</tr>
<tr>
<td>$[\text{PtCl}(\mu-\text{PP})]_2$</td>
<td>2115</td>
<td>6.0</td>
<td>2150</td>
<td>1751</td>
</tr>
</tbody>
</table>

From Table 14 it is clear that the chelating-bridging ligand in general exhibits lower $^3J_{M-X'}$ and $^1J_{M-A}$ coupling than does the analogous compound with monodentate ligands. A large decrease in the $^1J_{M-A}$ value in $[\text{PtCl}(\mu-\text{PP})]_2$ on replacement of Cl by CH$_3$ is also evident.

![Figure 35. Spin Labelling Convention for AA'M'M'X Spectra of $[\text{PtCl}(\mu-\text{PP})]_2$ and Analogous Compounds.](image-url)

It is clear from the $^{31}\!P\{^{1}\!H\}$ NMR data that complexes $[\text{PtCl}(\mu-P\text{Ph}_2)\text{(PR}_3)]_2$ bear a strong structural resemblance to $[\text{PtCl}(\mu-PP)]_2$ and $[\text{PtCl}(\mu-\text{CyPP})]_2$. The signs and magnitude of all of the coupling constants in these complexes are nearly identical. A comparison of the cis coupling $^2J_{A-X}$ to those of the CH$_3$ analogs, however, reveals that the $^2J_{A-X}$ value in the CH$_3$ compound has increased in magnitude from $\sim$-4 to $\sim$-20. Simultaneously, the trans $^2J_{AX}$ coupling between terminal phosphine and bridging phosphido ligands has decreased.

Kreter suggested that the high cis coupling between the phosphido-nuclei in this type of compound was a consequence of the interaction of the phosphorus 3d and 3p orbitals through space.$^{26}$ Available X-ray structural data for $[\text{Pt}(\text{CH}_3)(\mu-PP)]_2$ and $[\text{PtCl}(\mu-P\text{Ph}_2)(\text{HPPh}_2)]_2$ does indeed indicate that the phosphido-phosphorus atoms are farther apart (3.02 Å) in $[\text{Pt}(\text{CH}_3)(\mu-PP)]_2$ than in $[\text{PtCl}(\mu-P\text{Ph}_2)(\text{HPPh}_2)]_2$ (2.86 Å). The same X-ray data permit an attempt at a direct correlation of the other NMR data with the structural features of these two compounds.

The most striking difference between the structures of $[\text{Pt}(\text{CH}_3)(\mu-PP)]_2$ and $[\text{PtCl}(\mu-P\text{Ph}_2)(\text{HPPh}_2)]$ is that the former complex has a bent "open book" structure, whereas the latter is rigorously planar (Figure 36). The angle $\phi$ in $[\text{Pt}(\text{CH}_3)(\mu-PP)]_2$ is 143°.$^{76}$

Both the "open-book" and planar structures of dimeric complexes of the d$^8$ metals each have ample literature precedent.$^{93}$ Theoretical studies of complexes with halide and phosphide (PH$_2^-$) bridging
Figure 36. The X-ray Crystal Structures of $\left[\text{PtCl}(\mu-\text{PPh}_3)/\text{HPPPh}_3\right]_2$ (Top, Reference 25) and $\left[\text{PtCH}_3(\mu-\text{PP})\right]_2$ (Bottom)
ligands\textsuperscript{94} have indicated that there are no major energetic or electronic effects in 32-electron systems which influence the distortion from planarity. These studies conclude that steric and crystal packing forces are the primary factors which determine the size of the dihedral angle between the coordination planes of the two metal atoms.\textsuperscript{93,95}

On careful comparison of the bond angles and bond distances of the \( \text{M}_2\text{P}_2 \) core there does not seem to be any obvious cause for the different geometries of \([\text{Pt(CH}_3](\mu-\text{PP})]_2\) and \([\text{PtCl}(\mu-\text{PPh}_3)(\text{HPPh}_2)]\). The platinum-phosphorus bond distances are comparable in the two complexes and are within the range of other platinum-phosphorus bond lengths. In \([\text{Pt(CH}_3](\mu-\text{PP})]_2\) the Pt-P bond distance \textit{trans} to methyl is longer than the comparable Pt-P bond in \([\text{PtCl}(\mu-\text{PPh}_3)-\text{HPPh}_2]\), which is \textit{trans} to chloride; this is a consequence of the high \textit{trans}-influence of the methyl ligand. The longer phosphido-phosphido distance in \([\text{Pt(CH}_3](\mu-\text{PP})]_2\) already alluded to is due to this bond lengthening.

The carbon-carbon bond angles within the backbone of the chelating-bridging ligand are all in excess of \(109^\circ\) (111.1, 112.8, 112.2\(^\circ\)). A larger deviation from the tetrahedral angle in the ligand backbone was observed in the X-ray structure determination of \(\text{PdCl}_2\)(dppp) (112.9, 118.1, 117.0) of Palenik \textit{et al.}\textsuperscript{74} This angle strain arises primarily from the eclipsing of C-H bonds in the trimethylene backbone. As a result of this strain, one ligand phosphorus atom is
pushed 0.053 Å above the coordination plane and the second phosphorus atom pushed 0.31 Å below the plane in PdCl₂(dppp). Similar twisting of the coordination geometry about the platinum atoms in [Pt(CH₃)₂(μ-PP)]₂ may account for the observed open-book configuration of [PtCH₃(μ-PP)]₂. If this twist argument is valid, then [PtCl(μ-PP)]₂ would probably have a more sharply bent structure, since a decrease in the Pt-P bond length trans to X(X=CH₃ or Cl) would then be expected to compress the ligand backbone and increase the carbon-carbon bond angle strain. Since the transmission of ³Jₜₙ-ₓ coupling occurs through the phosphido-bridge, the magnitude of this coupling may be sensitive to ϕ. The ³Jₜₙ-ₓ coupling decreases in the order [PtCl(μ-PPh₂)(HPPH₂)]₂ > [Pt(CH₃)(μ-PP)]₂ > [PtCl(μ-PP)], and this is also the expected order of decrease (from 180°) of the dihedral angle. The ¹Jₜₙ₋ₓ coupling decreases in the same order as ³Jₜₙ₋ₓ, and this may again be the result of the folding of the dimer structure.

A second contributing steric factor is the interaction of the phenyl substituents of the phosphido-phosphorus atoms of [Pt(CH₃)₂(μ-PP)]₂. Both phenyl groups are on the same side of the intersecting planes of the metal atoms and the direction of the interplane bonding is away from the phenyl groups; this may serve to minimize steric interactions between the phenyl groups of the phosphido-phosphorus atoms and the phenyl groups of the terminal tertiary phosphorus atoms. Such a deformation in the more symmetrical [PtCl(μ-PPh₂)(HPPH₂)]₂ could not give such steric relief. Examination of the X-ray structure of [PtCl(μ-CyPP)]₂ would show a larger deviation from planarity if the
interactions of the phosphido phenyl groups with other phosphorus substituents are significant.

The $^{195}$Pt($^1$H) NMR spectrum of $[\text{PtCl}(\mu-\text{PP})]_2$ was also obtained, and is shown in Figure 37. This spectrum provides the chemical shift of the $^{195}$Pt nucleus (520 ppm) and the $^{195}$Pt-$^{195}$Pt coupling constant (360 Hz). The splitting and assignments of the major peaks in the spectrum are also detailed in Figure 37. The spin labels used in Figure 37 are the same as those of Figure 36.

The syntheses of $[\text{PtCl}(\mu-\text{PP})]_2$ (and $[\text{PtCl}(\mu-\text{CyPP})]_2$) carried out via the thermal and allyl elimination routes (Equations 38 and 39) each result in the isolation of a single product with the $^{31}$P NMR parameters presented in Table 13 (vide supra). However, when the synthesis of these compounds is carried out from the corresponding monomers at temperatures below 80°C, the $^{31}$P($^1$H) NMR spectrum of the isolated reaction product reveals the presence of approximately an 1:1 mixture of two compounds. In the case of $[\text{PtCl}(\mu-\text{CyPP})]_2$, for example, the organophosphido (high field) region of the $^{31}$P($^1$H) NMR spectrum ($\text{CH}_2\text{Cl}_2$) consists of two ten-line multiplets; one centered at $\delta = -142.6$ ppm and the other at $\delta = -170.2$ ppm (See Figure 38). A second pair of ten-line multiplets is present in the low-field (phosphino) region of the $^{31}$P NMR spectrum; the chemical shifts of these two multiplets are -2.68 and -5.66 ppm.

The multiplets at -2.68 and -142.6 ppm which constitute an AA'XX' pattern possess chemical shifts identical to those of the
Figure 37. The $^{195}$Pt($^1$H) NMR Spectrum of [PtCl($\mu$-PP)$_2$] in CH$_2$Cl$_2$. 
Figure 38. The $^{31}\text{P{}^{1}H}$ NMR Spectrum of the Phosphido-Region of a Mixture of the Geometrical Isomers of $[\text{PtCl}(\mu-\text{CyPP})]_2$
complex \([\text{PtCl}(\mu-\text{CyPP})]_2\) synthesized by the thermal and allyl routes. The second compound, which also displays an AA'XX' pattern in its \(\text{\(^{31}\)P NMR}\) spectrum, was successfully separated from the first by fractional recrystallization from dichloromethane and acetone. Investigation of this second, less soluble reaction product by \(\text{\(^1\)H NMR}\) and infrared spectroscopy reveals that it is also of composition \([\text{PtCl}(\mu-\text{CyPP})]_2\). There is no infrared or \(\text{\(^1\)H NMR}\) evidence for the presence of coordinated \(\text{NEt}_3\); this second product is therefore not the result of a substitution reaction between \([\text{PtCl}(\mu-\text{CyPP})]_2\) and \(\text{NEt}_3\). A mixture of isomers in an approximately 1:1 ratio is also obtained when \([\text{PtCl} (\mu-\text{PP})]_2\) is synthesized from \(\text{PtCl}_2(\text{PPH})\) by the action of base at room temperature.

Thus, the presence of four different groups bonded to each organophosphide phosphorus atom results in the formation of geometrical isomers (Figure 39). The \(\text{\(^{31}\)P NMR}\) chemical shift data for the observed isomers of \([\text{PtCl}(\mu-\text{CyPP})]_2\) and \([\text{PtCl}(\mu-\text{PP})]_2\) comprise Table 15.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>(phosphino)</th>
<th>(phosphido)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha- [\text{PtCl} (\mu-\text{PP})]_2)</td>
<td>-5.80</td>
<td>-144.6 ppm</td>
</tr>
<tr>
<td>(\beta- [\text{PtCl} (\mu-\text{PP})]_2)</td>
<td>-5.80</td>
<td>-171.4 ppm</td>
</tr>
<tr>
<td>(\alpha- [\text{PtCl} (\mu-\text{CyPP})]_2)</td>
<td>-2.68</td>
<td>-142.6 ppm</td>
</tr>
<tr>
<td>(\beta- [\text{PtCl} (\mu-\text{CyPP})]_2)</td>
<td>-5.66</td>
<td>-170.2 ppm</td>
</tr>
</tbody>
</table>
Similar geometrical isomerism in phosphido-bridged iron complexes of formula $\text{Fe}_2(\text{CO})_6(\mu-\text{PRR'})_2$ ($R = \text{C}_6\text{H}_5$, $R' = \text{CH}_3$, $\text{H}$) has previously been reported, the absolute configuration of one such compound was determined by X-ray crystallography.\textsuperscript{79},\textsuperscript{96}

The absolute configuration of the two isomers of $[\text{PtCl}(\mu-\text{CyPP})]_2$ has been determined from their $^1\text{H}$ NMR spectra and by comparison with the known structure of $[\text{Pt}(\text{CH}_3)(\mu-\text{PP})]_2$. Examination of the phenyl resonances of the $\alpha$ and $\beta$ isomers of $[\text{PtCl}(\mu-\text{CyPP})]_2$ by $^1\text{H}$ NMR spectroscopy (Figure 39) indicated that the $\alpha$ isomer has the structure with axial phenyl groups while the $\beta$ isomer has the structure with equatorial phenyl groups. The increased shielding of the phenyl protons of the $\alpha$ isomer is due to a ring current shielding contributions from the phenyl substituent of the neighboring phosphido phosphorus atom. In the previously cited iron compounds, the phenyl proton resonances of the isomer with eclipsed axial phenyl groups also appeared upfield from the corresponding resonances of the isomer with one axial and one equatorial phenyl group or two equatorial phenyl groups. The assignment of this structure to the $\alpha$ isomer is in agreement with the X-ray structure of $[\text{Pt}(\text{CH}_3)(\mu-\text{PP})]_2$, which like $\alpha-[\text{PtCl}(\mu-\text{CyPP})]_2$ resulted from a thermolysis reaction.

Thus, during the formation of $[\text{PtCl}(\mu-\text{CyPP})]_2$ at room temperature two products are formed in approximately equal quantities. The $\alpha$ isomer is favored at higher temperatures, presumably because of steric considerations, which include the conformation of the carbon
Figure 39. The 300 MHz\(^{1}\text{H}\) NMR Spectra of the Phenyl Protons of the Separated Isomers of \([\text{PtCl}(\mu-\text{CyPP})]_2\). Solvent: CD\(_2\)Cl\(_2\) Top: \(\beta\) isomer Bottom: \(\alpha\) isomer
backbone of the chelate ligand. An attempt to interconvert the 
\( \beta \) isomer to the \( \alpha \) isomer by refluxing a quantity of it in toluene 
was unsuccessful due to the strength of the organophosphido-
platinum bonds, since such an interconversion probably requires 
phosphorus-platinum bond breaking. The large difference in the 
phosphorus chemical shifts of the organophosphido-bridging groups 
in the two isomers is probably due mainly to variations in the 
bond angles about the phosphido phosphorus atoms. Chelate ring 
strain, resulting from the conformations of the ligand backbones, 
may lead to differences in the C-P-C bond angles at the phosphido 
phosphorus atoms.

None of the dimeric platinum(II) complexes heretofore mentioned 
possess platinum-platinum bonds. However, numerous examples are 
known in which metal-metal bonds and strong bridging ligands 
(e.g., \( \text{Ph}_2\text{P}^- \), \( \text{S}^- \), \( \mu\text{-dppm} \)) stabilize the unusual platinum 
(I) oxidation state. One such example is \( \text{[Pt}(\mu\text{-PPh}_2)(\text{PPh}_3)]_2 \), 
which has been synthesized in low yield via the thermal degradation 
of \( \text{Pt(PPh}_3)_2 \). This potentially interesting species might be 
synthesized from readily available \( \text{[PtCl}(\mu\text{-PPh}_2)(\text{PPh}_3)]_2 \) by the 
route of Equation 44.

\[
\text{[PtCl}(\mu\text{-PPh}_2)(\text{PPh}_3)]_2 + 2\text{e}^- \rightarrow \text{[Pt}(\mu\text{-PPh}_2)(\text{PPh}_3)]_2 + 2\text{Cl}^- \quad [44]
\]

Whereas such a reduction of a Pt(II)-phosphido-bridged 
species has not been reported, the reduction of \( \text{PtCl}_2 \text{(dppm)} \) by
excess NaBH₄, followed by reacidification with HCl, is a procedure used to obtain Pt(I) complexes containing bridging dppm. Therefore, [PtCl(μ-CyPP)]₂ was similarly treated with NaBH₄ in an attempt to obtain a complex containing a platinum-platinum bond.

The treatment of [PtCl(μ-CyPP)]₂ with an equimolar amount of NaBH₄ followed by reflux in ethanol or THF produced a red, glassy material. The infrared spectrum of this glass exhibits the normal ligand absorption bands, as well as a broad absorption at 1920 cm⁻¹. This band has been assigned to a Pt-H stretching vibration. The unusually low frequency of the Pt-H absorbance (common range for νₚₜ-H (terminal): 2400-2000 cm⁻¹) is typical of a hydrido ligand, situated trans to a phosphine or phosphide ligand. The value of νₚₜ-H in the literature example [PtH(μ-PPh₃)(PET₃)]₂ is reported to be 2002 cm⁻¹.

The room temperature P{¹H} NMR spectrum (solvent: C₂H₅) of this red material consists only of a featureless hump centered at about -20 ppm. No significant change in the NMR spectrum was observed when the sample was cooled to 223°K. Therefore, the product of the reaction of [PtCl(μ-CyPP)]₂ with NaBH₄ is apparently not a fluxional species. When a solution of the material was treated with HCl, a gas (H₂) was evolved and [PtCl(μ-CyPP)]₂ was regenerated. The characteristic AA'XX' spin pattern of [PtCl(μ-Cypp)]₂, with ten-line multiplets at -2.64 and -144.6 ppm, reappeared in the ³¹P NMR spectrum. From the preceding evidence, it may be concluded that the unidentified species is a hydrido-platinum complex in which the P₂Pt₂ core is intact. However, the material is not simply [PtH(μ-Cypp)],
which would be the result of the replacement of chloride from 
$[\text{PtCl}(\mu-\text{CyPP})]_2$ by hydride. In that case, it would still be possible to obtain a $^{31}\text{P}$ NMR spectrum; the $^{31}\text{P}$ NMR spectrum of the analogous complex, $[\text{PtH}(\mu-\text{PPh}_3)(\text{PPh}_3)]_2$ has been reported. Therefore, it seems likely that at least partial reduction of platinum or perhaps cluster formation may also have occurred during the reaction of $[\text{PtCl}(\mu-\text{CyPP})]_2$ with NaBH₄.

A second type of organophosphido-bridged compound, a non-
symmetrical dimeric Pt(II) species, was prepared by addition of solid PtCl₂(PPH) to a suspension of PtCl₂(COD), made basic by triethylamine. The addition of solid PtCl₂(PPH) to the suspension was carried out slowly, so that PtCl₂(COD) remained in excess. Thus, the competing reaction, the formation of $[\text{PtCl}(\mu-\text{PP})]_2$, was minimized. After the addition of the PtCl₂(PPH) was completed, a dimeric species, formulated as $[\text{Pt}(\mu-\text{Cl})(\mu-\text{PP})\text{Pt(COD)}]Cl$, precipitated cleanly from THF. The $^1\text{H}$ NMR spectrum of the precipitate displays the usual ligand proton resonances centered at 7.4δ (aromatic) and a low, broad resonance in the aliphatic region. Additional resonances at 4.25δ and 2.30δ in the ratio of 1:2 have been assigned to coordinated 1,5-COD.

The $^{31}\text{P}(^1\text{H})$ NMR spectrum of $[\text{Pt}(\mu-\text{Cl})(\mu-\text{PP})\text{Pt(COD)}]Cl$ in CHCl₃ is shown in Figure 40. This spectrum is actually a combination of four subspectra, each of which corresponds to one of the four possible isotopomers. The four isotopomers and their approximate abundances are also shown in Figure 40. The assignments of the satellite spectra to the respective isotopomers are included in
the figure. The $^{31}$P($^1$H) spectral parameters of [Pt($\mu$-Cl)(P-PP)Pt(COD)]Cl are given in Table 16.

Table 16. $^{31}$P($^1$H) NMR Parameters of [Pt($\mu$-Cl)(P-PP)Pt(COD)]Cl

<table>
<thead>
<tr>
<th>$J_{P-A-P_1}$</th>
<th>$J_{P-A-P_2}$</th>
<th>$J_{P-B-P_1}$</th>
<th>$J_{P-B-P_2}$</th>
<th>$\delta P_1$</th>
<th>$\delta P_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.06</td>
<td>-8.86</td>
<td>24.1</td>
<td>3720</td>
<td>3121</td>
<td>0</td>
</tr>
</tbody>
</table>

a. Chemical shifts in ppm relative to 85% H$_3$PO$_4$; upfield shifts are negative.

b. Coupling values are in Hz.

The observed strong coupling of phosphorus $P_A$ to the two different platinum atoms reveals that $P_A$ is acting as a bridging group between the metal atoms. The $^{31}$P NMR spectrum also shows that only a single organophosphido bridge is present in the dimer. From this NMR spectral evidence alone, it is not possible to determine whether or not the complex has both halide and phosphido bridges, as in Figure 40, or simply a single phosphido bridge which links both
Figure 40. The Four Isotopomers of $[\text{PtCl}_2(\mu-\text{Cl})(\mu-\text{PP})\text{Pt(COD)}]^+$ and the $^{31}\text{P}^{1}H$ NMR Spectrum of the Mixture. The * denotes platinum-195. The assignment of the satellite spectra to the respective isotopomers is shown.
platinum atoms, and only terminal chloride ligands. The minimal solubility of the dimer in most solvents (except CHCl₃, with which it slowly reacted) did not permit conductivity measurements, which would have distinguished between the two structures. However, the value of \(^J_{\text{Pt-A-P}}\) (3720 Hz) is considerably larger than the \(^1\text{Pt-P}\) value of PtCl₂(PPH) or PtCl₂(dppp) (3400 Hz) in which the Ph₃P-group is trans to a terminal chloride ligand. In contrast, the \(^1\text{J}_{\text{Pt-P}}\) for phosphorus trans to a bridging chloride ligand in [PtCl(μ-Cl)(PBu₃)]₂ (3715 Hz)\(^{37}\), is nearly identical to the \(^1\text{J}_{\text{Pt-A-P}}\), value of [PtCl(μ-PP)Pt(COD)]Cl. Thus, the \(^3\text{P}\) NMR spectral evidence supports the structural assignment of Figure 40.

The close similarity in the chemical shifts of the phosphino and phosphido groups of [PtCl(μ-Cl)(μ-PP)Pt(COD)]Cl is probably a result of the bond angles about the phosphido phosphorus atom. Carty has correlated increasing (i.e., more positive) phosphido chemical shifts with decreasing bond angles about the phosphorus atom. On this basis, the bond angles at the organophosphide phosphorus of [PtCl(μ-Cl)(μ-PP)Pt(COD)]Cl are expected to be smaller than those of [PtCl(μ-PP)]₂. Decreased shielding of the organophosphide phosphorus atom as a result of the presence of chloride rather than phosphate at the other bridging position in [PtCl(μ-Cl)(μ-PP)Pt(COD)]Cl may also contribute to the low-field value of \(\delta_{\text{Phosphide}}\).
I. Reactions of PPH and CyPPH with Platinum(0) Compounds.

In attempts to prepare phosphido-bridged complexes of Pt(II), the ligands PPH and CyPPH were combined with Pt(0) compounds. The object of these experiments was the preparation of intermediate phosphido-hydrido complexes by the oxidative addition of the P-H moiety to Pt(0). The intermediates would then combine via phosphido-bridges to form dimers or clusters. Rauchfuss and Roundhill reported analogous oxidative additions (of S-H) between chelating mercapto-ligands and zerovalent nickel, palladium, and platinum complexes.¹⁰¹

The treatment of Pt(PPh3)₄ or Pt(PPh₃)₃ with CyPPH or PPH in benzene afforded either flocculent yellow-orange solids or oils. The infrared spectra of these materials display the normal ligand substituent absorbances. In addition, the reaction products display broad absorbances centered at about 1960 cm⁻¹ (See Figure 41). No changes are evident in the infrared spectra when solutions of the products are treated with CO; thus, the 1960 cm⁻¹ absorbance is itself probably not a CO absorbance. The absorbance at 1960 cm⁻¹ has therefore been assigned to \( \nu \) \( _{\text{Pt-H}} \). The somewhat low frequency is probably due to the hydrido-ligand's presence \textit{trans} to a strong ligand (phosphine or phosphide). It is apparent, from this infrared evidence, that oxidative addition of P-H does occur. The \( ^{31}P(\text{H}) \) NMR spectrum of the reaction products consists of unresolved broad resonances, accompanied by a singlet due to free triphenylphosphine (\( \delta = 5.6 \) ppm). The limited evidence available suggests that oxidative
Figure 41. The 4000-1300 cm\(^{-1}\) portion of the Infrared Spectrum of the Product of the Reaction of \([\text{PtCl(µ-CyPF)}]_2\) with $\text{NaBH}_4$. (KBr pellet)
addition of P-H to Pt(0) is accompanied by oligomerization of the resulting compounds. The oligomer does not exhibit a resolvable $^3P(^1H)$ NMR spectrum because of a combination of its low symmetry and large number of nuclei which possess nuclear spins. There are similar situations reported in which suspected cluster compounds of platinum and rhodium could not be characterized by NMR spectroscopy.\textsuperscript{102,103} The results of the reactions of CyPPH and PPH with Pt(0) compounds are essentially the same whether the starting material is Pt(PPh$_3$)$_4$, Pt(PPh$_3$)$_3$, or Pt(C$_4$H$_4$)(PPh$_3$)$_2$.

Attempts were made to prepare an unsymmetrical phosphido-bridged dimer via oxidative addition of an already coordinated P-H group to a Pt(0) complex. When PtCl$_2$(PPH) and Pt(PPh$_3$)$_3$ were refluxed together in THF, the products isolated were the $\alpha$ and $\beta$ isomers of [PtCl($\mu$-PP)]$_2$ (\textit{vide supra}) and \textit{trans}-PtHCl(PPh$_3$)$_2$. Both of the isomers of [PtCl($\mu$-CyPP)]$_2$ were readily identified by the characteristic AA'XX' patterns in the $^3P$ NMR spectrum of the material isolated from the reaction mixture.

Positive identification of PtHCl(PPh$_3$)$_2$ was made primarily from its infrared spectrum ($\nu_{Pt-H} = 2220$ Hz), and the hydrido-resonance in the $^1H$ NMR spectrum ($\delta_H = -16.30$ ppm, $J_{P-H} = 12.70$ Hz, $J_{Pt-H} = 1186$ Hz).\textsuperscript{102} Thus, Pt(PPh$_3$)$_3$ acts as a base to abstract HCl from PtCl$_2$(PPH) similar to the action of NEt$_3$. When PtCl$_2$(PPH) is refluxed in THF alone, the self-dimerization reaction does not occur.
An attempted preparation of a mixed mercury-platinum species was unsuccessful. When PtCl₂(PPH) and HgCl(CH₃) were refluxed together in THF, no reaction occurred. It was thought that perhaps an intermolecular elimination of CH₄ between the two complexes would lead to a platinum-mercury organophosphido-bridged dimer. However, there was no spectral evidence that a reaction occurred.

J. Complexes of PPH and CyPPH with Rhodium.

Earlier workers have reported that reactions of rhodium (I) halides with secondary phosphines have often resulted in poorly defined or uncharacterizable products. Such results have been ascribed to elimination of HCl from intermediate compounds, which oligomerize via organophosphido bridges. Only in those cases where more than three secondary phosphino-ligands are coordinated to a single rhodium atom (e.g. RhCl(HPR₃)₃), have stable, molecular complexes been isolated.⁰⁸,⁰⁹

When Rh(µ-Cl)(COD)₂ is treated with one equivalent (per rhodium atom) of the ditertiary phosphine ligands dppe or dppp at room temperature, cleavage of the halide bridge occurs, and complexes formulated as [Rh(COD)(L-L)]Cl or [RhCl(COD)(L-L)] are isolated as orange microcrystalline materials.¹₀⁵ In contrast, if [Rh(µ-Cl)(COD)]₂ is treated with CyPPH or PPH under identical conditions, only red-brown or purplish materials can be isolated. When these materials are examined by ³¹P[¹H] NMR spectroscopy, broad undefined resonances appear. The NMR spectra are not temperature dependent; thus the luck
of spectral resolution is not due to sterochemical nonrigidity of
the reaction products. As in the case of the reaction of CyPPH
and PPH with Pt(0), the uncharacterized reaction products of rhodium
seem likely to be oligomeric materials.

If [Rh(μ-Cl)(COD)]₂ is treated with PPH at low temperature,
a yellow solid is obtained. This material is postulated to be the
five-coordinate intermediate RhCl(COD)(PPH). It is thermally
sensitive, and it decomposes above +10°C even when dry and under N₂.
Therefore, this compound's ³¹P(¹H) and ¹H NMR spectra were examined
in situ from 210°C to room temperature, in 10° increments. The ³¹P(¹H)
NMR spectra of RhCl(COD)(PPH) at 213°C and at room temperature are
combined in Figure 42.

The loss of detail in the room temperature spectrum was due to
decomposition rather than to a fluxional process. After the sample
stood at room temperature for 30 minutes, only a baseline spectrum
was obtained. When the sample was re-cooled to 213°C, no improvement
occurred in the spectrum.

The ³¹P(¹H) NMR spectrum of RhCl(COD)(PPH) at 213°C consists of
the AM pattern of an AMX spin pattern, (A=Ph₂P, M=P(H)Ph, X=Rh),
which is that expected for two dissimilar phosphines coordinated to
rhodium and mutually cis. The phosphorous chemical shifts and coupling
constants of RhCl(COD)(PPH) are included in Table 17, along with
those of several analogous rhodium diolefin-diphosphine complexes.

The chemical shifts of the Ph₂P- group of RhCl(COD)(PPH),
30.3 ppm, is comparable to the chemical shift of the Ph₃P- group
Figure 42. The $^{31}$P-{$^1$H} NMR Spectrum of RhCl(COD)(PPH) at 213$^\circ$K (Bottom) and 298$^\circ$K (Top) in C$_7$H$_8$. The resonance at -21.0 ppm could not be assigned.
Table 17. The $^3P$ NMR Spectral Parameters for Several Rh(I) Diphosphine Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta P_1$</th>
<th>$\delta P_2$</th>
<th>$^2J_{P_1-P_2}$</th>
<th>$^1J_{Rh-P_1}$</th>
<th>$^1J_{Rh-P_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{RhCl}(\text{NBD})(\text{dppp})^c$</td>
<td>16.7</td>
<td>-</td>
<td>-</td>
<td>129</td>
<td></td>
</tr>
<tr>
<td>$\text{RhCl}(\text{COD})(\text{PPH})$</td>
<td>30.3</td>
<td>-15.8</td>
<td>128</td>
<td>224</td>
<td>223</td>
</tr>
<tr>
<td>$[\text{Rh}(\text{COD})(\text{dppp})]BF_4^d$</td>
<td>9.5</td>
<td>-</td>
<td>-</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Rh}(\text{NBD})(\text{dppp})]BF_4^c$</td>
<td>14.1</td>
<td>-</td>
<td>-</td>
<td>148</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Rh}(\text{COD})(\text{PPH})]AsF_6$</td>
<td>12.3</td>
<td>-15.6</td>
<td>52.9</td>
<td>138</td>
<td>136</td>
</tr>
<tr>
<td>$[\text{Rh}(\text{COD})(\text{CyPPH})]AsF_6$</td>
<td>11.9</td>
<td>-11.5</td>
<td>47.8</td>
<td>134</td>
<td>141</td>
</tr>
<tr>
<td>$[\text{Rh}(\mu-\text{Cl})(\text{dppp})]_2^c$</td>
<td>30.3</td>
<td>-</td>
<td>-</td>
<td>187</td>
<td>-</td>
</tr>
</tbody>
</table>

a. $P_1$ = tertiary phosphine, $P_2$ = secondary phosphine
Chemical shifts are in ppm from 85% $H_2PO_4$; upfield shifts are negative.

b. Coupling constants are in Hz.

c. Reference 106

d. Reference 107
of dppp in [Rh(µ-Cl)(dppp)]₂. The similar chemical shift values suggest that the Ph₃P⁻ moiety of the PPH ligand is also trans to a chloride ligand. The chemical shift of the -P(H)Ph end of PPH in RhCl(COD)(PPH), at -15.9 ppm, is virtually identical to the chemical shift of -P(H)Ph in [Rh(COD)(PPH)]As₂. Thus, it is probable that the structure of RhCl(COD)(PPH) is that shown in Figure 42.

The extremely high phosphorus-phosphorus and phosphorus-rhodium coupling constants (Table 17) suggest either an unusual geometry for the complex or a low oxidation state for the rhodium atom. Unfortunately, since similar studies have previously been undertaken only with symmetrical diphosphines or diphosphines which contain only -CH₂CH₂- linkages, Jₚ₋ₚ data for comparison is not available. The value of an unsymmetrical diphosphine ligand in gathering data of this type is obvious from this example. Additional structural evidence supporting the proposed five-coordinate structure with COD bound to the metal comes from the series of ¹H NMR spectra which were obtained under the same conditions as the ³¹P(¹H) NMR series. These ¹H NMR spectra indicate that COD remains bound to rhodium up to the temperature at which complex decomposition occurs. Uncomplexed COD then appears in the spectra and can be identified by its characteristic ¹H resonances at 5.56 and 3.956 in the proper 1:2 ratio. The appearance of the resonances of free COD at the decomposition temperature is probably due to the displacement of COD by bridging organophosphido groups during the oligomerization reaction.

There were no Rh-H resonances observed in the ¹H NMR spectrum.
The mechanism of the deprotonation of the secondary phosphine may not proceed through a Rh-H intermediate. However, a Rh-H intermediate would probably be short-lived, and might not appear in the $^1$H NMR spectra.

Since HCl elimination was the apparent mode of decomposition of the proposed RhCl(COD)(PPH) species, a synthetic scheme was devised to remove chloride ion so that HCl elimination from the complex could not occur. A two-phase system was employed. An aqueous layer containing NaAsF$_4$ was mixed rapidly with a dichloromethane layer which contained [Rh(u-Cl)(COD)]$_4$. Addition of either PPH or CyPPH to this two-phase system led to the isolation of [Rh(COD)(PPH)]AsF$_6$ or [Rh(COD)(CyPPH)]AsF$_6$. A similar method was employed by Schrock and Osborn in syntheses of [Rh(COD)(PR$_3$)$_2$]PF$_6$ complexes.$^{105}$

The yellow-orange complexes [Rh(COD)(PPH)]AsF$_6$ and [Rh(COD)(CyPPH)]AsF$_6$ were contaminated by a red benzene-soluble material. Concentrated solutions of this red material did not give a $^{31}$P NMR signal. This red material was not obtained if a small quantity of HAsF$_6$ was added to the aqueous layer prior to the addition of the diphosphine. Therefore, it seems likely that the red material is an oligomer which arises as a result of the loss of H$^+$ from initially formed [Rh(COD)(PPH)]AsF$_6$ or RhCl(COD)(PPH), and that addition of acid in the form of HAsF$_6$ limits the loss of H$^+$. The $^{31}$P($^1$H) NMR spectrum of [Rh(COD)(PPH)]AsF$_6$ is shown in Figure 43. Phosphorus $-31$ NMR data for the PPH and CyPPH complexes
Figure 43. The $^{31}P$ $^1H$ NMR Spectrum of [Rh(COD)(PPH)] AsF$_6$ in CH$_2$Cl$_2$. 

(MeO)$_3$P=0 (Std.)

+12.3 ppm

-15.6 ppm
are collected in Table 17. The $^3\!\!\!\!\!\P$ NMR spectra consist of simple first-order AMX spectra like that of RhCl(COD)(PPH). The 90 MHz $^1\!\!\!\!\!\H$ NMR spectrum reveals ligand resonances at approximately 7.2-7.6 δ (aromatic) and the accompanying characteristic aliphatic resonances of either PPH or CyPPH. In addition, the presence of coordinated COD is revealed by a broad peak at 3.7 δ (coordinated C=C). The aromatic:aliphatic integration ratios are correct for complexes of formula [Rh(COD)(diphosphine)] AsF$_6$. Bands at 1005 cm$^{-1}$ and 840 cm$^{-1}$, attributable to COD, are present in the infrared spectra of both [Rh(COD)(PPH)]AsF$_6$ and [Rh(COD)(CyPPH)]AsF$_6$. These infrared spectra also contain the strong absorbance of the AsF$_6^-$ counterion at 700 cm$^{-1}$.

These results with rhodium seem to parallel observations made earlier in this study with palladium. In cases where free Na$^+$ was present, the formation of HCl was suppressed and dimerization or oligomerization of complexes did not take place.

A number of attempts to synthesize phosphido-bridged complexes from the [Rh(COD)(diphosphine)] AsF$_6$ complexes were made. Deprotonation of the complexes by triethylamine resulted in the isolation of deep red materials with unresolved $^3\!\!\!\!\!\P\{^1\!\!\!\!\!\H\}$ NMR spectra. These results suggest uncontrolled oligomer formation, as was observed in the case of RhCl(COD)(PPH).

Addition of two equivalents of either PPH or CyPPH to [Rh(µ-Cl)(COD)]$_2$ in THF or ethanol resulted in the isolation of good yields of [Rh(PPH)$_2$]Cl and [Rh(CyPPH)$_2$]Cl. No decomposition via loss of HCl was evident during the formation of these complexes;
i.e., no dark red or purple soluble components were observed in either the reaction mixtures or filtrates.

The $^{31}P\{^1H\}$ NMR spectra of the two complexes are similar to each other and to the spectra of the bis-CyPPH and bis-PPH palladium and platinum complexes discussed earlier in this dissertation. The $^{31}P\{^1H\}$ NMR spectrum of $[\text{Rh}(\text{PPH})_2]\text{Cl}$ is resolved sufficiently well to permit the computation of all phosphorus-phosphorus coupling constants present in the AA$'$MM$'$X spectrum. The computer-simulated and experimental (EtOH) $^{31}P\{^1H\}$ NMR spectra of the complex are shown in Figure 44. In contrast, $[\text{Rh}(\text{CyPPH})_2]\text{Cl}$ displays only pseudo-triplets in its deceptively simple $^{31}P\{^1H\}$ NMR spectrum. Consequently, only the average cis-phosphorus—phosphorus coupling values can be extracted from the $^{31}P\{^1H\}$ NMR spectrum. The $^{31}P\{^1H\}$ NMR spectral data for the bis-PPH, -CyPPH, and -dppp complexes of rhodium(I) are contained in Table 18.

The difference between the chemical shifts of the Ph$_2$P- groups of the PPH and dppp complexes reflects the differing trans influences of Ph$_2$P- and -P(H)Ph groups. In contrast to $[\text{Pd}(\text{PPH})_2][\text{BF}_4]_2$ and $[\text{Pt}(\text{PPH})_2][\text{AsF}_6]_2$, the $^{31}P\{^1H\}$ NMR spectra of the rhodium bis-diphosphine compounds do not exhibit any resonances attributable to the presence of a minor diastereomer. Both $[\text{Rh}(\text{CyPPH})_2]\text{Cl}$ and $[\text{Rh}(\text{PPH})_2]\text{Cl}$ are ionic species in polar solvents. This is evident from examination of the $^{31}P\{^1H\}$ NMR spectra of the two cations with AsF$_6$${}^-$ as the counterion. The variations in the phosphorus chemical shifts between
Figure 44. The Computer Simulated (Top) and Experimental (Bottom) \textsuperscript{31}P('H) NMR Spectra of \([\text{Rh}(PPH)_2]\text{Cl}\) in EtOH.
Table 18. \(^{31}\text{P}[^1\text{H}]\) NMR Spectral Parameters for Complexes of Formula \([\text{Rh}(L-L)L] \text{Cl}\) and \([\text{RhCO}(L-L)L] \text{Cl}\)

<table>
<thead>
<tr>
<th></th>
<th>(\delta^P_{A,A'})</th>
<th>(\delta^P_{M,M'})</th>
<th>(2J_{A-M})</th>
<th>(2J_{A-A'})</th>
<th>(2J_{A'-M})</th>
<th>(2J_{A'-M'})</th>
<th>(2J_{M'-M})</th>
<th>(2J_{A'-M'})</th>
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<tr>
<td>([\text{Rh}(\text{PPH})_2] \text{Cl})</td>
<td>11.96</td>
<td>-12.21</td>
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<td>46.1</td>
<td>46.1</td>
<td>358</td>
<td>52.5</td>
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<td>-17.66</td>
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<tr>
<td>([\text{Rh}(\text{dppp})_2] \text{Cl})</td>
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<td>([\text{RhCO}(\text{PPH})_2] \text{Cl})</td>
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<td>-27.5</td>
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<tr>
<td>([\text{RhCO}(\text{CyPPH})_2] \text{Cl})</td>
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<td>-30.2</td>
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<td>---</td>
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<tr>
<td>([\text{RhCO}(\text{dppp})_2] \text{Cl})</td>
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<td>-15.7</td>
<td>46.0</td>
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\(1J_{X-A,A'}\) | \(1J_{X-M,M'}\)
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<td>118</td>
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<tr>
<td>79</td>
<td>118</td>
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<td>86</td>
<td>115</td>
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</tbody>
</table>

\(a.\) Chemical shifts are in ppm from 85\% H\(_3\)PO\(_4\), upfield shifts are negative.

\(b.\) Coupling constants are in Hz.
the chloride salts and AsF₆⁻ salts are both less than 0.2 ppm.

By similar evidence, Baird has shown that the rhodium atom in the complex [Rh(dppp)₄]Cl is four-coordinate in polar solvents.⁵⁶

In solution, both [Rh(CyPPH)₂]Cl and [Rh(PPH)₄]Cl add CO to give monocarbonyl-substituted species. However, the large difference in the value of ν CO for the two complexes ([RhCO(CyPPH)₂]Cl, 1945 cm⁻¹; [RhCO(PPH)₄]Cl, 2030 cm⁻¹) suggests that the two complexes are of different structures. The carbonyl adducts of the AsF₆⁻ salts display the same values of ν CO as the chloride salts. Turning to rhodium bis-ditertiary phosphine complexes for comparison, ν CO = 1920 cm⁻¹ in [RhCO(dppp)₂]Cl and ν CO = 1952 cm⁻¹ in [RhCO(dppb)₂]Cl. The structure of RhCO(dppp)₂ Cl has been proposed to be the trigonal bipyramidal structure as shown in 5.¹⁰⁸ The structure determined for [IrCO(dppe)₂]⁺ by X-ray methods also has this trigonal bipyramidal geometry.¹⁰⁹

$$\begin{align*}
\text{Ph}_3\text{P}-(\text{CH}_2)_2 & \\
\text{OC} & \text{Rh} \\
\text{Ph}_2\text{P}-(\text{CH}_2)_2
\end{align*}$$

As may be seen from the data compiled in Table 18, there are strong similarities in the ³¹P{¹H} NMR spectra of [RhCO(dppp)₂]⁺, [RhCO(PPH)₂]⁺, and [RhCO(CyPPH)₂]⁺. Thus, the CyPPH and PPH complexes apparently also exist in the trigonal bipyramidal geometry. In the PPH and CyPPH complexes, the ³¹P NMR data point to the
structure shown in Figure 45, in which the bulkiest groups (i.e., Ph$_2$P- and Cy$_2$P-) are axial and the -P(H)Ph groups are equatorial. The large decrease in the values of $^{1}J_{	ext{Rh-P}}$ in the carbonyl complexes compared to the precursor compounds implies that these phosphorus atoms are oriented trans to strong $\sigma$ donors. The large differences in the values of $\nu_{\text{CO}}$ between [RhCO(PPH)$_2$]Cl and [RhCO(CyPPH)$_2$]Cl are particularly unusual considering the expected similarities in their respective structures.

A square pyramidal structure for [RhCO(PPH)$_2$]Cl, with the CO ligand at the apex of the pyramid could account for the anomalous $\nu_{\text{CO}}$ observed in the complex. Although the NMR evidence implies that the complex is trigonal pyramidal, the geometry may, in fact, be intermediate between the two ideal structures. Such an intermediate geometry would be most likely to be observed in a PPH complex, because that ligand is the least sterically demanding of the three diphosphines cited.

Figure 45. Probable Geometry of [RhCO(PPH)$_2$]$^+$ and [RhCO(CyPPH)$_2$]$^+$
If [Rh(µ-Cl)(COD)]₂ is treated with one equivalent per rhodium of a tertiary monophosphine such as PPh₃ (which cleaves the chloride bridges) and is then treated with CyPPH, it is possible to isolate a complex of formula RhCl(PPh₃)(CyPPH). The yield of complex is optimized if addition of the diphosphine is carried out at -78°C, since the low temperature limits decomposition of the complex. Once formed, RhCl(CyPPH)(PPh₃) is fairly stable in nonpolar solvents. In a polar solvent, particularly in alcohol, the yellow-orange complex undergoes irreversible decomposition to a red, highly soluble species which can not be characterized by ³¹P NMR spectroscopy.

The ³¹P ¹H NMR spectrum of RhCl(CyPPH)(PPh₃) is extremely complex because of its second-order character. The spectrum can be solved assuming an ABCX spectral pattern (X = ¹⁰³Rh). The computer-simulated and experimental ³¹P ¹H NMR spectrum of RhCl(PPh₃)(CyPPH) and the spin-label assignments are depicted in Figure 46. The spectral data for this complex comprises Table 19. The phosphorus-phosphorus coupling constants, which were derived from the iterated ³¹P NMR spectrum, are within the normal range of phosphorus-phosphorus coupling in rhodium(I) complexes. The values are also comparable to those found by Tau for the ABCX ³¹P NMR pattern of PhCl(dppp)(PPh₃).

The apparent increase in stability toward loss of HCl on going from RhCl(COD)(PPh) to RhCl(CyPPH)(PPh₃) to [Rh(PPh₃)]Cl suggests that increasing electron density on the rhodium atom with increasing number of phosphine ligands stabilizes and strengthens the P-H bond.
Figure 46. The Computer Simulated (Top) and Experimental (Bottom) $^3$P{H} NMR Spectra of RhCl(CyPPH)(PPh$_3$) in C$_6$H$_6$. 
Table 19. $^{31}$P($^1$H) Spectral Parameters for RhCl(CyPPH)(PPh₃)

<table>
<thead>
<tr>
<th></th>
<th>$P_A$</th>
<th>$P_B$</th>
<th>$P_C$</th>
<th>$2J_{P_A-P_B}$</th>
<th>$2J_{P_A-P_C}$</th>
<th>$2J_{P_B-P_C}$</th>
<th>$J_{Rh-P_A}$</th>
<th>$J_{Rh-P_B}$</th>
<th>$J_{Rh-P_C}$</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>25.9</td>
<td>14.7</td>
<td>6.2</td>
<td>330</td>
<td>51.2</td>
<td>41.5</td>
<td>129</td>
<td>127</td>
<td>172</td>
</tr>
</tbody>
</table>

a. Chemical shifts are in ppm from 85% H₃PO₄; upfield shifts are negative.

b. Coupling constants are in Hz.

Corroborative evidence is seen in the infrared spectra of these complexes; as the number of phosphine ligands increases, the $\nu_{P-H}$ absorbance at about 2350 cm⁻¹ increases in intensity, although it remains weak. The increased electron density on rhodium also explains why secondary phosphine complexes RhCl(HPR₃)$_n$ have been synthesized and have been shown to be stable when $n = 3$ or 4.

The syntheses of tridentate phosphine ligands in the coordination sphere of Rh(I) was accomplished using an adaptation of the synthesis of RhCl(CyPPH)(PPh₃). A two-step synthesis was employed:

$$[\text{Rh}(\mu-\text{Cl})(\text{COD})]_2 + 2\text{Cy}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{E.T.}} 2\text{RhCl(COD)}(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl})$$ [45]

$$\text{I + CyPPH} \xrightarrow{\text{Base}} \text{RhCl(Cyttpp)} \xrightarrow{-78^\circ \text{r.t.}}$$ [46]

Equation 45 represents the well-known cleavage of halide-bridged rhodium complexes by a monophosphine.$^5$ Displacement of
diolefin from the bridge-cleavage product at low temperature prevents loss of HCl from the presumed intermediate complex RhCl(CyPPH)-(Cy2PCH2CH2CH2Cl). As the reaction products are allowed to warm to room temperature, the base (NEt3) deprotonates the secondary phosphine. The phosphide group thus generated attacks the alkyl halide tail of the coordinated Cy2PCH2CH2CH2Cl group, causing ring closure. The ring closure reaction yielded the known compound RhCl(Cytpp). The 31P{1H}NMR spectrum of RhCl(Cytpp) is shown in Figure 47. The chemical shifts and coupling constants of the AB2X pattern displayed in Figure 47 are identical to those of authentic RhCl(Cytpp) prepared by Mazanec from free Cyttpp and [Rh(u-Cl)(COD)]. If chelate ring closure had not taken place, the 31P{1H} NMR of the complex RhCl(CyPPH)(Cy2PCH2CH2CH2Cl) would be much more complex because of the non-equivalence of the two Cy2P-groups. Additional confirmation of the ring closure reaction is given by the 1H NMR spectrum of RhCl(Cytpp) after recrystallization from a benzene-ethanol mixture; the triplet resonance due to the CH2Cl group (3.58 in CyPCH2CH2CH2Cl) is not present in the 1H NMR spectrum; thus, displacement of chloride from Cy2PCH2CH2CH2Cl must have occurred. The resulting RhCl(Cytpp) complex is stable in ethanol, whereas RhCl(CyPPH)(PPh3) decomposes in ethanol. It may be inferred that the decomposition of the latter complex is due to the loss of H+ from the coordinated secondary phosphino ligand.
Figure 47. The $^{31}$P $^1$H NMR Spectrum of RhCl(Cyttp) in C$_6$H$_6$. 
All of the attempts to synthesize an asymmetrical triphosphine ligand on Rh(I) using vinylidiphenylphosphine or allyldiphenylphosphine as the monophosphine were unsuccessful. Cleavage of the chloride bridge occurred as expected, but ring closure could not be accomplished although several experiments were attempted. The reasons for the failure are not known. One possibility is that the allyl or vinyl groups themselves coordinated to the rhodium atom and were unavailable for reaction with the P-H moiety.

A new synthesis for Rh(III) metallocycles was devised. When the steps shown in Equations 45 and 46 are carried out without addition of a base, a product is isolated in which oxidative addition of the CH$_2$CH$_2$CH$_2$Cl substituent to the metal atom has occurred. The structure of this complex along with its $^3$P($^1$H) NMR spectrum (solvent: CH$_2$Cl$_2$) is shown in Figure 48. The spectral parameters for the complexes RhCl$_2$(CH$_2$CH$_2$CH$_2$PCy$_2$)(CyPPH) and RhCl$_3$(CH$_2$CH$_2$CH$_2$PCy$_2$)(PPH) comprise Table 20.

The $^3$P($^1$H) NMR spectrum of RhCl$_2$(CH$_2$CH$_2$CH$_2$PCy$_2$)(CyPPH) can be interpreted as an ABMX spectrum ($X = ^{103}$Rh). The presence of the A nucleus in a five-membered chelate ring is evident from the low field chemical shift of that nucleus (47.1 ppm). The second half of AB pattern consists of the doublet of quartets centered at -4.29 ppm. The large value of $J_{PA-PB}$ (406 Hz) indicates that $P_A$ and $P_B$ are mutually trans. This trans assignment is further confirmed by the values of $^1$J$_{Rh-PA}$ and $^1$J$_{Rh-PB}$, which are typical phosphorus-rhodium couplings for phosphine ligands trans to strong
donor ligands. Nucleus $P_M^*$ is the secondary phosphino group of the CyPPH ligand. The multiplet of $P_M^*$ centered at 14.4 ppm, displays cis coupling to both $P_A$ and $P_B$. In addition, the $^1H$ coupled spectrum displays a $J_{P_M^*-H}$ value of 370 Hz. The value of $J_{\text{Rh}-P_M^*}$ indicates that $P_M^*$ is trans to a weak trans influence ligand; thus, the structure of $\text{RHCl}_2(\text{CH}_3\text{CH}_2\text{CH}_2\text{PCy}_3)(\text{CyPPH})$ is that shown in Figure 48. The $^{31}P$ NMR spectrum of $\text{RHCl}_2(\text{CH}_3\text{CH}_2\text{CH}_2\text{PCy}_3)(\text{PPH})$ is almost identical to that of its CyPPH analog. The most significant difference is in the chemical shift values of the Ph$_2$P- group of PPH and the Cy$_2$P- group of CyPPH. The similarity in the spectra aid in confirming the spectral assignments.

The oxidation state of the rhodium atom in the metalloycles can be confirmed from the $J_{\text{Rh}-P}$ coupling constants. A comparison of $J_{\text{Rh}-P}$ of the metalloycles to the corresponding values of other Rh(III) species that include the ttp or Cyttpp ligands$^{62,110}$ shows good agreement. The $J_{\text{Rh}-P}$ values of $\text{RHCl}(\text{Cyttpp})\cdot\text{O}_2$, for example, (114 Hz, P trans to P; 136 Hz, P trans to Cl) support the conclusion of a Rh(III) oxidation state for the metalloycles.

The exclusive isolation of the species in which the bulky tertiary phosphines are mutually trans is a consequence of steric considerations as well as possible trans-labilization by phosphorus during initial formation of the complex. The $^{31}P$ NMR spectrum of the reaction mixture was collected at low temperature. The low temperature spectrum is extremely complex, and it suggests that
Figure 48. The $^{31}$P($^1$H) NMR Spectrum of RhCl$_2$(CH$_2$CH$_2$CH$_2$PCy$_2$)–(CyPPH) in CH$_2$Cl$_2$.
Table 20. $^{31}P(^1H)$ Spectral Data for Two Rhodium(III) Metallocycles

<table>
<thead>
<tr>
<th>Compound</th>
<th>$P_A$</th>
<th>$P_B$</th>
<th>$P_X$</th>
<th>$^{2}J_{P_A-P_B}$</th>
<th>$^{2}J_{P_A-P_X}$</th>
<th>$^{2}J_{P_B-P_X}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{RhCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)(\text{CyPPH})$</td>
<td>47.07</td>
<td>-4.29</td>
<td>14.41</td>
<td>406</td>
<td>27.9</td>
<td>39.0</td>
</tr>
<tr>
<td>$\text{RhCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)(\text{PPH})$</td>
<td>46.66</td>
<td>0.44</td>
<td>10.94</td>
<td>414</td>
<td>20.7</td>
<td>42.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{1}J_{\text{Rh}-P_A}$</th>
<th>$^{1}J_{\text{Rh}-P_B}$</th>
<th>$^{1}J_{\text{Rh}-P_X}$</th>
<th>$^{1}J_{P_X-H}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{RhCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)(\text{CyPPH})$</td>
<td>94.9</td>
<td>86.03</td>
<td>137.5</td>
<td>370</td>
</tr>
<tr>
<td>$\text{RhCl}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)(\text{PPH})$</td>
<td>101.4</td>
<td>91.5</td>
<td>133.8</td>
<td>360</td>
</tr>
</tbody>
</table>

a. Chemical shifts are in ppm from 85% $\text{H}_3\text{PO}_4$, upfield shifts are negative.

b. Coupling constants are in Hz.
all of the possible isomeric products are formed initially. The spectrum simplifies gradually over several hours until only a single product appears.

The 90 MHz 1H NMR spectrum of RhCl₂(CH₃CH₂CH₂PCy₂)(CyPPH) in CD₂Cl₂ displays the appropriate ratio of aliphatic:aromatic protons of 10:1. In addition, the triplet resonance normally observed at 3.56 for the -CH₃Cl group of Cy₂PCH₂CH₂CH₂Cl is not present in the 1H spectrum. The lack of a triplet resonance is a sign that cyclization has occurred. The 13C NMR spectrum of RhCl₂(CH₃CH₂CH₂PCy₂)(PPH) was obtained, and it also indicates displacement of Cl from the -CH₂Cl group. Such a group, if present, would appear at approximately 44.6 ppm in the 13C NMR spectrum. Unfortunately, the resonance of the carbon atom directly bound to rhodium could not be distinguished from the numerous carbon peaks of the cyclohexyl group.

The mass spectrum of RhCl₂(CH₃CH₂CH₂PCy₂)(CyPPH) displays its most intense peak at m/e = 724, which corresponds to the loss of HCl from the molecular ion. Although such loss of HCl is not unusual for an organic system containing an amine hydrochloride, it is unusual for a transition metal complex. The observed loss of HCl may reflect the acidity of the rhodium-secondary phosphine complexes.

The synthesis of metallocycles through alkyl halide-substituted arsines and phosphines has been performed previously. Such
metallic cycles, derived from ligands Me₂AsCH₂CH₃CH₂Cl and
R₂PCH₂CH₂CH₂Cl have been synthesized on Mo, W, Fe, Ni, and
Re. However, in the prior syntheses, a Grignard reagent
or some reducing reagent such as sodium was necessary to cause
cyclization. In view of the tendency of Rh(I) toward oxidative
addition of alkyl and aryl halides, however, it is not surprising that
addition of the alkyl halide tail to rhodium does occur. Shaw
has shown that bulky substituents on coordinated phosphine ligands
favor cyclometallation reactions when there are appropriate sub-
stituent groups present on the ligands. The presence of the
 sterically demanding cyclohexyl groups on the monophosphine
Cy₃PCH₂CH₂CH₂Cl undoubtedly promotes the cyclometallation reaction.

K. Complexes of CyPPH and PPH with Iridium(I).

In contrast to the rhodium case, a stable five-coordinate
species was easily isolated from the reaction of PPH or CyPPH with
[Ir(μ-Cl)(COD)]₂. The yellow-green complexes IrCl(COD)(PPH) and
IrCl(COD)(CyPPH) were synthesized in benzene or toluene. The
complexes are five-coordinate in nonpolar solvents, as evidenced
by the molar conductivity of IrCl(COD)(CyPPH) in acetone:

\[ \Lambda_M = 8.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1} \]  \quad (In acetone, \( \Lambda_M \) for 1:1 electrolytes
commonly ranges from 100-160 ohm⁻¹ cm² mole⁻¹). However, when
the five-coordinate complexes are dissolved in alcohols, a
dramatic color change from yellow-green to deep red occurs.
The deep red complexes are formulated as \([\text{Ir(COD)(PPH)}]\text{Cl}\) and \([\text{Ir(COD)(CyPPH)}]\text{Cl}\). Supporting evidence for the ionic formulations is seen in the molar conductivity of \([\text{Ir(COD)(CyPPH)}]\text{Cl}\) in methanol: \(A = 103 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}\). This value is close to the average molar conductance value for 1:1 electrolytes in methanol of 120 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}\. Park and Meek observed the same type of behavior in the complexes \([\text{IrCl(COD)(ppol)}]\text{Cl}\) and \([\text{Ir(COD)(ppol)}]\text{Cl}\). The former was five-coordinate in nonpolar solvents, but when it was dissolved in alcohol, it was transformed into the ionic complex.

The four-coordinate ionic species \([\text{Ir(COD)(PPH)}]\text{AsF}_5\) and \([\text{Ir(COD)(CyPPH)}]\text{AsF}_5\) were prepared from the corresponding neutral complexes by metathesis with \(\text{NaAsF}_5\) in ethanol. A second method of preparation of \([\text{Ir(COD)(PPH)}]\text{AsF}_5\) employed the two-solvent "phase-transfer" type of reaction which was used in the preparation of \([\text{Rh(COD)(PPH)}]\text{AsF}_5\).

The \(^{31}\text{P} - ^1\text{H}\) NMR spectra of five-coordinate \([\text{IrCl(COD)(PPH)}]\) and \([\text{IrCl(COD)(CyPPH)}]\) differ considerably from the spectra of the four-coordinate cations. Despite the considerable changes in the coupling constants and chemical shifts, however, the \(^{31}\text{P}\) NMR patterns remain first-order AB patterns. These \(^{31}\text{P}\) NMR data are compiled in Table 21, along with data for analogous iridium(I) complexes of the diphosphine ligands dppp and ppol. Although they are not included in the table, \(^1\text{J}_{\text{P-H}}\) values were measured for the PPH and CyPPH complexes of
iridium. Within experimental error (due to line-broadening in the $^1$H-coupled NMR spectrum) the value of $^1J_{P-H}$ is about 350 Hz.

The chemical shifts of the phosphorus atoms of the respective iridium complexes increase (i.e., move to lower field) when the neutral complexes are converted to the corresponding ionic complexes. This is a result of the increase in the positive charge of the iridium atom, which leads to decreased shielding of phosphorus. In those cases in which phosphorus–phosphorus coupling can be observed because of the nonequivalence of the phosphorus atoms, the coupling decreases along with the decrease in coordination number from five to four. The $^{31}P$($^1$H) NMR spectrum of $\text{IrCl(COD)(PPH)}_2$, which consists of a simple first order AB pattern, is depicted in Figure 49.

The $^1$H NMR spectrum of $[\text{Ir(COD)(CyPPH)}]_{AsF_6}$ differs markedly from that of $\text{IrCl(COD)(CyPPH)}$ in the shape of the olefinic resonances of the coordinated COD ligand. The $^1$H NMR spectra of the two complexes are shown in Figure 50. The $^1$H NMR spectrum of $\text{IrCl(COD)(CyPPH)}$ shows a single large peak for olefinic COD protons centered at 3.76. In the $^1$H NMR spectrum of four-coordinate $[\text{Ir(COD)(CyPPH)}]_{AsF_6}$, there are four distinct resonances ranging from 3.36 to 5.46. The two 60 MHz spectra are shown together for comparison; a 300 MHz NMR spectrum of $[\text{Ir(COD)(CyPPH)}]_{AsF_6}$ shows the COD proton resonances more distinctly.
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta P_A$</th>
<th>$\delta P_B$</th>
<th>$^2J_P^P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrCl(COD)(PPH)</td>
<td>-10.7</td>
<td>-35.6</td>
<td>47.0</td>
</tr>
<tr>
<td>[Ir(COD)(PPH)]AsF$_6$</td>
<td>-2.8</td>
<td>-27.9</td>
<td>-34.5</td>
</tr>
<tr>
<td>IrCl(COD)(CyPPH)</td>
<td>-29.9</td>
<td>-36.6</td>
<td>-39.7</td>
</tr>
<tr>
<td>[Ir(COD)(CyPPH)]AsF$_6$</td>
<td>1.2</td>
<td>-23.1</td>
<td>28.6</td>
</tr>
<tr>
<td>IrCl(COD)(dppp)</td>
<td>-14.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ir(COD)(dppp)]PF$_6$</td>
<td>-0.3</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>IrCl(COD)(ppol)</td>
<td>-11.9</td>
<td>-27.2</td>
<td>44.5</td>
</tr>
<tr>
<td>[Ir(COD)(ppol)]Cl</td>
<td>-3.5</td>
<td>-30.0</td>
<td>36.6</td>
</tr>
</tbody>
</table>

a. $P_A$ is a tertiary phosphine, $P_B$ is a secondary phosphine. Chemical shifts are in ppm from 85% H$_3$PO$_4$, upfield shifts are negative.

b. Coupling constants are in Hz.

c. Reference 118

d. Reference 117
Figure 49. The 31P 1H NMR Spectrum of IrCl(COD)(PPH) in C6H6.
Presumably, the olefinic COD protons of \([\text{Ir(COD)(CyPPH)}]^+\) are in four different environments, as shown in 6. In the case of the five-coordinate species, either the geometry (probably trigonal bipyramidal) or a fluxional process is causing equivalence of the COD protons on the NMR time scale. No evidence of fluxional behavior on the NMR time scale was seen in the \(^{31}\text{P NMR}\) spectrum of \(\text{IrCl(COD)(CyPPH)}\). Additional variable temperature studies should be done on these materials in order to resolve this question.

The author was unable to prepare \(\text{bis-PPH}\) or \(\text{bis-CyPPH}\) iridium complexes. The forceful conditions required to remove the coordinated diolefin from the iridium complexes in order to add a second diphosphine inevitably led to degradation of the complexes.

Also, it was impossible to characterize iridium-PPH or -CyPPH complexes derived from \(\text{IrCl(CO)(PPh}_3\)) by \(^{31}\text{P NMR}\).
Figure 50. The 60 MHz $^1$H NMR Spectra of IrCl(COD)(CyPPh) (Top) in C$_6$D$_6$ and Ir(COD)(CyPPh) AsF$_6$ in (CD$_3$)$_2$C=O (Bottom). Both spectra were recorded at room temperature.
Infrared evidence suggests that an iridium hydrido complex was formed ($\nu_{\text{Ir-H}} = 2210 \text{ cm}^{-1}$), but as in the case of the suspected oxidative additions of the ligand to platinum(0) complexes, no structural information could be gleaned from the $^{31}\text{P}$ NMR spectrum.
APPENDIX

INFRARED, $^1$H NMR, AND $^{31}$P NMR SPECTRAL DATA FOR PPH
Figure 51. The Infrared Spectrum of PPH (Neat).
Figure 51 (cont.). The Infrared Spectrum of PPH (Neat).
Figure 52. The 60 MHz $^1$H NMR Spectrum of PPH in $\text{C}_6\text{D}_6$. 
Figure 53. The $^1$H-coupled (Top) and $^1$H-decoupled (Bottom) $^{31}$P NMR Spectra of PPH in C$_6$H$_6$ at Room Temperature.
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