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Synthesis and characterization of bimetallic palladium and platinum complexes resulting from chelating tertiary/secondary diphosphine ligands

Supplee, Carolyn, Ph.D.
The Ohio State University, 1989

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SYNTHESIS AND CHARACTERIZATION OF BIMETALLIC
PALLADIUM AND PLATINUM COMPLEXES RESULTING
FROM 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
Carolyn Supplee, B.A., M.S.

* * * * *

The Ohio State University

1989

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Carolyn Supplee
1989
To My Parents
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FIELDS OF STUDY

Major Field: Inorganic Chemistry

Studies in Coordination Chemistry,
Professor Devon W. Meek
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Me ............................................................... CH₃
Et .............................................................. C₂H₅
Pr¹ ............................................................ C₃H₇
But ............................................................ C₄H₉
Cp ............................................................... C₅H₅
Ph ............................................................... C₆H₅
Cy ............................................................... C₆H₁₁
COD .......................................................... 1,5-cyclooctadiene
PPH ............................................................ Ph₂P(CH₂)₃P(H)Ph
CyPPH ....................................................... Cy₂P(CH₂)₃P(H)Ph
PPMPh ....................................................... Ph₂P(CH₂)₃P(H)Me
CyPPMPh ................................................... Cy₂P(CH₂)₃P(H)Me
p-CF₃PPH ................................................... (p-CF₃C₆H₄)₂P(CH₂)₃P(H)Ph
PR₃ ............................................................ generalized phosphine
L~L ............................................................ generalized chelating diphosphine ligand
dppm .......................................................... Ph₂PCH₂PPh₂
dppe .......................................................... Ph₂P(CH₂)₂PPh₂
dppp .......................................................... Ph₂P(CH₂)₃PPh₂
dpet .......................................................... Ph₂P(CH₂)₂PPhEt
CHAPTER I
INTRODUCTION

A. General

Development of new catalysts for organic syntheses has resulted in an enormous amount of research in organophosphorus transition metal chemistry. Transition metal phosphine complexes have been shown to be active catalysts for olefin hydrogenation, isomerization, oxidation, polymerization and hydroformylation reactions.\textsuperscript{1-12}

The selectivity and reactivity of transition metal catalysts can be modified by varying the steric and electronic properties of the phosphine ligands bound to the metal center. The properties of phosphine ligands (PR\textsubscript{3}) are controlled by the R-groups bound to the phosphorus atoms.\textsuperscript{13} By changing one, two or all of the R-groups of the ligand transition metal catalysts can be fine-tuned. In order to inhibit dissociation of monodentate phosphine ligands (PR\textsubscript{3}) from a metal center and to increase the stability of a transition metal complex, the phosphorus atom can be incorporated into a chelate ring. Therefore, chelating bi- and tridentate phosphine ligands (R\textsubscript{3-m}P[(CH\textsubscript{2})\textsubscript{n}PR\textsubscript{2}]\textsubscript{m}, m = 1,2; n = 2,3,4; R = alkyl, aryl, hydrogen) allow for more control over the coordination number, stereochemistry, basicity and magnetic properties of the resulting metal complex (catalyst).\textsuperscript{14-19}
Tertiary-phosphine metal complexes are capable of undergoing phosphorus-carbon bond cleavage under catalytic conditions. Although the resulting complexes contained bridging organophosphido ligands between two or more metal centers, the reactivity of the catalysts was not necessarily destroyed.\textsuperscript{20} Hence, studies of the reactivity and stability of both secondary phosphino and phosphido bridged transition metal complexes are of interest.

In general, organophosphido ligands have the formula shown below, \( \text{I} \); they can be synthesized by either deprotonation of a secondary phosphine or cleavage of a tertiary phosphorus-carbon bond. In the 1960's, these types of ligands were studied as an extension of organosulfide chemistry.\textsuperscript{21-29} The results of these investigations showed organophosphido groups to be extremely flexible bridging ligands holding two metal centers in close proximity of each other in bi- and poly-metallic complexes.

In the 1970's, bi- and poly-metallic complexes (metal clusters) became an active area of research in homogeneous catalysis. An advantage of cluster catalysis is that aggregation of two or more metal centers is thought to resemble the surface of a heterogeneous catalyst, yet allow for easy modification of the catalyst via ligand substitution.
The major disadvantage is that clusters have a tendency to undergo fragmentation under catalytic conditions.\textsuperscript{30}

In order to inhibit fragmentation, bridging ligands of Groups V and VI, i.e., nitrogen, selenium, arsenic and phosphorus, were incorporated into the metal cluster framework. Clusters containing these types of bridging ligands, have been shown by Carty,\textsuperscript{31,32} Vahrenkamp,\textsuperscript{33,34} and others\textsuperscript{35-38} to have less tendency for fragmentation than their non-bridging counterparts. Therefore, bridging Group V and VI ligands, most commonly organophosphido, were thought to reduce fragmentation of the metal cluster by acting as a flexible support to the metal-metal framework.

In the 1980's reports by Carty,\textsuperscript{39} Collman,\textsuperscript{40} Geoffroy,\textsuperscript{41,42} Meek,\textsuperscript{43,44} and Wojcicki\textsuperscript{45,46} indicated that organophosphido bridges between two metal centers were more reactive than originally assumed. Therefore, if the bridging phosphido unit were incorporated into a chelate ring, then the reactivity at the metal-phosphido bond would be expected to decrease, analogous to the cases for phosphines. In contrast to the numerous reports for bridging phosphido bimetallic complexes, $[MX(\mu-PR_2)_2PR_3]_2$ ($R$ = aryl, alkyl; $X$ = halogen, CO, aryl, alkyl), only a few reports of bimetallic complexes containing a chelated bridging phosphido ligand are known.\textsuperscript{47-53}

Nonchelating phosphido bridged bimetallic complexes of planar transition metals [e.g., platinum(II), palladium(II), iridium(I), and rhodium(I)] can exist as either a cis- or trans-isomer (2 and 3, respectively).
If the bridging phosphido ligand is incorporated into a chelate ring of the general type, $R_2P(CH_2)_3PR'(H)$, then only the trans isomeric form of the metallic complex is possible (4).

Therefore, bridging phosphido units connected to a terminal tertiary phosphino group via a trimethylene chelate chain provide a controlled synthesis of bimetallic complexes containing bridging phosphido ligands.

The tetraatomic core ($M(\mu-P-M(\mu-P)$) will be planar if at least one of the three following criteria is met:

1) the presence of a $\sigma$ plane through all four atoms, 2 ($C_{2v}$ symmetry) and 3 ($C_{2h}$ symmetry);
(2) the presence of a $C_2$-axis through both phosphido-atoms, 2 ($C_2$ symmetry);
(3) the presence of an inversion center in the metal-phosphido core, 3 and 4 ($C_1$ symmetry).

Only in the first case will each tetra-coordinated platinum(II) center also be ideally planar. Only in the third case may the phosphido atoms exist as asymmetric phosphorus atoms.

In 1984, Glaser, Meek, Waid and others\textsuperscript{51} reported the existence of the three possible stereoisomers for complexes of type 4 (where $M = \text{Pd, Pt}$; $R = \text{Ph, Cy}$; $R' = \text{Ph}$; $X = \text{Cl, Me}$). Two of the isomers were chiral and existed as an enantiomeric $d$/\$-pair ($C_2$ symmetry). The third, which is diastereomeric to the pair, was the meso compound ($C_1$ symmetry). The three major results of this work showed that:

(1) the metal-phosphido tetraatomic core for the $d$/\$-pair was bent (5), whereas the meso-stereoisomer exhibited a planar core (6). (Based on the three criteria mentioned above, this was expected and was proven via X-ray diffraction studies.);
(2) In the phosphorus-31 NMR spectrum the resonance for the phosphido phosphorus atoms of the meso-stereoisomer appears at higher field than for the d/z-pair and;

(3) In the platinum-195 NMR spectrum the resonance for the platinum atoms of the meso-stereoisomer resonates at lower fields than those for the corresponding d/z-pair.

B. Preparation of Phosphido-Bridged Bimetallic Complexes

A difficulty encountered in synthesizing bi- and polynuclear phosphido bridged complexes is that there are only a few rational routes available. The four most commonly used methods are: 1) elimination reactions; 2) oxidative P-H addition; 3) ligand displacement via a metal substituted phosphide; and, 4) miscellaneous reactions.

1) Elimination Reactions

Elimination reactions are the most commonly used synthetic method for preparation of phosphido bridged dimers.32,38,40,44,52-82 These types of reactions are driven by elimination of stable small molecules with formation of a phosphido bridged bimetallic. Examples of elimination reactions are shown in Equations 1-4. These reactions include elimination of lithium chloride (Eqs. 1 and 2),45,55 potassium chloride and hydrogen chloride (Eq. 3)67,78,80 and propane (Eq. 4).71 Equations 1 and 2 illustrate the effects of reaction stoichiometry and the steric/electronic characteristics of the terminal phosphide on formation of the bimetallic complex, whereas in Equation 4, a secondary phosphine is bound to the metal center before formation of the phosphido
bridged bimetallic species. Reactions of the last type may also be used in formation of heterobimetallic complexes.

\[
\begin{align*}
2 \text{LIPPh}_2 + [\text{RhCl(COD)}]_2 & \quad \text{THF} \quad \rightarrow \quad [\text{Rh(μ-PPh}_2\text{(COD)})_2] + 2 \text{LICl} \\
\text{LIP(1-Bu)}_2 + [\text{RhCl(COD)}]_2 & \quad \text{hexane} \quad \rightarrow \quad \text{Rh}_2(μ-1-Bu_2P)(μ-\text{Cl})(η^4-\text{COD})_2 + \text{LICl}
\end{align*}
\]

\[
\begin{align*}
2 \text{K}_2\text{MCl}_4 + 4 \text{PPh}_2\text{H} & \quad \text{FIOH} \quad \rightarrow \quad [\text{M(μ-PPh}_2(\text{PPh}_2\text{H})\text{Cl})_2] + 4 \text{KCl} + 2 \text{HCl} \\
\text{M} & = \text{Pd, Pt}
\end{align*}
\]

\[
\begin{align*}
(\text{CO})_3\text{Ni(PMe}_2\text{H}) + (\eta^3-\text{C}_3\text{H}_5)\text{Co(CO)}_3 & \quad \rightarrow \quad (\text{CO})_3\text{Ni(μ-PMe}_2\text{)Co(CO)}_3 + \text{C}_3\text{H}_6
\end{align*}
\]

2) Oxidative Addition Reactions of P-H Bonds

A second synthetic route to prepare phosphido bridged bimetallic complexes involves oxidative addition of the P-H bond to a metal center. In these types of reactions the bimetallic contains both a
bridging phosphido ligand and a hydrido ligand. Examples of oxidative addition reactions of P-H are presented in Equations 5, 6, 73, 76. The former reaction yields a bimetallic complex that contains a bridging hydrido ligand, as well as a bridging phosphido ligand, whereas, the latter reaction yields a phosphido bridged bimetallic that contains a terminal hydrido ligand. Equation 6 also provides a direct method into the synthesis of heterobimetallic complexes. However, this route is limited by the availability of suitable starting materials. To date only a few types of heterobimetallic complexes have been synthesized by this method. 76, 78, 80, 83, 84

\[
\begin{align*}
\text{Rh}_4(\text{CO})_{12} &+ 4 \text{t-Bu}_2\text{PH} &\text{toluene} &\rightarrow & &2 \text{Rh}_2(\mu-\text{t-Bu}_2\text{P})(\mu-\text{H})(\text{CO})_2(\text{t-Bu}_2\text{PH})_2 &+ 8 \text{CO} \\
\text{Li}[\text{W}(\text{CO})_4(\text{PPh}_2\text{H})(\text{PPh})_2] &+ \text{trans-IrCl(CO)(PPh}_3)_2 &\text{THF} &\rightarrow & &\text{W}(\mu-\text{PPh}_2)_2\text{Ir(H)(CO)(PPh}_3) &+ \text{LiCl}
\end{align*}
\]

3) Ligand Displacement via Metal-Substituted Phosphide
This method is probably the most direct synthetic route used to prepare heterobimetallic complexes with bridging phosphido ligands. 85-90 An example is given in Equation 7. 85 Since only a few mononuclear bisphosphido transition metal complexes have been
synthesized and characterized,\textsuperscript{91,95} this method is also limited by the availability of starting materials.

\[
\text{Cp}_2\text{Hf(PEt}_2)_2 + M(\text{CO})_n\text{L}_2 \xrightarrow{\text{n = 4, 3, 2}} \text{Cp}_2\text{Hf(PEt}_2)_2M(\text{CO})_n + 2\text{L}
\]

4) Miscellaneous Reactions

Phosphido bridged complexes were prepared initially by cleavage of a phosphorus-carbon bond (Eq. 8),\textsuperscript{96,97} phosphorus-phosphorus bond (Eq. 9),\textsuperscript{21,22,48,98,99} phosphorus-hydrogen bond (Eq. 10).\textsuperscript{49-51,100-103} In general, the desired phosphido bridged bimetals were obtained in low yields. Therefore, they were not good preparative routes for large-scale syntheses. However, in 1982 Carty reported on the synthesis of a

\[
2 \text{IrH(CO)(PPh}_3)_3 \xrightarrow{\text{DMF, } \Delta} [\text{Ir(μ-PPh}_2)(\text{CO})(\text{PPh}_3)]_2 + \text{C}_6\text{H}_6 + 1/2 \text{H}_2
\]

\[
2 \text{CpCo(CO)}_2 + \text{Ph}_2\text{P-PPh}_2 \xrightarrow{\text{toluene}} [\text{CpCo(μ-PPh}_2)_2]_2 + 4\text{CO}
\]
monophosphido monoacetylide bridged bimetallic iron carbonyl complex (Eq. 11).\textsuperscript{31,39} This synthesis involves oxidative addition of diphenylphosphinoacetylide (phosphorus-carbon bond cleavage) to

\[
\text{Fe}_2(\text{CO})_9 + \text{Ph}_2\text{P} = \text{CR} \rightarrow \begin{array}{c}
\text{(CO)}_3\text{Fe} \\
\text{Fe(CO)}_3
\end{array} + 3 \text{CO}
\]

the metal center, and appears to be a good way of synthesizing bridging acetylide complexes.

In 1984, Meek and coworkers\textsuperscript{51} reported on the syntheses of palladium(II) and platinum(II) bimetallic complexes containing chelating phosphido ligands. The synthetic route is given in Equation 12 and takes advantage of known phosphorus acid/base chemistry (secondary phosphorus hydrogen bond cleavage). Although this method appears to be
a good way into phosphido bridged bimetallic complexes, it is severely limited by the availability of chelating tertiary/secondary diphosphine ligands.¹⁰⁴

C. Stability of the Phosphido Bridged Bimetallic Complexes

As stated previously, when organophosphido ligands were first used in the syntheses of bi- and polymetallic complexes, they were expected to be relatively inert chemically. However, in the 1980's it was reported that organophosphido ligands did not just act as simple bridges between two metal centers, but instead showed reactivity at the metal-phosphido bond. The five types of reactions which can occur at the metal-phosphido bond are: 1) metathesis; 2) reduction; 3) reductive elimination of P-H (or P-C) bond; 4) intramolecular nucleophilic displacement; and, 5) elimination reactions.

1) Metathesis of the Phosphido Bridge with a Halide Bridge

In 1982, Geoffroy and coworkers reported the cleavage of a rhodium phosphido bond under thermal conditions (Eq. 13).¹⁰⁵ A possible
mechanism for this reaction involves dissociation of the two dimers into monomeric species, followed by recombination to form a bridging phosphido/halide bimetallic complex.

\[
\text{(COD)}\text{Rh} \quad \text{Rh(COD)} \quad + \quad \text{(COD)}\text{Rh} \quad \text{Rh(COD)}
\]

\[
(COD)\text{Rh} \quad \text{Rh(COD)} \quad \xrightarrow{\Delta} \quad 2 \quad (COD)\text{Rh} \quad \text{Rh(COD)}
\]

2) Reduction of the Metal Phosphido Bond

When two phosphido groups are linked by an ortho-phenylene bridge, the metal-phosphido bond becomes the site for Na/Hg reduction in contrast to the expected reduction of the metal-metal bond.

\[
\text{PhP} \quad \text{PPh} \quad \xrightarrow{\text{Na/Hg}} \quad \text{PhP} \quad \text{PPh}^-
\]

3) Reductive Elimination of P-H (or P-C) Bond

Geoffroy, Meek, and Wojcicki have suggested this type of reaction in the mechanism for the rupture of the metal-phosphido bond. The driving force of this reaction may be formation of
a stable phosphorus-carbon bond (i.e., a tertiary phosphine) or a phosphorus-hydrogen bond (i.e., a secondary phosphine). For example, Meek and Kreter showed that treatment of $[\text{Rh(COD)(\mu-\text{PPh}_2)}]_2$ with the tertiary/secondary diphosphine ligand Ph$_2$P(CH$_2$)$_3$P(H)Ph, PPH, yielded a product that contained coordinated diphenylphosphine (Eq. 16). The proposed mechanism involved oxidative P-H addition to the rhodium metal center followed by either reductive elimination or rearrangement of the diphenylphosphido ligand and a rhodium hydride bond, or perhaps both. In a different system, Wojcicki and Shyu have found strong spectroscopic evidence for the conversion shown in Equation 17.
4) Intramolecular Nucleophilic Displacement

This type of reaction was first reported in 1984 by Seyferth et al. and is represented by Equation 18.

5) Elimination Reactions

Although transition metal triphenylphosphate complexes are known to eliminate one mole of benzene in order to form bridging diphenylphosphido bimetallic complexes (Eq. 8), elimination of a second mole of benzene from the bimetallic complex to form a phenylphosphinideno complex is not as common. However, in 1983 Geoffroy and coworkers reported the formation of a phenylphosphinideno rhodium cluster. The formation of the phenylphosphinideno rhodium cluster is thought to proceed via benzene elimination from a bridging phosphido rhodium bimetallic complex followed by dimerization of the bridging phenylphosphinideno rhodium bimetallic species (Eq. 19).

Similar types of reactions have been reported for metal clusters containing both bridging phosphido and hydrido ligands. For example,
\[
\begin{align*}
\text{CH}_2 & \quad \text{PhP} \quad \text{PPh} \quad \text{Fe(CO)}_3 \\
\text{CH} & \quad \text{CH} \\
\text{P(Me)Ph} \quad \text{PhP} \quad \text{PPh} \quad \text{Fe(CO)}_3 \\
\end{align*}
\]

\text{n-BuLi} \quad -78^\circ \text{C} \quad \rightarrow \quad \text{1 hour} \quad -20^\circ \text{C} \quad (18)

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH} \\
\text{PhP} & \quad \text{PPh} \quad \text{Fe(CO)}_3 \\
\text{CH} & \quad \text{CH} \\
\text{P(Me)Ph} & \quad \text{PhP} \quad \text{PPh} \quad \text{Fe(CO)}_3 \\
\end{align*}
\]
\[
\text{(COD)RhCl} \xrightarrow{\text{Li[BHET]}} \text{Rh(COD)} \]

\[
\text{Ph2} \quad \text{Ph2} \\
\text{(COD)Rh} \quad \text{Rh(COD)} \\
\text{Cl} \quad \text{H} \\
\text{25 °C, THF} \\
\text{- C6H6} \\
\text{dimerization} \\
\text{Ph} \quad \text{Ph} \\
\text{(COD)Rh} \quad \text{Rh(COD)} \\
\text{Ph} \quad \text{Ph} \\
\text{(COD)Rh} \quad \text{Rh(COD)} \\
\text{(COD)Rh} \quad \text{Rh(COD)}
\]
recently Stelzer and co-workers reported elimination of isopropane from a trimetallic iron carbonyl cluster which contained an isopropyl-methylphosphido ligand (Eq. 20).84

\[
\begin{align*}
&\text{(CO)}_3\text{Fe} \quad \text{Fe(CO)}_3 \\
&\text{H} \quad \text{Fe(CO)}_3 \\
&\text{PMePr}^1
\end{align*}
\]

6 days
110 °C

\[
\begin{align*}
&\text{(CO)}_3\text{Fe} \quad \text{Fe(CO)}_3 \\
&\text{H} \quad \text{Fe(CO)}_3 \\
&\text{PMePr}^1
\end{align*}
\]

D. Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy

Phosphorus-31 NMR spectroscopy has been used extensively in identification and structural characterization of both phosphino and bridging phosphido transition metal complexes. The phosphorus-31 nucleus is 100% naturally abundant with a spin of 1/2 and a receptivity value equal to $6.7 \times 10^{-2}$, relative to a proton; thus obtaining data on a Fourier Transform NMR spectrometer is relatively easy. The four most important characteristics of a P-31 NMR spectrum are the chemical shift(s), the phosphorus-phosphorus coupling constants, metal-phosphorus coupling constants, and the spectral pattern. In fact, the spectral pattern is a reflection of the first three characteristics.
1) Phosphorus-31 NMR Chemical Shifts

The chemical shift range for phosphorus-31 NMR is approximately 600 ppm (225 ppm for PBr₃ to 460 ppm for P₄). Because of this large range, small changes of the phosphorus atom's environment can be easily detected. The phosphorus-31 chemical shift, $\delta_{31P}$, is determined by several factors including the steric and electronic demands of the substituents bound to the phosphorus atom, the bond angles around the phosphorus atom, the oxidation state of phosphorus (P(III) vs. P(V)), the transition metal to which the phosphine is bonded, and whether the phosphorus atom is incorporated into a five-membered chelate ring. Upon close inspection of these factors, it becomes evident that they are interrelated. Therefore, when discussing the phosphorus-31 chemical shift, it is often impossible to attribute changes in the $\delta_{31P}$ to only one factor.

In general, the electronic effects for phosphines can be summarized as follows:

Electron releasing groups, R (where R = alkyl, hydrogen), provided that R is not sterically hindered will cause the phosphorus nucleus to become more shielded or shift to higher fields. In contrast, electron-withdrawing groups, X (where X = aryl, alkoxy, halogen) will cause the phosphorus resonance to become more deshielded or shift to lower fields. Thus, the chemical shifts for trialkylphosphines appear upfield from triarylphosphines. Similarly, resonances for secondary phosphines occur upfield from tertiary phosphines that contain similar R-groups (See Table 1).
The flexibility of the angles at phosphorus is used to determine the steric demands of the R- (or X) groups bound to phosphorus. The C-P-C angle is said to "open" as the steric requirements of R increase and causes $\delta_{31P}$ to shift downfield. This downfield shift occurs owing to the decreasing s-character of the phosphorus atom's lone pair of electrons. Therefore, reducing the steric demands of R ("closing" the C-P-C angle) will cause the phosphorus atom to become more shielded and $\delta_{31P}$ to move upfield (See Table 2).

Upon complexation, the chemical shift of the phosphorus atom becomes dependent on the oxidation state, coordination number and the periodic location of the metal, the geometry of the complex, the number of metal-metal bonds, the influence ability of the trans-ligand, as well as the phosphine itself. In general, coordination of monodentate phosphines causes $\delta_{31P}$ to shift downfield relative to $\delta_{31P}$ for the free ligand. The difference between the two chemical shifts is known as the coordination chemical shift, $\Delta$.

Transition metal complexes of chelating phosphine ligands also exhibit a coordination chemical shift. However, the coordination chemical shift is dependent on the size of the chelate ring. This dependence on the chelate ring size is known as the ring effect, $\Delta_R$, and is defined as the coordination chemical shift of the chelate complex minus the chemical shift of the corresponding monodentate cis-disubstituted complex. Garrou has found that when a phosphorus atom is incorporated into either a four- or a six-membered ring system, $\delta_{31P}$ appears at somewhat higher field than their analogous cis-disubstituted
<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
</table>

Phosphorus-31 NMR Chemical Shift Data\(^a\) of Several Phosphines

<table>
<thead>
<tr>
<th>Monodentate Phosphines</th>
<th>(\delta_{31^p}) (ppm)</th>
<th>Chelating Phosphines</th>
<th>(\delta_{31^p})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMeH(_2)</td>
<td>-164</td>
<td>(\text{H}_2\text{P(CH}_2\text{)}_3\text{PH}_2)</td>
<td>-139</td>
</tr>
<tr>
<td>PH(_2)(C(_4)H(_9))</td>
<td>-135</td>
<td>(\text{H}_2\text{PCH}_2\text{PH}_2)</td>
<td>-122</td>
</tr>
<tr>
<td>PEtH(_2)</td>
<td>-131</td>
<td>(\text{HPhP(CH}_2\text{)}_2\text{PPPhH})</td>
<td>-48</td>
</tr>
<tr>
<td>PPh(_2)Et</td>
<td>-73</td>
<td>(\text{Ph}_2\text{CH}_2\text{PPPh}_2)</td>
<td>-23</td>
</tr>
<tr>
<td>PMe(_2)Ph</td>
<td>-28</td>
<td>(\text{Et}_2\text{P(CH}_2\text{)}_3\text{PET}_2)</td>
<td>-24</td>
</tr>
<tr>
<td>P(_2)Et</td>
<td>-19</td>
<td>(\text{Et}_2\text{P(CH}_2\text{)}_2\text{PET}_2)</td>
<td>-19</td>
</tr>
<tr>
<td>PPh(_2)Et</td>
<td>-12</td>
<td>(\text{Ph}_2\text{P(CH}_2\text{)}_3\text{PPPh}_2)</td>
<td>-17</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Monodentates</th>
<th>(\delta_{31^p}) (ppm)</th>
<th>Unsymmetrical Chelates(^b)</th>
<th>(\delta_{31^p}) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh(_2)Et</td>
<td>-12</td>
<td>(\text{Ph}_2\text{P(CH}_2\text{)}_3\text{PPhMe})</td>
<td>-18, -34</td>
</tr>
<tr>
<td>PPhEtMe</td>
<td>-33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPh(_2)Et</td>
<td>-12</td>
<td>(\text{Ph}_2\text{P(CH}_2\text{)}_3\text{PPhEt})</td>
<td>-17, -22</td>
</tr>
<tr>
<td>PPhEt(_2)</td>
<td>-16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPh(_2)Et</td>
<td>-12</td>
<td>(\text{Ph}_2\text{P(CH}_2\text{)}_4\text{PMe}_2)</td>
<td>-16, -50</td>
</tr>
<tr>
<td>PMe(_2)Ph</td>
<td>-50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPh(_2)Et</td>
<td>-12</td>
<td>(\text{Ph}_2\text{P(CH}_2\text{)}_3\text{PET}_2)</td>
<td>-16, -23</td>
</tr>
<tr>
<td>P(_2)Et</td>
<td>-19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPh(_2)Et</td>
<td>-12</td>
<td>(\text{Ph}_2\text{P(CH}_2\text{)}_3\text{PPPhH})</td>
<td>-18, -54</td>
</tr>
<tr>
<td>PPhEtH</td>
<td>-73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(_2)Ph</td>
<td>-16</td>
<td>(\text{PhP}((\text{CH}_2\text{)}_3\text{PPPh}_2)_2)</td>
<td>-28, -18</td>
</tr>
<tr>
<td>PPh(_2)Et</td>
<td>-12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PE(_2)Ph</td>
<td>-16</td>
<td>(\text{PhP}((\text{CH}_2\text{)}_3\text{PCy}_2)_2)</td>
<td>-28, -8</td>
</tr>
<tr>
<td>PCy(_2)Et</td>
<td>-28</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Chemical shifts are reported in ppm relative to 85\% \text{H}_3\text{PO}_4; downfield values are positive.

\(^b\)First phosphorus atom corresponds to first \(\delta_{31^p}\) value reported.
Table 2
Comparison of Phosphorus-31 NMR Chemical Shift Data\textsuperscript{a} versus Tolman's Cone Angle\textsuperscript{13}

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>(^{31}\text{P} )</th>
<th>Cone Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH(_3)</td>
<td>-240</td>
<td>87</td>
</tr>
<tr>
<td>PMe(_3)</td>
<td>-62</td>
<td>118</td>
</tr>
<tr>
<td>PEt(_3)</td>
<td>-20.1</td>
<td>132\textsuperscript{b}</td>
</tr>
<tr>
<td>PPh(_3)</td>
<td>-6.0</td>
<td>145</td>
</tr>
<tr>
<td>PPr(_3)</td>
<td>20.0</td>
<td>160</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Chemical shifts are reported in ppm relative to 85\% H\(_3\)PO\(_4\); downfield values are positive.

\textsuperscript{b}Ernst \textit{et al.}\textsuperscript{118} report the cone angle to be 137.
countersparts. Thus, $\Delta R$ values for four- or six-membered rings are negative. When the phosphorus atom is a part of a five-membered ring system, $\delta_{31P}$ appears, by approximately 30-50 ppm, at lower fields than the monodentate analogues. Therefore, $\Delta R$ values for five-membered rings are positive with magnitudes between 30 and 50 ppm.\textsuperscript{117}

As an extrapolation, the low field phosphorus-31 resonances observed for bridging phosphido ligands between two metal centers containing a metal-metal bond (7a) can be rationalized by the "three-member ring effect." The high field shifts found for phosphido atoms between nonbonded metal centers (7b) are attributed to a "four-member ring effect." Examples of phosphorus-31 NMR data for some phosphido bridged complexes are given in Table 3.

Currently, theoretical justification for the "three-membered ring effect" is unavailable. However, it is believed the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is the major factor in producing downfield phosphorus-31 NMR chemical shifts. Theoretical work by Burdett,\textsuperscript{119} and Teo et al.\textsuperscript{120} suggests the HOMO-LUMO gap for phosphido bridged iron complexes, e.g., Fe$_2$(CO)$_6$(µ-PR$_2$), increase with decreasing metal-metal distances.
Mott and Carty\textsuperscript{31,121-125} found complexes of the type $\text{Fe}_2(\text{CO})_6-(\mu-\text{PR}_2)(X)$ $\delta_{31P}$ were dependent on the Fe-P-Fe angle (or, the Fe-Fe bond distance). As the Fe-P-Fe angle became more obtuse, $\delta_{31P}$ shifted downfield. Similarly, Glaser, Meek and Waid\textsuperscript{51} reported chemical shifts for the phosphido-phosphorus nuclei for Pt(II) and Pd(II) bimetals were sensitive to the metal phosphido core geometry. For the bimetals differing only in the $\text{M}_2\text{P}_2$ core geometry, $\delta_{31P}$ for the planar diastereomers were shifted -40 ppm upfield from the bent diastereomers. Chen and Meek\textsuperscript{52,53} have also reported on $\delta_{31P}$-structure correlations for bis(cyclopentadienyl) bisphosphido bridged cobalt complexes (Table 4). These complexes, which include examples of linked phosphido bridges, exhibit phosphido resonances at low fields for the metal-metal bonded species. The $\text{SO}_2$ adducts, [Cp$_2\text{Co}(\mu-\text{PR}_2)]_2^+(\mu-\text{SO}_2)$, exhibit dramatic shifts to high field, as expected for non-bonded metal atoms. In contrast, protonation of the Co-Co bond causes the phosphido-phosphorus nuclei to display the $^{31P}$ resonance at lower fields than the parent complex. However, an X-ray structural determinations of the protonated cations showed the Co-Co bond lengths had decreased, thus explaining the shifts to lower fields.\textsuperscript{52,53} These results illustrate the sensitivity of $\delta_{31P}$ on the $\text{M}_2\text{P}_2$ core geometry.

Recently several examples of phosphido bridged complexes which contradict this correlation have been published. The examples include phosphido bridged bimetals of early transition metals (such as Zr and Hf)\textsuperscript{55,58,86} and bimetallic complexes of Fe, Ni, Co, Rh, and Ir which contain di-t-butylphosphido ligands.\textsuperscript{38,76,77,126,127} Such exceptions make it necessary to use the phosphido bridged phosphorus-31 NMR chemical
Table 3
Phosphorus-31 NMR Data for Phosphido Bridged Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta^{31p}$</th>
<th>Metal-Metal Bond</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Rh}_2(u\text{-PPh}_2)_2\text{COD(PEt}_3)_2$</td>
<td>217</td>
<td>yes</td>
<td>44</td>
</tr>
<tr>
<td>$[\text{CpCo(u-PPh}_2]_2$</td>
<td>119.6</td>
<td>yes</td>
<td>52, 53</td>
</tr>
<tr>
<td>$<a href="u%5Ctext%7B-SO%7D_2">\text{CpCo(u-PPh}_2</a>$</td>
<td>-75.7</td>
<td>no</td>
<td>52, 53</td>
</tr>
<tr>
<td>$d/\text{l-}[\text{PtCl(CyPP)}_2$</td>
<td>-144.4</td>
<td>no</td>
<td>49, 51</td>
</tr>
<tr>
<td>$\text{Fe}_2(\text{CO})_6(u\text{-PPh}_2)_2$</td>
<td>142.8</td>
<td>yes</td>
<td>115</td>
</tr>
<tr>
<td>$[\text{Fe}_2((\text{CO})_6(u\text{-PPh}_2)_2]^{-2}$</td>
<td>-62.4</td>
<td>no</td>
<td>108</td>
</tr>
<tr>
<td>$\text{Rh}_2(u\text{-t-Bu}_2)(u\text{-H})(\text{CO})_2(t\text{-Bu}_2\text{PH})$</td>
<td>264.3</td>
<td>yes</td>
<td>78, 80</td>
</tr>
<tr>
<td>$\text{Rh}_2(u\text{-t-Bu}_2\text{P})(u\text{-Cl})(n^4\text{-COD})_2$</td>
<td>43.2</td>
<td>no</td>
<td>78, 80</td>
</tr>
<tr>
<td>$(\text{CO})_4\text{H}(u\text{-PPh}_2)_2\text{Ir(CH}_3\text{)COD}$</td>
<td>170.7</td>
<td>yes</td>
<td>73</td>
</tr>
<tr>
<td>$(\text{CO})_4\text{H}(u\text{-PPh}_2)_2\text{Ir(H)COD}$</td>
<td>157.6</td>
<td>yes</td>
<td>73</td>
</tr>
<tr>
<td>$t\text{-Bu}_2\text{PH(O)}_2\text{Fe(u-CO)(u-t-Bu}_2\text{P)Rh(COD)}$</td>
<td>186.6</td>
<td>yes</td>
<td>79</td>
</tr>
</tbody>
</table>

*Chemical shifts are reported relative to $85\% \text{ H}_3\text{PO}_4$; downfield values are positive.*
### Table 4
Phosphorus-31 NMR Data for Phosphido Bridged Cyclopentadienyl Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{31}\text{P}$</th>
<th>$^{31}\text{P} - \text{SO}_2$</th>
<th>$^{31}\text{P}(\mu-\text{H})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpCo($\mu$-PPh$_2$)$_2$CoCp</td>
<td>119.6</td>
<td>-75.7</td>
<td>132.0</td>
</tr>
<tr>
<td>CpCo($\mu$-PET)$_2$CoCp</td>
<td>133.4</td>
<td>-61.4</td>
<td>169.7</td>
</tr>
<tr>
<td>CpCo($\mu$-PMePh)$_2$CoCp</td>
<td>112.8</td>
<td>-82.0</td>
<td>138.0</td>
</tr>
<tr>
<td>CpCo($\mu$-PPh(CH$_2$)$_2$PPh)CoCp</td>
<td>139.7</td>
<td>-12.7</td>
<td>161.7</td>
</tr>
</tbody>
</table>

$^a$SO$_2$ Adducts: CpCo($\mu$-PR$_2$)(\mu-SO$_2$)CoCp

$^b$Bridging Hydride Cation complexes: [CpCo($\mu$-PR$_2$)$_2$(\mu-H)CoCp]$^+$
shift/metal-metal interaction correlation with caution. However, the majority of data suggests that one can use the correlation for a series of closely related complexes, if structural data are available for one or more of its members.

2) Phosphorus-Phosphorus Coupling Constants

Phosphorus-phosphorus coupling constants, $2J_{pp}$, provide useful information into the structure and bonding of transition metal phosphino- and/or phosphido-complexes. For trans-phosphine ligands, the magnitude of $2J_{pp}$ is on the order of ~200 Hz, compared to ~30 Hz for cis-disposed phosphine ligands.\textsuperscript{113-115} In monodentate phosphine complexes, $2J_{pp}$ can occur through space or through orbital overlap between the metal and phosphorus atoms, or both. The magnitude of $2J_{pp}$ for chelating phosphine complexes has been shown to be the summation of the coupling through the metal, $2J_{pp}^M$, and the coupling occurring via the carbon backbone, $nJ_{pp}^B$. In other words, $2J_{pp} = 2J_{pp}^M + nJ_{pp}^B$. Since these two components may not have the same sign, $2J_{pp}$ for chelating phosphine complexes may be larger or smaller than $2J_{pp}$ for analogous cis-disubstituted monodentate phosphine complexes.\textsuperscript{128} For ligands of the general type $R_2P(CH_2)_nPR'R''$ (R = alkyl, aryl, hydrogen), when $n \geq 3$ the coupling magnitude through the backbone is unimportant ($nJ_{pp}^B = 0$ Hz). Therefore for six-membered, or larger, chelate ring systems, the values of the phosphorus-phosphorus coupling constants are similar to observed values for the cis-disubstituted monodentate phosphine complexes.\textsuperscript{128-131} Typical $2J_{pp}$ values for both mono- and polydentate phosphine complexes are given in Table 5.
Phosphorus-phosphorus coupling constants for phosphido bridged bimetallic complexes can be divided into two categories: 1) phosphido-phosphido coupling constants, $J_{pp}$, and 2) cis/trans phosphido-phosphino coupling constants, $2J_{pip}$. The former coupling constants have been shown by Brandon and Dixon\textsuperscript{137} to vary between -162 to -208 Hz for Pt(II) bimetallic complexes and -261 to -350 Hz for Pd(II) complexes, whereas, the latter values were between 0 and +5 Hz and 20 and 32 Hz for the cis-Pt(II)- and Pd(II)-bimetallic complexes, respectively. Trans-$2J_{pip}$ values for the Pt(II)- and Pd(II)-compounds ranged from 292 to 396 Hz and 311 to 443 Hz, respectively (See Table 6). It should be noted that in all the above complexes, the metal phosphido core was planar and there were no direct metal-metal interactions (internuclear metal-metal distances > 3.5Å).

The relationship between the $M_2P_2$ core and the coupling constants was furthered in a 1982 report by Glaser and Meek.\textsuperscript{51} Glaser and Meek showed that bimetallic complexes which contain chelating phosphino/phosphido ligands existed as three diastereomers, a $d/z$-pair with a bent $M_2P_2$ core and a meso-complex with a planar core. The results of this work are presented in Table 7. The values for both $J_{pp}$ and $2J_{pip}$ reported for planar diastereomers are in good agreement with those reported earlier by Dixon et al.\textsuperscript{137} However, the $2J_{pip}$ for the bent $d/z$-pair is -18 Hz smaller for the Pt(II)-bimetallic complexes and -60 Hz smaller for the Pd(II)-complexes. However, both the cis- and the trans-$2J_{pip}$ coupling constants are larger for the bent diastereomers than the planar complex. These results may be attributed to the
Table 5

Representative Phosphorus-31 NMR Data for Transition Metal Complexes Containing Phosphorus Ligands

<table>
<thead>
<tr>
<th>Complex</th>
<th>$2J_{pp} \text{a}$</th>
<th>cis trans isomers</th>
<th>$1J_{MP} \text{a}$ (trans ligand)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdCl$_2$(PMe$_3$)$_2$</td>
<td>8</td>
<td>610</td>
<td>---</td>
<td>113, 132, 133</td>
</tr>
<tr>
<td>PdI$_2$(PMe$_3$)$_2$</td>
<td>-</td>
<td>572</td>
<td>---</td>
<td>113, 133</td>
</tr>
<tr>
<td>PtCl$_2$(PMe$_3$)$_2$</td>
<td>19</td>
<td>570</td>
<td>3489 (Cl), 2386 (PMe$_3$)</td>
<td>113, 133, 134</td>
</tr>
<tr>
<td>PtI$_2$(PMe$_3$)$_2$</td>
<td>14</td>
<td>489</td>
<td>3317 (I), 2236 (PMe$_3$)</td>
<td>133, 133, 134</td>
</tr>
<tr>
<td>PtCl$_2$(PET$_3$)$_2$</td>
<td>- 20</td>
<td>436</td>
<td>3502 (Cl), 2394 (PET$_3$)</td>
<td>113, 133, 134</td>
</tr>
<tr>
<td>PtCl$_2$(P-n-Bu$_3$)$_2$</td>
<td>- 10</td>
<td>-</td>
<td>3505 (Cl), 2379 (P(n-Bu)$_3$)</td>
<td>115, 133, 134</td>
</tr>
<tr>
<td>Pt(Me)Cl(dppm)</td>
<td>43</td>
<td>-</td>
<td>3876 (Cl), 1248 (Me)</td>
<td>115, 135</td>
</tr>
<tr>
<td>Pt(Me)Cl(dppe)</td>
<td>0</td>
<td>-</td>
<td>4224 (Cl), 1737 (Me)</td>
<td>115, 136</td>
</tr>
<tr>
<td>Pt(Me)Cl(dppp)</td>
<td>21</td>
<td>-</td>
<td>4116 (Cl), 1644 (Me)</td>
<td>115, 136</td>
</tr>
</tbody>
</table>

$^a$Hz
Table 6
Phosphorus-31 NMR Data for Phosphido Bridged Bimetallic Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{2}\text{J}_{\text{pp}}$</th>
<th>cis-$^{2}\text{J}_{\text{pp}}$</th>
<th>trans-$^{2}\text{J}_{\text{pp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{PdCl}(u-\text{PPh}_2)(\text{PET}_3)]_2$</td>
<td>-289.5</td>
<td>31.9</td>
<td>405.9</td>
</tr>
<tr>
<td>$[\text{PdCl}(u-\text{PPh}_2)(\text{PHPh}_2)]_2$</td>
<td>-261.1</td>
<td>20.9</td>
<td>423.1</td>
</tr>
<tr>
<td>$[\text{PdCl}(u-\text{PMe}_2)(\text{PHPh}_2)]_2$</td>
<td>-310.0</td>
<td>24.1</td>
<td>442.9</td>
</tr>
<tr>
<td>$[\text{PdCl}(u-\text{PMe}_2)(\text{PET}_3)]_2$</td>
<td>-344.2</td>
<td>31.7</td>
<td>408.4</td>
</tr>
<tr>
<td>$[\text{PdCl}(u-\text{PMe}_2)(\text{PPh}_3)]_2$</td>
<td>-341.0</td>
<td>23.5</td>
<td>373.6</td>
</tr>
<tr>
<td>$[\text{PdCl}(u-\text{PPh}_2)(\text{dppe})]_2^{2+}$</td>
<td>-349.0</td>
<td>28.2</td>
<td>311.0</td>
</tr>
<tr>
<td>$[\text{PtCl}(u-\text{PPh}_2)(\text{PPh}_3)]_2$</td>
<td>-177.7</td>
<td>4.5</td>
<td>374.3</td>
</tr>
<tr>
<td>$[\text{PtCl}(u-\text{PPh}_2)(\text{PHPh}_2)]_2$</td>
<td>-162.0</td>
<td>7.6</td>
<td>395.4</td>
</tr>
<tr>
<td>$[\text{PtCl}(u-\text{PPh}_2)(\text{dppe})]_2^{2+}$</td>
<td>-207.5</td>
<td>7.1</td>
<td>291.9</td>
</tr>
</tbody>
</table>

$^{a}$Hz
differences in the P-M-P bond angles and M-P lengths for the planar and bent diastereomers.

3) Metal-Phosphorus Coupling Constants

Another important diagnostic feature found in the phosphorus-31 NMR spectrum of magnetically active transition metal complexes is the one bond metal-phosphorus coupling constant, \( ^{1}J_{\text{MP}} \). One such spin-active metal is platinum-195 (33.7% natural abundance; \( I = 1/2 \)).\(^{112}\) The \( ^{1}J_{\text{MP}} \) values obtained have been correlated to the length of the metal-phosphorus bond; in general, a short metal-phosphorus bond results in a large \( ^{1}J_{\text{MP}} \) value.\(^{18,113}\) Also, \( ^{1}J_{\text{MP}} \) for platinum phosphine complexes has been used to determine the trans-influence series, as well as the oxidation state of the metal.\(^{113,138,139}\) The magnitudes for both metal-phosphino, \( ^{1}J_{\text{MP}} \), and metal-phosphido, \( ^{1}J_{\text{MP}} \), coupling constants, in general, are found to lie in the same range. Typical values for \( ^{1}J_{\text{PtP}} \) and \( ^{1}J_{\text{PtP}} \) are presented in Tables 5 and 8.

E. Platinum-195 NMR Spectroscopy

Since the introduction of Fourier Transform NMR spectroscopy in the 1970's, the direct measurement of magnetically active transition metal nuclei is becoming increasingly common. The most commonly observed transition metal nucleus is platinum-195 (\( I = 1/2 \), natural abundance = 33.7%, relative sensitivity to proton = \( 9.94 \times 10^{-3} \)).\(^{112}\) Owing to its large chemical shift range (> 15,000 ppm), platinum-195 NMR spectroscopy is extremely sensitive to the oxidation state of the metal, the type, number and bonding mode of ligands bound to the metal center, as well as temperature, solvent and sample concentration. Thus, comparisons of
Table 7
Phosphorus-31 NMR Data for Chelated Phosphido Bridged Diastereomers\textsuperscript{49,51}

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{2}J_{pip}$\textsuperscript{a}</th>
<th>cis-$^{2}J_{pip}$\textsuperscript{a}</th>
<th>trans-$^{2}J_{pip}$\textsuperscript{a}</th>
<th>$\text{H}_2\text{P}_2$ core geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d/&amp;[\text{PdCl}(\mu-\text{PP})]_2$\textsuperscript{b}</td>
<td>-246.0</td>
<td>12.5</td>
<td>417.8</td>
<td>bent</td>
</tr>
<tr>
<td>$d/&amp;-[\text{PdCl}(\mu-\text{CyPP})]_2$\textsuperscript{c}</td>
<td>-235.2</td>
<td>16.4</td>
<td>396.7</td>
<td>bent</td>
</tr>
<tr>
<td>meso-$[\text{PdCl}(\mu-\text{PP})]_2$</td>
<td>-299.8</td>
<td>26.7</td>
<td>435.0</td>
<td>planar</td>
</tr>
<tr>
<td>meso-$[\text{PdCl}(\mu-\text{CyPP})]_2$</td>
<td>-303.6</td>
<td>33.3</td>
<td>416.2</td>
<td>planar</td>
</tr>
<tr>
<td>$d/&amp;-[\text{PtCl}(\mu-\text{PP})]_2$</td>
<td>-155.9</td>
<td>-4.4</td>
<td>383.0</td>
<td>bent</td>
</tr>
<tr>
<td>$d/&amp;-[\text{PtCl}(\mu-\text{CyPP})]_2$</td>
<td>-158.1</td>
<td>-2.3</td>
<td>362.3</td>
<td>bent</td>
</tr>
<tr>
<td>$d/&amp;-[\text{PtMe}(\mu-\text{PP})]_2$</td>
<td>-131.1</td>
<td>-23.3</td>
<td>336.6</td>
<td>bent</td>
</tr>
<tr>
<td>$d/&amp;-[\text{PtMe}(\mu-\text{CyPP})]_2$</td>
<td>-138.3</td>
<td>-19.1</td>
<td>324.4</td>
<td>bent</td>
</tr>
<tr>
<td>meso-$[\text{PtCl}(\mu-\text{PP})]_2$</td>
<td>-173.3</td>
<td>0.7</td>
<td>395.6</td>
<td>planar</td>
</tr>
<tr>
<td>meso-$[\text{PtCl}(\mu-\text{CyPP})]_2$</td>
<td>-176.6</td>
<td>3.1</td>
<td>374.2</td>
<td>planar</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Hz

\textsuperscript{b}$\mu$-PP equals \([\text{Ph}_2\text{P(\text{CH}_2)_3P(\text{Ph})}]^-$

\textsuperscript{c}$\mu$-CyPP equals \([\text{Cy}_2\text{P(\text{CH}_2)_3P(\text{Ph})}]^-$
Table 8
Selected Platinum-195 Phosphorus-31 Coupling Constants for Phosphido Bridged Bimetallic Complexes$^{51,137}$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^1J_{PtP,a,b}$</th>
<th>$^1J_{PtP}$ $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="PEt(_3)">PtCl(u)-PPh(_2)</a>(_2)</td>
<td>1690.5</td>
<td>2171.8</td>
</tr>
<tr>
<td><a href="PHPH(_2)">PtCl(u)-PPh(_2)</a>(_2)</td>
<td>1991.1</td>
<td>2184.0</td>
</tr>
<tr>
<td><a href="dppe">Pt(u)-PPh(_2)</a>(_2)(^{2+})</td>
<td>1774.7</td>
<td>2112.6</td>
</tr>
<tr>
<td>d/t-[PtCl(u)-PP)](_2)</td>
<td>1820.2</td>
<td>2115.2</td>
</tr>
<tr>
<td>d/t-[PtCl(u)-CyPP)](_2)</td>
<td>1725.4</td>
<td>2122.4</td>
</tr>
<tr>
<td>meso-[PtCl(u)-PP)](_2)</td>
<td>1875.4</td>
<td>2139.5</td>
</tr>
<tr>
<td>meso-[PtCl(u)-CyPP)](_2)</td>
<td>1768.4</td>
<td>2135.1</td>
</tr>
</tbody>
</table>

$^a$Hz

$^b$Bridging phosphido atoms are magnetically inequivalent.
platinum-195 NMR shift data are most useful when similar complexes are compared and experimental conditions remain constant.\textsuperscript{140,141}

Although platinum-195 NMR chemical shifts are dependent on the above mentioned factors, several empirical trends have emerged: 1) for a series of closely related complexes the resonances are shifted upfield in the order P > As > S > N > Cl\textsuperscript{-} > O; 2) as one descends a group, the platinum-195 NMR resonances shift upfield; 3) chemical shifts of Pt(II)-complexes appear at higher fields than those for Pt(IV) complexes. (Chemical shifts for Pt(0) complexes appear in the same region as those for Pt(II) compounds.); 4) for Pt(II) compounds, PtX\textsubscript{2}L\textsubscript{2} (X = Cl; L = PR\textsubscript{3}), the platinum-195 NMR chemical shifts for the cis-isomers are upfield from the trans-isomers by - 400 ppm; and, 5) replacement of an alkyl group by an aryl group of a coordinated phosphine ligand causes the chemical shift for the platinum-195 nucleus to move upfield.\textsuperscript{140-142} An examination of the platinum-195 chemical shifts presented in Table 9 is consistent with the trends listed above.

When a chelating ligand is bound to a platinum metal center, then the platinum-195 NMR chemical shift, \(\delta_{195Pt}\), like the phosphorus-31 NMR chemical shift, \(\delta_{31P}\), becomes dependent on the size of the ring. As previously stated, when a phosphorus atom is part of a five-membered ring, \(\delta_{31P}\) appears significantly downfield from an analogous monodentate phosphine complex. However, the five-membered chelate ring effect for the platinum-195 nucleus is a shift to higher fields.\textsuperscript{141} Thus, downfield phosphorus-31 chemical shifts are apparently concomitant with upfield platinum-195 chemical shifts (See Table 10).
Platinum-195 NMR spectra for bi- and polymetallic complexes have also been obtained. Perhaps the most important feature of these spectra is the direct observation of the metal-metal coupling constants, $J_{\text{Pt-Pt}}^{140,141}$. Obviously, this parameter might be a source of information concerning metal-metal bonds. Complexes which have no direct metal-metal interaction, $d(\text{Pt-Pt}) > 2.7\AA$, would be expected to have small $J_{\text{Pt-Pt}}$ values. Alternatively, a large $J_{\text{Pt-Pt}}$ value would be associated with a metal-metal bond. $^{149-151}$ Representative platinum-platinum coupling constants for bi- and poly-metallic complexes are presented in Table 11. With the exception of $\text{Pt}_3(\mu_2-\text{CNBu}^t)_3(\text{CNBu}^t)_3$, generally a large $J_{\text{Pt-Pt}}$ value ($> 1000$ Hz) is indicative of direct, metal-metal bonding. A possible explanation of the small $J_{\text{Pt-Pt}}$ coupling constant for $\text{Pt}_3(\mu_2-\text{CNBu}^t)_3(\text{CNBu}^t)_3$ is that two possible pathways for coupling exist: 1) direct Pt-Pt coupling, $^1J_{\text{Pt-Pt}}$; and, 2) Pt-Pt coupling via the bridging ligand(s), $^2J_{\text{Pt-Pt}}$ (See Figure 8). Therefore, the total metal-metal coupling could be the sum of the coupling via the two pathways. In other words, $J_{\text{NN}} = ^1J_{\text{Pt-Pt}} + ^2J_{\text{Pt-Pt}}$.

![Diagram of Pt-Pt coupling](image)

Other empirical trends that have been found for $J_{\text{Pt-Pt}}$ are: 1) for $\text{Pt}_2X_2(\text{dppm})_2$ ($X = \text{halide}$), the magnitude of $J_{\text{Pt-Pt}}$ increases in the order
Table 9
Platinum-195 NMR Chemical Shift Data
for Several Platinum Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_{195}^{Pt}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PtCl$_3$PMe$_3$]$^-_3$</td>
<td>-3500</td>
<td>143</td>
</tr>
<tr>
<td>[PtCl$_3$AsMe$_3$]$^-_3$</td>
<td>-3173</td>
<td>143</td>
</tr>
<tr>
<td>[PtCl$_3$SMe$_2$]$^-_3$</td>
<td>-2769</td>
<td>143</td>
</tr>
<tr>
<td>[PtCl$_3$NMe$_3$]$^-_3$</td>
<td>-1715</td>
<td>143</td>
</tr>
<tr>
<td>cis-PtCl$_2$(PMe$_3$)$_2$</td>
<td>-4408</td>
<td>143</td>
</tr>
<tr>
<td>cis-PtCl$_2$(SbMe$_3$)$_2$</td>
<td>-4612</td>
<td>143</td>
</tr>
<tr>
<td>cis-PtCl$_2$(SMe$_2$)$_2$</td>
<td>-3551</td>
<td>143</td>
</tr>
<tr>
<td>cis-PtCl$_2$(SeMe$_2$)$_2$</td>
<td>-3735</td>
<td>143</td>
</tr>
<tr>
<td>cis-PtCl$_2$(TeMe$_2$)$_2$</td>
<td>-4369</td>
<td>143</td>
</tr>
<tr>
<td>trans-PtCl$_2$(PMe$_3$)$_2$</td>
<td>-3950</td>
<td>143</td>
</tr>
<tr>
<td>trans-PtBr$_2$(PMe$_3$)$_2$</td>
<td>-4473</td>
<td>143</td>
</tr>
<tr>
<td>trans-PtI$_2$(PMe$_3$)$_2$</td>
<td>-5539</td>
<td>143</td>
</tr>
<tr>
<td>cis-PtCl$_2$(PET$_3$)$_2$</td>
<td>-4475</td>
<td>144</td>
</tr>
<tr>
<td>trans-PtCl$_2$(PET$_3$)$_2$</td>
<td>-3916</td>
<td>144</td>
</tr>
<tr>
<td>cis-PtCl$_2$(PMe$_2$Ph)$_2$</td>
<td>-4403</td>
<td>145</td>
</tr>
<tr>
<td>cis-PtCl$_2$(PMePh$_2$)$_2$</td>
<td>-4439</td>
<td>145</td>
</tr>
</tbody>
</table>

$^a\delta_{195}^{Pt}$ is given relative to H$_2$PtCl$_6$ at 0 ppm; negative values are upfield of the standard.
Table 10
Comparison of Phosphorus-31 and Platinum-195 Chemical Shifts
for Five-Membered Chelate Ring Systems

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ring Size</th>
<th>$^{31}$P&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$^{195}$Pt&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtCl&lt;sub&gt;2&lt;/sub&gt;(dpet)</td>
<td>5</td>
<td>--</td>
<td>-4613</td>
<td>142</td>
</tr>
<tr>
<td>PtCl&lt;sub&gt;2&lt;/sub&gt;(dppe)</td>
<td>5</td>
<td>41.0</td>
<td>-4554</td>
<td>146, 147</td>
</tr>
<tr>
<td>PtCl&lt;sub&gt;2&lt;/sub&gt;(dppp)</td>
<td>6</td>
<td>-5.6</td>
<td>-4514</td>
<td>142</td>
</tr>
<tr>
<td>PtCl&lt;sub&gt;2&lt;/sub&gt;(PPH)</td>
<td>6</td>
<td>-5.7, -28.9&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-4506</td>
<td>142</td>
</tr>
<tr>
<td>PtCl&lt;sub&gt;2&lt;/sub&gt;(CyPPH)</td>
<td>6</td>
<td>7.5, -28.8&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-4544</td>
<td>142</td>
</tr>
<tr>
<td>PtMe&lt;sub&gt;2&lt;/sub&gt;(dppm)</td>
<td>4</td>
<td>-40.4</td>
<td>-3890.1</td>
<td>148</td>
</tr>
<tr>
<td>PtMe&lt;sub&gt;2&lt;/sub&gt;(dppe)</td>
<td>5</td>
<td>54.0</td>
<td>-4603.2</td>
<td>148</td>
</tr>
<tr>
<td>PtMe&lt;sub&gt;2&lt;/sub&gt;(dppp)</td>
<td>6</td>
<td>3.2</td>
<td>-4589.3</td>
<td>148</td>
</tr>
</tbody>
</table>

<sup>a</sup> ppm relative to 85% H<sub>3</sub>PO<sub>4</sub> at 0 ppm, downfield being positive
<sup>b</sup> ppm relative to H<sub>2</sub>PtCl<sub>6</sub> at 0 ppm, downfield being positive
<sup>c</sup> $^{31}$P at higher field is assigned to the secondary phosphino-group of the ligand.
Table 11
Representative Platinum-Platinum One- and Two-Bond Coupling Constants

<table>
<thead>
<tr>
<th>Complex</th>
<th>$J_{PtPt}$</th>
<th>Direct Metal-Metal Interaction</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pt_3(v_2-CO)_3(PCy_3)_3$</td>
<td>1571</td>
<td>yes</td>
<td>140</td>
</tr>
<tr>
<td>$Pt_3(v_2-CO)_3(PBu^t_2He)_3$</td>
<td>1770</td>
<td>yes</td>
<td>140, 141</td>
</tr>
<tr>
<td>$Pt_3(v_2-CNBut)_3(CnBu^t)_3$</td>
<td>188</td>
<td>yes</td>
<td>140, 141</td>
</tr>
<tr>
<td>$Pt_2Cl_2(dppm)_2$</td>
<td>8197</td>
<td>yes</td>
<td>140, 141</td>
</tr>
<tr>
<td>$Pt_2Br_2(dppm)_2$</td>
<td>8828</td>
<td>yes</td>
<td>140</td>
</tr>
<tr>
<td>$Pt_2I_2(dppm)_2$</td>
<td>9007</td>
<td>yes</td>
<td>140, 141</td>
</tr>
<tr>
<td>$d/\epsilon-[PtCl(u-PP)]_2$</td>
<td>342</td>
<td>no</td>
<td>49, 51</td>
</tr>
<tr>
<td>$d/\epsilon-[PtCl(u-CyPP)]_2$</td>
<td>259</td>
<td>no</td>
<td>49, 51</td>
</tr>
<tr>
<td>meso-[$PtCl(u-CyPP)]_2$</td>
<td>639</td>
<td>no</td>
<td>49, 51</td>
</tr>
</tbody>
</table>

$^a$Values in Hz.
$Cl < Br < I.^{151}$ (This trend follows the expected order, according to the trans-influence of halide.); and, 2) for the diastereomers $d/t$- and $meso-[PtCl(\mu-CyPP)]_2$, the magnitude of $J_{PtPt}$ is larger for the $meso$-complex (planar $M_2P_2$-core) than the $d/t$-pair (bent $H_2P_2$-core).$^{49,51}$

F. Tertiary/Secondary Diphosphine Ligands

The ligand PPH, $Ph_2P(CH_2)_3P(H)Ph$ was first synthesized by Tau as an intermediate for preparation of either substituted diphosphine ligands or triphosphine ligands such as ttp, $PhP[(CH_2)_3PPh_2]_2$. However, it was recognized that PPH and CyPPH, $Cy_2P(CH_2)_3P(H)Ph$, possessed ligand properties themselves. The chelation of the ligands to suitable metals followed by deprotonation of the secondary phosphine was shown by Waid to be a good synthetic method for preparation of phosphido bridged transition metal complexes (Eq. 21).$^{49}$ Thus, tertiary/secondary diphosphine ligands seemed to be promising starting materials with which to extend the known chemistry of organophosphido compounds.

$$PtMe_2COD + PPH \xrightarrow{\Delta} d/t- [PtMe(\mu-PP)]_2$$ (21)
G. Statement of Research Problems

The goals of this research were:

1. to synthesize the chelating tertiary/secondary diphosphine ligand, Ph$_2$P(CH$_2$)$_3$P(H)Bu$^t$, PPBu$^t$H;

2. to synthesize d$^8$-transition metal mono- and binuclear complexes containing the tertiary/secondary diphosphine ligands, R$_2$P(CH$_2$)$_3$P(H)R', where R = Ph, Cy, p-CF$_3$C$_6$H$_4$ and R' = Me, Ph;

3. to investigate the $^{31}$P NMR spectral characteristics of these complexes;

4. to investigate the $^{195}$Pt NMR spectral characteristics of the platinum complexes containing organophosphorus ligands; and

5. to correlate the steric and electronic properties of the ligands, PPH, CyPPH, PPMH, CyPPMH and p-CF$_3$PPH, to the NMR spectral parameters.
A. Reagents

Diphenylphosphine was purchased from Pressure Chemical Company, Pittsburgh, Pennsylvania and was used without further purification. Allyl bromide, which was purchased from Aldrich Chemical Company, Milwaukee, Wisconsin, was distilled from anhydrous magnesium sulfate under argon prior to use. Dichloro-t-butylphosphine was purchased from Strem Chemical Company, Newburyport, Massachusetts and used without further purification. The reagents diisobutylaluminum hydride (70% weight toluene solution), lithium diisopropylamide (1.5 M cyclohexane solution), and n-butyllithium (1.6 M hexane solution) were obtained from Aldrich Chemical Company. All other chemicals were reagent-grade and, unless stated otherwise, used as obtained.

The tertiary/secondary diphosphine ligands diphenyl(3-phenylphosphinopropyl)phosphine, PPH, and dicyclohexyl(3-phenylphosphinopropyl)phosphine, CyPPH, were prepared by Urrarte's modification of Tau's method. The diphosphine ligand di-p-trifluoromethylphenyl(3-phenylphosphinopropyl)phosphine, p-CF₃PPH was synthesized by L.M. Green. The ligands, diphenyl(3-methylphosphinopropyl)phosphine, PPMH and dicyclohexyl(3-methylphosphinopropyl)phosphine, CyPPMH were prepared by the present author according to reference 104.
The transition metal salt sodium tetrachloropalladate, Na$_2$PdCl$_4$ was obtained from Engelhard Industries, Newark, New Jersey. Potassium tetrachloroplatinate (K$_2$PtCl$_4$) was prepared from platinum metal or from recycled platinum-containing laboratory waste.155,156 These salts were converted to their 1,5-cyclooctadiene complexes by established procedures.157-159

All solvents were reagent grade and were distilled from appropriate dry agents under argon prior to use.160

B. Instrumentation

Infrared spectra were measured on a Perkin-Elmer Model 283B grating spectrophotometer from 200 to 4000 cm$^{-1}$. The samples were examined as Nujol mulls between potassium bromide plates or potassium bromide pellets. All spectra were calibrated with a polystyrene film.

Mass spectra were measured by C.R. Weisenberger at The Ohio State University Chemical Instrumentation Center and were obtained on a Kratos MS30 mass spectrometer by electron ionization (E.I.) or fast atom bombardment (FAB) techniques.

Melting points were recorded on a Mel-Temp melting point apparatus and are uncorrected.

Fourier mode proton NMR spectra were obtained on either a Bruker AM-250 spectrometer operating at 250.134 MHz or a Bruker AM-500 spectrometer operating at 500.136 MHz. Proton spectra were obtained in deuterated solvents and standardized against tetramethyilsilane (TMS, $\delta = 0.00$ ppm) or residual solvent proton peaks.
Fourier mode carbon-13 NMR spectra were collected on either the Bruker AM-250, MSL-300 or AM-500 NMR spectrometers operating at 62.896, 75.49 or 125.70 MHz, respectively. Spectra were obtained in deuterated dichloromethane solutions and were standardized against the solvent peak ($\delta_{13}^C = 43.6$ ppm).

Phosphorus-31 spectra were obtained on either the Bruker HX-90, AM-250 or AM-500 spectrometers operating at 36.43, 101.26 or 202.42 MHz, respectively. Spectra recorded on either the Bruker HX-90 or AM-500 were recorded in nondeuterated solvents and calibrated by use of a coaxial insert tube containing both trimethylphosphate ($\delta_{31}^P 1.59$ ppm relative to $85\%$ H$_3$PO$_4$) and deuterated acetone. During the acquisition period, the coaxial insert remained in the sample tube. Spectra collected on the Bruker AM-250 were recorded in deuterated solvents in 5mm NMR tubes and calibrated against predetermined values according to the deuterated solvent. Spectra were obtained in either the $^1$H-coupled or broadband-noise $^1$H-decoupled mode. Phosphorus-31 NMR chemical shifts are reported in ppm relative to $85\%$ H$_3$PO$_4$ with positive numbers being downfield from the standard.

Broadband-noise $^1$H-decoupled platinum-195 NMR spectra were recorded at 297K on the Bruker MSL-300 operating at 64.39 MHz. The samples were prepared in 10% deuterated dichloromethane/90% dichloromethane solvent mixtures as 0.03 M solutions and recorded in 10mm NMR tubes fit with vortex plugs. Spectra were referenced to external 0.6 M H$_2$PtCl$_6$ in D$_2$O/HCl ($\delta_{195}^{Pt} = 0$ ppm).

Both the phosphorus-31 DEPT (Distortionless Enhancement by Polarization Transfer) and the coupled DEPT NMR experiments were
performed on the Bruker AM-250 spectrometer by Mr. C. Engelman. The two-dimensional NMR experiments were performed by Dr. C.E. Cottrell at The Ohio State University Campus Chemical Instrumentation Center on the Bruker AM-500 spectrometer. Computer simulations of experimental spectra were performed with the PANIC (Parameter Adjustment in NMR by Iteration Calculation) program provided by Bruker Instruments, Inc.

Elemental analyses were done by M-H-W Laboratories, Phoenix, Arizona. In the presence of heavy metals, percent carbon is sometimes decreased by the formation of metal carbides during analysis.

C. General Experimental Procedures

All reactions were performed in a well-ventilated fume hood under an atmosphere of argon using standard techniques for the manipulation of air-sensitive materials. Solutions of air-sensitive reagents were transferred between reaction vessels using syringes flushed with argon or stainless steel cannulae. Triethylamine was purged with argon for 20 minutes before use. All other solvents were distilled from appropriate drying agents under argon prior to use.

D. Attempted Synthesis of Diphenyl(3-t-butylphosphinopropyl)phosphine, PPBu₃H

1) Attempted Reduction of Diphenyl[3-(ethyl-t-butylphosphinate, 
Ph₂P(CH₂)₃P(O)(OEt)₃-Bu]¹⁰⁴,¹⁶³

Diphenyl[3-(ethyl-t-butylphosphinate) (12.2 g, 3.23 x 10⁻² moles) dissolved in ~100 mL of THF was added dropwise to a THF slurry of lithium aluminum hydride (2.3 g, 5.9 x 10⁻² moles in ~100 mL THF).
During addition of the phosphinite, the solution was stirred vigorously and maintained at 0°C by external cooling. When the addition of the phosphinite was complete, the reaction mixture was refluxed at 60°C for 48 hours. Unreacted LAH was destroyed by the addition of 9.30 mL of distilled water in 1.00 mL increments, while the reaction flask was maintained at 0°C via external cooling. After the H₂O addition was complete, a white precipitate (Al₂O₃) was formed. The THF solution was removed from the aluminum oxide slurry by passing it through a celite column via a cannula. The precipitate was then washed with three 25.0 mL portions of THF. The phosphorus-31 NMR spectrum of the THF solution showed two peaks at -18.57 and 58.40 ppm, indicating that the phosphinite had not been reduced.

2) Tertiarybutylphosphine, t-BuPH₂

Dichloro-t-butylyphosphine (10.0g, 6.29 x 10⁻² moles) dissolved in 100 mL THF was added dropwise to a 70% Vitrile/toluene solution (32.5 mL, 1.17 x 10⁻¹ moles). During the addition, the reaction temperature was maintained at 0°C by external cooling. After the addition was complete, the solution was heated to reflux for 12 hours. Excess Vitrile was destroyed by the addition of 20 mL of methanol in 2 mL increments at 0°C. Pure t-butylyphosphine was obtained as a clear viscous oil by fractional distillation at 760 torr. Yield was quantitative. Boiling point range: 57-60°C/760 torr (literature value 54°C/760 torr). ³¹P NMR data: δ = -82.31 ppm, ¹JPH = 186.2 Hz, ³JPH 11.8.
3) Attempted Synthesis of Diphenyl(3-t-butylphosphinopropyl)phosphine, $\text{Ph}_2\text{P(CH}_2\text{)}_3\text{P(H)Bu}^t$

A solution consisting of 15.0 g (5.71 x $10^{-2}$ moles) of diphenyl(3-chloropropyl)phosphine in 100 mL toluene was added dropwise from a pressure-equalizing funnel to a mechanically stirred solution of liquid ammonia at -78°C containing 2.08 g of Na metal, 13.3 g (1.47 x $10^{-1}$ moles) t-butylphosphine, and ~75 mL of diethyl ether. After the addition was complete, the ammonia was allowed to evaporate overnight. The residue in the flask was first treated with 8 x 2 mL of distilled water. The $^{31}$P($^1$H) NMR spectrum of the organic layer gave rise to two peaks at -18.91 and -82.29 ppm due to diphenyl(3-chloropropyl)phosphine and t-butylphosphine, respectively, thus indicating that no reaction had occurred.

4) Attempted Synthesis of Diphenyl(3-t-butylphosphinopropyl)phosphine, $\text{PPBu}^t\text{H}$

A 1.5 M cyclohexane solution of lithium diisopropylamide, LDA (25.0 mL, 3.75 x $10^{-2}$ moles) diluted with 20 mL of hexane was added dropwise to a solution of diphenyl(3-chloropropylphosphine) (5.45 g, 2.04 x $10^{-2}$ moles) and t-butylphosphine (2.50 g, 2.77 x $10^{-2}$ moles) in 200 mL of toluene. During the addition of the LDA, the reaction temperature was maintained at -78°C via an isopropanol/dry ice bath. After the addition of the LDA was complete, the resulting solution was allowed to warm to room temperature and was stirred overnight. The solution was then refluxed for three hours. Upon cooling, the reaction mixture was hydrolyzed with 200 mL of distilled water. The $^{31}$P NMR spectrum of the
toluene layer revealed that no appreciable reaction had occurred. (See Results and Discussion.)

E. Synthesis of Palladium(II) and Platinum(II) Monometallic Complexes

1) Preparation of Chelating Tertiary/Secondary Diphosphine Palladium(II) and Platinum(II) Chloride Complexes

The complexes $\text{PdCl}_2(\text{PPH})$, $\text{PdCl}_2(\text{PPMH})$, $\text{PdCl}_2(\text{CyPPMH})$, $\text{PdCl}_2(\text{p-CF}_3\text{PPH})$, $\text{PtCl}_2(\text{PPMH})$, $\text{PtCl}_2(\text{CyPPMH})$, and $\text{PtCl}_2(\text{p-CF}_3\text{PPH})$ were prepared by treating a solution of either $\text{PdCl}_2$ COD or $\text{PtCl}_2$ COD with PPH, PPMH, CyPPMH, or p-CF$_3$PPH in the presence of $\text{H}^+$. For example, a solution of 0.58 M CyPPMH in benzene (1.4 mL, $8.2 \times 10^{-4}$ moles) was added to a solution of $\text{PdCl}_2$ COD (0.235 g, $8.23 \times 10^{-4}$ moles) and 1 drop of 6 M HCl solution in 25 mL of CH$_2$Cl$_2$. After stirring the reaction mixture for ~2 hours, the solution was concentrated under a stream of Ar to ~2 mL. To complete precipitation of the orange-yellow solid, ~10 mL were added. The orange-yellow solid was then collected on a Schlenk frit, washed two times with 2.0 mL aliquots of hexane and dried overnight in vacuo. Yield: 0.25 g (65%).

2) Preparation of Chelating Tertiary/Secondary Diphosphine Platinum(II) Iodide Complexes

The complexes $\text{PtI}_2(\text{PPH})$, $\text{PtI}_2(\text{CyPPH})$, $\text{PtI}_2(\text{PPMH})$, $\text{PtI}_2(\text{CyPPMH})$, and $\text{PtI}_2(\text{p-CF}_3\text{PPH})$ were synthesized by treating a solution of $\text{PtI}_2$ COD with 1 equivalent of PPH, CyPPH, PPMH, CyPPMH or p-CF$_3$PPH, respectively. For example, a solution of 0.32 M PPH in benzene (0.88 mL, $2.8 \times 10^{-4}$ moles) was added to $\text{PtI}_2$ COD (0.157 g, $2.82 \times 10^{-4}$ moles) in 25 mL of benzene.
## Table 12
Reaction Conditions and Yields for Chelating Tertiary/Secondary Diphosphine Palladium(II) and Platinum(II) Chloride Complexes

<table>
<thead>
<tr>
<th>Complex (description of solid)</th>
<th>[MC1₂COO] (g, moles)</th>
<th>Phosphine Ligand (mole)</th>
<th>Reaction Solvent (mL)</th>
<th>Reaction Time (hours)</th>
<th>Yield (g) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdCl₂PPH³</td>
<td>PdCl₂-COD (0.211g, 7.39x10⁻⁴)</td>
<td>PPH (7.4x10⁻⁴)</td>
<td>CH₂Cl₂ (25)</td>
<td>1 1/2</td>
<td>0.22 g (57)</td>
</tr>
<tr>
<td>PdCl₂PPMH (yellow)</td>
<td>PdCl₂-COD (0.263g, 9.23x10⁻⁴)</td>
<td>PPMH (9.2x10⁻⁴)</td>
<td>CH₂Cl₂ (25)</td>
<td>1 1/2</td>
<td>0.24 g (69)</td>
</tr>
<tr>
<td>PdCl₂CyPPMH (orange-yellow)</td>
<td>PdCl₂-COD (0.234g, 8.23x10⁻⁴)</td>
<td>CyPPMH (8.2x10⁻⁴)</td>
<td>CH₂Cl₂ (25)</td>
<td>2</td>
<td>0.25 g (65)</td>
</tr>
<tr>
<td>PdCl₂(p-CF₃PPH)² (yellow)</td>
<td>PdCl₂-COD (0.144g, 5.04x10⁻⁴)</td>
<td>p-CF₃PPH (5.0x10⁻⁴)</td>
<td>CH₂Cl₂ (25)</td>
<td>1 1/2</td>
<td>---</td>
</tr>
<tr>
<td>PtCl₂(PPMH) (white)</td>
<td>PtCl₂-COD (0.211g, 5.63x10⁻⁴)</td>
<td>PPMH (5.7x10⁻⁴)</td>
<td>CH₂Cl₂ (30)</td>
<td>1</td>
<td>0.20 g (67)</td>
</tr>
<tr>
<td>PtCl₂(CyPPMH) (yellow-white)</td>
<td>PtCl₂-COD (0.325g, 8.69x10⁻⁴)</td>
<td>CyPPMH (8.8x10⁻⁴)</td>
<td>Benzene (20)</td>
<td>2</td>
<td>0.38 g (70)</td>
</tr>
<tr>
<td>PtCl₂(p-CF₃PPH)²(c) (white)</td>
<td>PtCl₂-COD (0.203g, 5.43x10⁻⁴)</td>
<td>p-CF₃PPH (5.4x10⁻⁴)</td>
<td>Benzene (20)</td>
<td>1</td>
<td>0.37 g (92)</td>
</tr>
</tbody>
</table>

³Recrystallized from CH₂Cl₂

²See Results and Discussion

³Data from reference 154, pages 74-75.
Upon addition of the ligand the solution turned a bright yellow color which faded in ~ 10 minutes as a yellow solid precipitated. The solution was concentrated under a stream of Ar to ~ 2 mL and then 10 mL of hexane was added to complete precipitation. The yellow solid was collected on a Schlenk frit, washed two times with 5.0 mL aliquots of hexane and dried overnight in vacuo. Yield: 0.21 g (96%).

F. Bimetallic Palladium(II) and Platinum(II) Complexes Containing Chelated Bridging Phosphido Ligands

1) \([\text{PdCl} (\mu-p-\text{CF}_3\text{PP})]_2\)

Recrystallization of \(\text{PdCl}_2(\mu-\text{CF}_3\text{PPH})\) from nitromethane afforded the title complex. On the basis of its \(^{31}\text{P}(^1\text{H})\) NMR spectrum, the complexe was assigned to be \(\text{d/}\text{a-}[\text{PdCl}(\mu-p\text{-}\text{CF}_3\text{PP})]_2\). Yield 0.56 g (90% based on \(\text{PdCl}_2\text{COD}\)).

Analysis for \(\text{C}_{46}\text{H}_{38}\text{F}_{12}\text{Cl}_2\text{P}_4\text{Pd}_2\):

\[
\begin{array}{ccc}
\% & \% & \% \\
\text{calcd.} & 45.05 & 3.12 & 10.10 \\
\text{found} & 44.33 & 3.61 & 10.16 \\
\end{array}
\]

2) \([\text{PtI}(\mu-\text{PP})]_2\)

A suspension of \(\text{PtI}_2(\text{PPH})\) (0.414 g, \(5.27 \times 10^{-4}\) moles) in 20 mL of THF was treated with 0.5 mL of \(\text{Et}_3\text{N}\). Addition of the amine caused part of the suspended solid to dissolve. The above mixture was stirred for 12 hours. Removal of the solvent in vacuo afforded a light yellow solid. The \(\text{Et}_3\text{N}\cdot\text{HCl}\) was removed from the \([\text{PtI}(\mu-\text{PP})]_2\) by redissolving
Table 13

Reaction Conditions and Yields for Chelating Tertiary/Secondary Diphosphine Platinum(II) Iodide Complexes

<table>
<thead>
<tr>
<th>Complex (description of solid)</th>
<th>PtI₂COD (g, moles)</th>
<th>Phosphine Ligand (moles)</th>
<th>Reaction Solvent (mL)</th>
<th>Reaction Time (minutes)</th>
<th>Yield (g) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtI₂(PPH) (yellow)</td>
<td>0.157 (2.82×10⁻⁴)</td>
<td>PPH (2.8×10⁻⁴)</td>
<td>Benzene</td>
<td>30</td>
<td>0.21 g (96)</td>
</tr>
<tr>
<td>PtI₂(CyPPH) (yellow)</td>
<td>0.381 (6.83×10⁻⁴)</td>
<td>CyPPH (6.9×10⁻⁴)</td>
<td>Benzene</td>
<td>30</td>
<td>0.45 g (83)</td>
</tr>
<tr>
<td>PtI₂(PPMH) (yellow)</td>
<td>0.257 (4.61×10⁻⁴)</td>
<td>PPMH (4.9×10⁻⁴)</td>
<td>Benzene</td>
<td>30</td>
<td>0.28 g (83)</td>
</tr>
<tr>
<td>PtI₂(CyPPMH) (orange/yellow)</td>
<td>0.254 (4.23×10⁻⁴)</td>
<td>CyPPMH (4.2×10⁻⁴)</td>
<td>Benzene</td>
<td>30</td>
<td>0.29 g (92)</td>
</tr>
<tr>
<td>PtI₂(p-CF₃PPH) (yellow)</td>
<td>0.337 (6.05×10⁻⁴)</td>
<td>p-CF₃PPH (6.1×10⁻⁴)</td>
<td>Benzene</td>
<td>30</td>
<td>0.37 g (67)</td>
</tr>
</tbody>
</table>
Table 14
Elemental Analysis for Representative Monometallic Palladium(II) and Platinum(II) Diphosphine Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Empirical Formula</th>
<th>% C</th>
<th>% H</th>
<th>% P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>calcd (found)</td>
<td>calcd (found)</td>
<td>calc (found)</td>
</tr>
<tr>
<td>PtI₂(PPH)</td>
<td>C₂₁H₂₂I₂P₂Pt·3/4 C₆H₅</td>
<td>36.29 (36.39)</td>
<td>3.17 (3.10)</td>
<td>7.70 (7.34)</td>
</tr>
<tr>
<td>PtI₂(p-CF₃PPH)</td>
<td>C₂₃H₂₀F₆I₂P₂Pt</td>
<td>29.99 (30.17)</td>
<td>2.19 (2.24)</td>
<td>6.74 (6.86)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Complex</th>
<th>Empirical Formula</th>
<th>% C</th>
<th>% H</th>
<th>% Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>calcd (found)</td>
<td>calcd (found)</td>
<td>calcd (found)</td>
</tr>
<tr>
<td>PtCl₂(PPMH)</td>
<td>C₁₆H₂₀Cl₂P₂Pt·1/2 C₆H₁₄</td>
<td>39.12 (38.92)</td>
<td>4.67 (4.53)</td>
<td>12.15 (12.48)</td>
</tr>
</tbody>
</table>
the yellow solid in 5 mL of benzene, and filtering the resulting solution. The benzene solution was concentrated to 1 mL under a stream of Ar and then 10 mL of hexane was added to complete the precipitation of the yellow solid. The yellow solid was collected on a Schlenk frit, washed two times with 2.0 mL aliquots of hexane and dried in vacuo. The $^{31}$P($^1$H) NMR spectrum of the compound revealed that it was a mixture of two geometrical isomers. Yield: 0.61 g (87%).

3) [PtI($\mu$-CyPP)]$_2$

Substitution of PtI$_2$(CyPPH) (0.451 g, $5.66 \times 10^{-4}$ moles) in the preceding experimental procedure yields both d/â- and meso-[PtI($\mu$-CyPP)]$_2$ in 86% yield.

4) [PtI($\mu$-p-CF$_3$PP)]$_2$

Substitution of PtI$_2$(p-CF$_3$PPH) (0.176 g, $1.91 \times 10^{-4}$ moles) in the preceding experimental procedure yields both d/â- and meso-[PtI($\mu$-p-CF$_3$PP)]$_2$ in 89% yield.

5) [PtCl($\mu$-p-CF$_3$PP)]$_2$

Method A

A suspension of PtCl$_2$COD (0.592 g, $1.58 \times 10^{-3}$ moles) in 35 mL of benzene was treated with 5.3 mL of 0.30 M p-CF$_3$PPH ($1.6 \times 10^{-3}$ moles) in benzene. Upon addition of the ligand the solution turned bright yellow and then a white solid precipitated. The reaction mixture was stirred for 15 minutes before the solution was concentrated under a stream of Ar to - 1 mL. To complete precipitation of the white solid - 5 mL of hexane was added. The solid was then collected on a Schlenk frit.
washed two times with 3 mL aliquots of hexane and dried overnight in vacuo. The $^{31}$P($^1$H) NMR spectrum of the compound revealed that it was a mixture of two geometrical isomers. Yield: 1.0 g (92%).

**Method B**

A suspension of PtCl$_2$COD (0.255 g, $6.81 \times 10^{-4}$ moles) in 10 mL of toluene was treated with 1 equivalent of p-CF$_3$PPH and refluxed for 90 minutes. The resulting white suspension was allowed to cool to room temperature. The solution was concentrated to ~5 mL under an Ar stream and then 40 mL of hexane was added to complete precipitation. The white solid was then collected on a Schlenk frit and dried overnight in vacuo. The $^{31}$P($^1$H) NMR spectrum of the solid revealed that it was a mixture of two compounds: $\eta^1$-[PtCl($\mu$-p-CF$_3$PP)]$_2$ and [Pt(p-CF$_3$PPH)$_2$]$_2^{2+}$ [(Cl)$_2$].

6) Separation of $\eta^1$-[PtCl($\mu$-p-CF$_3$PP)]$_2$ from [Pt(p-CF$_3$PPH)$_2$]$_2^{2+}$ [(Cl)$_2$]

Treatment of 0.255 g ($6.81 \times 10^{-4}$ moles) of PtCl$_2$COD suspended in 10 mL of toluene with 1 equivalent of p-CF$_3$PPH according to Method 5B yielded 0.442 g of an approximately 2:1 ratio (determined by $^{31}$P NMR spectroscopy) of both $\eta^1$-[PtCl($\mu$-p-CF$_3$PP)]$_2$ and [PtCl(p-CF$_3$PPH)$_2$]$_2^{2+}$ [(Cl)$_2$], respectively. This mixture was dissolved in 30 mL of benzene and the resulting slurry was stirred for 30 minutes. The white precipitate was then collected on a Schlenk frit and washed two times with 1.0 mL aliquots of benzene. Removal of the benzene from the filtrate in vacuo afforded a second white precipitate. Based on both $^{31}$P- and $^{195}$Pt-NMR spectroscopy, the white precipitate collected on the Schlenk frit was
identified as \([\text{Pt(p-CF}_3\text{PPH})_2]^{2+}\text{[Cl]}_2\), and the white precipitate obtained from the filtrate was identified as \(d/\alpha-\text{[PtCl(u-p-CF}_3\text{PP})_2}\).

7) \([\text{PdCl(u-PPM)}]_2\)

Substitution of \(\text{PdCl}_2(\text{PPM})\) (0.11 g, \(2.4 \times 10^{-4}\) moles) into the experimental procedure for \([\text{PtI(u-PP)}]_2\) afforded both \(d/\alpha-\) and \(\text{meso-}\) \([\text{PdCl(u-PPM)}]_2\) in 51% yield.

8) Attempted Synthesis of \([\text{PtCl(u-PPM)}]_2\)

Substitution of \(\text{PtCl}_2(\text{PPM})\) (0.15 g, \(2.8 \times 10^{-4}\) moles) into the experimental procedure for \([\text{PtI(u-PP)}]_2\) does not yield the bimetallic complex, \([\text{PtCl(u-PPM)}]_2\) (See Results and Discussion).

9) Attempted Synthesis of \([\text{PdCl(u-CyPPM)}]_2\)

Substitution of \(\text{PdCl}_2(\text{u-CyPPM})\) (0.0748 g, \(1.61 \times 10^{-4}\) moles) into the experimental procedure for \([\text{PtI(u-PP)}]_2\) does not afford the bimetallic complex, \([\text{PdCl(u-CyPPM)}]_2\) (See Results and Discussion).

10) Reaction of \(\text{PdCl}_2(\text{PPM})\) with Proton Sponge

A suspension of \(\text{PdCl}_2(\text{PPM})\) (0.0954 g, \(2.11 \times 10^{-4}\) moles) in 10 mL of THF was treated with 1.1 equivalents of 1,8-dimethylaminonapthalene (proton sponge). Addition of the non-coordinating amine base caused the precipitate to momentarily dissolve. After the mixture was then stirred overnight, the solution was concentrated under a stream of Ar to ~2 mL and then to complete precipitation, 5 mL of diethyl ether was added. The yellow solid was collected on a Schlenk frit, washed two times with 1 mL
aliquots of diethyl ether and dried overnight in vacuo. The $^{31}$P($^1$H) NMR spectrum of this material revealed that the bimetallic [PdCl-(μ-PPM)]$_2$ was not formed (See Results and Discussion).

11) Reaction of PdCl$_2$(PPM) with 2,6-Lutidene

A suspension of PdCl$_2$(PPM) (0.0744 g, $1.65 \times 10^{-4}$ moles) in 10 mL of diethyl ether was treated with 1.1 equivalents of 2,6-lutidene. Addition of the amine base caused the solid to momentarily dissolve. After the mixture was stirred overnight, the solvent was removed under reduced pressure and the yellow residue was dried overnight in vacuo. The $^{31}$P($^1$H) NMR spectrum of the yellow residue revealed that [PdCl-(μ-PPM)]$_2$ was not formed (See Results and Discussion).

G. Reactions to Determine Intermediate in Bimetallic Formation

1) [Pt(PPH)$_2$]$^{2+}$[Cl]$_2$ 49

A suspension of PtCl$_2$COD (0.305 g, $8.15 \times 10^{-4}$ moles) in 15 mL of benzene was treated with two equivalents of a 0.32 M PPH solution in benzene (5.0 mL, $1.6 \times 10^{-3}$ moles). Addition of the ligand caused the suspended solid to momentarily dissolve. After stirring the slurry for an hour, the solution was concentrated to ~2 mL under an Ar stream. The white precipitate was then collected on a Schlenk frit, washed three times with 10 mL aliquots of benzene and dried overnight in vacuo. Yield: 0.69 g (90%).
2) Thermolysis of \([\text{Pt(PPH)}_2]^{2+}[\text{Cl}]_2\)

A suspension of \([\text{Pt(PPH)}_2]^{2+}[\text{Cl}]_2\) (0.124 g, \(1.32 \times 10^{-4}\) moles) in 10 mL of toluene was refluxed for 3 hours. The solvent was removed under reduced pressure, and the remaining white residue was dissolved in a minimum amount of dichloromethane. Examination of the white residue by \(^{31}\text{P}\) NMR spectroscopy revealed only the presence of starting material, \([\text{Pt(PPH)}_2]^{2+}[\text{Cl}]_2\).

3) Reaction of \([\text{Pt(PPH)}_2]^{2+}[\text{Cl}]_2\) with \(\text{Et}_3\text{N}\)

A suspension of \([\text{Pt(PPH)}_2]^{2+}[\text{Cl}]_2\) (0.235 g, \(2.50 \times 10^{-4}\) moles) in 20 mL of THF was treated with 0.5 mL of \(\text{Et}_3\text{N}\). Addition of the amine caused part of the suspended solid to dissolve. The mixture was stirred overnight. Removal of the solvent in vacuo afforded a yellow residue. This material failed to give an observable \(^{31}\text{P}(^1\text{H})\) NMR spectrum.

4) Reaction of \([\text{Pt(PPH)}_2]^{2+}[\text{Cl}]_2\) with \(\text{PtCl}_2\text{COD}\) in the Presence of \(\text{Et}_3\text{N}\)

A solution of \([\text{Pt(PPH)}_2]^{2+}[\text{Cl}]_2\) (0.0779 g, \(8.30 \times 10^{-5}\) moles) and \(\text{PtCl}_2\text{COD}\) (0.0313 g, \(8.37 \times 10^{-5}\) moles) in 20 mL of dichloromethane was treated with 0.25 mL of \(\text{Et}_3\text{N}\). Addition of the amine caused the colorless solution to turn immediately yellow. After the solution was stirred for 12 hours, all solvent was removed under reduced pressure. The resulting yellow-white solid was dissolved in \(\text{CD}_2\text{Cl}_2\) and examined by \(^{31}\text{P}\) NMR spectroscopy. The \(^{31}\text{P}(^1\text{H})\) NMR spectrum revealed the presence of \(d/\alpha\)- and \(\text{meso-}[\text{PtCl}(\mu-\text{PP})]_2\) as the major product (See Results and Discussion).
CHAPTER III
RESULTS AND DISCUSSION

A. Attempted Syntheses of $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{P}(\text{H})\text{t-Bu}$

The three attempted syntheses used to prepare the tertiary/secondary diphosphine ligand, $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{P}(\text{H})\text{t-Bu}$, $\text{PPBu}_2^\text{H}$, are presented in Schemes 1, 2, and 3. The methods involved in attempts at synthesis of $\text{PPBu}_2^\text{H}$ included the Michaelis-Arbuzov reaction (Eq. 22), free radical phosphorus-hydrogen addition across an activated carbon-carbon bond (Eq. 23) followed by reduction (Eq. 24), and phosphorus carbon coupling via an organophosphide (Eqs. 25-27). Although all of these methods have been demonstrated to be useful in the syntheses of bi-, tri-, and polydentate organophosphine ligands, none proved to be a viable synthetic route for $\text{PPBu}_2^\text{H}$.

Scheme 1

\[ \text{t-BuP(OEt)}_2 + \text{CH}_2=\text{CHCH}_2\text{Br} \xrightarrow{\Delta, 3 \text{ hr}} -\text{EtBr} \xrightarrow{\text{Ph}_2\text{P}(\text{H})} \text{t-BuP(O)(OE)} \text{t-BuP(O)(OE)(CH}_2\text{CH}=\text{CH}_2} \]

\[ \text{t-BuP(O)(OE)} \text{t-BuP(O)(OE)(CH}_2\text{CH}=\text{CH}_2 + \text{Ph}_2\text{PH} \xrightarrow{\text{AIBN}} \text{t-BuP(O)(OE)(CH}_2\text{H}_3\text{PPh}_2} \]

\[ \text{t-BuP(O)(OE)(CH}_2\text{H}_3\text{PPh}_2 + \text{LAH} \xrightarrow{\Delta} \text{N.R.} \]
Scheme 3

\[
\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Cl} + \text{t-BuPH}_2 \xrightarrow{\text{LDA}, -78^\circ\text{C}} \text{N.R.}
\]  

Scheme A presents a three-step synthesis designed to prepare PPBu\textsuperscript{t}H. Although it was not the most direct route for preparing tertiary/secondary diphosphine ligands containing flexible trimethylene linkages, it is, perhaps, the safest. The first two reactions in Scheme A have already been discussed in detail by the author\textsuperscript{104} and, therefore, only the final step (Eq. 24) will be discussed at this time.

Reduction of phosphine oxides and phosphinates have been carried out with hexachlorodisilane, Si\textsubscript{2}Cl\textsubscript{6}\textsuperscript{173} trichlorosilane, SiHCl\textsubscript{3}\textsuperscript{174,175}, calcium hydride, CaH\textsubscript{2}\textsuperscript{179} sodium borohydride, NaBH\textsubscript{4}\textsuperscript{180} and, lithium aluminum hydride, LAH\textsuperscript{179,181}. Since an earlier attempt at reducing diphenyl[(3-ethyl t-butylphosphinate)propyl]phosphine, Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{3}P(O)(OEt)Bu\textsuperscript{t}, with diphenylsilane had failed, reduction of Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{3}P(O)(OEt)Bu\textsuperscript{t} (9) was attempted using a LAH/THF slurry. After compound 9 was dissolved in THF, it was added dropwise to a LAH/THF slurry. Since the reduction of phosphorus(V) to phosphorus(III) compounds is highly
exothermic, the reaction mixture was maintained at 0°C during the addition. To insure complete reduction, the reaction mixture was refluxed for 2 days. After destruction of excess LAH with distilled H₂O and separation of the THF layer from the H₂O layer, a phosphorus-31 NMR spectrum was obtained. The phosphorus-31 NMR spectrum afforded two signals at 58.2 ppm and -18.6 ppm for the ethyl t-butylphosphinate end and the diphenylphosphino end of compound 9, respectively.

Since LAH has been demonstrated to reduce isopropyl methylphosphinates and isopropyl phenylphosphinates, and diphenylsilane, Ph₂SiH₂, was shown to be a non-selective reducing agent for phosphine oxides and phosphinates, it was surprising that no appreciable reduction of compound 9 occurred. Because reduction of phosphinates and phosphates is a common method of preparing primary, secondary and tertiary phosphines, an explanation for the lack of reactivity of compound 9 is warranted.

Reaction mechanisms involving phosphines and metal phosphine complexes are often interpreted on the basis of the steric and electronic properties of the phosphines. Tolman's cone angle, θ, and substituent contribution x₁ (where x₁ is additive and x₁ = 0 for t-Bu) are measures of the steric and electronic (σ-donor and π-donor or π-acceptor) properties of phosphines. An attempt to correlate the cone angle and substituent contribution of phosphinates and phosphine oxides to their ability to undergo reduction with either diphenylsilane, Ph₂SiH₂, or lithium aluminum hydride, LAH, has been made, the results of which are presented in Table 15.
### Table 15

A Survey of the Reduction Reactions Used to Synthesize Tertiary and Secondary Phosphines

\[
\begin{align*}
R_3P(0) + Ph_2S1H_2 & \rightarrow R_3P \\
R_3P(0) + LAH & \rightarrow R_3P \\
R_2P(0)(OR') + Ph_2S1H_2 & \rightarrow R_2PH \\
R_2P(0)(OR') + LAH & \rightarrow R_2PH
\end{align*}
\]

<table>
<thead>
<tr>
<th>Phosphine Oxide</th>
<th>1a</th>
<th>1b</th>
<th>2a</th>
<th>2b</th>
<th>Cone Angle</th>
<th>( \theta_1 \times \theta_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph(_3)P(0)</td>
<td>yes</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>145</td>
<td>12.9</td>
</tr>
<tr>
<td>(CH(_2)_3)Ph(_2)EtP(0)(^a)</td>
<td>yes</td>
<td>no</td>
<td>---</td>
<td>---</td>
<td>127</td>
<td>10.4</td>
</tr>
<tr>
<td>Ph(_2)P(0)(OMe)</td>
<td>---</td>
<td>---</td>
<td>yes</td>
<td>---(^b)</td>
<td>132</td>
<td>16.3</td>
</tr>
<tr>
<td>(CH(_2)_3)P(0)(OPr(^i))(^2)(^a)</td>
<td>---</td>
<td>---</td>
<td>---(^b)</td>
<td>yes</td>
<td>116(^c)</td>
<td>14.4</td>
</tr>
<tr>
<td>(CH(_2)_3)PhP(0)(OPr(^i))(^a)</td>
<td>---</td>
<td>---</td>
<td>---(^b)</td>
<td>yes</td>
<td>123(^c)</td>
<td>12.4</td>
</tr>
<tr>
<td>(CH(_2)_3MeP(0)(OPr(^i))(^a)</td>
<td>---</td>
<td>---</td>
<td>yes</td>
<td>yes</td>
<td>113(^c)</td>
<td>10.7</td>
</tr>
<tr>
<td>(CH(_2)_3t-BuP(0)(OEt)(^a)</td>
<td>---</td>
<td>---</td>
<td>no</td>
<td>no</td>
<td>127(^c)</td>
<td>8.6</td>
</tr>
</tbody>
</table>

\(^a\)For diphosphine ligands of the general type, \(R_2P(CH_2)_3PR_2\), when \(n = 3\), \(\theta\) for the trimethylene backbone for the chelating phosphine was assumed to be 90°.\(^{13}\)

\(^b\)Data not available.

\(^c\)Cone angles are approximated using the equation \(\theta = 2/3 \theta_1 (\theta_1/2)\).
A comparison of the reactions with the steric and electronic properties of the phosphorus(V) compounds suggests that reduction reactions with \( \text{Ph}_2\text{SiH}_2 \) are favored when the sum of the net substituent contributions, \( \sum x_i \), is large. Steric factors do not seem to be as important in reductions with \( \text{Ph}_2\text{SiH}_2 \). For example, the cone angle for triphenylphosphine oxide (\( \theta = 145^\circ, \sum x_i = 129 \)) is much larger than the cone angle for the isopropyl methylphosphinate group (\( \theta = 113, \sum x_i = 10.7 \)), which have similar net contributions, and react with \( \text{Ph}_2\text{SiH}_2 \) to yield the corresponding phosphines. However, \( \sum x_i \) is much larger for triphenylphosphine oxide than for the ethyl t-butylphosphinate moiety (\( \theta = 127, \sum x_i = 8.6 \)), which also has a large cone angle, but fails to react with \( \text{Ph}_2\text{SiH}_2 \).

In contrast to reductions with \( \text{Ph}_2\text{SiH}_2 \), LAH reductions appear to be more dependent on steric factors than electronic factors. LAH reductions seem to be favored when cone angles are small. The isopropyl methylphosphinate group (\( \theta = 113, \sum x_i = 10.7 \)) has a much smaller cone angle than the diphenylphosphine oxide group (\( \theta = 127, \sum x_i = 10.4 \)), which has nearly identical net substituent contribution, and fails to undergo reduction with LAH. The other remaining phosphorus(V) compounds that were reduced also have relatively small cone angles (113-123°). In conclusion, it appears that phosphorus(V) can be reduced with net substituent contributions that are large (\( \sum x_i > 10.4 \)) or with LAH if cone angles are small (\( \theta < 127^\circ \)).

Careful inspection of the steric and electronic parameters for the phosphinate end of compound 9, \( \text{t-BuP}(\text{O})(\text{OEt})_2 \), reveal that neither of the two previously mentioned criteria for reduction exist. The approximate
cone angle for the phosphinate is 127°, which is too large for LAH reduction, and a net substituent contribution equal to 8.6, which is too small for Ph₂SiH₂ reduction.

Since the attempted reductions of compound 9 failed, two alternative syntheses (Schemes B and C) were tried. Both of these reaction schemes involve the direct coupling between diphenyl(3-chloropropyl)phosphine, Ph₂P(CH₂)₃Cl, and t-butylphosphide, t-BuP(H)M (M = Na, Li). The major difference between the two schemes is the manner in which the organophosphide was generated. In Scheme B, a toluene solution of Ph₂P(CH₂)₃Cl was added dropwise to a flask containing t-butylphosphine and sodium metal in liquid ammonia at -78°C. As the reaction vessel was allowed to warm to room temperature, the liquid ammonia evaporated. To insure reaction completion, the mixture was stirred overnight. After destruction of excess sodium metal was complete, a phosphorus-31 NMR spectrum of the organic layer was obtained. The ³¹P(¹H)-NMR spectrum afforded two signals at -18.9 and -82.3 ppm, assignable to starting material. The diphenyl(3-chloropropyl)phosphine, Ph₂P(CH₂)₃Cl, has a ³¹P(¹H) NMR chemical shift at -18.9 ppm. The t-butylphosphine, which was prepared from the reduction of t-BuPCl₂ (δ³¹P = 185.1 ppm) with vitride, has a ³¹P NMR chemical shift of -82.3 ppm (¹JₚH = 186 Hz, ³JₚH = 11.8 Hz), whereas the known diphenyl(3-t-butylethylphosphino)phosphine, Ph₂P(CH₂)₂P(H)Bu⁺, has ³¹P chemical shifts at -13.0 ppm and -19.8 ppm for the Ph₂P group and P(H)Bu⁺ group, respectively.

A coupling reaction between Ph₂P(CH₂)₃Cl and t-butylphosphine in the presence of lithium diisopropylamide, LDA, was attempted to produce
PPBu\textsuperscript{t}H in a manner exactly analogous to that used by Green\textsuperscript{154} to prepare (p-CF\textsubscript{3})\textsubscript{6}C\textsubscript{6}H\textsubscript{4})\textsubscript{2}P(\textsubscript{2}CH\textsubscript{2})\textsubscript{3}P(H)Ph. p-CF\textsubscript{3}PPH, another chelating tertiary/secondary diphosphine ligand used in this study. (Refer to Scheme C.) Lithium diisopropylamide was added slowly to a flask containing Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{3}Cl and t-BuPH\textsubscript{2} maintained at -78°C. The resulting solution was allowed to warm to room temperature and stir overnight. To insure reaction completion, the solution was refluxed for three hours. The \textsuperscript{31}P NMR spectrum gave rise to three signals at -18.9, -27.6, and -81.8 ppm. The signals at -18.9 and -81.8 were assigned to the starting materials, Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{3}Cl and t-BuPH\textsubscript{2}, respectively. The signal at -27.6 ppm was assigned to the t-BuP(H) end of the ligand PPBu\textsuperscript{t}H. Since the \textsuperscript{31}P chemical shifts for the diphenylphosphino group for both Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{3}Cl and PPBu\textsuperscript{t}H would be expected to be nearly identical, a separate signal for the diphenylphosphino group of PPBu\textsuperscript{t}H would not be expected. Based on the \textsuperscript{31}P NMR intensities only -13% of the desired ligand was formed. A possible explanation for the lack of coupling between diphenyl(3-chloropropyl)phosphine and t-butylphosphine represented in Schemes B and C is the lack of formation of the t-butylphosphide.

Deprotonation of primary and secondary phosphines with LDA to form the corresponding organophosphides was found to be favored when the net substituent contributions of phosphines are large (\(\varepsilon_1x_1 > 11\)) and the cone angles are small (\(\phi < 130^\circ\)).\textsuperscript{154} Based on this generalization, t-BuPH\textsubscript{2} (\(\varepsilon_1x_1 = 16.6, \phi = 119^\circ\)) would have been predicted to react with Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{3}Cl in the presence of LDA to yield the ligand PPBu\textsuperscript{t}H. However, this reaction does not occur. Since organophosphide formation
with LDA occurs through deprotonation of either the primary or secondary phosphine, the strength of the phosphorus-hydrogen bond, pKₐ value, appears to be the most important factor in predicting reactions with LDA.

Streuli and others⁹³,⁹⁴ have shown that tertiary alkyl phosphines are more basic than tertiary aryl phosphines and any tertiary phosphine is more basic than its corresponding secondary phosphine which in turn is more basic than the primary phosphine. Analogous to amines, Streuli et al. utilized the Taft equation,¹⁸⁵ \( \log \frac{k}{k_0} = \sigma \sigma^* \), to correlate the pKₐ of phosphines to the sum of the inductive effects of the substituent, \( \sigma \sigma^* \). This author has made an attempt to correlate the pKₐ values of some primary and secondary phosphines to their reactivity with LDA.

A comparison of pKₐ values for both primary and secondary phosphines with their reactivity towards LDA, presented in Table 16, suggests that the phosphines can be divided into two classes: primary and secondary,⁹³ and that successful reactions between phosphines and LDA appear to be favored when pKₐ values are relatively small. In conclusion, reactions of LDA with primary phosphines appear to be favored when pKₐ ≤ 0.3, whereas reactions with secondary phosphines seem to be favored when pKₐ ≤ 4.4.

The major impetus for synthesizing tertiary/secondary phosphine ligands is to investigate the steric and electronic effects of the substituents bound to the phosphorus atom in both organophosphino and organophosphido transition metal complexes. Earlier reports by Meek and Waid on palladium(II) and platinum(II) transition complexes containing the tertiary/secondary phosphine ligands, \( \text{R}_2\text{P(CH}_2\text{)}_3\text{P(H)Ph} \) (R = Ph, Cy:...
Table 16
A Survey of Reactions of Primary and Secondary Phosphines with Lithium diisopropylamide

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>$\kappa^a$</th>
<th>$pK_{a}^{b,c}$</th>
<th>Deprotonation with LDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhPH$_2$</td>
<td>1.58</td>
<td>-1.71</td>
<td>yes</td>
</tr>
<tr>
<td>CyPH$_2$</td>
<td>.83</td>
<td>.269</td>
<td>yes</td>
</tr>
<tr>
<td>$t$-BuPH$_2$</td>
<td>.68</td>
<td>.665</td>
<td>N.R.</td>
</tr>
<tr>
<td>Ph$_2$PH</td>
<td>1.69</td>
<td>.719 (.03)$^d$</td>
<td>yes</td>
</tr>
<tr>
<td>Et$_2$PH</td>
<td>.29</td>
<td>4.37</td>
<td>yes</td>
</tr>
<tr>
<td>$t$-Pr$_2$PH</td>
<td>.11</td>
<td>4.84</td>
<td>N.R.</td>
</tr>
<tr>
<td>Cy$_2$PH</td>
<td>.19</td>
<td>4.63 (4.55)$^d$</td>
<td>N.R.</td>
</tr>
</tbody>
</table>

$^a$Data from reference 185, page 619.

$^b$ $pK_{a}$ values for primary phosphines are approximated using the equation $pK_{a} = 2.46 - 2.64 \times \kappa^a.^{183}$

$^c$ $pK_{a}$ values for secondary phosphines are approximated using the equation $pK_{a} = 5.13 - 2.61 \times \kappa^a.^{183}$

$^d$Data presented in parentheses was taken from reference 184.
PPH, CyPPH, respectively), prompted the author to synthesize the ligands \( R_2P(\text{CH}_2)_3\text{P(H)Me} \) (\( R = \text{Ph, Cy; PPMH, CyPPMH, respectively} \)). Comparisons of the differences of the steric and electronic properties of these four ligands, as well as the ligand \((p-\text{CF}_3\text{C}_6\text{H}_4)_2\text{P(\text{CH}_2)_3P(H)Ph, p-\text{CF}_3\text{PPH}}\), have been noted and are described herein.

B. Mononuclear Palladium(II) and Platinum(II) Complexes of the Ligands PPH, CyPPH, PPMH, CyPPMH and p-CF\(_3\)PPH

In order to investigate the physical properties of the chelating tertiary/secondary diphosphine ligands, both palladium(II) and platinum(II) chloro and iodo complexes were synthesized (10).

These complexes are prepared by displacing the coordinated diolefin from \( \text{MX}_2\text{COD} \) (\( M = \text{Pd, Pt; } X = \text{Cl, I} \)) with the appropriate diphosphine ligands at room temperature in either benzene or dichloromethane according to Equation 28. The infrared spectra for these types of compounds (Figure 1) display the characteristic pattern for the diphosphine ligands, with the exception that the PH stretching frequency, \( \nu_{\text{PH}} \), observed between 2440 and 2275 cm\(^{-1}\), was absent.
Figure 1. The infrared spectrum of PtI$_2$(p-CF$_3$PPH)
The $^{31}\text{P}(^1\text{H})$ NMR spectra for the palladium or platinum monometallic complexes give rise to either an AB- or an ABX- spin system pattern, respectively. A typical $^{31}\text{P}(^1\text{H})$ NMR spectrum for the monometallic complexes is presented in Figure 2. The spectrum consists of a first-order AB subspectra (the two large transitions) and four smaller transitions due to the large coupling of each phosphorus nucleus with the platinum-195 nucleus ($I = 1/2$, natural abundance $= 33.7\times 112$). The small coupling, which turns all transitions into doublets, is due to the cis-phosphorus-phosphorus coupling, $^2J_{pp}$, between the two inequivalent phosphorus atoms of the coordinated ligand. Unequivocal assignment of the secondary phosphino nucleus was accomplished by obtaining phosphorus-31 DEPT$^{187}$ (Distortionless Enhancement by Polarization Transfer) and proton-coupled DEPT NMR spectra (See Figures 3 and 4.) Since DEPT experiments require polarization transfer from protons to phosphorus, only phosphorus nuclei which are bound directly to a proton will display a signal in the NMR spectrum. (In these cases, only the signal for the secondary phosphino group will be displayed.) Elimination of the broadband $^1\text{H}$ decoupling causes the signal due to the secondary phosphino group to be split into a doublet ($^1J_{PH} = 400$ Hz). Both the coupled and decoupled DEPT experiments prove that the upfield signals in the $^{31}\text{P}(^1\text{H})$ NMR spectra are due to the secondary phosphino...
Figure 2. The $^{31}P(\text{\textsuperscript{1}H})$ NMR Spectrum of PtI$_2$(CyPPM$_4$)
Figure 3. The $^{31}P(\text{H})$ DEPT NMR spectrum of PtI$_2$(CyPPNH)
Figure 4. The $^{31}$p NMR coupled DEPT NMR spectrum of Pt$_2$(CyPPMH)
group. The phosphorus-31 NMR data for both the palladium and platinum monometallic complexes are presented in Table 17.

1) $^{31}$P NMR Spectra for the Monomeric Complexes

From close inspection of the data presented in Table 17, some correlations concerning the phosphorus-31 NMR chemical shifts ($\delta_{P(1)}$ and $\delta_{P(2)}$), where $\delta_{P(1)}$ denotes the $^{31}$P NMR chemical shift for the secondary phosphino group and $\delta_{P(2)}$ the shift for the tertiary phosphino group, the two-bond phosphorus-phosphorus coupling constant ($^{2}J_{PP}$), the one-bond phosphorus-hydrogen coupling constant ($^{1}J_{PH}$), and when $M = Pt$, the one-bond platinum-phosphorus coupling constants ($^{1}J_{PtP(1)}$ and $^{1}J_{PtP(2)}$), can be made. It has been shown that $^{1}J_{PtP}$ values depend on the Fermi contact term and can be described by Equation 29, where $Pt^{2}$ (or $P^{2}$) is

$$|^{1}J_{PtP}| = \alpha_{Pt}^{2}\alpha_{P}^{2}\frac{S_{Pt}(6S)(0)}{\Delta E}b_{P}(3S)(0)$$

the s-character of the relevant bonding orbital, $S_{Pt}(6S)(0)$ (or $S_{P}(3S)(0)$) is the density of the ns orbital at the platinum (or phosphorus) nucleus, and $\Delta E$ is a mean singlet-quartet excitation energy. Therefore, changes in the s-character of the bonding orbital, $\alpha_{Pt}^{2}\alpha_{P}^{2}$, result in differences in the values of $^{1}J_{PtP}$. Trans-influence series have been observed on the basis of $^{1}J_{HX}$ ($X = ^{13}C$ or $^{31}P$) trans to the ligand which is varied. When the trans ligand is more tightly bound to the metal center, it demands more s and d character from the metal hybrid orbitals, thus lowering the amount of s-character available for the phosphorus-31 nucleus. Therefore a high trans-influence ligand results in a low $^{1}J_{HX}$. A similar result might be
# Table 17

**Phosphorus-31 NMR Data for Palladium and Platinum Monometallic Type Complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \delta (P1) )</th>
<th>( \delta (P2) )</th>
<th>( J_{PP} )</th>
<th>( J_{PH} )</th>
<th>( J_{PtP(1)} )</th>
<th>( J_{PtP(2)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{PdCl}_2(\text{PPH}) )</td>
<td>-15.7</td>
<td>10.4</td>
<td>12.2</td>
<td>438</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>( \text{PdCl}_2(\text{PPMH}) )</td>
<td>-31.4</td>
<td>10.6</td>
<td>13.1</td>
<td>434</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>( \text{PdCl}_2(\text{CyPPH}) )</td>
<td>-14.1</td>
<td>31.1</td>
<td>7.3</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>( \text{PdCl}_2(\text{CyPPMH}) )</td>
<td>-27.1</td>
<td>30.7</td>
<td>0.0</td>
<td>431</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>( \text{PdCl}_2(\text{CF}_3\text{PPH}) )</td>
<td>-15.6</td>
<td>10.9</td>
<td>0.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>( \text{PtCl}_2(\text{PPH}) )</td>
<td>-28.9</td>
<td>-5.7</td>
<td>24.4</td>
<td>460</td>
<td>3256</td>
<td>3403</td>
</tr>
<tr>
<td>( \text{PtI}_2(\text{PPH}) )</td>
<td>-32.8</td>
<td>-11.7</td>
<td>18.7</td>
<td>444</td>
<td>3030</td>
<td>3206</td>
</tr>
<tr>
<td>( \text{PtCl}_2(\text{PPMH}) )</td>
<td>-48.8</td>
<td>-5.7</td>
<td>23.6</td>
<td>427</td>
<td>3160</td>
<td>3443</td>
</tr>
<tr>
<td>( \text{PtI}_2(\text{PPMH}) )</td>
<td>-47.5</td>
<td>-10.4</td>
<td>19.2</td>
<td>446</td>
<td>2918</td>
<td>3249</td>
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<tr>
<td>( \text{PtCl}_2(\text{CyPPH}) )</td>
<td>-28.8</td>
<td>7.5</td>
<td>19.7</td>
<td>430</td>
<td>3390</td>
<td>3303</td>
</tr>
<tr>
<td>( \text{PtI}_2(\text{CyPPH}) )</td>
<td>-32.6</td>
<td>3.7</td>
<td>14.7</td>
<td>433</td>
<td>3188</td>
<td>3143</td>
</tr>
<tr>
<td>( \text{PtCl}_2(\text{CyPPMH}) )</td>
<td>-45.0</td>
<td>7.9</td>
<td>20.1</td>
<td>420</td>
<td>3271</td>
<td>3356</td>
</tr>
<tr>
<td>( \text{PtI}_2(\text{CyPPMH}) )</td>
<td>-47.4</td>
<td>4.2</td>
<td>15.2</td>
<td>424</td>
<td>3064</td>
<td>3186</td>
</tr>
<tr>
<td>( \text{PtMe}_2(\text{PPH}) )</td>
<td>-18.1</td>
<td>3.3</td>
<td>17.7</td>
<td>--</td>
<td>1654</td>
<td>1805</td>
</tr>
<tr>
<td>( \text{PtMe}_2(\text{CyPPH}) )</td>
<td>-17.3</td>
<td>4.6</td>
<td>18.7</td>
<td>--</td>
<td>1748</td>
<td>1773</td>
</tr>
<tr>
<td>( \text{PtCl}_2(\text{CF}_3\text{PPH}) )</td>
<td>-29.0</td>
<td>-5.2</td>
<td>22.7</td>
<td>449</td>
<td>3199</td>
<td>3422</td>
</tr>
<tr>
<td>( \text{PtI}_2(\text{CF}_3\text{PPH}) )</td>
<td>-34.5</td>
<td>-12.8</td>
<td>19.0</td>
<td>429</td>
<td>2979</td>
<td>3233</td>
</tr>
</tbody>
</table>

---

*Chemical shifts are reported in ppm relative to 85% H\(_3\)PO\(_4\); P(1) denotes the secondary phosphine; P(2) the tertiary phosphine.*

*Coupling constants reported in Hz.*

*Data from reference 49.*

*Data from reference 154.*
expected for the cis-ligand and in 1987 Hersh and Honeychuck reported on the cis-effect for some tungsten carbonyl nitrosyl complexes. Their results showed $^1J_{HP}$ was largest for complexes which contained weakly coordinated ligands, and that as the donating ability of the cis-ligand increase, $^1J_{HP}$ decreased. By similar reasoning, complexes containing unsymmetrical cis-phosphine ligands might be expected to display a linear correlation between $^1J_{PtP(1)}$ and $^1J_{PtP(2)}$ as the donor ability of the phosphine ligands was varied and the trans-ligands remained constant. The complexes described in this manuscript are such systems. As expected a correlation between $^1J_{PtP(1)}$ and $^1J_{PtP(2)}$ is observed (See Figure 5). Simply stated if P(2) requires more s- and d-character from the metal hybrid orbitals then the amount of s-character available for P(1) will be less and $^1J_{PtP(1)}$ will be smaller than $^1J_{PtP(2)}$ (See Table 17).

Ligand effects on the phosphorus-31 NMR chemical shift, $\delta_31p$, for metal complexes are difficult to interpret, since $\delta_31p$ is affected by the steric requirements and electronic contributions of the substituents bound to the phosphorus nucleus, as well as the other ligands bound to the metal. From the data presented in Table 17, high field shift of $\delta_31p$ and a decrease in $^1J_{PtP}$ occurs when $X$ is changed from Cl to I. These changes are consistent with the trans-influence ability of I compared to Cl. However, for similar complexes, i.e., PtCl$_2$(PPH) and PtCl$_2$(PPhH), changes in $^1J_{PtP(2)}$ which do not correspond to changes in $\delta P(2)$ may be related to the σ-donor ability of the cis-secondary phosphino group. Plots of $^1J_{PtP(2)}$ versus $\delta P(2)$ give rise to a nearly linear correlation which, in general, shows that as $^1J_{PtP(2)}$
Figure 5. Plots of $^{1}J_{PtP(2)}$ versus $^{1}J_{PtP(1)}$ for PtX$_2$(diphosphine) complexes.
Figure 6. Plots of $^{1}J_{PtP}(2)$ versus $\delta_{P(2)}$ for Pt$_{2}$X$_{2}$(diphosphine) complexes
increases $\delta p(2)$ is shifted upfield. Since the larger $^1J_{PtP}(2)$ values (shorter Pt-P bonds) are presumably due to the $\sigma$-donor ability of the differing secondary cis-phosphino groups (i.e., P(H)Ph versus P(H)Me), it seems that the methylphosphino group is a better $\sigma$-donor than the phenylphosphino group. However, inspection of the $^1J_{PtP}(1)$ values presented in Table 17 appears to contradict this conclusion, i.e., $^1J_{PtP}(1) = 3160$ Hz and 3256 Hz for P(H)Me and P(H)Ph, respectively.

An explanation for this apparent reversal of the $^1J_{PtP}(1)$ values can be found by examining the steric and electronic properties for the diphosphine ligands (Table 18). Giering et al. reported that phosphines could be divided into three classes: I) $\sigma$-donor/$\pi$-donor phosphines; II) $\sigma$-donor phosphines; and, III) $\sigma$-donor/$\pi$-acceptor phosphines. Phosphines belonging to class I were found to have pKa values from 8.69 to 9.70 and cone angles ranging from 132° to 170°. Examples of class I phosphines are Bu$_3$P and Cy$_3$P. Class II phosphines consisted mainly of mixed aryl/alkyl tertiary phosphines with pKa's from 2.73 to 8.65 and cone angles between 118° and 145°. Class III phosphines (more correctly phosphites) had pKa's ranging from -1.20 to 4.0 and cone angles between 107° to 145°. The difference between these three classes of phosphines is their ability to accept $\pi$-electron density from the metal center into the $\pi^*$ orbital of the ligand. If the phosphine can accept electron density from the metal center, then the metal-phosphorus bond would be expected to have more double bond character and therefore be shorter. This decrease in bond length should be reflected by a larger $^1J_{MP}$. 


Table 1B
Steric and Electronic Properties for the Tertiary/Secondary Diphosphine Ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$e$ $^{bc}$</th>
<th>$\varepsilon_{x_1}$</th>
<th>$\varepsilon^d$</th>
<th>$pK_a$ $^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPH</td>
<td>127 (107)</td>
<td>10.2 (14.2)</td>
<td>1.085 (0.975)</td>
<td>5.25 (2.59)</td>
</tr>
<tr>
<td>CyPPH</td>
<td>143 (107)</td>
<td>1.8 (14.2)</td>
<td>-0.415 (0.975)</td>
<td>6.74 (2.59)</td>
</tr>
<tr>
<td>PPMH</td>
<td>127 (98)</td>
<td>10.2 (12.5)</td>
<td>1.085 (0.375)</td>
<td>5.25 (4.15)</td>
</tr>
<tr>
<td>CyPPMH</td>
<td>143 (98)</td>
<td>1.8 (12.5)</td>
<td>-0.415 (0.375)</td>
<td>6.74 (4.15)</td>
</tr>
<tr>
<td>p-CF$_3$PPH</td>
<td>--- (107)</td>
<td>--- (14.2)</td>
<td>--- (0.975)</td>
<td>--- (2.59)</td>
</tr>
</tbody>
</table>

$^a$Values in parentheses are for the secondary phosphino-group of the ligand, P(1).

$^b$Approximate cone angles were obtained using the equation

$\theta = 2/3 \varepsilon_{x_1} \theta_1/2$. $^{13}$

$^c$For diphosphine ligands of the general type, $R_2P(CH_2)_nPR_2$, when $n = 3$, $\theta$ for the trimethylene linkage was assumed to be 90°. $^{13}$

$^d$Data from reference 185, page 619.

$^e$p$K_a$ values calculated according to reference 183.
Based on their $pK_a$ values, the tertiary phosphino end of the diphosphine ligands used in this investigation can be classified, according to Giering's findings, as class II (α-donor) phosphines, whereas the secondary phosphino end of the ligands are class I (α-donor/π-acceptor) phosphines. Therefore, if the length of the metal-phosphorus bond is reflected by the magnitude of $1J_{HP}$, then $1J_{PtP(1)}$ for $P(\text{H})\text{Me}$ would be expected to be smaller than $1J_{PtP(1)}$ for $P(\text{H})\text{Ph}$, not because $P(\text{H})\text{Ph}$ is a better α-donor than $P(\text{H})\text{Me}$, but because $P(\text{H})\text{Ph}$ is a better π-acceptor.

Since $1J_{HP}$ has traditionally been thought to depend solely on the α-donor ability of the phosphine ligand, it would be interesting to see which factor, α-donor ability or π-acceptor capability, is predominate in determining $1J_{HP}$. Since the tertiary phosphino end of the ligand is class II (α-donor) and the secondary phosphino end is class I (α-donor/π-acceptor), comparing $1J_{PtP(2)}$ with $1J_{PtP(1)}$ obtained for the PtX$_2$(diphosphine) complexes ($X = \text{Cl, I};$ diphosphine = PPH, CyPPH, PPMH, CyPPMMH, p-CF$_3$PPH) should allow for such an evaluation. If π-acceptor capability is more important in determining the magnitude of $1J_{PtP}$ than α-donor ability, then $1J_{PtP(1)}$ would be expected to be larger than $1J_{PtP(2)}$. This, however, is not the case, with the exception of PtX$_2$(CyPPH) ($X = \text{Cl, I}$), $1J_{PtP(2)} > 1J_{PtP(1)}$, thereby indicating that α-donor ability is the predominate factor in determining $1J_{HP}$. Perhaps $1J_{PtP(1)}$ is greater than $1J_{PtP(2)}$ for PtX$_2$(CyPPH) and not PtX$_2$(CyPPMMH) because the electron density placed on the metal center by the Cy$_2$P group is so large that π-backbonding becomes important. (Recall that $P(\text{H})\text{Ph}$ is a better π-acceptor group than $P(\text{H})\text{Me}$.)
Examination of the $^2J_{pp}$ cis-coupling constants presented in Table 17 shows that substitution of platinum for palladium causes $^2J_{pp}$ to increase, whereas substitution of I for Cl causes a decrease in $^2J_{pp}$. Again, these trends are as expected and have previously been reported. Since the magnitudes of $^2J_{pp}$ coupling constants for both Pt(0) and Pt(II) complexes have been shown to be affected by the electronegativity of the substituents bound to phosphorus, plots of Taft's constant versus $^2J_{pp}$ should give rise to linear correlations. (See Figures 7 and 8). Linear correlations are obtained between $\xi \sigma^*$ for the tertiary phosphino group ($\xi \sigma^*_P(\text{II})$) and $^2J_{pp}$, but not for $\xi \sigma^*_P(\text{I})$ and $^2J_{pp}$. These results can also be explained by examining the $\sigma$-donor ability and $\pi$-acceptor capability of the tertiary phosphino and secondary phosphino groups of the ligands. As stated previously, the $\sigma$-donor ability of phosphines seems to be the dominate factor in determining the magnitude of $^1J_{PtP}$, and the $\sigma$-donor ability of the tertiary phosphino groups ($\text{Cy}_2\text{P}$, $\text{Ph}_2\text{P}$, ($\text{p-CF}_3\text{C}_6\text{H}_4$)$_2\text{P}$) is greater than the secondary phosphino groups ($\text{P(H)}\text{Ph}$, $\text{P(H)}\text{Me}$). Therefore, since the two-bond phosphorus-phosphorus coupling is transmitted through the metal center, $\sigma$-donor ability should also be reflected in and predominate $^2J_{pp}$ couplings. The phosphino end of the ligands which has a greater $\sigma$-donor ability ($\text{Cy}_2\text{P}$, $\text{Ph}_2\text{P}$, ($\text{p-CF}_3\text{C}_6\text{H}_4$)$_2\text{P}$) would be expected to, and does, linearly correlate to $\xi \sigma^*$ (Figure 7), whereas the other end would not (Figure 8). This similarity between $^1J_{PtP}(\text{II})$ and $^2J_{pp}$ can also be seen in Figures 9 and 10.

For the free ligands PPH, CyPPH, PPMH, CyPPMH and p-CF$_3$PPH, the one-bond phosphorus-hydrogen coupling constants are 207, 205, 194, 194.
Figure 7. Plots of $\sigma^*$ versus $^{2}J_{pp}$ for PtX$_2$(diphosphine) complexes
Figure 8. Plots of $I \sigma^*_{P(1)}$ versus $^2J_{pp}$ for Pt$X_2$(diphosphine) complexes
Figure 9. Plots of $^{1}J_{PtP(2)}$ versus $^{2}J_{pp}$ for PtX$_2$(diphosphine) complexes.
Figure 10. Plot of $^1J_{pp}(2)$ versus $^2J_{pp}$ for PtX$_2$(diphosphine) complexes
and 207 Hz, respectively. Coordination of the ligands to a metal center causes the magnitude of $^1J_{PH}$ to increase by -200 Hz (see Table 17). This large increase has previously been observed\textsuperscript{49,101} and was attributed to increases in s-orbital character of the phosphorus-hydrogen bonding orbital upon complexation of the ligand. As stated earlier, the Fermi contact term is the dominant factor in determining the magnitude of the one-bond couplings to phosphorus and is dependent on the amount of s-orbital character in the phosphorus-hydrogen bond. Therefore, increase of $^1J_{PH}$ could be due to increases in the s-character of the phosphorus-hydrogen bond due to rehybridization of the sp$^3$ orbitals of the coordinated phosphine. The magnitude of $^1J_{PH}$ for the P(H)Ph moiety is larger than $^1J_{PH}$ for the P(H)Me group, e.g., $^1J_{PH} = 460$ and 427 Hz, respectively, for PtCl$_2$(diphosphine). Although replacing chloride with iodide causes the magnitude of $^1J_{PH}$ to decrease for the P(H)Ph group and to increase for the P(H)Me group (e.g., $^1J_{PH} = 444$ and 446 Hz, respectively, for PtI$_2$(diphosphine)), in general, $^1J_{PH}$ for the P(H)Ph moiety is still larger than $^1J_{PH}$ for the P(H)Me moiety. Unfortunately, attempts to correlate the $^1J_{PH}$ for the secondary phosphino group with their respective $pK_a$ or $\sigma^*$ values to investigate the basicity of the coordinated secondary phosphino-group or to examine $\sigma$-donor/$\pi$-acceptor strength in $^1J_{PH}$, proved to be unsuccessful.

The phosphorus-31 NMR chemical shifts for the PtX$_2$(diphosphine) complexes appear to be dependent on both the steric requirements and electronic contributions of the substituents bound to the phosphorus nucleus. The phosphorus-31 NMR chemical shift, $\delta_{31P}$, moves upfield as the cone angle decreases (Figure 11).\textsuperscript{13} As the phosphine basicity
Figure 11. Plots of $\delta_{31p}$ versus Tolman's cone angle, $\theta$, for Pt$\text{II}_2$-(diphosphine) complexes
Figure 12. Plots for $\delta_{31}$ versus $\Sigma \sigma^*$ for PtI$_2$(diphosphine) complexes.
increases for the secondary phosphino group, $\delta_{P(1)}$ is shifted upfield. In contrast, the resonance for the tertiary phosphino group moves downfield with increasing basicity (Figure 12). A possible explanation for this contradiction in the basicity trend is that steric considerations are more important in determining $\delta_{31P}$.

2) $^{195}\text{Pt}(^{1}H)$ NMR for the Monomeric Complexes

The $^{195}\text{Pt}(^{1}H)$ NMR spectra for the PtX$_2$(diphos) complexes consist of a doublet of doublets owing to the presence of the magnetically inequivalent phosphorus nuclei of the diphos ligand. A typical $^{195}\text{Pt}(^{1}H)$ NMR spectrum for the monometallic complexes is presented in Figure 13. The $^{195}\text{Pt}(^{1}H)$ NMR data for the PtX$_2$(diphos) complexes are given in Table 19.

Since the main contribution to the nuclear magnetic shielding of a heavy nucleus such as Pt-195 is the paramagnetic term, $\sigma_P$, the platinum-195 chemical shift, $\delta_{^{195}\text{Pt}}$, is affected by: (1) the mean inverse cube of the distance between the 5d and 6s orbitals of platinum ($r^{-3}$); (2) the inverse of the energy difference between the ground and excited states of the 5d and 6s electrons ($[E_n - E_0]^{-1}$); and (3) the asymmetry of the valence electron distribution about the platinum nucleus. Thus explanations and definition of simple trends in the platinum-195 NMR chemical shift, $\delta_{^{195}\text{Pt}}$, are difficult to make owing to the complex interactions of these three factors. However, three empirical trends which have emerged from the platinum data are: (a) replacing an alkyl substituent by an aryl substituent of a coordinated phosphine ligand causes $\delta_{^{195}\text{Pt}}$ to shift upfield; (b) decreases in the
Figure 13. The $^{195}\text{Pt}^{1\text{H}}$ NMR spectrum for PtI$_2$(PPMH)
Table 19

Platinum-195 NMR Data for Platinum(II) Monometallic Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{195}\text{Pt}$</th>
<th>$^{1}\text{J}_{\text{PtP}(1)}$</th>
<th>$^{1}\text{J}_{\text{PtP}(2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtCl$_2$(PPH)</td>
<td>-4506</td>
<td>3256</td>
<td>3403</td>
</tr>
<tr>
<td>PtI$_2$(PPH)</td>
<td>-5355</td>
<td>3033</td>
<td>3206</td>
</tr>
<tr>
<td>PtCl$_2$(PPMH)</td>
<td>-4486</td>
<td>3157</td>
<td>3447</td>
</tr>
<tr>
<td>PtI$_2$(PPMH)</td>
<td>-5291</td>
<td>2917</td>
<td>3252</td>
</tr>
<tr>
<td>PtCl$_2$(CyPPH)$_b$</td>
<td>-4544</td>
<td>3390</td>
<td>3303</td>
</tr>
<tr>
<td>PtI$_2$(CyPPH)</td>
<td>-5345</td>
<td>3189</td>
<td>3142</td>
</tr>
<tr>
<td>PtCl$_2$(CyPPMH)</td>
<td>-4535</td>
<td>3272</td>
<td>3357</td>
</tr>
<tr>
<td>PtI$_2$(CyPPMH)</td>
<td>-5287</td>
<td>3058</td>
<td>3187</td>
</tr>
<tr>
<td>PtCl$_2$(p-CF$_3$PPH)</td>
<td>-4513</td>
<td>3209</td>
<td>3435</td>
</tr>
<tr>
<td>PtI$_2$(p-CF$_3$PPH)</td>
<td>-5374</td>
<td>2979</td>
<td>3232</td>
</tr>
<tr>
<td>[Pt(PPH)$_2$]$^{2+}$[Cl$_2$]</td>
<td>-5191</td>
<td>2360</td>
<td>2144</td>
</tr>
</tbody>
</table>

$^a$Chemical shifts are reported in ppm values relative to H$_2$PtCl$_6$; negative values are upfield from the standard. P(1) is the secondary phosphine part of the ligand, whereas P(2) is the tertiary end.

$^b$Data from reference 49.
electronegativity of the ligands bound to platinum cause the platinum-195 nucleus to become more shielded ($\delta_{195\text{Pt}}$ moves upfield); and, (c) increased covalent bonding between the platinum-195 nucleus and its ligand adds electron density to the metal center causing more negative chemical shifts. Concentration, temperature and solvent effects on $\delta_{195\text{Pt}}$ have been minimized by the use of nearly equal concentrations ($M = .03$) and the same solvent. Therefore, the chemical shift data presented in Table 19 should be consistent and empirical trends concerning the $\sigma$-donor/$\pi$-acceptor properties of the diphosphine ligands and $\delta_{195\text{Pt}}$ should be valid.

Replacement of iodide for chloride in the monomeric complexes causes $\delta_{195\text{Pt}}$ to shift upfield. Since the iodo ligand is both more electropositive and softer than chloro, this observation was as expected and consistent with empirical trends b and c. The platinum-195 chemical shift ordering for the PtCl$_2$(diphosphine) complexes is PtCl$_2$(CyPPH) > PtCl$_2$(CyPPM) > PtCl$_2$(p-CF$_3$PPH) > PtCl$_2$(PPH) > PtCl$_2$(PPMH) ($\delta_{195\text{Pt}}$ equals -4544, -4535, -4513, -4506, -4486 ppm, respectively). In contrast, the $\delta_{195\text{Pt}}$ ordering for the iodo complexes is PtI$_2$(p-CF$_3$PPH) > PtI$_2$(PPH) > PtI$_2$(CyPPH) > PtI$_2$(PPMH) > PtI$_2$(CyPPMH) (-5374, -5355, -5345, -5291, and -5287 ppm, respectively). Although the chemical shift orderings are different, they both are consistent with empirical trend a. For the chloro complexes, substitution of phenyl for methyl at the secondary phosphino group appears to be more important in determining $\delta_{195\text{Pt}}$ than at the tertiary phosphino group. In contrast, aryl/alkyl substitution at both the tertiary phosphino and secondary phosphino moiety appear to be equally important for the iodo complexes.
Another generality observed for platinum phosphine complexes is upfield phosphorus-31 NMR chemical shifts are concomitant with downfield platinum-195 chemical shifts. And although the chemical shift ordering trends appear to be dependent on either secondary or tertiary aryl/alkyl substitution, the $\delta_{31P}$ upfield/$\delta_{195Pt}$ downfield trend is observed for the monometallic chloro complexes. For example, for both PtCl$_2$(CyPPH) and PtCl$_2$(PPH)$_2$ $\delta_{P(1)} = -28.9$ ppm, but $\delta_{P(2)} = 7.5$ and $-5.7$ ppm, respectively. Based on the $\delta_{P(2)}$, the $\delta_{195Pt}$ for PtCl$_2$(CyPPH) would be expected to appear upfield from $\delta_{195Pt}$ for PtCl$_2$(PPH) ($\delta_{195} = -4544$, $-4513$ ppm, respectively). Similarly, for both PtCl$_2$(PPH) and PtCl$_2$(PMMH) ($\delta_{P(2)} = -5.7$ ppm), the $\delta_{P(1)} = -28.9$ and $-48.8$ ppm and $\delta_{195Pt} = -4535$ and $-4486$ ppm, respectively. For the PtI$_2$(diphosphine) complexes, the generalization was not observed. For example, for both PtI$_2$(CyPPH) and PtI$_2$(PPH) $\delta_{P(1)} = -32.7$ ppm, but $\delta_{P(2)} = 3.7$ and $-11.7$ ppm, respectively. Again based on $\delta_{P(2)}$, $\delta_{195Pt}$ for PtI$_2$(CyPPH) would be expected to be upfield from $\delta_{195Pt}$ for PtI$_2$(PPH). This, however, is not the case ($\delta_{195Pt} = -5345$ and $-5355$ ppm for PtI$_2$CyPPH and PtI$_2$(PPH), respectively). In contrast, the $\delta_{P(1)} = -32.6$ and $-47.4$ ppm for PtI$_2$(CyPPH) and PtI$_2$(CyPMMH), respectively, with $\delta_{195Pt} = 5345$ and $-5287$ ppm. Therefore, it would appear that the generalization of $\delta_{31P}$ upfield/$\delta_{195Pt}$ downfield also depends on whether aryl/alkyl substitution at the tertiary phosphino moiety is more important than at the secondary phosphino moiety.

For the chloro complexes this generalization does not appear to be dependent on either P(1) or P(2) substitution. However, for the iodo complexes this generalization only holds when substitution occurs at the
secondary phosphino moiety. Correlations of $\delta_{^{195}Pt}$ with $\delta P(1)$ and/or $\delta P(2)$ for both the chloro and iodo diphosphine platinum(II) complexes are presented in Figures 14 and 15. From the plots it would appear that $\delta_{^{195}Pt}$ is shifted downfield as $\delta P(2)$ shifts upfield for the PtCl$_2$-(diphosphine) complexes. However, for the PtI$_2$(diphosphine) complexes, $\delta_{^{195}Pt}$ is shifted downfield as $\delta P(1)$ shifts upfield. Exact linear correlations do not exist between $\delta_{^{195}Pt}$ and $\delta_{^{31}P}$ for either the chloro or iodo complexes, since the phosphorus-31 nucleus should not be affected by changes in the electronic environment to the same extent as the platinum-195 nucleus.

Since empirical trend a suggests, in apparent contrast to Figures 14 and 15, that changes at the secondary phosphino end of the ligand (P(1)) are more important than at the tertiary end (P(2)) for the chloro complexes and vice versa for the iodo complexes, a possible explanation is warranted. Larger steric requirements normally have the effect of deshielding the platinum-195 nucleus, possibly by distorting the angles about platinum, thus causing $\delta_{^{195}Pt}$ to become more positive.$^{139,140}$ Perhaps, the large difference in size between P(2) (for Cy$_2$P $\phi = 143^\circ$) and P(1) ($\phi = 107$ and 98 for P(H)Ph and P(H)Me, respectively) is the predominant factor in determining $\delta_{^{195}Pt}$ for the PtCl$_2$(diphosphine) complexes. Thus, making aryl/alkyl substitution at the secondary phosphino moiety more important for trend a and causing $\delta_{^{195}Pt}$ to be more dependent on $\delta P(2)$ (Figure 14). By virtue of the same argument, steric effects due to the diphosphine ligand may be less important in determining $\delta_{^{195}Pt}$ for the iodo complexes. Replacing a chloride ligand with an iodine ligand causes the steric crowding due to
Figure 14. Plots of $\delta_{195Pt}$ versus $\delta_{31P}$ for PtCl$_2$(diphosphine) complexes
Figure 15. Plots of $\delta_{195\text{Pt}}$ versus $\delta_{31\text{p}}$ for PtI$_2$(diphosphine) complexes
the halide ligand and the covalency of the platinum-halide bond to increase. (Recall $J_{Pt}^{(2)}$ is larger for the chloro complexes than the iodo complexes.) As the covalency of the platinum-halide bond increases, the electron density at the metal center increases. Therefore, the ability of the phosphine to remove electron density from platinum should be the predominant factor in determining $\delta_{195}^{Pt}$. Thus, a linear correlation between $\delta_{195}^{Pt}$ and $\delta_P^{(1)}$ suggests that the steric considerations for the phosphine are less important than the $\pi$-acceptor ability of the phosphine. (Recall: P(H)Ph was determined to be a better $\pi$-acceptor than P(H)Me.)

Downfield shifts in either the phosphorus-31 or the platinum-195 NMR spectrum are associated with deshielding of the magnetically active nucleus, whereas shielding of the nucleus causes $\delta$ to move upfield. In the preceding section, it was observed that as $J_{Pt}^{(2)}$ increased $\delta_P^{(2)}$ decreased (Figure 6). Since downfield chemical shifts in the phosphorus-31 NMR are associated with upfield shifts in the platinum-195 NMR, the correlation between $J_{Pt}^{(2)}$ and $\delta_{195}^{Pt}$ may be opposite in the platinum-195 NMR. In other words, as $J_{Pt}^{(2)}$ increases $\delta_{195}^{Pt}$ would decrease (See Figure 16). Both $J_{Pt}^{(1)}$ and $J_{Pt}^{(2)}$ correlate to $\delta_{195}^{Pt}$ in a synergistic manner (See Figure 17). Again, based on previous observations noted by the author, this is as expected.

The primary reason for synthesizing the monometallic palladium(II) and platinum(II) diphosphine complexes was to convert them into their respective bimetallic complexes. Earlier reports by Waid and Meek showed that diastereomeric mixtures of the bimetallics were obtained upon treatment of a monometallic complex with excess base (Eq. 30). In
Figure 16. Plots of $^1J_{PtP}$ versus $\delta_{195P}$ for PtCl$_2$(diphosphine) complexes.

$y = -1.175e+4 \cdot 3.3223x \; R = 0.89$

$y = 1.400e+4 + 2.349x \; R = 0.92$
Figure 17. Plot of $\delta_{195Pt}$ versus $^1J_{PtP}$ for PtCl$_2$(diphosphine) complexes
contrast, refluxing the ligand and PtCl$_2$COD in benzene for 1 1/2 hours yielded only the $\sigma/\pi$-bimetallic (Eq. 31).

$$\text{PtX}_2(L \quad \text{LH}) \quad \xrightarrow{\text{xEt}_3\text{N}} \quad \frac{12 \text{ hours}}{\text{12 hours}} \quad \sigma/\pi- \text{ and meso-[PtX(u-PP)]}_2$$ (30)

$$\text{PtX}_2\text{COD} + \text{ligand} \quad \xrightarrow{\text{benzene}} \quad \frac{1.5 \text{ h}}{\text{1.5 h}} \quad \sigma/\pi-\text{[PX(u-L L')]}_2$$ (31)

Since this author had replaced the phenyl-substituent of the secondary phosphino-moiety with a methyl, it was hoped that changes in the steric and electronic properties at the bridging phosphido-ligand would invoke changes in the relative formation of the $\sigma/\pi$- and meso-diastereoisomers, as well as provide insight into the metal-phosphorus and metal-metal interactions via phosphorus-31 and platinum-195 NMR spectroscopy.

C. Bimetallic Palladium(II) and Platinum(II) Organophosphido Complexes

The bimetallic complex $\sigma/\pi$-[PdCl(u-p-CF$_3$PP)]$_2$, where "u-p-CF$_3$PP" designates the deprotonated form of p-CF$_3$PPH, was made fortuitously by recrystallization of PdCl$_2$(p-CF$_3$PPH) from nitromethane. The determination that the bimetallic complex had formed was based on its phosphorus-31 NMR spectra (See Figure 18). The bonding mode for the deprotonated ligand is illustrated in Figure 19.

Although the $^{31}\text{P}(^1\text{H})$ NMR spectrum for $\sigma/\pi$-[PdCl(u-p-CF$_3$PP)]$_2$ show the major resonances expected for an AA'BB' spin system, the spectrum is deceptively simple. For an AA'BB' spin system ten transitions are
Figure 18. The calculated versus experimental $^{31}$P($^1$H) NMR spectra for $[\text{PdCl(μ-p-CF}_3\text{PP})_2]$
expected (See Figure 20). However for the bimetallic complexes, e.g., [PdCl₂(μ-p-CF₃PP)]₂, only six of the ten transitions were resolved.

Since Wald and Meek reported previously that these bimetallics could be produced by treating the monomers with excess base, attempts to synthesize [PdCl(μ-PPM)]₂ and [PdCl(μ-CyPPM)]₂ via this route were made. Both d/l- and meso- [PdCl(μ-PPM)]₂ were synthesized according to Equation 30 in low yield. The formation of the bimetallics was determined on the basis of the ³¹P(¹H) NMR spectrum for the reaction.
mixture (Figure 21). Attempts to separate the diastereomers by column chromatography resulted in decomposition and loss of the products. Upon changing the ligand from PPMH to CyPPMH, no bimetallic formation occurred.

In contrast to PdCl$_2$(PPH), PdCl$_2$(CyPPH), and PdCl$_2$(p-CF$_3$PPH) which either react spontaneously or with excess base to produce their respective bimetallics, PdCl$_2$(PPMH) and PdCl$_2$(CyPPMH) do not (or do so in very low yields). Since the steric and electronic considerations at the tertiary phosphino moiety apparently do not affect bimetallic formation, this lack of reactivity must be associated with either the steric or electronic properties of the secondary phosphino group.

Since the bimetallics of PPH and CyPPH were originally prepared by known phosphorus acid/base chemistry, the lack of formation of [PdCl(μ-PPM)]$_2$ and [PdCl(μ-CyPPM)]$_2$ was at first attributed to the basicity of the methylphosphino moiety, P(H)Me.$^{183}$ The calculated pK$_a$ values for P(H)Ph and P(H)Me are 2.59 and 4.15, respectively (See Table 18). Therefore, the phenylphosphino moiety is a better acid than the methylphosphino group. Thus, removal of a proton from P(H)Ph should be easier than from P(H)Me. Since triethylamine was presumably not basic enough to remove the "acidic" methylphosphino proton, reactions between the PPMH and CyPPMH monomers and proton sponge or 2,6-lutidene were attempted. Unfortunately, these non-coordinating bases also failed to produce the desired bimetallics. Therefore, formation of the bimetallic complexes could possibly occur via the mechanism illustrated in Scheme 4.
Figure 21. The phosphido region of the $^{31}\text{P}(^1\text{H})$ NMR spectrum for both $d/\&$- and meso-$[\text{PdCl}(\mu-\text{PPM})]_2$. 
Removal of the proton by triethylamine produces a coordinated chelating tertiary phosphino/secondary phosphido ligand, 11. Intermediate 11 is then quickly converted into 12 by attack of the lone pair of electrons on the phosphido moiety on the metal center, thus displacing chloride ion and making triethylamine-hydrochloride. Subsequent dimerization of 12 produces the bimetallic complex. Therefore, the formation of the bimetallic complex could be dependent on the formation of 11. Intuitively, the formation of 11 would depend on the secondary phosphido ligands' ability to delocalize the negative charge after the proton is abstracted by the amine base. Since the phenylphosphido moiety should be able to delocalize the charge better than the methylphosphido moiety due to the \( \pi \)-cloud of the phenyl ring, formation of 11 would be favored when \( R' = \text{Ph} \) but not when \( R' = \text{Me} \).

Up to now the steric and electronic properties of the tertiary phosphino end have been ignored. However, these properties of the tertiary phosphino end of the ligand must contribute to the formation of the bimetallics, since \( \text{PdCl}_2(\text{PPH}) \) and \( \text{PdCl}_2(p-\text{CF}_3\text{PPH}) \) react spontaneously to produce the bimetallics and \( \text{PdCl}_2(\text{CyPPH}) \) does not. Similarly, \( \text{PdCl}_2(\text{PPMH}) \) reacts with excess triethylamine whereas \( \text{PdCl}_2(\text{CyPPMH}) \) does not. The relative stability of \( \text{PdCl}_2(\text{CyPPH}) \) and \( \text{PdCl}_2(\text{CyPPMH}) \) compared to \( \text{PdCl}_2(\text{PPH}) \) and \( \text{PdCl}_2(\text{PPMH}) \) may be attributed to the electron donating ability of the dicyclohexylphosphino moiety versus the diphenylphosphino moiety. Based on the findings of Giering et al.,\(^{193,194}\) the dicyclohexylphosphino moiety is a better \( \sigma \)-donor than the diphenylphosphino moiety (\( \text{pK}_a = 6.74 \) and 5.25, respectively).
Therefore, stabilization (formation) of intermediate 11 would also be favored when tertiary phosphino end of the ligands is a poorer σ-donor.

Steric effects due to both the tertiary phosphino and secondary phosphino moieties may also play a role in bimetallic formation. However, since the tertiary phosphino group is far removed from the reactive site when dimerization of 12 occurs, steric effects due to the tertiary phosphino group appear to be minimal. Steric crowding due to the secondary phosphino groups also appear to be negligible, since the difference in the cone angles for the P(H)Ph and P(H)Me groups is calculated to be 9°. Therefore, bimetallic formation does not appear to be dependent on the steric considerations of either the tertiary or secondary phosphino moieties, but rather on their electronic contributions.

1) Phosphorus-31 NMR Spectra of Bimetallic Palladium(II) Complexes

The phosphorus-31 NMR data for the phosphido-bridged bimetallic complexes, [PdCl(μ-p-CF₃PP)]₂ and [PdCl(μ-PPM)]₂ are presented in Table 20. Data for both [PdCl(μ-PP)]₂ and [PdCl(μ-CyPP)]₂ are presented for comparison. The assignments of the NMR spin labels, AA'BB', are shown in Figure 19.

The phosphorus-31 NMR chemical shifts for the bridging phosphido atoms, δₐₐ', appear at higher field than the phosphorus-31 NMR chemical shifts for the phosphino atoms, δ₇₇. Assignment of the low-field resonances to the tertiary phosphino nuclei are consistent with similar chemical shift values observed for the tertiary phosphino nuclei of the
Table 20
Phosphorus-31 NMR Data for Phosphido Bridged Complexes of Palladium(II)\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_{AA'}$</th>
<th>$\delta_{BB'}$</th>
<th>$^2J_{AA'}$</th>
<th>$^2J_{AB}$</th>
<th>$^2J_{A'B}$</th>
<th>$^4J_{BB'}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{PdCl}(u-\text{PP})]_2$</td>
<td>-144.4</td>
<td>-11.9</td>
<td>-246.0</td>
<td>12.5</td>
<td>417.8</td>
<td>0.0</td>
</tr>
<tr>
<td>$[\text{PdCl}(u-\text{CyPP})]_2$</td>
<td>-126.6</td>
<td>-0.3</td>
<td>-235.2</td>
<td>16.4</td>
<td>396.7</td>
<td>0.0</td>
</tr>
<tr>
<td>$[\text{PdCl}(u-p-\text{CF}_3\text{PP})]_2$</td>
<td>-145.1</td>
<td>-11.1</td>
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<td>9.1</td>
<td>416.4</td>
<td>0.1</td>
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<tr>
<td>$[\text{PdCl}(u-\text{PPM})]_2$</td>
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<td>-10.9</td>
<td>-267.8</td>
<td>31.5</td>
<td>430.3</td>
<td>-1.7</td>
</tr>
</tbody>
</table>

\textit{d/4-}

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_{AA'}$</th>
<th>$\delta_{BB'}$</th>
<th>$^2J_{AA'}$</th>
<th>$^2J_{AB}$</th>
<th>$^2J_{A'B}$</th>
<th>$^4J_{BB'}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{PdCl}(u-\text{PP})]_2$</td>
<td>-171.5</td>
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<td>26.7</td>
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<td>0.1</td>
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<tr>
<td>$[\text{PdCl}(u-\text{CyPP})]_2$</td>
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<td>33.3</td>
<td>416.2</td>
<td>0.0</td>
</tr>
<tr>
<td>$[\text{PdCl}(u-\text{PPM})]_2$</td>
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<td>-12.0</td>
<td>-304.5</td>
<td>18.2</td>
<td>438.6</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\textit{meso-}

\textsuperscript{a}Chemical shifts are reported in ppm relative to 85\% H$_3$PO$_4$; $AA'$ denotes the phosphido moiety; $BB'$ denotes the phosphino moiety.

\textsuperscript{b}Coupling constants reported in Hz.

\textsuperscript{c}Data from references 49 and 51.
monometallic complexes. The highfield resonances of the phosphido nuclei indicate that there is no direct interaction between the palladium centers (Refer to Table 3). In fact, X-ray structures of isoelectronic compounds \( d/\alpha-, \text{meso-}[\text{PtCl(\mu-CyPP)\_2} \) revealed that there was no metal-metal bonding in these cases.\(^\text{51}\)

As stated previously, the difference between the \( d/\alpha-\) and \( \text{meso-}\)stereoisomers is the geometry of the \( \text{M}_2\text{P}_2 \) core. In the case of the \( d/\alpha-\) pair the \( \text{M}_2\text{P}_2 \) core was shown to be bent, whereas a planar \( \text{M}_2\text{P}_2 \) core was found for the \( \text{meso-}\)stereoisomer.\(^\text{49,51}\) This difference in the \( \text{M}_2\text{P}_2 \) core is reflected in the phosphorus-31 NMR chemical shifts for the phosphido nuclei, \( \delta_{\text{AA}'} \). As the \( \text{M-P-M} \) angle becomes more acute, \( \delta_{\text{AA}'} \) is shifted downfield, and obviously, as the \( \text{M-P-M} \) angle becomes more obtuse, \( \delta_{\text{AA}'} \) is shifted upfield.\(^\text{49,51}\) Therefore assignment of the \( d/\alpha-\) and \( \text{meso-}\)diastereomers is based on the phosphorus-31 NMR chemical shift for the phosphido nuclei.

Replacement of phenyl with methyl on the bridging phosphido atom causes \( \delta_{31\text{P}} \) to shift upfield by -35 and -23 ppm for the \( d/\alpha-\) and \( \text{meso-}\)stereoisomers, respectively. This expected upfield shift observed for \( \delta_{\text{AA}'} \) for both \( d/\alpha-\) and \( \text{meso-}[\text{PdCl(\mu-PPM)}\_2 \) may be attributed to the electron releasing ability of methyl versus phenyl. (Recall: electron releasing groups provided that they are not sterically hindered cause the phosphorus nucleus to become more shielded.) In contrast, changing the substituent on the tertiary phosphino moiety from phenyl to cyclohexyl causes the resonances for the phosphido nuclei, \( \delta_{\text{AA}'} \), to shift downfield by -18 and -4.2 ppm for the \( d/\alpha-\) and \( \text{meso-}\)stereoisomers, respectively. This downfield shift observed for \( \delta_{\text{AA}'} \) may be attributed
to either the steric or electronic properties of the Cy2P group compared to the Ph2P group.

If the electron donating ability of the tertiary phosphino moiety is an important factor in determining δAA', then the tertiary phosphino moiety which is a better σ-donor would cause the phosphido nuclei to be more shielded and δAA' to appear at higher fields. This, however, is not the case. When a poorer σ-donor was replaced with a better σ-donor (i.e., Ph2P with Cy2P) δAA' shifted downfield. Therefore, it may be implied that the steric requirements of the dicyclohexylphosphino moiety are more dominant than the electronic contributions in influencing δAA'. Since steric considerations appear to dominate δAA', the bulkier the tertiary phosphino group is the less able it will be to shield the phosphido nucleus trans to itself. Thus, δAA' would be expected and does shift downfield (e.g., δAA' = -144.4 and -126.6 ppm for [PdCl(μ-PP)]2 and [PdCl(μ-CyPP)]2, respectively).

Since the steric considerations of the tertiary phosphino-group trans to the phosphido nucleus appear to be an important factor in determining δAA' (the most important factor being changes in the substituents bound directly to the phosphido nucleus), the trans-two-bond coupling constant, 2J_A'B, should also be influenced by the steric demands of the phosphino moiety. That is, the more electron density shared between the phosphido and phosphino nuclei, the better the orbital overlap. Therefore, we expect shorter phosphido/phosphino internuclear distances and larger values for 2J_A'B. Substitution of methyl for phenyl at the phosphido-nuclei causes a slight increase in 2J_A'B. Again, the increase in 2J_A'B may be attributed to the relative
α-donor abilities of methyl versus phenyl, whereas substitution of cyclohexyl groups for phenyl groups at the tertiary phosphino nuclei causes $^{2}J_{A'B}$ to decrease by -20 Hz in both the $d$/$l$- and meso-stereo-isomers. The decrease in $^{2}J_{A'B}$ may again be attributed to the steric demands of the dicyclohexylphosphino moiety. Hopefully, more insight into the nature of $^{2}J_{A'B}$ will be gained upon close inspection of the phosphorus-31 NMR parameters for the bimetallic platinum complexes.

The cis-phosphido-phosphino coupling constants, $^{2}J_{AB}$, obtained for the bimetallic complexes are comparable in magnitude to cis-phosphino/phosphino and cis-phosphido/phosphino coupling constants reported in the literature (refer to Tables 5, 6 and 17). Deviations in $^{2}J_{AB}$, e.g., $^{2}J_{AB} = 23.5$ and 31.5 Hz for $[\text{PdCl} (\mu-\text{PMe}) (\text{PPh}_3)]_2^{137}$ and $d/l-[\text{PdCl} (\mu-\text{PPM})]_2$ can be rationalized by Grim's suggestion that the magnitude of phosphorus-phosphorus coupling in a chelate ring is the summation of coupling through the metal and coupling occurring via the carbon backbone. Although the phosphorus-phosphorus couplings for the free diphosphine ligands, PPH, CyPPH, PPMH, CyPPMH and p-CF$_3$PPH are -0 Hz, it is possible that chelation locks the backbone into a rigid conformation, thus allowing transmission of phosphorus-phosphorus coupling through the backbone. Since the coupling through the metal orbital and the backbone are of opposite sign, the magnitude of $^{2}J_{AB}$ may be decreased. In fact, $^{2}J_{AB}$ was found to be -0 Hz for both PdCl$_2$(p-CF$_3$PPH) and PdCl$_2$(CyPPMH), thereby indicating that the coupling transmitted through the metal center and the backbone are equal in magnitude as well as opposite in sign.
Substitution of the phenyl groups with cyclohexyl groups on the tertiary phosphino nuclei causes $2J_{AB}$ to increase by -5 Hz. An increase in $2J_{AB}$ concomitant with a decrease in $2J_{A'B}$ is expected since both the phosphido nuclei and the phosphino nuclei compete for the same metal hybrid orbitals. A similar cis-effect was noted for the platinum monometallic diphosphine complexes (Refer to Figure 5). Changing the phenyl substituent to methyl on the bridging phosphido atom causes a 19 Hz increase in $2J_{AB}$ for the $d/\pi$-pair and a -8 Hz decrease in $2J_{AB}$ for the meso-stereoisomer. A possible explanation for the inconsistency in $2J_{AB}$ for $d/\pi$- and meso-$[PdCl(u-PPM)]_2$ is that the coupling through the backbone is more positive for $d/\pi$-$[PdCl(u-PPM)]_2$ than for meso-$[PdCl-(u-PPM)]_2$.\textsuperscript{128,129} Another possible explanation for this inconsistency may be that since there are three phosphorus atoms bound to one palladium atom which compete for the same metal hybrid orbitals, a second cis-effect between the phosphido/phosphino nuclei and the phosphido/phosphido nuclei is being observed.

The cis-phosphido/phosphido coupling constants, $2J_{AA'}$, are -247 Hz and -303 Hz for the $d/\pi$- and meso-stereoisomers, respectively. These values are much larger in magnitude than cis-phosphino/phosphino coupling constants (vide supra). Kreter\textsuperscript{200} suggested that the unusually high cis-coupling between the phosphido nuclei was due in part to the steric demands of the substituents on the phosphido atoms. Substitutents with low steric demands would allow the phosphido nuclei to approach more closely, presumably increasing the orbital overlap of the phosphorus 3s and 3p orbitals and thus increasing $2J_{AA'}$. Changing the phenyl substituent to methyl causes an increase in $2J_{AA'}$. Since the
methyl substituent is both sterically less demanding and a better 
σ-donor than the phenyl substituent an increase in $^2J_{AA'}$ was expected. 
Substitution of cyclohexyl groups for the phenyl groups on the phosphino 
nuclei causes a decrease of $\sim11$ Hz for the $d$/l-pair, presumably due to 
the steric requirements of the dicyclopentylphosphino moiety. However, 
for the meso-stereoisomers a slight increase for $^2J_{AA'}$ was noted. 
Perhaps, this increase is caused by the planarity of the $M_2P_2$ core. 
Orbital overlap for the planar stereoisomers should be better, 
presumably increasing the electronic contributions and decreasing the 
steric requirements of the dicyclopentylphosphino moiety. Therefore all 
the coupling constants $^2J_{AA'}$, $^2J_{AB}$, and $^2J_{A'B}$ should be and are larger 
for the meso-stereoisomers than the $d$/l-pair. Similarly, $\delta_{AA'}$ should be 
and is shifted downfield to a lesser extent for the meso-stereoisomer 
than the $d$/l-pair.

The exact causes of the many differences in the phosphorus-31 NMR 
parameters of the chelating phosphido/phosphino bridged bimetallic 
palladium complexes at present is still speculative. Perhaps the 
phosphorus-31 NMR parameters for the platinum bimetallic complexes will 
provide more insight into the nature of the phosphorus-phosphorus 
couplings.

D. Bimetallic Platinum(II) Organophosphido Complexes

Unfortunately attempts to synthesize both [PtX($\mu$-PPM)]$_2$ and [PtX-
($\mu$-CyPPM)]$_2$, where $X = \text{Cl, I}$, according to Equation 30 proved to be 
unsuccessful. Since reactivity of metal complexes decreases upon 
descending a triad (i.e., palladium is more reactive than platinum),
this result is not surprising. Attempts to remove the "acidic" proton before complexation according to Equation 33 proved to be futile.

\[ \text{R}_2\text{P(CH}_2\text{)}_3\text{P(H)R'} + \text{xs nBuL} \xrightarrow{\text{hexane}} \frac{2}{2 \text{ hrs}} \rightarrow \text{N.R.} \quad (33) \]

\( \text{R} = \text{Ph, Cy} \)

\( \text{R'} = \text{Me} \)

In order to gain further insight into the relationships between the \( \text{M}_2\text{P}_2 \) core stereochemistry and NMR spectral parameters, \([\text{PtCl(u-p-CF}_3\text{PP})_2], [\text{PtI(u-p-CF}_3\text{PP})_2], [\text{PtI(u-PP})_2], \) and \([\text{PtI(u-CyPP})_2] \) were synthesized. These bimetallic complexes were prepared according to Equations 30 or Equation 31, so that all of the diastereomers could be obtained.

1) Phosphorus-31 NMR Spectra of Bimetallic Platinum(II) Complexes

As stated previously, examination of reaction products by \(^{31}\text{P}(^1\text{H})\) NMR spectroscopy was the most convenient method of distinguishing the bimetallic complexes from the monometallic compounds. A typical phosphorus-31 NMR spectrum, for the phosphido region only, is presented in Figure 22. Since platinum has a natural abundance magnetic nucleus (ca. 33.8%, I = 1/2), the phosphorus-31 NMR spectra displayed relatively intense patterns for \( \text{AA'BB}' \), \( \text{AA'BB}'\text{X} \) plus a very weak \( \text{AA'BB}'\text{XX}' \) pattern. The three patterns reflect the natural abundance of platinum-195 which yields 44.9%, 44.2%, 10.9% of the isotopmeric diplatinum complexes containing zero, one, or two platinum-195 nuclei, respectively (Refer to Figure 23). The spectra obtained for these platinum bimetallic
Figure 22. The phosphido region of the $^{31}\text{P}[^1\text{H}]$ NMR spectrum for $d/t-\text{[PtI(\text{u-PP})]}_2$
complexes closely resemble those reported earlier by Dixon et al.,137 and Meek et al.49,51

![Complex structures](image)

**Figure 23.** The three isotopomers for the platinum bimetallic complexes

The $^{31}\text{P}^{(1}\text{H})$ NMR spectral data for the AA'BB' portion of the bimetallic chelating phosphido/phosphino ligands are presented in Table 21. The AA'BB' spin labels for the major isotopomer are assigned according to Figure 24.

![Spin label assignments](image)

**Figure 24.** NMR spin label assignments for the isotopomers of the bimetallic platinum(II) complexes

Analogous to the palladium bimetallic complexes, the assignment of the phosphorus signal at relatively high fields is assigned to the bridging phosphido nuclei, $\delta_{AA'}$, whereas the low field resonances are assigned to the phosphino nuclei, $\delta_{BB'}$. Again, this assignment is
Table 21
Phosphorus-31 NMR Data for Phosphido Bridged Complexes of Platinum(II)\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\delta_{AA'})</th>
<th>(\delta_{BB'})</th>
<th>(2J_{AA'})</th>
<th>(2J_{AB})</th>
<th>(2J_{A'B})</th>
<th>(4J_{BB'})</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{d/1-}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{PdCl(u-PP)}]_2)\textsuperscript{c}</td>
<td>-146.5</td>
<td>-8.3</td>
<td>-155.9</td>
<td>-4.4</td>
<td>383.0</td>
<td>6.0</td>
</tr>
<tr>
<td>([\text{PtI(u-PP)}]_2)</td>
<td>-165.7</td>
<td>-10.6</td>
<td>-166.2</td>
<td>-1.9</td>
<td>374.6</td>
<td>---</td>
</tr>
<tr>
<td>([\text{PtCl(u-CyPP)}]_2)\textsuperscript{c}</td>
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<td>-4.5</td>
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<td>-3.0</td>
<td>377.4</td>
<td>---</td>
</tr>
<tr>
<td>\textit{meso-}</td>
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</tr>
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<tr>
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<td>-5.6</td>
<td>-186.1</td>
<td>5.1</td>
<td>395.7</td>
<td>---</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Chemical shifts are reported in ppm relative to 85\% H\textsubscript{3}PO\textsubscript{4}; AA' denotes the phosphido moiety; BB' denotes the phosphino moiety.

\textsuperscript{b}Coupling constants reported in Hz; \textsuperscript{195}Pt-P coupling data omitted.

\textsuperscript{c}Data from references 49 and 51.
consistent with the similar chemical values for the tertiary phosphino moiety of the monometallic complexes (Refer to Tables 17 and 21). Moreover, the high field resonances due to the bridging phosphido moiety are consistent with the absence of a metal-metal bond (Refer to Table 3). Assignment of the d/z- and meso-diastereomers is based on the phosphorus-31 NMR chemical shifts for the phosphido nuclei. Signals for the phosphido nuclei of meso-stereoisomer appear at significantly higher fields than the d/z-pair (See Figure 25).

As noted previously, ligand effects on the phosphorus-31 NMR chemical shifts are difficult to interpret, since the chemical shift is affected by both the steric and electronic contributions of the substitutents bound to the phosphorus nucleus, as well as the other ligands bound to the metal center. From the data presented in Table 21, the phosphorus-31 NMR chemical shifts for the phosphido nuclei, δ_{AA'}, are shifted upfield when the halogen ligand is changed from Cl to I by -21 Hz and -33 Hz for the d/z- and meso-stereoisomers, respectively. This increase in δ_{AA'} is consistent with the known trans-influence ability of I versus Cl.113,131,191 Unlike for the palladium bimetallic complexes, δ_{AA'} for the platinum bimetallic complexes do not appear to be influenced by substituent changes on the tertiary phosphino moiety (δ_{AA'} = -146.7 and -167.9 ppm for d/z-[PtCl(μ-L-L)]_2 and d/z-[PtI(μ-L-L)]_2, respectively).

Substitution of an iodo ligand for a chloro ligand causes a decrease in the two-bond cis-phosphido/phosphido and trans-phosphido/phosphino coupling constants, J_{AA'} and J_{A'B}, respectively. The
Figure 25. The phosphido region of the $^{31}p_{^1H}$ NMR spectrum for both $d/\alpha$- and meso-$[PtI(u-CyPP)]_2$
decreases in $^{2}J_{AA}$ are on the order of 12 Hz for the $d/\alpha$-stereoisomers and 19 Hz for the meso-complexes. Decreases of -12 Hz and -1 Hz were observed for $^{2}J_{A'B}$ in both the $d/\alpha$- and meso-stereoisomers, respectively. Again, this is consistent with the trans-influence ability of I$^{-}$ compared to Cl$^{-}$. Replacement of phenyl with cyclohexyl substituents on the phosphino atom causes $^{2}J_{A'B}$ to decrease for all the stereoisomers (e.g., $^{2}J_{A'B} = 350.6$ and 37.4 Hz for $d/\alpha$-[PtI($\mu$-CyPP)]$_2$ and $d/\alpha$-[PtI($\mu$-p-CF$_3$PP)]$_2$, respectively). In contrast to $^{2}J_{A'B}$, $^{2}J_{AA'}$ does not appear to be influenced by substitution of the phosphino atom.

Concomitant with the observed decreases in $^{2}J_{AA'}$ and $^{2}J_{A'B}$ when the chloro-ligand is replaced with an iodo ligand are increases in the two-bond cis-phosphido/phosphino coupling constant, $^{2}J_{AB}$. $^{2}J_{AB}$ increases by -3 Hz and -7 Hz for the $d/\alpha$- and meso-stereoisomers, respectively. Similarly, replacement of the phenyl groups with cyclohexyl groups on the phosphino atom causes $^{2}J_{AB}$ to increase (e.g., $^{2}J_{AB} = -3.0$ and -1.2 Hz for $d/\alpha$-[PtI($\mu$-p-CF$_3$PP)]$_2$ and [PtI($\mu$-CyPP)]$_2$, respectively).

A comparison of the NMR parameters presented in Tables 20 and 21 reveals that the trends mentioned above for the phosphido/phosphido and phosphido/phosphino coupling constants, $^{2}J_{AA'}$, $^{2}J_{AB}$ and $^{2}J_{A'B}$ are valid for similar palladium and platinum bimetallic complexes. Inspection of both sets of data also shows that the coupling constants are larger in magnitude for the bimetallic palladium complexes. Of the three coupling constant mentioned, $^{2}J_{A'B}$ appears to be the least sensitive to substituent changes at the phosphino atom. Brandon and Dixon$^{137}$ have reported similar observations in comparing phosphido bridged palladium and platinum complexes have similar structures (Refer to Table 6).
While only a limited amount of data is available regarding the magnitudes of the phosphido/phosphido and phosphido/phosphino coupling constant in Ni, Pd, and Pt complexes of comparable structures, their values (with a few exceptions) seem to decrease down the nickel triad.51,137

2) $^{195}$Pt($^1$H) NMR Spectra of Bimetallic Complexes

The $^{195}$Pt($^1$H) NMR spectra for the bimetallic complexes consists of a highly ordered pattern due to the presence of the two isotopomers of the complexes which contain the spin active platinum-195 nucleus and the presence of the three magnetically inequivalent phosphorus nuclei. A typical $^{195}$Pt($^1$H) NMR spectrum for the bimetallic complexes is presented in Figure 26. The additional data which these spectra provided are the platinum-195 NMR chemical shifts, $\delta_{195^{\text{Pt}}}$, and the two-bond platinum-platinum coupling constant, $^{2}J_{XX}$. The splitting pattern assignments are outlined in Figure 26 and the NMR spin-labels were presented in Figure 24. The data obtained from these spectra is given in Table 22.

Exactly analogous to the platinum(II) monometallic diphosphine complexes, replacement of chloride with iodide cause $\delta_{195^{\text{Pt}}}$ to shift upfield for both the $d$/$l$- and meso-stereoisomers. Again, since the iodo ligand is both more electropositive and softer than the chloro ligand, this upfield shift for the platinum-195 resonances was expected. Substitution of cyclohexyl groups for phenyl groups on the phosphino-atom causes $\delta_{195^{\text{Pt}}}$ to appear downfield for both $d$/$l$- and meso-$[\text{PtX(}\mu-\text{L})_2]$, where X = Cl, I. Again this is consistent with the empirical trend reported previously.140-142,198
Figure 26. The calculated versus experimental $^{195}\text{Pt}(^1\text{H})$ NMR spectrum for $[\text{PtCl}(\mu-p-\text{CF}_3\text{PP})]_2$
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_{XX}$</th>
<th>$J_{AX}$</th>
<th>$J_{BX}$</th>
<th>$J_{B'X}$</th>
<th>$J_{XX'}$</th>
</tr>
</thead>
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<tr>
<td>$d/\lambda$ -</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{PtCl}(\mu-\text{PP})]_2$</td>
<td>-4050.2</td>
<td>2024.3</td>
<td>2215.2</td>
<td>6.0</td>
<td>342</td>
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<tr>
<td>$[\text{PtI}(\mu-\text{PP})]_2$</td>
<td>-4394.7</td>
<td>1845.3</td>
<td>2128.6</td>
<td>6.1</td>
<td>263</td>
</tr>
<tr>
<td>$[\text{PtCl}(\mu-\text{CyPP})]_2$</td>
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<td>2358.5</td>
<td>2122.4</td>
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<td>259</td>
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<td>$[\text{PtI}(\mu-\text{CyPP})]_2$</td>
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<td>1824.6</td>
<td>2137.1</td>
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<td>325</td>
</tr>
<tr>
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<td>-4057.1</td>
<td>2033.9</td>
<td>2081.8</td>
<td>8.3</td>
<td>354</td>
</tr>
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<td>$[\text{PtI}(\mu-p-\text{CF}_3\text{PP})]_2$</td>
<td>-4397.6</td>
<td>1894.6</td>
<td>2099.4</td>
<td>7.2</td>
<td>254</td>
</tr>
<tr>
<td>$\text{meso}$ -</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{PtCl}(\mu-\text{PP})]_2$</td>
<td>---</td>
<td>2058.9</td>
<td>2139.5</td>
<td>39.2</td>
<td>---</td>
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<tr>
<td>$[\text{PtCl}(\mu-\text{CyPP})]_2$</td>
<td>---</td>
<td>2028.0</td>
<td>2135.1</td>
<td>32.6</td>
<td>639</td>
</tr>
<tr>
<td>$[\text{PtI}(\mu-\text{CyPP})]_2$</td>
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<td>1781.3</td>
<td>2207.9</td>
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<td>$[\text{PtCl}(\mu-p-\text{CF}_3\text{PP})]_2$</td>
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<td>$[\text{PtI}(\mu-p-\text{CF}_3\text{PP})]_2$</td>
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<td>1882.9</td>
<td>2132.9</td>
<td>39.2</td>
<td>525</td>
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</table>

*a* Chemical shifts are reported in ppm relative to 0.6 M $\text{H}_2\text{PtCl}_6$ in $\text{D}_2\text{O}/\text{HCl}$ ($\delta_{195\text{Pt}} = 0$ ppm); AA' denotes the phosphido moiety; BB' denotes the phosphino moiety.

*b* Coupling constants in Hz.

*c* Average platinum-phosphido coupling constants.

*d* Data from references 49 and 51.
Another empirical trend observed for platinum phosphine complexes is upfield phosphorus-31 NMR chemical shifts are concomitant with downfield platinum-195 NMR chemical shifts. This trend is also observed for the bimetallic complexes. In general, the $\delta_{31p}$ for the phosphido- ligands of the $d/\alpha$-stereoisomers appears downfield from the $\delta_{31p}$ for the meso-stereoisomer by -25 and -38 ppm for $[PtCl(u-L)\square]$ and $[PtI(u-L)\square]_2$, respectively. In contrast, $\delta_{195Pt}$ for the $d/\alpha$-stereoisomers is upfield from $\delta_{195Pt}$ for the meso-stereoisomers by -38 and -73 ppm for $[PtCl(u-L)\square]$ and $[PtI(u-L)\square]_2$, respectively (Refer to Figures 25 and 27). Therefore, the $\delta_{195Pt}$ also appears to be very sensitive to the nature of the $M_2P_2$ core geometry. These upfield/downfield shifts noted for the $\delta_{195Pt}$ and $\delta_{31p}$ can be easily explained by synergistic effects occurring between the platinum-195 nucleus becomes more shielded, the phosphorus-31 nucleus becomes more deshielded.

The coupling constants which appear to be most sensitive to changes in the metal core geometry are the three-bond the two-bond platinum/platinum coupling constant, $^2J_{XX}$. In a comparison of the eleven compounds studied, the six values of $^3J_{B\chi\chi}$ are considerably smaller for the $d/\alpha$-stereoisomers than the meso-stereoisomers. The values found for $^3J_{B\chi\chi}$ for the $d/\alpha$-isomers are -6 Hz compared to -33 Hz for the meso-isomer. Similarly, smaller values for $^2J_{XX}$ were observed for the $d/\alpha$-stereoisomers than the meso-stereoisomer, i.e., $^2J_{XX} = 300$ and 600 Hz, respectively (Refer to Figures 26 and 27). Rationalization of the smaller coupling constants for the $d/\alpha$-stereoisomers than meso- isomers can be found in comparing the $M_2P_2$ core geometry. For the $d/\alpha$- stereoisomers the $M_2P_2$ core was found to be bent, whereas a planar core
Figure 27. The $^{195}\text{Pt}(^1\text{H})$ NMR spectrum for $d\overline{e}$- and meso-$\text{PtI}(\mu-\text{p-CF}_3\text{PP})_2$
was found for the meso-stereoisomers. Therefore, better orbital overlap between the platinum and phosphorus atoms in the case of the planar core results in larger coupling constants. Changing the halide ligand from chloride to iodide also decreases the value of $^{2}J_{XX}$ for both the $d/t$- and meso-stereoisomers. Since iodide is a stronger trans-influence ligand than chloride, the orbital overlap in the $M_2P_2$ core should decrease and thereby decrease the values observed for $^{2}J_{XX}$.

Changing the phenyl substituents for cyclohexyl substituents at the phosphino atom decreased $^{2}J_{XX}$, by -83 Hz for the $d/t$-[PtCl($\mu$-$\perp$-$L$)]$_2$ and increased $^{2}J_{XX}$, by -62 Hz for [PtI($\mu$-$\perp$-$L$)]$_2$. However, for the meso-stereoisomers, $^{2}J_{XX}$, increased by -40 Hz for both the chloro and iodo complexes. These observations can be rationalized on the basis of the steric and electronic contributions due to the dicyclohexylphosphino moiety. If the steric demands of the dicyclohexylphosphino moiety are important, $^{2}J_{XX}$, will be larger and the one-bond platinum/phosphino coupling constant, $^{1}J_{BX}$, will be smaller. Conversely, if the $\sigma$-donor ability of the phosphino moiety is important, $^{2}J_{XX}$, will be smaller and $^{1}J_{BX}$ will be larger. Therefore, for the meso-complexes and the $d/t$-iodo complexes it appears that electronic contributions of the phosphino moiety are more important than steric considerations (Refer to Table 22).

Substitution of cyclohexyl for diphenyl groups on the phosphino moiety causes $^{1}J_{AX}$ to increase for the $d/t$-[PtI($\mu$-$\perp$-$L$)]$_2$ and decrease for the $d/t$-[PtI($\mu$-$\perp$-$L$)]$_2$. However, $^{1}J_{AX}$ for the meso-stereoisomers decreases when the phenyl substituents are replaced with cyclohexyl groups. Rationale for the increases and decreases associated with the
substituent changes at the phosphino moiety have been previously discussed by the author. The stronger trans-influence of the iodo versus the chloro ligand is demonstrated by the larger $^{1}J_{AX}$ values for the corresponding complexes. Similarly, the stronger trans-influence ability of the phosphine versus chloro ligand can be seen in the different one-bond platinum-phosphido coupling constants, $^{1}J_{AX}$ and $^{1}J_{A'X}$, which are presented in Table 23. Strong trans-influence ligands (i.e., I, R$_3$P) are known to reduce one-bond metal phosphorus coupling constants.139-142,198

E. The Role of [Pt(PPH)$_2$]$^{2+}$[Cl]$_2$ in Bimetallic Formation

During the formation of the bimetallic platinum complex [PtCl(u-p-CF$_3$PP)]$_2$ trace amounts of [Pt(p-CF$_3$PPH)$_2$]$^{2+}$[Cl]$_2$ were detected by $^{31}$P($^1$H) NMR spectroscopy, therefore the reactivity of [Pt(PPH)$_2$]$^{2+}$[Cl]$_2$, under the conditions used in synthesizing the bimetallic complexes, was examined. The three attempted reactions of [Pt(PPH)$_2$]$^{2+}$[Cl]$_2$ are illustrated in Equations 34, 35, and 36.

$$[\text{Pt(PPH)}_2]^{2+}[\text{Cl}]_2 \xrightarrow{\Delta, \text{toluene}} \text{N.R.}$$  \hspace{1cm} (34)

$$[\text{Pt(PPH)}_2]^{2+}[\text{Cl}]_2 \xrightarrow{\text{Et}_3\text{N, THF}} \text{N.R.}$$  \hspace{1cm} (35)

$$[\text{Pt(PPH)}_2]^{2+}[\text{Cl}]_2 + \text{PtCl}_2\text{COD} \xrightarrow{\text{Et}_3\text{N, CH}_2\text{Cl}_2} [\text{PtCl(u-PP)}]_2$$  \hspace{1cm} (36)
Table 23

Platinum-195 NMR Data for the Phosphido Bridged Complexes(II)^a,b

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1J_{AX}$</th>
<th>$^1J_{A'X}$</th>
</tr>
</thead>
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<tr>
<td>$d/ε-$</td>
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<td></td>
</tr>
<tr>
<td>$[PtCl(u-PP)]_2^C$</td>
<td>2228.4</td>
<td>1820.2</td>
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<tr>
<td>$[PtCl(u-CyPP)]_2^C$</td>
<td>2991.5</td>
<td>1725.4</td>
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<tr>
<td>$[PtCl(u-p-CF_3PP)]_2$</td>
<td>2200.2</td>
<td>1867.8</td>
</tr>
<tr>
<td>$meso-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[PtCl(u-PP)]_2^C$</td>
<td>2242.5</td>
<td>1875.4</td>
</tr>
<tr>
<td>$[PtCl(u-CyPP)]_2^C$</td>
<td>2287.6</td>
<td>1768.4</td>
</tr>
</tbody>
</table>

^aChemical shifts are reported in ppm relative to $85\% \text{H}_3\text{PO}_4$.

^bCoupling constants in Hz.

^cData from references 49 and 51.
Since [Pt(PPH)$_2$]$^{2+}$[Cl]$^2_2$ failed to react with itself at either elevated temperatures or in the presence of triethylamine and reacted with PtCl$_2$COD in the presence of triethylamine, it was concluded that an alternative pathway for the formation of the bimetallic complexes may exist. Earlier the author suggested that formation of the bimetallics may occur via intermediate 11 (Refer to Scheme 4). However, these results seem to suggest that the formation of the bimetallics (according to Equation 31) proceed via a [Pt(PPH)$_2$]$^{2+}$[Cl]$^2_2$ intermediate. Since envisioning a mechanism similar to Scheme 4 involving [Pt(PPH)$_2$]$^{2+}$[Cl]$^2_2$ is difficult, a simpler explanation is sought. Perhaps [Pt(PPH)$_2$]$^{2+}$[Cl]$^2_2$ is formed more readily than the monometallic diphosphine complex, however once formed it disproportionates in the presence of PtCl$_2$COD to yield PtCl$_2$(PPH). The monometallic diphosphine complex may then react with the excess triethylamine base as indicated in Scheme 4.
REFERENCES


163. Supplee, C.; Engelman, C.; Meek, D.W. Phosphorus and Sulfur, in press.


