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A PHOSPHORUS-31 NMR STUDY OF PLATINUM(0) COMPLEXES AND UNSATURATED TERTIARY PHOSPHINE COMPLEXES OF RHODIUM AND IRIDIUM

The Ohio State University

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A PHOSPHORUS-31 NMR STUDY OF PLATINUM(O) COMPLEXES
AND UNSATURATED TERTIARY PHOSPHINE COMPLEXES
OF RHODIUM AND IRIDIUM

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

By
Young-ae Park, B.S., M.S.

The Ohio State University
1980

Reading Committee:
Dr. Devon W. Meek
Dr. Andrew Wojcicki
Dr. Gary G. Christoph

Approved By
Advisor
Department of Chemistry
To my parents, parents-in-law,
my husband, and Mingyun
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VITA

July 9, 1947 .............. Born - Seoul, Korea

1970 ..................... B.S. (Chemistry) Seoul National University, Seoul, Korea


1976 - 1978, ............. Teaching Associate, The Ohio State University Columbus, Ohio

1979 - 1980 ............. Evans and McPherson Fellowship, The Ohio State University, Columbus, Ohio

PUBLICATIONS


FIELDS OF STUDY

Major Field: Inorganic Chemistry

Studies in Coordination Chemistry. Dr. Devon W. Meek.
LIST OF ABBREVIATIONS

L \hspace{0.5cm} \text{Monodentate neutral ligand}
X \hspace{0.5cm} \text{Coordinated anionic ligand}
Y \hspace{0.5cm} \text{PF}_6^-, \text{AsF}_6^- \text{ or } \text{BF}_4^-
t-Bu \hspace{0.5cm} \text{C}(\text{CH}_3)_3
Me \hspace{0.5cm} \text{CH}_3
Et \hspace{0.5cm} \text{CH}_2\text{CH}_3
i-Pr \hspace{0.5cm} \text{CH(\text{CH}_3)_2}
Ph, \emptyset \hspace{0.5cm} \text{C}_6\text{H}_5
Cy \hspace{0.5cm} \text{Cyclohexyl}
cod \hspace{0.5cm} \text{Cyclo-1,5-octadiene}
coe \hspace{0.5cm} \text{Cydooctene}
tripod \hspace{0.5cm} \text{CH}_3\text{C(\text{CH}_2\text{PPh}_2)_3}
mbp \hspace{0.5cm} \text{Ph}_2\text{P(\text{CH}_2)_2CH=CH}_2
spp \hspace{0.5cm} \text{\textomega-CH}_2=\text{CH}_2-\text{C}_6\text{H}_4\text{PPh}_2
spas \hspace{0.5cm} \text{\textomega-CH}_2=\text{CH-C}_6\text{H}_4\text{AsMe}_2
bdpps \hspace{0.5cm} \text{\textomega-Ph}_2\text{PC}_6\text{H}_4\text{CH=CHC}_6\text{H}_4\text{PPh}_2-\text{\omega}
1-bdpb \hspace{0.5cm} \text{\textomega-Ph}_2\text{PC}_6\text{H}_4-\text{\pm-CH=CHCH(CH}_3)\text{C}_6\text{H}_4\text{PPh}_2-\text{\omega}
ttp \hspace{0.5cm} \text{PhP(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2}
ppol \hspace{0.5cm} \text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P(Ph)CH}_2\text{CH}_2\text{CH=CH}_2
py \hspace{0.5cm} \text{Pyridine}
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PART I

A PHOSPHORUS-31 NMR STUDY OF PLATINUM(0) COMPLEXES
INTRODUCTION

The measurement and study of phosphorus-phosphorus coupling in the nuclear magnetic resonance spectroscopy of transition metal complexes have attracted considerable interest among chemists.\textsuperscript{1,2} The interest is of theoretical value for bonding arguments and of utilitarian value for its relationship to structural determination of these complexes in solution. There are mainly two categories of interactions contributing to a nuclear magnetic resonance scalar coupling constant; first, those arising from interaction of the nuclear magnetic moments with the orbital motion of the electrons, and secondly, the Fermi contact term. In general, the coupling, $J_{AB}$, where atoms A and B are bonded to each other through a covalent bond having nuclei with $I = \frac{1}{2}$, is believed to be dominated by the Fermi contact term.\textsuperscript{3-6} The coupling constant, $J_{AB}$ is then given by\textsuperscript{7}

$$J_{AB} \propto \gamma_A \gamma_B \alpha_A^2 \alpha_B^2 |\psi_A(ns)(0)|^2 |\psi_B(ns)(0)|^2 (\Delta E)^{-1}$$

(1)

where $\gamma_A$ is the gyromagnetic ratio for the nucleus A, $\alpha_A^2$ is the s-character of the bonding hybrid orbital used by A.
in the A-B bond, $|\psi_{A(ns)}(0)|^2$ is the electron density of
the ns valence orbital at the nucleus, and $3\Delta E$ is a mean
singlet-triplet excitation energy. A number of chemists have
studied a series of closely related transition metal-
phosphorus complexes where all the factors in the above
expression can be assumed to remain constant except $\alpha^2$ and
$|\psi_{ns}(0)|^2$. Based on a comparison of the magnitudes of
coupling to triphenylphosphite with couplings to trialkyl-
phosphine given in Table 1, $\alpha_P^2$ and $|\psi_P(3s)(0)|^2$ are
expected to increase with increasing electronegativity of
substituents on phosphorus by changes in the s-character
of the phosphorus donor orbital for $\alpha_P^2$ and by orbital
contraction for $|\psi_P(3s)(0)|^2$. Furthermore, alteration of
the substituents primarily associated with the phosphorus
atom can deliver a large effect on $\alpha_P^2$ and $|\psi_P(3s)(0)|^2$,
but it will have only a small effect on the corresponding
terms for the other atom.

The relatively small dependence of the ratio on the
nature of the acceptor atom shown in Table 2 supports the
evidence that substituents directly bonded to the phosphorus
atom are mainly responsible for $\alpha_P^2|\psi_P(3s)(0)|^2$. Verkade
and his coworkers investigated phosphorus-phosphorus
coupling constants in complexes containing two phosphorus
ligands. They found the trends in the ranges of coupling
### TABLE 1

**SELECTED $^{31}\text{P}$ NMR SPECTRAL PARAMETERS OF TRIPHENYL PHOSPHITE COMPLEXES DISSOLVED IN DICHLOROMETHANE**

| Complex                                      | $|^{1}J_{(M-P)}|_{(Hz)}$ | $|^{2}J_{PMP'}|_{(Hz)}$ |
|----------------------------------------------|--------------------------|--------------------------|
| cis-[$\text{PtCl}_2\{\text{(PhO)}_3\text{P}\}_2]$ | 5770                     |                          |
| cis-[$\text{PtCl}_2\{\text{(PhO)}_3\text{P}\}(\text{Bu}_3\text{P})]$ | 6282                     | 20.0                     |
| | (PhO)$_3$P | 3156                     |                          |
| | Bu$_3$P     |                          |                          |
| cis-[$\text{PtMe}_2\{\text{(PhO)}_3\text{P}\}(\text{Bu}_3\text{P})]$ | 3292                     | b                        |
| | (PhO)$_3$P | 1727                     |                          |
| | Bu$_3$P     |                          |                          |
| cis-[$\text{PtMeCl}\{\text{(PhO)}_3\text{P}\}(\text{Bu}_3\text{P})]$ | 7411                     | 23.3                     |
| | (PhO)$_3$P | 1628                     |                          |
| | Bu$_3$P     |                          |                          |
| trans-[$\text{PtCl}_2\{\text{(PhO)}_3\text{P}\}(\text{Bu}_3\text{P})]$ | 4068                     | 709                      |
| | (PhO)$_3$P | 2516                     |                          |
| | Bu$_3$P     |                          |                          |
| [PtCl{\text{(PhO)}_3\text{P}}(\text{Bu}_3\text{P})_2]Cl$^c$ | 6399                     | 24.0                     |
| | (PhO)$_3$P | 2028                     |                          |
| | Bu$_3$P     |                          |                          |
| mer-[$\text{RhCl}_3\{\text{(PhO)}_3\text{P}\}(\text{Bu}_3\text{P})_2]$ | 202.8                    | 30.3                     |
| | (PhO)$_3$P | 79.3                     |                          |
| | Bu$_3$P     |                          |                          |
Table 1 (continued)

All values are taken from Ref. 8.

^No coupling due to \( |^{2j}_{\text{PMP}}| \) not resolved.

°Prepared in situ.
TABLE 2

THE RATIO, $\frac{1J_{\text{Pt-P}}(L=(\text{PhO})_3P)}{1J_{\text{Pt-P}}(L=R_3P)}$, IN THE PLATINUM(II) COMPLEXES

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<td>$[\text{PtCl}(\text{Bu}_3\text{P})\text{L}]^+^a$</td>
<td>1.85</td>
<td>Cl</td>
</tr>
<tr>
<td>cis-$[\text{PtCl}_2(\text{Bu}_3\text{P})\text{L}]^a$</td>
<td>1.79</td>
<td>Cl</td>
</tr>
<tr>
<td>cis-$[\text{PtCl}_2(\text{PhO})_3\text{P}\text{L}]^a$</td>
<td>1.83</td>
<td>Cl</td>
</tr>
<tr>
<td>$[\text{PtMeCl}(\text{R}_3\text{P})\text{L}]^a$</td>
<td>1.79</td>
<td>Cl</td>
</tr>
<tr>
<td>trans-$[\text{PtCl}_2(\text{Bu}_3\text{P})\text{L}]^a$</td>
<td>1.70</td>
<td>Bu$_3\text{P}$</td>
</tr>
<tr>
<td>cis-$[\text{PtMe}_2(\text{R}_3\text{P})\text{L}]^a$</td>
<td>1.77</td>
<td>Me</td>
</tr>
<tr>
<td>L-BH$_3^b$</td>
<td>1.53</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$The values are copied from Ref. 8.

$^b$The ratio in this case is $\frac{1J_{\text{B-P}}(L=(\text{PhO})_3\text{P})}{1J_{\text{B-P}}(L=R_3\text{P})}$ and the value is taken from Ref. 9.
constants to parallel roughly the increase in the sum of Pauling's electronegativity of atoms immediately bound to phosphorus atom in substituents. Since P-P couplings in coordination compounds are transmitted through the metal atoms metal-phosphorus couplings might be expected to parallel the trends in $^{2}J_{P-P}$ values. Nelson $^{11}$ found, based on the experimental results on the Pd complexes of mixed phosphine ligands, that the magnitude of $^{2}J_{P-P}$ should be affected by the electronegativity of the substituents bound to phosphorus if $^{2}J_{P-P}$ is dominated by the Fermi contact term. Allen and Pidcock$^{12}$ examined a platinum complex having two phosphine ligands, cis-PtCl(CH$_{3}$)(PEt$_{3}$)$_{2}$, and its phosphorus-31 nuclear magnetic resonance spectrum shows the presence of two chemically shifted phosphorus resonances having coupling constants to platinum of 4179 and 1719 Hz. Since these two couplings must share a common $|\psi_{Pt(6s)}(0)|^{2}$ term, this result shows that the non-equivalent phosphorus-platinum bonds must differ widely in their $\alpha_{Pt}^{2}$ terms.

Electronic effects of phosphine ligands have been determined by examining a series of monosubstituted metal carbynyls; $^{13}$ Tolman uses the A$_{1}$ carbonyl stretching mode of Ni(CO)$_{3}$L in CH$_{2}$Cl$_{2}$ solution. This substituent parameter, designated $\chi_{L}$ for ligand PX$_{1}$X$_{2}$X$_{3}$ can be calculated from the following equation (2).
An excellent correlation between these parameters and the $pK_a$'s of the phosphonium ions $\text{HPR}_3^+$ reported by Henderson$^{14}$ and Streuli,$^{15}$ with the points for $\text{PR}_2\text{H}$ and $\text{PRH}_2$ phosphines falling on the same line. Kabachnik$^{16}$ has proposed the substituent parameters based on acid ionization constants in water of phosphorus acids of the type

$$\begin{align*}
\text{O} \\
R' - \text{P} - \text{OH} \\
R''
\end{align*}$$

Kabachnik's $\sigma$ values and the parameters based on CO stretching frequencies show excellent correlation.

However, it has been recently recognized that the steric effect is also of critical importance. The ligand cone angle $\Theta$ was introduced$^{17}$ after it became clear that the ability of phosphorus ligands to compete for coordination positions on Ni(O) could not be explained satisfactorily in terms of their electronic character alone. Figures 1 and 2 show the pictorial definition of the ligand cone angle, $\Theta$, and the method to measure an effective cone angle for an unsymmetrical ligand $\text{PX}_1\text{X}_2\text{X}_3$ shown in equation (3), respectively.
Figure 1. The Cone Angle.

Figure 2. Cone Angle for an Unsymmetrical Ligands.
It has been shown that the dissociation equilibrium constants \( K_d \) of NiL\(_4\) (\( L = P(OEt)_3, PMe_3, P(0-p-C_6H_4Cl)_3, P(0-p-tol)_3, PEt_3, P(0-o-tol)_3, PMePh_2, PPh_3 \))\(^{18,19}\) are not sensitive to changing para-substituents in aryl phosphites. However, a decrease in bonding ability has been observed when one increases steric congestion around the bonding face of the phosphine atom. Lately, Alyea and his coworkers\(^{20}\) developed an alternative method to estimate the bulkiness of the phosphorus ligand, which emphasizes the cog-like nature of the ligand and thus "ligand profiles" were defined. The maximum semicone angle, \( \Theta/2 \), can be obtained as shown in Figure 3.

\[
\Theta = \left( \frac{2}{3} \right) \sum_{i=1}^{3} \frac{\theta_i}{2}
\]

Figure 3. The maximum semicone angle \( \Theta/2 \).
The vector \( M - X \) is coplanar with the metal, phosphorus and hydrogen atoms. Based on this concept, the values of \( \theta \) are variable widely; \( \text{PBU}^t_3 \) ranges from 176 to 187° and \( \text{PCy}_3 \) from 163 to 181°. However, the trends in Tolman's concept remain unchanged in Alyea's concept.

It has been found from a study of a series of platinum-phosphorus complexes that the crowdedness of the bulky ligands causes an increase of the Pt-P distance, 2.348 Å in the case of \( \text{trans-[PtI}_2\{\text{P(C}_6\text{H}_4\text{Me-2)}_3\}_2 \), \(^{21}\) compared to the corresponding distances in \( \text{trans-[PtBr}_2\{\text{PET}_3\}_2 \) (2.315 Å)\(^ {22}\) and \( \text{trans-[PtH}_2\{\text{PCy}_3\}_2 \) (2.25 Å),\(^ {23}\) respectively, which have less bulky ligands. Another interesting result has been observed in the reactions of \( \text{[Rh(cod)Cl]}_2 \) with \( \text{PPh}_3 \), \( \text{P(i-Pr)}_3 \), and \( \text{PCy}_3 \) and the behavior on the nitrogen fixation of their corresponding compounds. In the reaction of \( \text{[Rh(cod)Cl]}_2 \) and \( \text{PPh}_3 \), the air-stable product, \( \text{Rh(PPh}_3)_3\text{Cl} \) was produced and it does not react with the nitrogen molecule. In the case of \( \text{P(i-Pr)}_3 \), the bisphosphine adduct was formed, which picks up nitrogen readily to produce the side-on bonded dinitrogen complex, \( \text{trans-[Rh[P(i-Pr)}_3\text{]_2ClN}_2 \),\(^ {24}\) in the nitrogen atmosphere. For the tricyclohexylphosphine ligand, the extremely air-sensitive, three-coordinated complex, \( \text{Rh(PCy}_3)_2\text{Cl} \) resulted, whose dinitrogen complex was formed in 4 days.\(^ {25}\) These results could be explained in terms of
the cone angles of three phosphine ligands. For PPh$_3$ ligand with cone angle of 145°, all three phosphine ligands can be coordinated to the metal, thus the nitrogen-fixation could not be occurred. However, P(i-Pr)$_3$ has a wider cone angle of 160°, which makes coordination of three phosphine ligands around rhodium impossible. A 14-electron species RhCl[P(i-Pr)$_3$]$_2$ might be formed in situ which undergoes facile reaction with the nitrogen molecule to form a dinitrogen complex. But, the tricyclohexylphosphine ligand with cone angle of 170° might form a three-coordinated complex which is stable; thus, it does not react with molecular nitrogen readily.

**Research Objectives**

The goal of this work was to prepare a series of platinum(O)-polyydentate phosphine ligand complexes and utilize the phosphorus-31 nuclear magnetic resonance spectroscopy to investigate the character of platinum-phosphorus and phosphorus-phosphorus couplings in platinum(O) complexes. Platinum was chosen as the metal since $^{195}$Pt has 33.6% natural abundance with $I = \frac{1}{2}$; thus platinum-phosphorus coupling constants can be related to the nature of the platinum-phosphorus bond. The tridentate phosphine ligand, 1,1,1-tris(diphenylphosphinomethyl)ethane (tripod)
was used since Pt(PR$_3$)$_4$ complexes can dissociate in solution and control of stoichiometry in preparing complexes of two different monodentate phosphine ligands is difficult.

The synthesis of a series of Pt(tripod)PR$_3$ complexes, the characterization of those complexes, the interpretation of the phosphorus-31 nuclear magnetic resonance results will be described in this part of the dissertation.
EXPERIMENTAL

A. Reagents and Chemicals

1,1,1-Tris(diphenylphosphinomethyl)ethane (tripod) was obtained from Orgmet, Inc., E. Hampstead, N.H. and was used as obtained. Diphenylmethyphosphine, tris(p-tolyl)phosphine, triphenylphosphine, tris(p-fluorophenyl)phosphine, diphenyl-(pentafluorophenyl)phosphine, tris(2-cyanoethyl)phosphine, bis(diphenylphosphino)acetylene, diphenylmethoxyphosphine, t-butyldifluorophosphine, and tris(p-chlorophenyl)phosphite were obtained from either Strem Chemical Company, Danvers, Massachusetts, or Pressure Chemical Company, Pittsburgh, Pennsylvania, and were used as obtained. Potassium tetra-chloroplatinate(II), $K_2PtCl_4$, was prepared from platinum metal as described in the literature. 26

All reagent grade solvents were dried by distillation over appropriate drying agents under nitrogen prior to use. All other chemicals were reagent-grade quality and were used without further purification unless stated otherwise.

B. Instrumentation and Physical Measurements

Infrared spectra were measured on a Perkin Elmer 337 grating spectrophotometer from 400 to 4000 cm$^{-1}$ as Nujol
mulls or hexachlorobutadiene mulls between potassium bromide plates. Sharp polystyrene absorptions at 1601 and 906.7 cm\(^{-1}\) were used for calibration of the spectra.

Fourier-mode, proton-noise-decoupled, phosphorus-31 nuclear magnetic resonance spectra were collected on a Bruker HX90 spectrometer operating at 36.43 MHz, with a Bruker B-NC 12 data system. These \(^{31}\text{P}[^{1}\text{H}]\) spectra were obtained using 10 mm nmr tubes. In some cases, deuterated solvents (10–20% of the sample volume) provided an internal deuterium lock. These spectra were standardized using an external reference by (a) obtaining the spectrum, (b) inserting a coaxial tube containing 85% phosphoric acid and collecting that spectrum, and (c) adding the two spectra together to obtain a referenced spectrum. In other cases, the deuterated solvent and a secondary standard, trimethylphosphate (\(\delta = 58.09\) Hz relative to \(\text{H}_3\text{PO}_4\)), were contained in a coaxial tube which was placed in the sample tube throughout the collection of data. Chemical shifts on the phosphorus-31 spectra are reported relative to 85% \(\text{H}_3\text{PO}_4\) with positive values being downfield from the standard.

Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona.
C. General Experimental Procedure

Standard techniques for the manipulation of air-sensitive compounds were used for all the experiments of this work. High-purity nitrogen was used to provide an inert atmosphere. Solvents were deaerated by purging them with nitrogen or by the freeze-thaw method.

D. Synthesis of Pt(0) Complexes

1. Pt(tripod)PPh₂Me

To a solution of tripod ligand (1.2050 g, 1.93 mmol) in 90 ml of hot ethanol was added \( \text{K}_2\text{PtCl}_4 \) (0.7673 g, 1.85 mmol) in 5 ml of distilled water. A white precipitate, \( \text{Pt(tripod)Cl}_2 \), was formed immediately and the solution turned pink. The resultant slurry was stirred for 1 hr to redissolve the white precipitate; the pink color of the solution slowly disappeared during that time. After the addition of diphenylmethylphosphine, \( \text{PPh}_2\text{Me} \) (0.4 g, 2.0 mmol), the solution was cooled to room temperature and \( \text{NaBH}_4 \) (0.1524 g, 4.01 mmol) in 20 ml of water was added dropwise using a pressure-equalizing funnel while the mixture was stirred. Immediately a bright yellow precipitate occurred, accompanied by vigorous evolution of \( \text{H}_2 \) gas. After the hydrogen evolution was completed, the bright yellow powder was collected on a Schlenk frit, washed with
water and ethanol in sequence and dried in vacuo. Yield: 1.282 g (68%).

Analysis for C_{54}H_{52}P_4Pt: Calcd: C, 63.59; H, 5.10.
Found: C, 63.44; H, 5.14.

2. Pt(tripod)L, L = P(p-C_6H_4F)_3, Ph_2P(C_6F_5), P(CH_2CH_2CN)_3

PPh_2C = CPPh_2

The synthetic method for the above compounds was the same as that used for Pt(tripod)PPh_2Me except that P(p-C_6H_4F)_3, Ph_2P(C_6F_5), P(CH_2CH_2CN)_3 and PPh_2C=CPPh_2 were used, respectively, instead of PPh_2Me for the monophosphine ligand.

3. Pt(tripod)P(p-tolyl)_3

A solution of K_2PtCl_4 (0.837 g, 2.01 mmol) in 5 ml of distilled water was added to a solution of tripod (1.253 g, 2.01 mmol) in 90 ml of hot ethanol. To the reaction mixture was added P(p-tolyl)_3 (0.680 g, 2.00 mmol) in 20 ml of ethanol and 20 ml of acetone while the solution was warm. After the reaction mixture was stirred for 1 hr, it was cooled to room temperature and NaBH_4 (0.227 g, 5.97 mmol) in 10 ml of water was added dropwise. A golden yellow product was collected, washed with distilled water and ethanol and dried in vacuo for 1 hr.
4. Pt(tripod)PPh$_3$

Tripod ligand (0.624 g, 1.00 mmol) was dissolved in 90 ml of boiling ethanol and the solution was cooled to 50°C. A solution of K$_2$PtCl$_4$ (0.400 g, 0.96 mmol) was added to the above solution and the reaction mixture was heated to 70°C to dissolve the white precipitate. After cooling the solution to 40°C again, NaBH$_4$ (0.076 g, 2.00 mmol) in 20 ml of distilled water was added dropwise to the solution. A bright yellow precipitate formed immediately; it was collected on a Schlenk frit by filtration, washed with water and ethanol and dried in vacuo for 3 hr.

Analysis for C$_{62}$H$_{60}$P$_4$Pt:  Calcd: C, 66.24; H, 5.38.  
Found: C, 65.80; H, 5.51.

5. Pt(tripod)L in situ; General Procedure

Equimolar quantities of Pt(tripod)PPh$_2$Me and the desired tertiary phosphine ligand were dissolved in THF. The bright yellow solution was transferred via syringe into a 10 mm nmr tube for phosphorus-31 nmr analysis. The following ligands were employed in this manner.

L:  PPh$_2$(OMe)$_2$,  P(OPh)$_3$,
P$_2$(t-Bu)$_2$,  P(O-C$_6$H$_4$Cl-p)$_3$,
PF$_2$NMe$_2$,  PF$_3$.  

RESULTS AND DISCUSSION

A. Synthesis and Characterization

A new series of platinum(0) complexes has been synthesized in this study. The reactions for the preparation of these complexes are summarized in Figure 4. There are two types of reactions: (1) direct synthesis of the complexes by the reaction of Pt(tripod)Cl$_2$ and the corresponding monodentate phosphorus ligand, followed by sodium borohydride reduction; and (2) synthesis using displacement reactions from the complexes Pt(tripod)PPh$_2$Me or Pt(tripod)PPh$_3$ by substitution of the corresponding monodentate phosphorus ligand by PR$_3$ ligands that have more electronegative substituents to prevent the possible hydrolysis in aqueous solution.

The products were characterized by elemental analyses, infrared spectroscopy, and phosphorus-31 nuclear magnetic resonance spectroscopy. The phosphorus-31 nmr data received a major emphasis in this work.

The intermediate, Pt$^{II}$ (tripod)Cl$_2$ (1), was isolated as a white powder, and its phosphorus-31 nmr spectrum (Table 3) consisted of a triplet of area 1 for P$_2$ due to
\[ \text{K}_2\text{PtCl}_4 + \text{tripod} \rightarrow [\text{Pt}(\text{tripod})\text{Cl}_2] + 2 \text{KCl} \]

\[ \text{a.} \text{L}_x \]

\[ \text{b.} \text{NaBH}_4 \]

\[ \text{Pt}(\text{tripod})\text{L}_x \]

\[ \text{L}_x = \text{PPh}_2\text{Me}, \]

\[ \text{P}(\text{p-tolyl})_3, \]

\[ \text{PPh}_3, \]

\[ \text{P}(\text{p-C}_6\text{H}_4\text{F})_3, \]

\[ \text{PPh}_2\text{C}_6\text{F}_5, \]

\[ \text{P(}\text{CH}_2\text{CH}_2\text{CN})_3, \]

\[ \text{Ph}_2\text{PC}═\text{CPPPh}_2. \]

\[ \text{Pt}(\text{tripod})\text{PPh}_2\text{Me} \quad \text{or} \quad \text{Pt}(\text{tripod})\text{PPh}_3 \quad \text{L}_y \quad \text{Pt}(\text{tripod})\text{L}_y + \]

\[ \text{PPh}_2\text{Me} \quad \text{or} \quad \text{PPh}_3. \]

\[ \text{L}_y = \text{PPh}_2(\text{OMe}), \]

\[ \text{PF}_2(\text{t-Bu}), \]

\[ \text{PF}_2\text{NMe}_2, \]

\[ \text{P(}\text{OPh})_3, \]

\[ \text{P(}\text{o-p-}\text{C}_6\text{H}_4\text{Cl})_3, \]

\[ \text{PF}_3. \]

**Figure 4.** Reaction scheme for the platinum(0) complexes.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Chemical Shift (ppm)</th>
<th>Coupling Constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5P₁</td>
<td>5P₂</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>-1.8</td>
<td>-29.8</td>
</tr>
</tbody>
</table>
the four-bond coupling with two \( P_1 \) nuclei, a doublet of area 2 for two \( P_1 \) nuclei coupled with \( P_2 \), and the corresponding \(^{195}\text{Pt} \) satellites (\(^{195}\text{Pt} \) in 33.8\% natural abundance, \( I = \frac{1}{2} \)), indicating that two phosphorus atoms of the tripod ligand and both chlorine atoms were bonded to the platinum leaving one phosphorus atom of the tripod ligand free.

\[
\begin{align*}
\text{Cl} & \\
\text{Pt} & \\
\text{Cl} & \\
\end{align*}
\]

In the series of Pt(0) complexes, the phosphorus-31 nmr spectra show that all three phosphorus nuclei are bonded to the metal. A few of the complexes in this study give first order \( A_3 BX \) spin systems with a doublet due to the \( P_3 \) nuclei and a quartet due to the \( P_1 \) nucleus being split by the set of the \( P_3 \) nuclei. The corresponding platinum-195 satellites for both doublet and quartet are also discussed. However, the majority of the compounds of this study are second-order \( A_3 BX \) spin systems; that is,
some additional lines are seen in the spectra. Thus the central position of these spectra (due to molecules containing Pt with I = 0) gives $A_3B$ pattern. A series of calculated $A_3B$ spectra is displayed in Figure 5 where $v_A > v_B$ and $J_{AB} > 0$ are assumed. In the case of $v_A < v_B$, the whole spectrum is turned over. When $J_{AB}$ is negative, the labelling of the transitions is altered but the appearance of the spectrum remains the same. The Larmor frequencies and the spin-coupling constant can be derived from the following equations.

$$
\begin{align*}
    v_A &= C + \frac{1}{2} \delta, \\
    v_B &= C - \frac{1}{2} \delta, \\
    C &= \frac{[v(A5) + v(B5)]}{2}, \\
    \delta &= \frac{[v(A7) - v(B6)]}{[v(A5) - v(B5)]^{1/2}}, \\
    |J_{AB}| &= v(A7) - v(A5) \text{ or } v(B5) - v(B6)
\end{align*}
$$

The $^{31}P\{^1H\}$ nmr spectrum of Pt(tripod)PPh$_2$NO (2) in tetrahydrofuran is illustrated in Figure 6. The spectrum can be analyzed as an $A_3BX$ pattern to give: $\delta P_1 = -7.8$ ppm, $\delta P_3 = -19.5$ ppm, $J_{P_1-P_3} = 51$ Hz, $J_{\text{Pt-P}_1} = 5370$ Hz.
Figure 5. Theoretical $A_3B$ spectra.$^{29}$
Figure 6. Proton-decoupled phosphorus-31 nmr spectrum of Pt(tripod)PMePh\textsubscript{2}
$^{1}J_{\text{Pt-P}} = 3076 \text{ Hz}$. Data for the series of Pt(tripod) (monophosphine) complexes are illustrated in Table 4. The $^{1}J_{\text{Pt-P}}$ values for the monodentate phosphines are much larger than for the triphosphine. The magnitude of the directly bonded coupling constants depends on the hybridization around each atom. The tripod ligand restricts the P-Pt-P angles to about 90-99°, thus three Pt-P bonds will have smaller s-character than tetrahedral Pt-P bonds. Therefore, the remaining Pt-P bond will be hydridized to include more s-character, and this would be expected to exhibit a larger Pt-P coupling constant. The crystal structure determination of Ni(tripod)\textsubscript{3} shows three P-Ni-P angles at 92.2°, 94.4° and 97.7°. The average of three P-Fe-P bond angles in the dimeric diiron complex [Fe\textsubscript{2}H\textsubscript{3}(tripod)\textsubscript{2}]PF\textsubscript{6} is 89°, thus the P-M-P angles are fairly consistent. Dr. G.A. Williams at the University of Sussex\textsuperscript{32} has determined the molecular structure of Pt(tripod)P(p-C\textsubscript{6}H\textsubscript{4}F)\textsubscript{3} by a single-crystal X-ray structural analysis to give: three P-Pt-P angles of 90.8°, 91.3°, and 99.6°. The relationship between the crystallographic data and the $^{31}$P nmr will be discussed in the next section.

The compounds Pt(tripod)PPh\textsubscript{2}Me, Pt(tripod)P(p-tolyl)\textsubscript{3}, Pt(tripod)PPh\textsubscript{3}, Pt(tripod)(p-C\textsubscript{6}H\textsubscript{4}F)\textsubscript{3} and Pt(tripod)Ph\textsubscript{2}PC\textsubscript{6}F\textsubscript{5} all contain phenyl or substituted phenyl groups; for this reason, they have similar infrared spectra. The infrared
<table>
<thead>
<tr>
<th>Compounds</th>
<th>$^{1}J_{\text{Pt-P}_1}$ \text{ Hz}</th>
<th>$^{1}J_{\text{Pt-P}_3}$ \text{ Hz}</th>
<th>$^{2}J_{\text{P}_1-P_3}$ \text{ Hz}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(tripod)PPh$_2$Me</td>
<td>5370</td>
<td>3076</td>
<td>51.2</td>
</tr>
<tr>
<td>Pt(tripod)P(p-tolyl)$_3$</td>
<td>5380</td>
<td>3054</td>
<td>51.0</td>
</tr>
<tr>
<td>Pt(tripod)PPh$_3$</td>
<td>5380</td>
<td>3100</td>
<td>51.3</td>
</tr>
<tr>
<td>Pt(tripod)P(p-C$_6$H$_4$F)$_3$</td>
<td>5450</td>
<td>3068</td>
<td>52.5</td>
</tr>
<tr>
<td>Pt(tripod)PPh$_2$C$_6$F$_5$</td>
<td>5470</td>
<td>3058</td>
<td>55.0</td>
</tr>
<tr>
<td>Pt(tripod)P(CH$_2$CH$_2$CN)$_3$</td>
<td>5470</td>
<td>2935</td>
<td>54.9</td>
</tr>
<tr>
<td>$[^{131}\text{P}]$Pt(tripod)PPh$_2$PC=CPPh$_2$</td>
<td>5521</td>
<td>3100</td>
<td>50.6</td>
</tr>
<tr>
<td>Pt(tripod)PPh$_2$(OMe)</td>
<td>6297</td>
<td>2882</td>
<td>62.0</td>
</tr>
<tr>
<td>Pt(tripod)PF$_2$(t-Bu)</td>
<td>7958</td>
<td>2760</td>
<td>78.8</td>
</tr>
<tr>
<td>Pt(tripod)PF$_2$NMe$_2$</td>
<td>8838</td>
<td>2893</td>
<td>83.0</td>
</tr>
<tr>
<td>Pt(tripod)P(OPh)$_3$</td>
<td>9150</td>
<td>2883</td>
<td>87.0</td>
</tr>
<tr>
<td>Pt(tripod)P(OCH$_2$CH$_2$Cl)$_3$</td>
<td>9200</td>
<td>2863</td>
<td>88.6</td>
</tr>
<tr>
<td>Pt(tripod)PF$_3$</td>
<td>2867</td>
<td>95.2</td>
<td></td>
</tr>
</tbody>
</table>

aNot observed due to low solubility.

bThese values are taken from reference 39.
spectra of Pt(tripod)PPh₃ are presented in Figures 7 and 8. The phosphorus-31 nmr spectrum of Pt(tripod)PPh₃ (Figure 9) shows an AₓPX spin system in which the quartet is partially overlapped with one satellite of the doublet.

The tris-2-cyanoethylphosphine complex, Pt(tripod)-P(CH₂CH₂CN)₃, has coupling constants similar to those of Pt(tripod)PPh₃. The phosphorus-31 nmr data of the complex will be discussed in the next section. The infrared spectrum shows that the C≡N stretching frequency (Figures 10 and 11) is a weak, broad band at 2250 cm⁻¹, indicating that the -C≡N group is not bonded to the metal.³³

The assumed dimeric complex, [Pt(tripod)]₂Ph₂PC≡CPPh₂ (3) was prepared using two equivalents of Pt(tripod)Cl₂ and one equivalent of Ph₂PC≡CPPh₂ followed by NaBH₄ reduction of the metal complex from Pt(II) to Pt(0). The infrared spectrum of the dimer (Figures 12 and 13) shows no C≡C stretching frequency; this suggests a center of symmetry of the molecule.³⁴ The phosphorus-31 nmr spectrum (Figure 14) of [Pt(tripod)]₂Ph₂PC≡CPPh₂ confirms that one phosphorus atom of bis(diphenylphosphino)acetylene is bonded to each Pt(tripod) moiety in a symmetrical manner, since the spectrum can be analyzed as a simple AₓBX pattern.
Figure 7. Infrared spectrum of Pt(tripod)PPh₃ in Nujol; 4000 - 1300 cm⁻¹.
Calibration peak is at 1601.4 cm⁻¹.
Figure 8. Infrared spectrum of Pt(tripod)PPh$_3$ in Nujol; 1350 - 400 cm$^{-1}$. Calibration peak is at 906.7 cm$^{-1}$.
Figure 9. Proton-decoupled phosphorus-31 nmr spectrum of Pt(tripod)PPh₃.
Figure 10. Infrared spectrum of Pt(tripod)P(CH₂CH₂CN)₃ in Nujol; 4000 - 1300 cm⁻¹. Calibration peak is at 1601.4 cm⁻¹.
Figure 11. Infrared spectrum of Pt(tripod)P(CH₂CH₂CN)₃ in Nujol; 1350 - 400 cm⁻¹. Calibration peak is at 906.7 cm⁻¹.
Figure 12. Infrared spectrum of $[\text{Pt(tripod)}]_2\text{Ph}_2\text{PC}≡\text{GPPPh}_2$ in Nujol; 4000 - 1300 cm$^{-1}$. Calibration peak is at 1601.4 cm$^{-1}$. 
Figure 13. Infrared spectrum of \([\text{Pt(tripod)}]_2 \text{Ph}_2 \text{PC} = \text{CPPh}_2\) in Nujol; 1350 - 400 cm\(^{-1}\). Calibration peak is at 906.7 cm\(^{-1}\).
Figure 14. Proton-decoupled phosphorus-31 nmr spectrum of 
\[
\left[\text{Pt(tripod)}\right]_2\text{PPh}_2\text{C}=\text{CPh}_2.
\]
Replacement of the monophosphine ligands PPh₂Me and PPh₃ from the complexes Pt(tripod)PPh₂Me and Pt(tripod)PPh₃, respectively, with PR₃ ligands containing more electronegative substituents proceeds readily in benzene or toluene at room temperature. The newly substituted complexes can, in most cases, be precipitated as bright yellow solids by the addition of hexane after evaporation of some of the solvent. Since the author had difficulty in isolating solids for some of the substituted platinum complexes, several reactions were investigated in situ to determine the relationship between the phosphorus-phosphorus coupling constant and the platinum-phosphorus coupling constant.

\[ \text{Pt(tripod)PPh}_3 + PR_3 \rightleftharpoons \text{Pt(tripod)PR}_3 + PPh_3 \]

R = a more electronegative substituent than phenyl.
The monophosphine ligand Ph$_2$P(OMe) gives a first order A$_3$PX spin system in the phosphorus-31 nmr spectrum (Figure 15). One additional line at $\delta = -27.2$ ppm is due to the free PPh$_2$Me ligand. The left satellite of the quartet is probably folded over at the starting line of the nmr chart and thus lost from this spectrum.

The phosphorus nmr spectrum of the solutions obtained by treating Pt(tripod)PPh$_2$Me with PF$_2$(t-Bu) shows a doublet of triplets due to the resonance of P$_3$ being split into a doublet by coupling to P$_1$; in turn, those doublets are split into triplets by the three-bond coupling with two fluorine nuclei on PF$_2$(t-Bu) with the corresponding satellite by platinum-195. And a triplet of quartets for P$_1$ was also observed with a set of satellites by platinum-195; a triplet by coupling with two gem-fluorines and the triplet was further split into a quartet due to the three P$_3$ nuclei. Besides the liberated PPh$_2$Me, the spectrum shows a small amount of impurity which might be the compound Pt(tripod)(PPh$_2$Me)PF$_2$(t-Bu) with one dangling phosphorus nucleus from the tripod ligand. However, due to the low intensity of the peak in the spectrum and overlapping with one satellite, the exact analysis of the impurity could not be made. The phosphorus-31 nmr spectral data for the major component gives: $\delta P_1 = 212.0$ ppm, $\delta P_3 = -18.0$ ppm,
Figure 15. Proton-decoupled phosphorus-31 nmr spectrum of Pt(tripod)PPh$_2$(OMe).
\[^1J_{\text{Pt-P}_1} = 7958 \text{ Hz}, \ ^1J_{\text{Pt-P}_3} = 2760 \text{ Hz}, \ ^3J_{\text{P}_1-P_3} = 78.8 \text{ Hz}, \ ^1J_{\text{P}_1-F} = 1099 \text{ Hz}, \ ^3J_{\text{P}_3-F} = 58 \text{ Hz}.\]

Pt(tripod)P(OC\_6H\_4Cl-E)\_3 was prepared by substituting P(0-C\_6H\_4Cl-P)\_3 for PPh\_2Me of Pt(tripod)PPh\_2Me in THF, and evaporating the solvent by blowing a slow stream of nitrogen across the solution. The broad, moderately strong peak at approximately 1200 cm\(^{-1}\) in the infrared spectrum (Figures 16 and 17) indicates the presence of the phosphite ligand. The \(^{31}\text{P}\{^1\text{H}\}\text{nmr spectrum is a first-order A}_3\text{P}X\) spin system.

The P(OPh)\_3 ligand also can easily replace PPh\_3 from Pt(tripod)PPh\_3 to give Pt(tripod)P(OPh)\_3, which gives a first-order \(^{31}\text{P}\{^1\text{H}\}\text{nmr spectrum (Figure 18).}\)

**B. Discussion of the Phosphorus-31 Nmr Data**

Since Pt(PR\_3)\_4 complexes dissociate in solution, synthesis of complexes containing mixed phosphine ligands are difficult. Consequently, there are not many \(^{31}\text{P}\text{nmr results that give the magnitudes of Pt-P and P-P couplings for platinum(O) complexes.}\)

The chelating triphosphine ligand, CH\_3C[CH\_2P(C\_6H\_5)\_2]\_3, tripod, is ideal for \(^{31}\text{P}\text{nmr study since it leads to dissociatively stable tetrahedral platinum(O) complexes in the presence of a fourth ligand. In this work, monodentate
Figure 16. Infrared spectrum of Pt(tripod)P(0-C₆H₄Cl-p)₃ in Nujol; 4000 - 1300 cm⁻¹. Calibration peak is at 1601.4 cm⁻¹.
Figure 17. Infrared spectrum of Pt(tripod)P(0-C₆H₄Cl-p)₃ in Nujol; 1350 - 400 cm⁻¹. Calibration peak is at 906.7 cm⁻¹.
Figure 18. Proton-decoupled phosphorus-31 nmr spectrum of Pt(tripod)PPh$_3$ + P(OPh)$_3$. 
phosphines were used as the fourth ligands. The main purpose was to find the relationship between $^{1}J_{Pt-P}$ and $^{2}J_{P-P}$ using various monodentate phosphorus ligands in Pt(tripod)PR$_3$ complexes. Also, it was important to determine the effect of the PR$_3$ substituents on the coupling constants and the chemical shifts. Among the interactions contributing to a nuclear magnetic resonance scalar coupling constant between two atoms bonded to each other through covalent bond, the Fermi contact interaction is assumed to be the dominant contribution. The Fermi contact term is a measure of the electron density at both nuclei. Since the s orbital has a finite probability at the nucleus and p, d and other orbitals have a node at the nucleus, the Fermi contact term should reflect the s-character of the bond.

Using Pople and Santry's equation for the Fermi contribution to directly bonded X-Y coupling constants, Pidcock and his coworkers obtained the following approximate expression for the coupling constant, $^{1}J_{Pt-P}$:

$$^{1}J_{Pt-P} \propto \gamma_{Pt} \gamma_{P} \alpha_{P}^{2} 2^{\alpha_{P}} |\Psi_{Pt}(6s)(0)|^{2} |\Psi_{P}(3s)(0)|^{2} (3\Delta E)^{-1}$$

where $\gamma_{Pt}$ and $\gamma_{P}$ are the magnetogyratic ratios for the nuclei with spin quantum number $I_x$, $3\Delta E$ is an average excitation energy, $\alpha_{X}^{2}$ is the s-character of the hybrid orbital used
by X in the platinum-phosphorus bond, and $|\psi_{(0)}|^2$ terms are the electron densities of the indicated orbitals evaluated at the parent nuclei. In that paper, they considered the relative importance of the parameters of the equation and concluded that changes in the magnitude of $^1J_{\text{Pt-P}}$ within a series of platinum-phosphine complexes are largely dependent on the changes in $\alpha_{\text{p}}^2 |\psi_{(3s)}(0)|^2$ and $\alpha_{\text{Pt}}^2$. Using a series of closely related platinum complexes, Pidcock and others correlated the Pt-P bond strength with the $^1J_{\text{Pt-P}}$ value assuming that $\alpha^2$ was proportional to the strength of the Pt-P bond. In many cases, the Pt-P bond strength seems to increase as the s-component of the bond increases. However, in a study of complexes of the type $\text{cis-PtCl}_2(\text{PET}_3)\text{L}$ (where L = Cl$^{-}$, C(NPhCH$_2$)$_2$, CNPh, C(OEt)NPh, PET$_3$, CO, P(OPh)$_3$, PF$_3$) no correlation was found between $^1J_{\text{Pt-P}}$ and the length of the Pt-P bond. Also, the Pidcock's correlation does not appear to fit with ligands that are capable of $\pi$-bonding, since there is no direct way for the Fermi contact term to reflect the $\pi$-bonding character and the $^1J_{\text{Pt-P}}$ values, unless changes in the $\pi$-electron system in a molecule alter the electron distribution in the $\sigma$-system. Therefore, $^1J_{\text{Pt-P}}$ values may or may not reflect accurately the strength of a bond, depending upon the relative contributions of $\sigma$ and $\pi$ wave functions.
toward the overall strength of the bond. Pidcock also proposed that alteration of the group bonded to one of the coupled atoms can have a large effect on $\alpha^2$ and $|\uparrow_{(0)}|^2$ for that atom, but it will have only a small effect on the corresponding terms for the other atom. $^8,^9$

In the present system, $\text{Pt(tripod)PR}_3$, the expression for $^1J_{\text{Pt-P}}$ used by Pidcock can be adopted. The relative importance of the parameters should be reconsidered for the system in this work. The terms involved in $\Delta E$ are singlet to triplet excitation energies, and the lowest-energy transitions are of greatest importance in determining $\Delta E^{-1}$. Thus, the complexes with weakest ligand fields would be expected to have the largest coupling constants. For example, in the case of cis- and trans-$[\text{PtX}_2(\text{PR}_3)_2]$ ($R = \text{Bu}$ and $\text{OEt}, X = \text{Cl}, \text{Br}$, and $I$), $J_{\text{Pt-P}}$ decreases as $X$ changes from $\text{Cl}$, $\text{Br}$ to $I$, that is, the ligand-field strength decreases; the actual trend of the changes of coupling constants is entirely reverse to what we expected. Consequently, we may conclude that the difference of $^1J_{\text{Pt-P}}$ is not dominated by the variation of $^3\Delta E^{-1}$. This leaves four parameters to be considered: $\alpha_{\text{Pt}}^2$, $|\uparrow_{\text{Pt}(6s)(0)}|^2$, $\alpha_{\text{P}}^2$ and $|\uparrow_{\text{P}(3s)(0)}|^2$. In our system, there are two kinds of phosphorus atoms: $\text{P}_1$ of the monodentate phosphine and a $\text{P}_3$
set from the tripod ligand. Since both couplings, $^{1}J_{\text{Pt-P}_1}$ and $^{1}J_{\text{Pt-P}_3}$, must share a common $|\psi_{\text{Pt}(6s)}(0)|^2$ term, the
nonequivalent $^{1}J_{\text{Pt-P}_1}$ may not be attributed to $|\psi_{\text{Pt}(6s)}(0)|^2$
as long as $^{1}J_{\text{Pt-P}_3}$ remains relatively constant. Thus,
phosphorus-31 nmr data for the platinum(0) complexes are
presented in Table 4 according to the increasing value of
$^{1}J_{\text{Pt-P}_1}$. The values of $^{1}J_{\text{Pt-P}_1}$ in the complexes produce
the order $\text{PPH}_2\text{Me} \approx \text{P(p-tolyl)}_3 < \text{PPH}_3 < \text{P(p-C}_6\text{H}_4\text{F)}_3 \approx$
$\text{Ph}_2\text{PC}_6\text{F}_5 < \text{P(CH}_2\text{CH}_2\text{CN)}_3 < \text{Ph}_2\text{PC}=\text{CPPH}_2 < \text{Ph}_2\text{P(OMe)} <$
$\text{PF}_2(t-Bu) < \text{PF}_2\text{NMe}_2 < \text{P(OPh)}_3 < \text{P(O-C}_6\text{H}_4\text{Cl-p)}_3 < \text{PF}_3$.
Table 7 also shows that generally the Pt-P$_1$ and P$_1$-P$_3$
coupling constants increase, whereas the $^{1}J_{\text{Pt-P}_3}$ values
decrease slowly. The fact that the Pt-P$_3$ coupling constants
are not very sensitive to the variation of the monodentate
tertiary phosphine is consistent with Pidcock's assumption
that the alteration of the group bonded to one of the
coupled atoms can have a large effect on $\alpha^2$ and $|\psi(0)|^2$ for
corresponding terms for the other atom. Since the
phosphorus-phosphorus couplings in these coordination
compounds are transmitted through the metal atom assuming
that there is no transmission through carbon chains, the
metal-phosphorus couplings might be expected to parallel
the trends in $^{2}J_{\text{p-p}}$ values. From the investigation of
palladium complexes of mixed phosphine ligands, Nelson
argued that the magnitude of $2J_{p-p}$ should be affected by the electronegativity of the substituent bound to phosphorus atom assuming $2J_{p-p}$ is dominated by the Fermi contact term. Figure 19 shows the linear relationship between $1J_{pt-P_1}$ and $2J_{p_1-P_3}$; this least-squares plot fits the equation (4).

$$1J_{pt-P_1} = 105 \times 2J_{p_1-P_3} - 144 \text{ Hz}$$ (4)

Since 144 Hz can be regarded as negligible compared to the range of $1J_{pt-P_1}$ (5000-9000 Hz), one could say that $1J_{pt-P_1}$ is directly proportional to $2J_{p_1-P_3}$ and the values of $1J_{pt-P_1}$ produce nearly the same order as does the electronegativity variation of the substituents on the monodentate phosphine ligand. By increasing the electronegativity on a substituent R, more p-character will be used in the bond between phosphorus and R; in turn, more s-character will be involved in the Pt-P bond and the $1J_{pt-P_1}$ values will be larger.

Tolman\textsuperscript{13} described a rapid method for determining electron donor-acceptor properties of triply connected phosphorus ligands based on the $A_1$ carbonyl stretching frequency of Ni(CO)$_3$L complexes in CH$_2$Cl$_2$. The measured frequencies for 70 ligands in his work shows that successive replacement of one substituent on phosphorus by another causes $\nu_{CO}(A_1)$ to change by nearly constant increments.
Figure 19. Relationship of $^1J_{Pt-P_1}$ vs $^2J_{P_1-P_3}$. 
This observation suggests that each substituent on phosphorus makes a contribution to the CO stretching frequency observed for a given Ni(CO)$_3$L complex. This assigned substituent contribution is designated $\chi_1$, and it has a magnitude (in cm$^{-1}$) such that the $\nu_{\text{CO}}$ for any Ni(CO)$_3$PX$_1$X$_2$X$_3$ combination can be represented by the equation

$$\nu_{\text{CO}}(A_1) = 2056.1 + \sum_{i=1}^{3} \chi_i \text{ cm}^{-1}.$$ 

The frequency 2056.1 cm$^{-1}$ is that of P(t-Bu)$_3$, the most basic ligand in the series. The values of $\nu_{\text{CO}}(A_1)$ given by other ligands can be predicted by the additivity rule even when direct data are not available. The $^{2}J_{P_1-P_3}$ values correlate reasonably well with Tolman's substituent constants for the ligands used in this study. The relationships between $^{2}J_{P_1-P_3}$ and various inductive parameters are listed in Table 5 for the platinum complexes.

A group of substituent parameters have been proposed by Kabachnik, based on acid ionization constants in water of phosphorus acids of the type $R'-\overset{\circ}{P}-OH$.\textsuperscript{16}

On the other hand, the basicities of substituted phosphines were determined in a nonaqueous solvent, nitromethane, by Streuli.\textsuperscript{15}
However, it is hard to make any meaningful conclusion for our work because there are not many data available from Kabachnik's and Streuli's experiments.

As we see from Figure 20, the $^{2}J_{P_1-P_3}$ values correlate well with Taft's substituent constants, $\sigma^*$, which are defined as measures of the electron withdrawing power of an atom or group of atoms in a molecule; Taft's $\sigma^*$ is based on transmission of inductive effects through carbon while the $^{2}J_{P_1-P_3}$ values are between phosphorus atoms.

It would be interesting to point out that the coupling constants of Pt-P$_1$ and P$_1$-P$_3$ for PPh$_2$Me, P(p-tolyl)$_3$, PPh$_3$, P(p-$C_6H_4F$)$_3$, Ph$_2$PC$_6F_5$, P(CH$_2$CH$_2$CN)$_3$ and Ph$_2$PC=CPPPh$_2$ complexes are very close to each other. It is not surprising to observe similar coupling constants for PPh$_2$Me, P(p-tolyl)$_3$ and PPh$_3$ complexes, since these ligands do not differ much from each other in the various inductive parameters. Although Tolman's constant for P(p-$C_6H_4F$)$_3$ is higher than the above three phosphine ligands, the electron inductive withdrawing power of the fluorine atom on the para-position of the phenyl group seems to be cancelled mostly by the resonance effect.

\[ -\overset{\text{V}}{P} - \overset{\text{F}}{\text{C}_6\text{H}_4} \leftrightarrow -\overset{\text{F}}{P} = \overset{\text{C}_6\text{H}_4}{\text{C}_6\text{H}_4} = \overset{\text{F}}{\text{C}_6\text{H}_4} \]
Figure 20. Relationship of $2J_{P_1-P_2}$ with sum of Taft's constant $\sum \sigma^*$. 
<table>
<thead>
<tr>
<th>$L$</th>
<th>$2J_{P_1-P_3}$</th>
<th>$\sum_{i=1}^{3} \chi_i^a$</th>
<th>$\sum_{i=1}^{3} \sigma_i^b$</th>
<th>$\Sigma EN^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$PPh_2Me$</td>
<td>51.2 Hz</td>
<td>11.2</td>
<td>1.20</td>
<td>7.5</td>
</tr>
<tr>
<td>$P(p$-tolyl)$_3$</td>
<td>51.0</td>
<td>10.5</td>
<td>NA</td>
<td>7.5</td>
</tr>
<tr>
<td>$PPh_3$</td>
<td>51.3</td>
<td>12.9</td>
<td>1.80</td>
<td>7.5</td>
</tr>
<tr>
<td>$P(p$-C$_6H_4F)_3$</td>
<td>52.5</td>
<td>15.0</td>
<td>NA</td>
<td>7.5</td>
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<tr>
<td>$PPh_2C_6F_5$</td>
<td>55.0</td>
<td>19.8</td>
<td>NA</td>
<td>7.5</td>
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<tr>
<td>$P(CH_2CH_2CN)_3$</td>
<td>54.9</td>
<td>21.9</td>
<td>2.40</td>
<td>7.5</td>
</tr>
<tr>
<td>$Ph_2PC CPPh_2$</td>
<td>50.6</td>
<td>NA</td>
<td>NA</td>
<td>7.5</td>
</tr>
<tr>
<td>$PPh_2(OMe)$</td>
<td>62.0</td>
<td>16.3</td>
<td>2.66</td>
<td>8.5</td>
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<tr>
<td>$PF_2(t$-Bu$)$</td>
<td>78.8</td>
<td>36.4</td>
<td>5.86</td>
<td>10.7</td>
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<tr>
<td>$PF_2NMe_2$</td>
<td>83.0</td>
<td>NA</td>
<td>NA</td>
<td>11.3</td>
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<tr>
<td>$P(OPh)_3$</td>
<td>87.0</td>
<td>29.1</td>
<td>7.14</td>
<td>10.5</td>
</tr>
<tr>
<td>$P(OC_6H_4Cl-P)_3$</td>
<td>88.6</td>
<td>33.3</td>
<td>NA</td>
<td>10.5</td>
</tr>
<tr>
<td>$PF_3$</td>
<td>95.2</td>
<td>54.6</td>
<td>9.24</td>
<td>12.3</td>
</tr>
</tbody>
</table>

$^a$Sum of Tolman's substituent constant.

$^b$Sum of Taft's constant

$^c$Sum of electronegativity of atoms immediately bound to phosphorus in substituent. EN = electronegativity.
An analogous explanation could be made for Ph₂PC₆F₅ if we assume that the inductive effect of the four fluorine atoms on the ortho- and meta-positions effectively cancels each other. A single-crystal X-ray structural analysis of Pt(tripod)P(p-C₆H₄F)₃ shows the compound contains one half of a disordered THF molecule. Table 6 lists bond angles and bond lengths for this compound. As expected, the tripod ligand restricts the P-Pt-P bond angles to 90.8°, 91.3°, and 99.6°, which are all smaller than the tetrahedral angle; thus, the bond between platinum and phosphorus of the monodentate phosphine will be rehybridized to include more s character. In fact, the P₁-Pt-P₂ angle is 118.30°, which is closer to the angle of sp² hybridization. As a consequence of the angles and possible rehybridization, the Pt-P₁ bond length is about 0.04 Å shorter than the Pt-P₃ bond length.

It has been recognized that steric effects are generally as important as electronic effects and can dominate in many cases. Ligand cone angles θ were introduced to explain the coordination ability of phosphorus θ ligands to nickel(0).
TABLE 6

BOND ANGLE AND BOND LENGTH DATA FOR Pt(tripod)P(p-C₆H₄F)₃

<table>
<thead>
<tr>
<th></th>
<th>Bond Angle</th>
<th>Bond Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₂-P₄-P₃</td>
<td>91.26(5)°</td>
<td>Pt-P₁</td>
</tr>
<tr>
<td>P₂-P₄-P₃</td>
<td>99.56(5)°</td>
<td>Pt-P₂</td>
</tr>
<tr>
<td>P₃-P₄-P₄</td>
<td>90.79(5)°</td>
<td>Pt-P₃</td>
</tr>
<tr>
<td>P₁-P₂-P₂</td>
<td>118.23(5)°</td>
<td>Pt-P₄</td>
</tr>
<tr>
<td>P₁-P₂-P₃</td>
<td>127.18(6)°</td>
<td></td>
</tr>
<tr>
<td>P₁-P₂-P₄</td>
<td>122.20(5)°</td>
<td></td>
</tr>
</tbody>
</table>

Figure 21. Numbering system for bond-angle and bond-length data.
The ligands showed a decreasing binding in the order of 
\[ P\text{(OCH}_2\text{)}_3\text{CCH}_3 \geq P\text{(OPh)}_3 \geq P\text{Ph}_3 > P\text{Cy}_3 > P\text{(t-Bu)}_3. \] CPK models of these ligands showed increasing atom congestion around the phosphorus atom in the same order. Cone angles for the ligands used in this study are presented in Table 7.

The steric effect may be responsible for the fact that we were unable to prepare the Pt(tripod)PCy_3 compound; the cone angle of PCy_3 is 172°. Instead of isolating the desired compound Pt(tripod)PCy_3, the bis complex Pt(tripod)_2 was isolated. The \( ^{31}\text{P} \) nmr spectrum of this compound (Table 8) showed an \( A_2B_2X \) spin system with two phosphorus atoms from each tripod bonded to the metal. The coupling constants observed for Pt-P are close to those of four-coordinate tetrahedral platinum(O) complexes. For Pt(ttp)CO and Pt(ttp)PPh_3 (ttp = bis-(3-diphenylphosphinopropyl)phenylphosphine) \( ^{31}\text{P} \) nmr data give: \(^{38}\)

\[
\begin{align*}
\text{Pt(ttp)CO} & : \quad J_{\text{Pt-PPh}_2} = 3359 \text{ Hz}, \quad J_{\text{Pt-PPh}} = 3179 \text{ Hz}; \\
\text{Pt(ttp)PPh}_3 & : \quad J_{\text{Pt-PPh}_2} = 3664 \text{ Hz}, \quad J_{\text{Pt-PPh}} = 3994 \text{ Hz}; \\
& \quad J_{\text{Pt-PPh}_3} = 3356 \text{ Hz}.
\end{align*}
\]

In the platinum compound of bis-diphenylphosphino-acetylene, the electron withdrawing power of the acetylene moiety seems to be reduced in the formation of the symmetrical dimer; thus, the complex gives a value of ca 5500 Hz for
<table>
<thead>
<tr>
<th>Ligand</th>
<th>Cone Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh₂Me</td>
<td>136</td>
</tr>
<tr>
<td>P(E-tolyl)₃</td>
<td>145</td>
</tr>
<tr>
<td>PPh₃</td>
<td>145</td>
</tr>
<tr>
<td>P(E-C₆H₄F)₃</td>
<td>NA</td>
</tr>
<tr>
<td>Ph₂PC₆F₅</td>
<td>158</td>
</tr>
<tr>
<td>P(CH₂CH₂CN)₃</td>
<td>132</td>
</tr>
<tr>
<td>Ph₂PC ≡ CPPh₂</td>
<td>NA</td>
</tr>
<tr>
<td>PPh₂(OMe)</td>
<td>132</td>
</tr>
<tr>
<td>PF₂(t-Bu)</td>
<td>131</td>
</tr>
<tr>
<td>P(OPh)₃</td>
<td>128</td>
</tr>
<tr>
<td>P(OCH₆Cl-P)₃</td>
<td>128</td>
</tr>
<tr>
<td>PF₃</td>
<td>104</td>
</tr>
<tr>
<td>PCy₃</td>
<td>172</td>
</tr>
</tbody>
</table>

*a*Copied from reference 17.
### TABLE 8

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>( \delta_{P_A} )</th>
<th>( \delta_{P_B} )</th>
<th>( J_{Pt-P_A} )</th>
<th>( J_{Pt-P_B} )</th>
<th>( 2J_{P_A-P_B} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(tripod)₂</td>
<td>THF + C₆D₇</td>
<td>12.3</td>
<td>17.0</td>
<td>3571</td>
<td>3721</td>
<td>50.2</td>
</tr>
</tbody>
</table>
\( ^1J_{\text{Pt-P}_1} \). The phosphorus-31 nmr spectrum of this compound shows an AB\(_3\)X spin system. The infrared spectrum shows no peak for the C\(=\)C stretching frequency, which further supports the presence of a symmetrical dimer.

However, for P(CH\(_2\)CH\(_2\)CN)\(_3\), the \( ^1J_{\text{Pt-P}_1} \) value of 5500 Hz cannot be explained by either an electronic effect or a steric effect. This result might suggest that the sum of Pauling's electronegativity of the atoms directly bound to phosphorus is important regardless of their hybridization. In fact, the sums of electronegativity for the first atoms bonded to phosphorus in the top seven complexes in Table 8 are identical. The correlation of \( ^1J_{\text{Pt-P}_1} \) values with the electronegativity sum of the first atoms is good for the whole series of the complexes in this study.

The complexes of PF\(_2\)(\(t\)-Bu), PF\(_2\)NMe\(_2\) and PF\(_3\) ligands have reasonable coupling constant values, considering their electronic and steric effects.

C. Summary and Conclusions

Based on equation (4), derived from the least squares plot (Figure 19), the intercept value (-144 Hz) is judged to be negligible compared to the order of magnitude of the
$^{1}J_{\text{Pt-P}}$ values, which are greater than 5000 Hz. Thus, we conclude that $^{1}J_{\text{Pt-P}}$ is directly proportional to $^{2}J_{\text{P-P}}$. The magnitudes of Pt-P and P-P coupling constants appear to be affected by the degree of hybridization. The coupling constant for Pt-P$_{1}$ is larger than that for Pt-P$_{3}$ where the platinum-phosphorus bond to the monodentate ligand uses more s-character than three platinum-phosphorus bonds of the tripod ligand. The bond length of Pt-P$_{1}$ for P(C$_{6}$H$_{4}$F-P)$_{3}$ is about 0.04Å shorter than the average length of three Pt-P$_{3}$ bonds. Although the variations in the values of Pt-P coupling constant are not necessarily reflected by the bond length, it would be desirable to correlate the platinum-phosphorus coupling constant with the Pt-P bond length by determining more crystal structures of compounds prepared in this study.

The electronegativity of substituents in trisubstituted phosphines is a very important factor in the magnitude of the Pt-P$_{1}$ coupling constant, and it appears that the electronegativity of atoms immediately bonded to phosphorus is the most important factor that affects the observed J's; there also appears to be a linear relationship between $^{1}J_{\text{Pt-P}}$ (as well as $^{2}J_{\text{P-P}}$) values and various inductive parameters. However, steric effects are also important, since we can
explain certain inconsistencies by using the steric effect argument. Therefore, the alternative reasonings, based on electronic effect or steric effect, of the results discussed in this study do not exclude one another. Each effect depends on environmental factors in the coordination sphere.
PART II
UNSATURATED TERTIARY PHOSPHINE COMPLEXES
OF RHODIUM AND IRIDIUM
INTRODUCTION

Inorganic chemists have pursued the chemistry of transition metal complexes containing unsaturated tertiary phosphines as a way of studying metal-catalyzed reactions of the olefin. These reactions include homogeneous hydrogenation, olefin isomerization, electrophilic attack by halogen or acids, nucleophilic attack by methoxide ion, deprotonation, and metallation.

The homogeneous hydrogenation of olefins catalyzed by RhCl(PPh₃)₃ was reported by Wilkinson and his coworkers. Catalytic hydrogenation involves a ligand dissociation to generate coordinatively unsaturated intermediates. Although transition metals are very important for catalysis, variation of ligands also causes changes in the catalytic activity of the complexes. For example, the rate of hydrogenation of olefins increases in the order X = Cl < Br < I for RhXL₃ (L = PPh₃) complexes.

Since the coordinated olefin can be reductively eliminated by hydrogenation to provide a vacant site on the metal, unsaturated tertiary phosphine complexes of transition metals are considered as the effective catalysts. Hartwell and Clark proposed a two-step mechanism for the
transfer of two hydrogen atoms to RhCl(CO)(mbp)_2 (mbp = Ph_2P(CH_2)_2CH=CH_2) to yield the corresponding butyl-diphenylphosphine complex. The proposed mechanism is shown in Scheme 1.

\[
\begin{align*}
\text{[(CO)L}_2\text{Rh}]^+ & \quad \text{H}_2 \\
\text{[(CO)L}_2\text{H}_2\text{Rh}]^+ \\
\text{[(CO)LH}_2\text{Rh}(\phi_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)]^+}
\end{align*}
\]

\text{SCHEME 1}
The Rh$_2$Cl$_2$(Ph$_2$PC$_4$H$_9$)$_4$ and RhCl(CO)(Ph$_2$PC$_4$H$_9$)$_2$ complexes have been obtained by hydrogenation of RhCl(mbpc)$_2$ and RhCl(CO)(mbpc)$_2$, respectively, in methanol. A rhodium complex, RhCl(CO)[Ph$_2$P(CH)$_2$)$_3$CH=CH$_2$] gives isomerization of the terminal olefin to yield the cis-pent-3-enylphosphine complex in the absence of hydrogen.

The tetraphenylborate salts of the planar rhodium(I) cations, Rh(spp)$_2^+$ (spp = o-CH$_2$=CH-C$_6$H$_4$PPh$_2$), absorb one mole of hydrogen per mole of complex forming the $\eta^6$-tetraphenylborate complex, Rh($\eta^6$-C$_6$H$_5$BPh$_3$)(spp), and o-C$_2$H$_5$C$_6$H$_4$-PPh$_2$. Scheme 2 shows a plausible mechanism for the
hydrogenation, which involves 1) the oxidative addition of hydrogen, 2) transfer of the hydrogen atoms to one of the bonded spp ligands, forming P-bonded (o-ethylphenyl)diphenylphosphine to create a vacant site on the metal; this is then occupied by one of the phenyl rings of the BPh₄⁻, and 3) the formation of η⁶-bonded BPh₄⁻ salt of rhodium and free (o-ethylphenyl)diphenyl phosphine.

The insertion of the ortho-olefinic part of the spp ligand into the platinum-hydrogen bond of trans-[PtHCl(PPh₃)₂] to form compounds containing a metal-carbon σ-bond was reported by Brooks and Nyholm. 45
Stable M-C σ-bonded complexes can also be obtained by intramolecular hydride addition to the free vinyl group in HM(CO)$_4$(spp).$^{46}$ When M is manganese, the predominant product, 4, contains the five-membered ring which results by Markownikoff addition; in the case of rhenium, the product in 5, which arises exclusively from anti-Markownikoff addition. The difference may be related to the fact that HRe(CO)$_5$ is a weaker acid than HMn(CO)$_5$, so that the addition in the sense $H^+\cdot M^-$ will be favored for the lighter element.

\[
\begin{align*}
\text{4} & \quad \phi_2P\text{Mn}\text{CHCH}_2\text{CH}_2\text{OC}\text{CO} \\
\text{5} & \quad \phi_2P\text{Re}\text{CH}_2\text{CH}_2\text{OC}\text{CO}
\end{align*}
\]

Dihydro-olefin complexes, which are believed to be intermediates in the homogeneous hydrogenation of olefins, have been isolated during the hydrogenation of cycloocta-1,5-diene by [IR(cod)L$_2$]PF$_6$ (cod = cycloocta-1,5-diene;
L = tertiary phosphine. A coplanar M(C=C)H system seems to be necessary for the insertion of the coordinated olefin into the M-H bond; cis-[IrH₂(cod)L₂PF₆] (6), which has the coplanar Ir(C=C)H system, was hydrogenated 40 times faster than cis,trans-[IrH₂(cod)L₂]PF₆ (7), which does not satisfy the coplanarity of Ir(C=C)H.

Besides hydrogenation and isomerization, unsaturated tertiary phosphine complexes can undergo halogenation and alcoholysis reactions. Bromination of PtBr₂(spas)₂ (spas = o-CH₂=CH-C₆H₄-AsMe₂), 8, results in a chelated Pt-C σ-bonded metallocycle 9; ethanolysis of the resulting adduct 9 involves a Wagner-Meerwein rearrangement, i.e., a 1,2-shift of a metal to form the ethoxy-substituted complex 10.
Similar reactions have been observed for the linear gold(I) complexes of spas and spp.
49,50
When the olefinic part of phosphine or arsine is an allylic group, a bromination reaction occurs to form a metallo-cycle, followed by a nucleophilic substitution and reduction of the metal upon heating with methanol.
Other examples of the electrophilic attack on iron(0), \(^{51}\) ruthenium(0), \(^{51}\) rhodium(I), \(^{52}\) and iridium(I) \(^{52}\) complexes are shown below.

\[
\begin{align*}
\text{M} & = \text{Fe or Ru} \text{, } \\
\text{X} & = \text{Cl or Br} \text{.}
\end{align*}
\]
Whereas unactivated olefins are not susceptible to nucleophilic attack, olefins complexed to metals with low electron density (e.g. Pt(II)) react readily with nucleophiles to form \( \sigma \)-bonded complexes.\(^{53}\) When the but-3-enyl-diphenylphosphine complex of platinum(II) was treated with sodium hydrogen carbonate in methanol, the methoxy-substituted \( \sigma \)-bonded complex was formed.\(^{54}\)

\[
\text{On the other hand, nucleophilic attack on the Pt}^{\text{II}} \text{ complex of the chelate ligand spas gives four geometrical isomers of a dimeric product containing Pt-C } \sigma \text{-bonds.}^{55}\n\]
The four isomers are considered to arise from two types of isomerization: 1) arsine groups cis or trans across the dimer, 2) methoxy groups cis or trans relative to the coordination plane of the dimer. The nmr spectra of monomers obtained by cleavage of the chlorine-bridged dimer with acetylacetone or hexafluoroacetone show that methoxide attack occurs exclusively at the β-carbon atom to give a five membered chelate ring.

Metal olefin complexes have been prepared from the dehydrogenation of the alkane chain in tertiary phosphate ligand by rhodium(I) and iridium(I) complexes. 56,57

$$\text{M}_2\text{Cl}_2(\text{C}_6\text{H}_{12})_2 \cdot (\text{C}_6\text{H}_3)_2\text{P(CH}_2)_6\text{P(C}_6\text{H}_5)_2 \xrightarrow{\text{mesitylene reflux}}$$

\[ \text{M} = \text{Rh} \]

\[ \text{Rh}(\text{bdpps})\text{Cl} \]
The 2,2'-bis(diphenylphosphine)stilbene (bdpps) (o-Ph₂PC₆H₄CH=CHC₆H₄PPh₂-o) ligand also undergoes deprotonation and metallation when it reacts with halide salts or complexes of transition metals; the reaction results in the elimination of hydrogen halide and formation of the complexes [MCl(o-Ph₂PC₆H₄CH=CHC₆H₄PPh₂-o)] (11). M = Ni, Pd, or Pt.

X = Cl, Br, or I.

R = C₆H₅ or o-CH₂C₆H₅.

The olefinic di(tertiary phosphine), o-Ph₂PC₆H₄-t-CH=CHCH(CH₃)C₆H₄PPh₂-o (1-bdpb) reacts with dichloro complexes of Ni(II), Pd(II), and Pt(II); In the case of nickel(II) the product is a mixture of isomers of the η₃-allyl complexes.

In the case of palladium(II) or platinum(II), the product is a planar, σ-alkyl compound (12), since the ligand is deprotonated at the tertiary carbon atom.
\[ X = H, \ Y = \text{CH}_3 \ . \ \text{anti-syn} \]

\[ X = \text{CH}_3, \ Y = H \ . \ \text{syn-anti} \]
However, the single crystal X-ray structure determination of the similar reaction product of rhodium(III) showed structure 13 which resulted from deprotonation and coordination of the double bond to form the $\eta^3$-allylic complex.  

The reaction of $R_2P(\text{allyl})$ ($R = t$-butyl, cyclohexyl), with $[(\text{coe})_2\text{IrCl}]_2$ (coe = cyclooctene) in the presence of $\gamma$-picoline at room temperature yields the six coordinated, metallated complexes, 14.  However, this metallation does not involve deprotonation in the overall stoichiometry since
one hydrogen atom from the allylic group is bonded to the metal as a hydride.
EXPERIMENTAL

Rhodium trichloride trihydrate (RhCl$_3$·3H$_2$O) and iridium trichloride trihydrate (IrCl$_3$·3H$_2$O) were purchased from Engelhard Industries, Newark, New Jersey.

All reagent grade solvents were dried by distillation over appropriate drying agents under nitrogen prior to use. All other chemicals were reagent-grade quality and were used without further purification unless stated otherwise.

Infrared spectra were measured on a Perkin Elmer 337 grating spectrophotometer from 400 to 4000 cm$^{-1}$ as Nujol mulls or hexachlorobutadiene mulls between potassium bromide plates. Sharp polystyrene absorptions at 1601.4 and 906.7 cm$^{-1}$ were used for calibration of the spectra.

Conductance measurements were made on solutions of approximately 10$^{-3}$ M concentration in ethanol, acetonitrile and tetrahydrofuran on an Industrial Instruments Inc. conductivity bridge Model RC 16B2 operating at 1000 c.p.s. Ethanol was reagent grade and degassed by flushing with nitrogen for 30 minutes prior to use. Acetonitrile was distilled from P$_4$O$_{10}$ prior to use. Tetrahydrofuran was refluxed over lithium aluminum hydride and distilled under nitrogen prior to use.
Proton magnetic resonance spectra were collected on a Varian A60A, EM360, or a Bruker HX90 spectrometer with tetramethysilane (TMS) as an internal standard, in general. In some cases, the proton resonance occurring from small amounts of non-deuterated solvent in the nominally deuterated solvents was also used for standardization.

Techniques for obtaining phosphorus-31 nuclear magnetic resonance spectra and assignments of chemical shifts are the same as were explained in Part I of this dissertation.

Mass spectra were measured on an AEI-MS902 spectrometer at an ionizing energy of 70 eV by Mr. C.R. Weisenberger at The Ohio State University.

Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona.

A. General Experimental Procedure

Standard techniques for the manipulation of air-sensitive compounds were used for all the experiments of this work. High-purity nitrogen was used to provide an inert atmosphere. Solvents were deaerated by purging with nitrogen or by the freeze-thaw method.

B. Ligand Synthesis

1. 3-Chloropropyldiphenylphosphine

To a solution of 25.0 g of Ph₂PH (0.134 mol) in 450 ml of freshly distilled tetrahydrofuran (THF) was added 58.4 ml
of 2.4 M n-butyllithium (0.140 mol) in hexane via a pressure-
equalizing dropping funnel; a deep red colored solution
resulted immediately. The mixture was stirred at room
temperature for two hours and at 55-65°C for an additional
hour. After the solution was transferred to a pressure-
equalizing funnel via a needle under a nitrogen atmosphere,
it was then added into a cold (-78°C) solution of 200 ml of
1,3-dichloropropane (2.10 mol) in 100 ml of THF contained in
a three-necked, 2 L round-bottomed flask over a period of
8 hours. The solution was washed with 150 ml of degassed
water and was dried over anhydrous sodium sulfate. After
filtration, the solvent was removed in vacuo at 50°C to
afford 32.0 g of a colorless oil; yield = 89%.

2. 1-Diphenylphosphino-3-phenylphosphinopropane

A 2 L, three-necked, round-bottomed flask fitted with
two Dry Ice-isopropyl alcohol condensers and a mechanical
stirrer was immersed in a Dry Ice-isopropyl alcohol slush
bath and charged with anhydrous liquid ammonia (ca. 450 ml)
and sodium chips (3.1 g, 0.13 mol). This blue solution was
stirred for 1 hour and then was treated with phenylphosphine
(15.2 g, 0.14 mol) slowly via a syringe to generate an
orange solution. After the reaction mixture had been stirred
for 1.5 hours, a solution of 3-chloropropylidiphenylphosphine
(32.0 g, 0.12 mol) in ether (200 ml) was added at -78°C
through a pressure-equalizing funnel which replaced one of the Dry Ice reflux condensers. The resulting mixture was stirred for 3 hours and an orange-yellow solid formed during this time. Ammonia was allowed to evaporate slowly as the reaction mixture warmed to room temperature under nitrogen overnight. Ethanol (30 ml) and distilled water were added in sequence to destroy excess phosphide and ether (200 ml) was added to dissolve the ligand and the resulting solution was stirred for 3 hours. The orange layer was transferred via needle into a Grignard flask containing anhydrous sodium sulfate (dried overnight). The solution was filtered and the solvent was removed \textit{in vacuo}; the resulting yellow oil was warmed to 80°C \textit{in vacuo} to remove residual phenylphosphine. Yield: 34 g (84%).

3. 3-Diphenylphosphinopropyl-3-butenylphenylphosphine (ppol)

To a benzene solution (300 ml) containing 1-diphenylphosphino-3-phenylphosphinopropane (34.0 g, 0.10 mol) was slowly added 50 ml of 2.3 M hexane solution of \( \eta \)-butyllithium (0.12 mol). A red color developed immediately and a pale yellow solid formed after 15 minutes. The mixture was stirred at room temperature for 3 hours and at 55-65°C for 1 hour. After the mixture was cooled to room temperature, a benzene (50 ml) solution of 4-chlorobutene (25 ml) was
added dropwise. The resulting mixture was stirred at room temperature for 1 hour and refluxed at 80-90°C for 2.5 hours. An additional 10 ml of 4-chlorobutene was added and refluxing was continued for 3 hr. The reaction mixture was stirred overnight while it cooled to room temperature. The resultant pale yellow mixture was then treated in sequence with absolute ethanol (50 ml) and distilled water (150 ml) to destroy any excess n-butyllithium or phosphide. The organic layer was separated and dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo at 70°C to leave a yellow oil. Yield: 36 g (92%).

C. Synthesis of Rhodium and Iridium Complexes

1. RhCl(ppo1)

To a solution of [RhCl(cod)]_2 (0.7543 g; 3.06 mmol Rh) in absolute ethanol (40 ml) was added a solution of ppo1 (6.1 ml; 0.5271 M in benzene) and the resultant solution was heated to reflux for 2 hr. After the solution had cooled to room temperature, orange crystals started to form. The product was collected on a Schlenk frit, washed with hexane (35 ml) and dried in vacuo.

2. RhI(ppo1)

To a boiling solution of [RhI(cod)]_2 (0.3361 g; 0.99 mmol Rh) in benzene (15 ml) was added a solution of ppo1
(2.0 ml; 0.5271 M in benzene) and the solution was refluxed for 10 minutes. After cooling the reaction mixture to room temperature, the solution was filtered to remove any impurity. Orange crystals started to form after the wall of the reaction vessel was scratched by a spatula. The resulting crystals were collected on a Schlenk frit, washed with ethanol and dried in vacuo.

$$^{31}\text{P nmr } (C_6H_6): \quad 45.9 \text{ ppm } (\delta \text{ PPh})$$

$$1.9 \text{ ppm } (\delta \text{ PPh}_2)$$

3. \(	ext{RhN}_3(\text{ppol})\)

To a solid mixture of \(\text{RhCl}(\text{ppol})\) (0.3851 g) and \(\text{NaN}_3\) (0.0486 g) was added 50 ml of ethanol and the reaction mixture was refluxed for 20 min. After the solution cooled to room temperature, orange crystals appeared in the flask. The crystals were collected on the frit of a Schlenk filter and washed with water and ethanol in sequence and dried in vacuo.

Analysis for \(\text{C}_{25}\text{H}_{28}\text{N}_3\text{P}_2\text{Rh}\):

Calcd: C, 56.07; H, 5.23; N, 7.85.

Found: C, 54.64; H, 5.17; N, 6.80.

4. \([\text{Rh}(\text{ppol})\text{py}]\text{AsF}_6\)

A solution of \(\text{RhCl}(\text{ppol})\) (0.4257 g) and \(\text{NaAsF}_6\) (0.1755 g) in ethanol (30 ml) was heated to reflux for
30 minutes. At this point, pyridine (0.6 ml) was added to the solution and refluxing was continued for 1 hr. Upon cooling the solution to room temperature, an orange-yellow precipitate appeared. The product was separated, washed with water and ethanol, and then dried in vacuo.

Analysis for $\text{C}_{30}\text{H}_{33}\text{AsF}_{6}\text{NP}_{2}\text{Rh}$:

Calcd: C, 47.31; H, 4.34; N, 1.84.

Found: C, 47.37; H, 4.31; N, 1.72.

5. $[\text{Rh(ppol)}_{2}]\text{AsF}_{6}$

To a boiling ethanol solution of $[\text{RhCl(cod)}]_{2}$ (0.2471 g; 1.00 mmol Rh) and ppol (4.0 ml; 0.5271 M in benzene) was added NaAsF$_6$ (0.2210 g); the resulting mixture was refluxed for 30 min. After the solution was cooled to room temperature, most of the solvent was evaporated and hexane (20 ml) was added to the solution. A quantity of yellow-orange product precipitated; it was washed with water and hexane and then dried in vacuo.

Analysis for $\text{C}_{50}\text{H}_{56}\text{AsF}_{6}\text{P}_{4}\text{Rh}$:

Calcd: C, 55.97; H, 5.22; F, 10.63.

Found: C, 55.52; H, 5.23; F, 13.24.

6. Attempted Reaction of RhCl(ppol) with HCl

To a solution of RhCl(ppol) (0.75 g) in ethanol (10 ml) was added HCl (conc. aq. 1.5 ml) and the mixture was
refluxed for 1 hr. After the solution was cooled to room temperature, the solvent was evaporated to 5 ml. A pale yellow product was obtained upon filtration; it was washed with hexane and dried in vacuo.

7. Attempted reaction of RhI(ppol) with CH₃I

To a solution of 0.3549 g of RhI(ppol) in 10 ml of ethanol was added 2 ml of methyl iodide. After the mixture was heated to reflux for 10 min, 2 ml of benzene was introduced to dissolve the solid. Refluxing was continued 5 additional minutes and the solution was cooled to room temperature. Hexane was added dropwise with constant stirring until the solution turned slightly cloudy. After the volume of the solution was reduced to 5 ml, a precipitate formed. Brown crystals formed along with a brown oil which stuck to the bottom of the reaction flask after it sat overnight in the freezer. The crystals were collected on a Schlenk frit and washed with hexane and then dried in vacuo.

8. [Ir(cod)(ppol)]Cl·2C₂H₅OH

A solution of [IrCl(cod)]₂₆³ (0.6732 g, 2.00 mmol) in absolute ethanol (25 ml) was treated with ppol (4.0 ml; 0.5271 M in benzene) and the mixture was stirred at room
temperature for 1 hour. The resultant pale yellow solution was evaporated almost to dryness under vacuum; a white precipitate separated after ether (30 ml) was added to the solution. The product was washed with ether and dried *in vacuo*.

Analysis for $C_{37}H_{50}ClIrO_2P_2$:
Calcd: C, 54.58; H, 6.11; Cl, 4.28.
Found: C, 51.37; H, 5.34; Cl, 4.50.

9. **IrCl(cod)(ppol)$\cdot C_6H_6$**

To a solution of $[\text{IrCl(cod)}]_2$ (0.3248 g; 0.48 mmol) in benzene (20 ml) was added ppol (2.3 ml; 0.478 M in benzene) and the solution was stirred at room temperature for 1 hour. After evaporating most of the solvent, hexane (30 ml) was added to isolate a pale yellow solid. The product was washed with hexane and dried *in vacuo*.

Analysis for $C_{39}H_{58}ClIrP_2$:
Calcd: C, 58.20; H, 5.72; Cl, 4.41.
Found: C, 57.10; H, 6.18; Cl, 4.29.

10. **[Ir(cod)(ppol)]AsF_6$\cdot \frac{1}{2}C_2H_5OH$**

A solution of $[\text{IrCl(cod)}]_2$ (0.28 g; 0.42 mmol) in ethanol (20 ml) was treated with ppol (2.0 ml; 0.478 M in benzene). To this was added a boiling ethanol solution
of NaAsF₆ (0.19 g; 0.90 mmol) and the resultant mixture was refluxed for 1 hour. After cooling the solution to room temperature, a white solid separated. The product was washed with water and diethyl ether and dried \textit{in vacuo}.

Analysis for C₃₄H₄₃AsF₆IrO₀.₅P₂:
Calcd: C, 45.26; H, 4.75; F, 12.63.
Found: C, 47.31; H, 4.79; F, 12.88.

11. \underline{Ir(cod)(ppol)PF₆·2CH₃CN}

To a solid mixture of [Ir(cod)(ppol)]Cl·2C₂H₅OH (0.30 g; 0.37 mmol) and NaPF₆ (0.08 g; 0.48 mmol) was added acetonitrile (20 ml). The mixture was refluxed for 30 min. A crystalline white solid separated during the refluxing. After cooling the solution to room temperature, that product was collected on a Schlenk frit and washed with water. The sample was then washed with diethyl ether and dried \textit{in vacuo}.

Analysis for C₃₄H₄₁.₅F₆IrN₀.₅P₃:
Calcd: C, 47.61; H, 4.90; N, 0.82.
Found: C, 47.46; H, 5.06; N, 0.85.

12. \underline{IrCl(CO)(ppol)}

A 0.20 g sample of [Ir(cod)(ppol)]Cl·2C₂H₅OH was dissolved in 20 ml of ethanol and CO was bubbled through
the solution for 20 min. The solvent was evaporated to ~ 5 ml by bubbling both CO and N₂ through the solution; then diethyl ether was added to help precipitation of a solid. The solution was allowed to stand several days and white crystals formed. The crystals were collected on a Schlenk frit, washed with ether and dried with a gaseous mixture of CO and N₂.

Analysis for C₂₆H₂₈ClIrOP₂:
Calcd: C, 48.30; H, 4.33; Cl, 5.50.
Found: C, 47.73; H, 4.63; Cl, 6.24.

13. The Reaction of [Ir(cod)(ppol)]Cl·2C₂H₅OH with HCl aq.

To a solution of [Ir(cod)(ppol)]Cl·2C₂H₅OH (0.25 g; 0.31 mmol) in 20 ml of ethanol was added concentrated aqueous HCl (0.5 ml) and the mixture was refluxed for 1 hour. After cooling the solution to room temperature, the solvent was evaporated to 3 ml under vacuum and ether (20 ml) was added. The solution was stirred overnight. A white precipitate was washed with ether and dried in vacuo.

IR: ν(Ir-H) = 2250 cm⁻¹.

Analysis for C₂₅H₂₉Cl₂IrP₂[IrHCl₂(ppol)]:
Calcd: C, 45.87; H, 4.43; Cl, 10.85.
Found: C, 45.82; H, 4.61; Cl, 10.61.
14. \([\text{Ir}(\text{cod})(\text{ppol})]\text{BF}_4\cdot\text{CH}_3\text{OH}\)

To a solution of \([\text{Ir}(\text{cod})(\text{ppol})]\text{Cl}\cdot\text{C}_2\text{H}_5\text{OH} (0.32 \text{ g})\) in methyl alcohol (20 ml) at \(-78^\circ\text{C}\) was added \(\text{HBF}_4\)-etherate concentration (1 ml). A white solid formed immediately; the resulting mixture was stirred for 1 hour at the same temperature. After filtration, the product was washed with ether and dried in \text{vacuo}.

Analysis for \(\text{C}_{34}\text{H}_{44}\text{BF}_4\text{IrOP}_2\):

Calcd: C, 50.62; H, 5.46; F, 8.93; Cl, 0.00.
Found: a) C, 49.48; H, 5.21; F, 8.71; Cl, 0.31.
       b) C, 49.73; H, 5.40.

15. \text{IrI(cod)(ppol)}

A mixture of \([\text{Ir}(\text{cod})(\text{ppol})]\text{Cl}\cdot\text{C}_2\text{H}_5\text{OH} (0.20 \text{ g}; 0.24 \text{ mmol})\) and \(\text{NaI} (0.05 \text{ g}; 0.33 \text{ mmol})\) in benzene (20 ml) was refluxed for 1 hour. The pale yellow precipitate was collected on a Schlenk frit, washed with water and ether, in sequence, and dried in \text{vacuo}.

\(\text{IR: free olefin stretch at 1640 cm}^{-1}\).

16. Reaction of \([\text{Ir}(\text{cod})(\text{ppol})]\text{Cl}\cdot\text{C}_2\text{H}_5\text{OH} with I}_2

To a solution of \([\text{Ir}(\text{cod})(\text{ppol})]\text{Cl}\cdot\text{C}_2\text{H}_5\text{OH} (0.30 \text{ g}; 0.37 \text{ mmol})\) in toluene (10 ml), was added \(\text{I}_2 (0.30 \text{ g}; 1.2 \text{ mmol})\) and the mixture was refluxed for 2 hours. Unreacted
iodine was filtered off and the solution was evaporated
to dryness with a rotary evaporator to obtain a yellow
solid. All the spectral data are identical to IrI(cod)(ppol).
RESULTS AND DISCUSSION

A. Rhodium Complexes of Unsaturated Tertiary Phosphines

The rhodium complex of the olefinic tertiary phosphine ligand used in this project, RhCl(ppol), was prepared from [RhCl(cod)]₂ and ppol in refluxing ethanol. The infrared spectra of the orange crystalline rhodium complex are given in Figures 22 and 23. The weak absorption at 1510 cm⁻¹ is due to the bonded C=C stretch. On exposure in the air this compound turns brown. The infrared spectrum of the compound that was exposed to the air for 5 days was identical to that of the authentic material. However, when oxygen is bubbled through the solution of RhCl(ppol) in benzene, the compound is decomposed.

The ^{31}P[^1H] nmr spectrum of RhCl(ppol) (Figure 24) in benzene consists of two nonequivalent doublets of doublets. The phosphorus resonance at δ 53.7 ppm is assigned to the central phosphorus nucleus from the =PPh group on the basis that the phosphorus atoms in the 5.5-membered rings usually exhibit large downfield chemical shift. The phosphorus-31 nmr data for three rhodium complexes are presented in Table 9. The ^{31}P[^1H] nmr and infrared spectra of RhI(ppol) have patterns similar to those of RhCl(ppol), indicating that the two compounds have similar structures.
Figure 22. Infrared spectrum of RhCl(ppol) in Nujol; 4000-1300 cm$^{-1}$. Calibration peak is at 1601.4 cm$^{-1}$.
Figure 23. Infrared spectrum of RhCl\textsubscript{(ppol)} in Nujol; 1350-400 cm\textsuperscript{-1}. Calibration peak is at 906.7 cm\textsuperscript{-1}.
Figure 24. Proton-decoupled phosphorus-31 nmr spectrum of RhCl(ppo1) in benzene.
<table>
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<th>Compound</th>
<th>Solvent</th>
<th>$\delta_{P_1}^{b}$</th>
<th>$\delta_{P_2}^{c}$</th>
<th>$J_{P_1-P_2}$</th>
<th>$J_{Rh-P_1}$</th>
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<td>RhCl(ppol)</td>
<td>Benzene</td>
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<td>5.3</td>
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<td>RhI(ppol)</td>
<td>Benzene</td>
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<td>157.5</td>
<td>147.7</td>
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<td>RhN$_3$(ppol)</td>
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<td>4.3</td>
<td>55.9</td>
<td>149.0</td>
<td>157.4</td>
</tr>
</tbody>
</table>

$^a$ Inserts containing deuterated solvents were used for an external deuterium lock.

$^b$ Chemical shifts are relative to 85% $H_3PO_4$, (+) is downfield from $H_3PO_4$.

$^{c}$ $P_1$: central phosphorus atom from the $=PPh$ group.

$^{d}$ $P_2$: terminal phosphorus atom from the $-PPh_2$ group.
The infrared spectra of RhN₃(ppol) (Figures 25 and 26) show a strong, slightly broadened band at 2060 cm⁻¹ due to the N≡N stretch. It is well known that the azido group in ionic compounds (for example, a structure like 15) is symmetrical and linear, whereas the structure of the azido group in covalent compounds like 16 is asymmetrical. 66

\[
\mathrm{NH}_4^+ \left[ N_1^{1,15\AA} N_{II}^{1,15\AA} N_{III} \right]^{-}
\]

\[
\mathrm{H} \overset{1,24\AA}{\mathrm{N}}_{II}^{1,10\AA} N_{III}
\]

Thus one might expect that the covalent azide has a higher N≡N stretching frequency than the ionic azide. 67-70 Fujita, Nakamoto and Kobayashi 70 reported that the cobalt-nitrogen bond in coordinated azide was more ionic than the corresponding chromium-nitrogen bond based upon the N≡N stretching frequencies in the infrared spectra. An X-ray crystal structure of azidopentammine-cobalt(III) azide was determined by Palenik 71 in order to compare the bonding of both anionic and coordinated azides in coordination compounds. It confirms that the Co-N bond is a resonance hybrid of a
Figure 25. Infrared spectrum of RhN$_3$(ppol) in Nujol; 4000-1300 cm$^{-1}$. Calibration peak is at 1601.4 cm$^{-1}$. 
Figure 26. Infrared spectrum of RhN$_3$(ppol) in Nujol; 1350-400 cm$^{-1}$. Calibration peak is at 906.7 cm$^{-1}$. 
covalent-bonded Co-N$_3$ and an ionic-bonded Co$^+N_3^-$, thus the bond angle Co-N-N (125°) is larger than the covalent bond angle. Based upon the infrared spectrum, the bond angle Rh-N-N in RhN$_3$(ppol) might be expected to be somewhat smaller than 125°.

The rhodium complex containing another nitrogen donor ligand, Rh(NO$_2$)(ppol) was obtained only in an extremely poor yield and the preparation of this compound was not reproducible. The infrared spectrum (Figures 27 and 28) has absorptions at 1330, 1315 and 814 cm$^{-1}$ which might correspond to the N-bonded nitro complex. The nitro complex is interesting because of the bonding mode of the NO$_2^-$ ligand to the transition metal; in addition the oxygen atom transfer reaction of the nitro compound with carbon monoxide to produce a corresponding nitrosyl compound and carbon dioxide is of current interest. Unfortunately no other data is available for the Rh(NO$_2$)(ppol) complex.

Several attempts were made to study the behavior of the olefinic moiety of the RhCl(ppol) complex toward nucleophiles and acids. Upon treatment of RhCl(ppol) with triethylamine in boiling methanol for 1.5 hour, no change was observed in the reaction vessel. But, when a solution of RhCl(ppol) and sodium hydroxide in ethanol was heated to reflux for 2 hr, the reaction mixture turned green. The
Figure 27. Infrared spectrum of Rh(NO$_2$)$_2$(ppol) in Nujol; 4000-1300 cm$^{-1}$. Calibration peak is at 1601.4 cm$^{-1}$.
Figure 28. Infrared spectrum of Rh(NO₂)(ppol) in Nujol; 1350-400 cm⁻¹. Calibration peak is at 906.7 cm⁻¹.
\[ \text{Following data: } \delta P_1 = 34.4 \text{ ppm, } \delta P_2 = 23.5 \text{ ppm, } J_{P_1-P_2} = 62.3 \text{ Hz, } J_{Rh-P_1} = 150.1 \text{ Hz, } J_{Rh-P_2} = 145.2 \text{ Hz.} \]

An attempt was made to isolate the corresponding product; by evaporating the solvent, however, only a brown oily material was obtained. Blum reported RhOH(ttp) as a by-product when she tried to make RhCH\(_3\)(ttp) using RhCl(ttp) and CH\(_3\)Li. The reported value of \( J_{Rh-P_1} \) (P\(_1\) being central phosphorus atom) is larger for RhOH(ttp) than for RhCl(ttp) since hydroxide is a very weak ligand. However, the value of \( J_{Rh-P_1} \) for the green solution is smaller than that for RhCl(ppol), thus it is unlikely that the product in the green solution is RhOH(ppol). Because of the difficulty in isolation, no other data were obtained.

Treatment with pyridine in the presence of NaAsF\(_6\), the chloride ligand of RhCl(ppol) was replaced by pyridine to give the cationic complex, [Rhpy(ppol)]AsF\(_6\). The infrared spectra (Figures 29 and 30) show an absorption at 700 cm\(^{-1}\) due to an asymmetric stretch of anionic AsF\(_6^+\). The symmetrical stretching mode of AsF\(_6^+\) could not be identified presumably because it was masked by the absorption band at 570 cm\(^{-1}\) due to the ppol ligand. For the same reason, the infrared bands due to the pyridine ligand could not be
Figure 29. Infrared spectrum of [Rh(ppo)py]AsF$_6$ in Nujol; 4000-1300 cm$^{-1}$. Calibration peak is at 1601.4 cm$^{-1}$. 
Figure 30. Infrared spectrum of [Rh(ppy)py]AsF$_6$ in Nujol; 1350-400 cm$^{-1}$. Calibration peak is at 906.7 cm$^{-1}$. 
identified. The $^{31}P\{^1H\}$ nmr spectrum of [Rh(ppol)py]AsF$_6$ gives: $\delta P_1 = 48.1$ ppm, $\delta P_2 = 10.2$ ppm, $J_{P_1-P_2} = 54.4$ Hz, $^1J_{Rh-P_1} = 141.6$ Hz, $^1J_{Rh-P_2} = 155.2$ Hz.

Because the pyridine ligand in [Rh(ppol)py]AsF$_6$ is a weak base and rather labile, a strong ligand such as carbon monoxide can replace the pyridine easily to give [Rh(CO)$_2$-(ppol)]AsF$_6$. The bond angle of CO-Rh-CO bonds in the dicarbonyl complex can be derived from the ratio of the intensities of two different CO stretching modes. For the case of two CO groups, the ratio of the intensities of the symmetric and antisymmetric bands is given by

$$\frac{R_{sym}}{R_{asym}} = \cot^2 \theta$$

thus

$$2\theta = 2 \arctan \left( \sqrt{\frac{R_{sym}}{R_{asym}}} \right)$$

The OC-Rh-CO bond angle of [Rh(CO)$_2$(ppol)]AsF$_6$ was calculated from the relative intensities of two stretching vibrations to be 114° (Figure 31). The structure of this complex is close to a trigonal bipyramid with both carbonyls on equatorial sites.

When an excess of ppol ligand is used in a reaction with [RhCl(cod)]$_2$, two ppol ligands are bonded to rhodium;
Figure 31. Infrared spectrum of $[\text{Rh}^{\text{ppol}}(\text{CO})_2]\text{AsF}_6$ in the range of 2500-2000 cm$^{-1}$. 
each ppol ligand is bonded via the two phosphorus nuclei and has the olefin dangling. The infrared spectra of [Rh(ppol)$_2$]AsF$_6$ (Figures 32 and 33) show the free olefin absorption at 1645 cm$^{-1}$. The phosphorus-31 nmr spectrum consists of two sets of doublets of triplets (Figure 34); one set due to the resonance of two terminal phosphorus nuclei, $P_X$, being split into a triplet by coupling to two central phosphorus atoms, $P_A$, and the triplet being further split into a doublet due to the coupling with rhodium atom. The other set is due to two central phosphorus nuclei coupled with two terminal phosphorus nuclei and the rhodium atom. The $^{31}P[^1H]$ nmr data for this compound is: $\delta P_X = 11.3$ ppm, $\delta P_A = -8.0$ ppm, $J_{PA-P_X} = 30.9$ Hz, $J_{Rh-P_A} = 82.4$ Hz, $J_{Rh-P_X} = 123.5$ Hz. Although two central or terminal phosphorus nuclei are not magnetically equivalent, the present spectrum does not show the inequivalence; $J_{PA-P_A}$ and $J_{P_X-P_X}$ are not observed.

Several reactions of the Rh(I) complexes with small molecules such as HCl, Cl$_2$, CH$_3$I, I$_2$ and CHCl$_3$ were attempted. The reaction of RhCl(ppol) with HCl was tried several times and the phosphorus-31 nmr spectrum of the isolated pale-yellow product shows that there are impurities besides the
Figure 32. Infrared spectrum of $[\text{Rh}(\text{ppol})_2]\text{AsF}_6$ in Nujol, 4000-1300 cm$^{-1}$. Calibration peak is at 1601.4 cm$^{-1}$.
Figure 33. Infrared spectrum of $[\text{Rh}(\text{ppol})_2]\text{AsF}_6$ in Nujol; 1350-400 cm$^{-1}$. Calibration peak is at 906.7 cm$^{-1}$. 
Figure 34. Proton-decoupled phosphorus-31 nmr spectrum of $[\text{Rh}(\text{ppol})_2]\text{AsF}_6$

in ethanol.
main product. Since those impurities were present in every reaction and they gave a very complicated pattern in the phosphorus-31 nmr spectrum, purification of the compound was not attempted. However, the $^{31}P\left(^1H\right)$ nmr spectrum of the major component gives: $\delta P_1 = 57.0$ ppm, $\delta P_2 = 18.2$ ppm, $J_{P_1-P_2} = 40.5$ Hz, $^{1}J_{Rh-P_1} = 133.0$ Hz, $^{1}J_{Rh-P_2} = 147.1$ Hz. The values of the rhodium-phosphorus coupling constants do not distinguish whether the oxidation state of rhodium is I or III, since the $J_{Rh-P}$ values are midway between typical Rh(I) and Rh(III) values. The infrared spectrum of the compound does not show a Rh-H absorption. However, the metal-hydride stretching peaks are sometimes too weak to be observed in the infrared spectrum. The proton nmr spectrum also does not show a peak at the hydride region; thus the reaction with HCl is not simply the oxidative addition reaction.

The addition of methyl iodide to RhI(ppol) also gave a similar problem. There are many extra peaks in the phosphorus-31 nmr spectrum. The major component gives the following phosphorus-31 nmr data: $\delta P_1 = 23.6$ ppm, $\delta P_2 = 10.1$ ppm, $J_{P_1-P_2} = 36.0$ Hz, $^{1}J_{Rh-P_1} = 125.1$ Hz, $^{1}J_{Rh-P_2} = 122.6$ Hz. Again, it is inconclusive whether methyl iodide adds oxidatively to the metal or reacts at the olefin
center. The $^{31}P^{1}H$ nmr spectra of Rh(I) complexes with other small molecules, i.e., Cl$_2$, I$_2$, and CHCl$_3$, gave only very broad peaks from $\sim$ 35 ppm to $\sim$ 25 ppm. Therefore, characterization of the reaction products, which were designed to show whether reactions occurred at the metal or at the olefin center were unsuccessful in this study for the rhodium complexes. Because of the serious difficulties in purification of the resultant products, we changed the transition metal from rhodium to iridium; these studies will be discussed in the following section.
B. Iridium Complexes of Unsaturated Tertiary Phosphines

The complex \([\text{Ir}(\text{cod})(\text{ppol})]\text{Cl} \cdot 2\text{C}_2\text{H}_5\text{OH}\) (A) was prepared from \([\text{IrCl}(\text{cod})]_2\) and ppol in ethanol at room temperature. The infrared spectra of A (Figures 35 and 36) show a broad band at \(-3300\ \text{cm}^{-1}\) due to the O-H stretching vibration of the ethanol molecules; however, the spectra show no band due to a free olefin at \(-1650\ \text{cm}^{-1}\), indicating the olefins of both ppol and cod are bonded to iridium. The stoichiometry that includes two ethanol molecules per iridium complex was confirmed by the proton nmr spectrum (Figure 37). The two ethanol molecules are equivalent in \(\text{CD}_2\text{Cl}_2\) solution since only one quartet and one triplet for the ethanol molecules were observed. The assignments for the \(^1\text{H}\) nmr spectrum in \(\text{CD}_2\text{Cl}_2\) are as follows:

\[
\begin{align*}
88.15-7.01 \text{ (m, phenyl)}; \\
65.33 \text{ (t, CDHC}_1\text{Cl}_2\text{)}; \\
64.64 \text{ (s, -OH of ethanol)}; \\
63.54 \text{ (q, -CH}_2\text{ of ethanol)}; \\
63.32-1.27 \text{ (m, -CH}_2\text{ of ppol and -CH}_2\text{ of cod)}; \\
61.08 \text{ (t, -CH}_3\text{ of ethanol)}.
\end{align*}
\]

The \(^1\text{H}\) nmr parameters for a free ethanol molecule in \(\text{CCl}_4\) are:

\[
\begin{align*}
64.40 \text{ (s, -OH)}; \\
63.58 \text{ (q, -CH}_2\text{)}; \\
61.17 \text{ (t, -CH}_3\text{)}.
\end{align*}
\]
Figure 35. Infrared spectrum of \([\text{Ir(cod)(ppol)}] \text{Cl}\cdot2\text{C}_2\text{H}_5\text{OH}\) in Nujol: 4000-1300 cm\(^{-1}\). Calibration peak is at 1601.4 cm\(^{-1}\).
Figure 36. Infrared spectrum of [Ir(cod)(ppol)]Cl.2C,H,OH in Nujol; 1350-400 cm$^{-1}$. Calibration peak is at 906.7 cm$^{-1}$. 
Figure 37. Proton nmr spectrum of $[\text{Ir}(\text{cod})(\text{ppol})]\text{Cl} \cdot 2\text{C}_2\text{H}_5\text{OH}$ in $\text{CD}_2\text{Cl}_2$. 
By comparing the above two sets of $^1$H nmr parameters for the ethanol molecule, the ethanol molecules in the iridium complex can be considered as those in the lattice. Small differences may be caused by the different solvents; i.e., CD$_2$Cl$_2$ for the iridium complex and CCl$_4$ for the pure ethanol.

Usually the protons of a bonded olefin shift upfield with a corresponding reduction in the H-H coupling constants. These effects are presumably due to a predominance of the $\sigma$-component over the $\pi$-component in the metal-olefin bond. Some proton nmr data for a phosphine ligand containing olefin substituents and the corresponding metal complexes are listed in Table 10. The proton nmr data for ppol ligand in benzene-$d_6$ are:

$$
\delta 7.55-6.65 \text{ (m, phenyl);} \\
\delta 5.9 - 5.4 \text{ (m, } -\text{CH=} ) \\
\delta 5.1 - 4.65 \text{ (m, } =\text{CH}_2 ) \\
\delta 2.35-0.6 \text{ (m, } -\text{CH}_2 ).
$$

On the other hand, the proton nmr spectrum of 1,5-cyclo-octadiene in CCl$_4$ gives peaks at $\delta$ 5.54 ppm for the olefinic protons and at $\delta$ 2.35 ppm for the methylene groups. The coordinated olefins of A could not be observed directly by the proton nmr spectroscopy, as the peaks may be hidden under the broad peak around $\delta$3-6 ppm.
### TABLE 10
SELECTED PROTON NMR DATA

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\tau_1) (ppm)</th>
<th>(\tau_2) (ppm)</th>
<th>(\tau_3) (ppm)</th>
<th>(J_{12}) (Hz)</th>
<th>(J_{13}) (Hz)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>mbp</td>
<td>4.19</td>
<td>5.11</td>
<td>5.06</td>
<td>10.0</td>
<td>17.0</td>
<td>81</td>
</tr>
<tr>
<td>Mo((\text{CO})_4) (mbp)</td>
<td>5.34</td>
<td>6.53</td>
<td>6.67</td>
<td>8.5</td>
<td>14.3</td>
<td>81</td>
</tr>
<tr>
<td>PtCl(_2) (mbp)</td>
<td>4.61</td>
<td>5.29</td>
<td>6.10</td>
<td>8.0</td>
<td>13.5</td>
<td>82</td>
</tr>
<tr>
<td>PtBr(_2) (mbp)</td>
<td>4.50</td>
<td>5.06</td>
<td>6.04</td>
<td>8.0</td>
<td>13.5</td>
<td>82</td>
</tr>
<tr>
<td>PtI(_2) (mbp)</td>
<td>4.42</td>
<td>4.75</td>
<td>5.82</td>
<td>8.2</td>
<td>13.7</td>
<td>82</td>
</tr>
</tbody>
</table>

\[ \text{mbp} = \text{Ph}_2\text{P-CH}_2\text{-CH}_2\text{-C\equiv C} \]

\[ \text{H}_1 \quad \text{H}_2 \]

\[ \text{H}_3 \]
Reactions performed on A are illustrated in Scheme 3. The phosphorus-31 nmr spectral data of A in ethanol (Figure 38) and in benzene (Figure 39) are listed in Table 11. Based upon the $^{31}P\{^1H\}$ nmr spectra, it appears that some structural reorganization occurs on changing the solvent from ethanol to benzene.

Scheme 3
The species present in benzene (B) can also be prepared directly from the reaction of [IrCl(cod)]₂ with ppol in benzene at room temperature.

The $^{31}$P{¹H} nmr spectra of B in ethanol and in benzene give identical spectra to those shown in Figures 38 and 39 respectively; thus, the structural reorganization between A and B is reversible.
Figure 38. Proton-decoupled phosphorus-31 nmr spectrum of [Ir(cod)(ppol)]Cl·2C₂H₅OH in ethanol.
Figure 39. Proton-decoupled phosphorus-31 nmr spectrum of $[\text{Ir(cod)(ppol)}] \text{Cl} \cdot 2\text{C}_2\text{H}_5\text{OH}$ in benzene.
There is only one component in ethanol, whereas there are two components in benzene. The ratio of the major component to the minor component in benzene is 2.0. Since the $J_{P_1-P_2}$ values for both components are the same, they are considered as isomers. The possible isomerization for B may arise from the position of the chlorine atom; in one case, the Cl atom is syn to the phenyl group on the phosphorus atom ($P_1$), and the Cl is anti in the second case. The syn-isomer would be the minor component since the phenyl group will experience more steric hindrance by the Cl atom in this case than in the anti-isomer. The free olefin $C=C$ stretch could not be observed in the infrared spectrum of B since the $-1650 \text{ cm}^{-1}$ area was masked by a broad weak band due to moisture in the solvent, which could not be completely removed under vacuum for 1 day. However, the proton nmr spectrum of B shows two broad peaks at $\delta 5.64-5.44 \text{ ppm}$ and $\delta 4.91-4.72 \text{ ppm}$ due to the non-bonded olefin group.

When A was treated with NaI in benzene, a yellow precipitate (C) formed; its infrared spectra (Figures 40 and 41) showed a non-bonded olefin absorption at 1640 cm$^{-1}$. The phosphorus-31 nmr spectrum of C in benzene shows a pattern similar to that shown in Figure 39; this suggests that the same type of structure and isomerization as B
Figure 40. Infrared spectrum of IrI(cod)(ppol) in Nujol; 4000-1300 cm\(^{-1}\). Calibration peak is at 1601.4 cm\(^{-1}\).
Figure 41. Infrared spectrum of IrI(cod)(ppol) in Nujol; 1350-400 cm$^{-1}$.
Calibration peak is at 906.7 cm$^{-1}$.
is occurring in \( \mathcal{C} \). The parameters of the \( ^{31}\text{P}[^{1}\text{H}] \) nmr spectrum are: \( \delta P_1 = -20.9 \text{ ppm}, \delta P_2 = -38.2 \text{ ppm}, J_{P_1-P_2} = 44.0 \text{ Hz} \) for the major component; \( \delta P_1 = -21.4 \text{ ppm}, \delta P_2 = -35.5 \text{ ppm}, J_{P_1-P_2} = 42.7 \text{ Hz} \) for the minor component. The ratio of the major component to the minor component is 4.0 in this case. Thus, the ratio is larger for the iodide complex than for the chloride complex since the phenyl group on \( P_1 \) in the syn-isomer will be more sterically hindered by the bulky iodide than by the chloride. Thus, the anti-isomer is more favored in the iodide complex than in the chloride complex.

In addition, the chemical shift of the central phosphorus nucleus, \( \delta P_1 \), in the phosphorus-31 nmr spectrum supports the presence of the free olefin. When the olefinic moiety is not bonded to the metal, the \( P_1 \) atom is no longer a member of the 5.5-membered ring. Thus, \( \delta P_1 \) for the complexes \( \mathcal{B} \) and \( \mathcal{C} \) is expected to be upfield compared to its resonance in \( \mathcal{A} \) in ethanol. Indeed, this shift is observed (eg. Table 11); thus, \( \delta P_1 \) for \( \mathcal{B} \) is shifted upfield by \( \sim 15 \text{ ppm} \) compared to \( \delta P_1 \) for \( \mathcal{A} \). The same trend was observed in the rhodium complex, \([\text{Rh(ppol)}_2]\text{AsF}_6\), which has two ppol ligands, both with non-bonded olefins. The chemical shift of the central phosphorus atom, \( \delta P_1 \), in \( \text{Rh(ppol)}\text{Cl} \) is 53.7 ppm, whereas
δP₁ in [Rh(ppol)₂]AsF₆ is at -8.0 ppm. Thus, both olefins of cod are bonded and the olefin position of ppol is not coordinated to iridium in benzene.

The presence of a benzene molecule in B could not be confirmed either by infrared spectroscopy or by proton nmr spectroscopy. Since the ppol ligand has several phenyl groups, it is impossible to determine whether the infrared absorption bands at ~ 3000 cm⁻¹ and ~ 1600 cm⁻¹ are due to the phenyl groups of the ligand or to the benzene molecule in the lattice. Also, the peaks of the proton nmr spectrum of this complex are too broad for accurate calculations of the ratio of the phenyl group region to any other peak. However, the analytical results fit reasonably well for one benzene molecule in B.

Thus, in ethanol A is an ionic compound which contains all olefins of ppol and cod bonded, and the chloride is an anion. On the other hand, B is a molecular compound that has the olefin of ppol uncoordinated, whereas the two olefins of cod are bonded along with the chloride. This kind of structural change has been reported in the literature. In methanol RhCl(CO)(mbp)₂ (mbp = but-3-enyldiphenylphosphine) ionizes to give a molar conductivity of 64.0 43 ohm⁻¹cm⁻²mol⁻¹ and a similar phenomenon has been seen in RhBr(tvpp) (tvpp = tris-2-vinylphenylphosphine) in
methanol. The chloride anion can be replaced by other anions, such as PF$_6^-$ and AsF$_6^-$.  

A white crystalline solid, [Ir(cod)(ppol)]AsF$_6$·$\frac{1}{4}$C$_2$H$_5$OH (D) was isolated by adding NaAsF$_6$ to A in ethanol; the infrared spectrum of the resultant solid indicates the presence of AsF$_6^-$ anion. A weak absorption band at 3570 cm$^{-1}$ might be due to an OH stretch of the ethanol molecule in the crystal lattice. Additionally, a weak absorption at 1970 cm$^{-1}$ is observed. This peak might be due to a small amount of a carbonyl impurity; this point will be discussed later.

When acetonitrile was used as a solvent for the reaction of A with NaPF$_6$, a white solid [Ir(cod)(ppol)]PF$_6$·$\frac{1}{4}$CH$_3$CN (E) was produced. The infrared spectrum of this compound shows absorption bands at 845 cm$^{-1}$ and 559 cm$^{-1}$ due to PF$_6^-$ anion. A weak absorption at 1970 cm$^{-1}$ is observed here, too. A weak band at 2270 cm$^{-1}$ indicates the presence of acetonitrile in the lattice and the elemental analysis confirmed the presence of acetonitrile.

The phosphorus-31 nmr spectral data of A, D, E are presented in Table 12. The observed similarity in the phosphorus-31 nmr spectra for those three compounds suggests that the species in ethanol or in acetonitrile have similar structures. The molar conductivities of D
(61.0 ohm\(^{-1}\)cm\(^{-2}\)mol\(^{-1}\) in ethanol) and \(E\) (137.0 ohm\(^{-1}\)cm\(^{-2}\)mol\(^{-1}\) in acetonitrile) show that both \(D\) and \(E\) are 1:1 electrolytes.\(^{84}\)

### TABLE 12

\(^{31}\)P\(_{\{\text{\(1\)H}\}}\) NMR DATA FOR THE CATIONIC COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>(\delta P_1) (ppm)</th>
<th>(\delta P_2) (ppm)</th>
<th>(J_{P_1-P_2}) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(cod) (ppol)]Cl • 2C(_2)H(_5)OH</td>
<td>C(_2)H(_5)OH</td>
<td>3.5</td>
<td>-30.0</td>
<td>36.6</td>
</tr>
<tr>
<td>[Ir(cod) (ppol)]AsF(_6) • ½C(_2)H(_5)OH</td>
<td>C(_2)H(_5)OH</td>
<td>3.2</td>
<td>-30.0</td>
<td>36.6</td>
</tr>
<tr>
<td>[Ir(cod) (ppol)]PF(_6) • ½CH(_3)CN</td>
<td>CH(_3)CN</td>
<td>4.4</td>
<td>-30.0</td>
<td>37.2</td>
</tr>
</tbody>
</table>
The crystal structure of [Ir(cod)(ppol)]AsF₆·½C₂H₅OH has been determined by X-ray crystallography by Dr. Pignolet at the University of Minnesota. There are two molecules per asymmetric unit, but they are chemically equivalent. The positional and thermal parameters and their estimated standard deviations are shown in Table 13. The perspective view of the coordination sphere around iridium is illustrated in Figure 42. Intramolecular distances and angles are shown in Table 14, and chemically equivalent distances are tabulated in the same row.

The geometry about iridium is trigonal bipyramidal structure; the central phosphorus atom of ppol and one olefin of cod occupy the apex positions including a half of distorted ethanol molecule in the crystal lattice. All the Ir-C(olefin) distances are in the ranges reported for bonded Ir-C(olefin) distances and the Ir-C(olefin of ppol) distances (2.216(7) Å and 2.222(8) Å) do not differ significantly from the Rh-C (olefin) distances (2.203 Å and 2.210 Å) in RhCl(ppol). The Ir-C₄' and Ir-C₅' bond distances are longer than the other Ir-C(olefin) distances, which may be due to a stronger trans-influence of the phosphorus than the olefin.
<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>B(1,1)</th>
<th>B(2,2)</th>
<th>B(3,3)</th>
<th>B(1,2)</th>
<th>B(1,3)</th>
<th>B(2,3)</th>
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<td>IR</td>
<td>-0.1917(2)</td>
<td>-0.8493(2)</td>
<td>0.1056(2)</td>
<td>0.0033(1)</td>
<td>0.0019(2)</td>
<td>-0.0039(2)</td>
<td>0.0056(3)</td>
<td>0.0019(2)</td>
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<tr>
<td>IR'</td>
<td>0.2915(2)</td>
<td>0.4722(2)</td>
<td>0.2812(2)</td>
<td>0.0049(2)</td>
<td>0.0044(2)</td>
<td>0.0062(2)</td>
<td>0.0017(3)</td>
<td>0.0027(2)</td>
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<tr>
<td>C1</td>
<td>0.1957(8)</td>
<td>0.1036(7)</td>
<td>-0.1062(8)</td>
<td>0.0085(17)</td>
<td>0.0034(4)</td>
<td>0.0047(7)</td>
<td>0.0018(9)</td>
<td>0.0011(1)</td>
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<tr>
<td>C2</td>
<td>0.1134(7)</td>
<td>-0.3233(6)</td>
<td>-0.2356(6)</td>
<td>0.0062(6)</td>
<td>0.0036(4)</td>
<td>0.0062(7)</td>
<td>0.0028(8)</td>
<td>0.0011(1)</td>
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<tr>
<td>F1</td>
<td>-0.0778(2)</td>
<td>-0.1351(1)</td>
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Table 13 (continued)
Figure 42. Perspective view of coordination sphere around iridium.
TABLE 14

INTRAMOLECULAR DISTANCES AND ANGLES WITHIN
THE COORDINATION SPHERE

Chemically equivalent distances and angles are
tabulated in the same row.

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</table>

*aNote that figure is for the primed molecule.*
As mentioned earlier, a weak absorption band at 1970 cm\(^{-1}\) is observed in the infrared spectrum of each cationic complex; i.e., A, D, and E. This band may be due to a small amount of a carbonyl impurity. Abstraction of CO from alcohols with basic and bulky phosphines has been reported previously\(^{88-91}\). For example, mixing alcoholic solutions of commercially available metal halides with PCy\(_3\) gives high yields of carbonyl complexes such as HRuCl\((CO)\)\(_2\)(PCy\(_3\))\(_2\), Ru\((CO)\)\(_3\)(PCy\(_3\))\(_2\), IrCl\((CO)(PCy\(_3\))\(_2\); thus, these syntheses of carbonyl complexes do not require the use of gaseous carbon monoxide.

To confirm that the 1970 cm\(^{-1}\) band is due to the CO stretch, the carbonyl complex, IrCl\((CO)(ppol)\) was prepared by bubbling CO gas through an ethanol solution of \([Ir(cod)(ppol)]Cl\cdot2C_2H_5OH\). The infrared spectra of IrCl\((CO)(ppol)\) are presented in Figures 43 and 44. A carbonyl absorption at the same frequency supports the assignment of the 1970 cm\(^{-1}\) frequency to a \(\nu_{CO}\) of the minor component in D and E. The lower carbonyl stretching frequency compared to those in \([Rh(CO)(PPh_3)(ppol)]AsF_6\) (1985 cm\(^{-1}\) in Nujol)\(^{38}\) and \([Rh(CO)_2(ppol)]AsF_6\) (2105 and 2060 cm\(^{-1}\)) can be attributed to the higher basicity of the iridium atom. The value is similar to those observed in IrCl(bdpss)\((CO)\) (1990 cm\(^{-1}\))\(^{52}\), IrCl\((CO)(C_8H_{14})_3\) (1994 cm\(^{-1}\)).\(^{92}\)
Figure 43. Infrared spectrum of IrCl(CO)(ppol) in Nujol; 4000-1300 cm\(^{-1}\). Calibration peak is at 1601.4 cm\(^{-1}\).
Figure 44. Infrared spectrum of IrCl(CO)(ppol) in Nujol; 1350-400 cm\(^{-1}\).
Calibration peak is at 906.7 cm\(^{-1}\).
which are presumed to have the trigonal-bipyramidal structures with CO in the equatorial position. However, it cannot be decided that IrCl(CO)(ppol) has a trigonal-bipyramidal structure simply because the carbonyl stretching frequency in this complex is similar to those in trigonal-bipyramidal complexes. For example, the $\nu_{\text{CO}}$ in [IrCl(CO)-(C$_8$H$_{14}$)$_2$]$_2$ containing two square-pyramidal units is 1980 cm$^{-1}$, and the $\nu_{\text{CO}}$ in the trigonal-bipyramidal [Ir(CO)(spp)$_2$]BF$_4$ is 2038 cm$^{-1}$. There is no free C=CH absorption observed, indicating that the olefin group is bonded to the metal. Both the elemental analysis and the effective atomic number rule suggest that cod is replaced by CO. Due to the extremely low solubility of the carbonyl complex in various solvents, no other significant phosphorus-31 nmr spectral data could be obtained, even after ~ 30,000 scans. Thus, the possible structures for this complex are 17 and 18.
The reaction product, G, of [Ir(cod)(ppol)]Cl·2C2H5OH with conc. HCl gives an Ir–H absorption at 2250 cm⁻¹ in the infrared spectrum. The phosphorus-31 nmr spectrum of this compound in acetonitrile gives the following data: \( \delta P_1 = -13.5 \text{ ppm}, \delta P_2 = -25.3 \text{ ppm}, J_{P_1-P_2} = 26.2 \text{ Hz.} \) The \( ^2J_{pp} \) values for Ir(I) complexes are in the range of 15-30 Hz; known \( ^2J_{pp} \) values for Ir(III) complexes vary from 15 to 35 Hz. Thus, one cannot tell whether the oxidation state of Ir of this compound is I or III at this point.

The proton nmr spectrum of G shows a doublet of doublets at -15.3 ppm, which confirms the presence of a hydride, and this chemical shift is close to the values found for H trans to Cl in IrHCl₂(bdpps)⁵² and IrHCl₂(CO)(PR₃)₂. A phosphorus-decoupled proton nmr spectrum gives a singlet at the same position. By selective decoupling one phosphorus nucleus at a time, the coupling constant for another phosphorus nucleus with the hydride ligand was obtained:

\[
^2J_{P_1-H} = 12.7 \pm 1.0 \text{ Hz}, \quad ^2J_{P_2-H} = 8.3 \pm 1.0 \text{ Hz.}
\]

The \( ^2J_{PH(cis)} \) couplings are normally in the range 10-30 Hz, whereas the \( ^2J_{PH(trans)} \) couplings are in the range 130-180 Hz for terminal hydrides and \( ^2J_{PH(trans)} \) couplings for bridging hydrides are 60-100 Hz.⁹⁵,⁹⁷-¹₀⁰ Therefore, the hydride in G is cis to both phosphorus nuclei since the observed \( ^2J_{PH} \) couplings are in the range expected for \( ^2J_{PH(cis)} \). The
MH stretching vibrations are sensitive to other substituents in the metal complex, particularly of ligands in positions trans to hydrogens. In iridium complexes, $\nu_{\text{Ir-H}}$ is ~1750 cm$^{-1}$ when hydrogen is the trans ligand, 2000-2100 cm$^{-1}$ for $\text{R}_3\text{P}$ and CO and 2180-2240 cm$^{-1}$ for halogen. The observed infrared absorption frequency at 2250 cm$^{-1}$ is in the range quoted for H trans to Cl in octahedral hydrido-iridium(III) complexes. Elemental analysis for $G$ indicates that two chlorine atoms are included. Therefore, it is concluded that the oxidation number of iridium is III, which gives the molecular formula IrCl$_2$H$_5$ for $G$. Thus, HCl adds oxidatively to iridium to give a six-coordinate geometry, and the cod ligand is displaced in this reaction.

The reaction of $A$ with I$_2$ was attempted to find out if iodination gives a similar result to that mentioned above. However, the phosphorus-31 nmr spectrum of the product, which was obtained after refluxing with I$_2$ for 2 hr in toluene, was identical to that of IrI(cod)(ppol). Thus, iodine did not oxidatively add to the iridium(I) complex; instead, it gave only the halogen substitution product.

Protonation of $[\text{Ir(cod)(ppol)}]\text{Cl} \cdot 2\text{C}_2\text{H}_5\text{OH}$ with HBF$_4$-etherate was attempted at -78°C in methanol. However, the
phosphorus-31 nmr spectrum shows that the chloride anion is simply displaced by the BF$_4^-$ anion to give the cationic complex, [Ir(cod)(ppol)]BF$_4$. The $^{31}$P-$^1$H nmr spectrum in CH$_3$OH, which is similar to those observed for the other cationic complexes, A, D, and E, gives the following data: $\delta P_1 = 3.5$ ppm, $\delta P_2 = -30.4$ ppm, $J_{PP} = 37.2$ Hz. Crabtree and coworkers performed the protonation and oxidative addition reactions with various acids on [Ir(cod)L$_2$]PF$_6$ ($L =$ PPh$_3$, PMePh$_2$). They showed that the cationic complexes, [Ir(cod)L$_2$]PF$_6$, did not react with HPF$_6$ in methanol; also, they did not react with HF or KF since the fluoride anion was insufficiently nucleophilic to effect the substitution. In addition, the complexes are insufficiently basic to become protonated. However, when [IrCl(cod)(PPh$_3$)$_2$] was reacted with HPF$_6$ at $-60^\circ$C, a product from the substitution reaction, [Ir(cod)(PPh$_3$)$_2$]PF$_6$ was obtained along with the protonated compound.

In conclusion, the reaction of [IrCl(cod)]$_2$ with ppol gives a complex which contains cod as well as ppol in the coordination sphere of iridium. This compound is ionic in the polar solvents EtOH and CH$_3$CN, and it is a molecular complex in non-polar solvents such as benzene and toluene. When CO is introduced to this complex, cod is replaced by carbon monoxide. Oxidative addition of HCl to this compound was accomplished, and the cod ligand was displaced.
However, in the case of an attempted oxidative addition of I₂, the simple iodide substitution product was obtained. An attempt to attack the olefin center with HBF₄-etherate resulted only in another cationic complex, whereby the anionic chloride was replaced by the BF₄⁻ anion. Thus, the olefinic moiety in this study seems to be stable to electrophilic attack.
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