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Synthesis, characterization and reactivity of platinum(0)-tetraphosphino complexes and group VIII metal phosphine complexes coordinated to alkoxide and hydroxide ligands

Green, Lisa Marie, Ph.D.
The Ohio State University, 1987
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SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF
PLATINUM(0)-TETRAPHOSPHINO COMPLEXES AND GROUP VIII METAL
PHOSPHINE COMPLEXES COORDINATED TO ALKOXIDE AND HYDROXIDE LIGANDS

DISSERTATION

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

By

Lisa Marie Green, B.S.

* * * * *

The Ohio State University
1987

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Approved By
Devon W. Meek,
Department of Chemistry
To

My Parents

James and Audrey Banovetz

and

My Husband

Michael
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PUBLICATIONS


"Crystal and Molecular Structure of a Dinuclear Uranyl(VI) Chloride (UO2Cl2(THF)2)2." R. D. Rogers, L. M. Green and M. M. Benning, Lanthanide Actinide Research 1986, 1, 185.


"A 195Pt(1H) and 31P(1H) NMR Investigation of the Platinum(0)-Tetrakisphosphino Complexes, Pt[CH3C(CH2PPh2)3]PR3." L. M. Green, Y. Park and D. W. Meek, submitted for publication.

FIELDS OF STUDY

Major Field: Inorganic Chemistry
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    in THF with C$_6$D$_6$ added as an internal lock ................... 237

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ABBREVIATIONS

Ph  \( \text{C}_6\text{H}_5 \)

R  Organic Group

tripod  \( 1,1,1\text{-tris(diphenylphosphinomethyl)ethane} \)

p-tolyl  \( \text{p-CH}_3\text{C}_6\text{H}_4 \)

Me  \( \text{CH}_3 \)

Et  \( \text{CH}_3\text{CH}_2 \)

n-Bu  \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \)

Bz  \( \text{C}_6\text{H}_5\text{CH}_2 \)

i-Pr  \( \text{CH(CH}_3)_2 \)

t-Bu  \( \text{C(CH}_3)_3 \)

n-Pr  \( \text{CH}_3\text{CH}_2\text{CH}_2 \)

DMF  \( \text{N,N-Dimethylformamide} \)

THF  \( \text{Tetrahydrofuran} \)

Cy  \( \text{C}_6\text{H}_{11} \)

COD  \( 1,5\text{-Cyclooctadiene} \)

ttp  \( \text{Bis(3-(diphenylphosphino)propyl)phenylphosphine} \)

cyttpp  \( \text{Bis(3-(dicyclohexylphosphino)propyl)phenylphosphine} \)

xs  excess

LDA  \( \text{Lithium diisopropylamide} \)

CF\text{3PPH}  \( \text{3-Bis(4-trifluoromethylphenylphosphino)propyl-phenylphosphine} \)

xviii
<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>CF&lt;sub&gt;3&lt;/sub&gt;ttpp</td>
<td>Bis(3-(4-trifluoromethylphenylphosphino)-propyl)phenylphosphine</td>
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<tr>
<td>NPh</td>
<td>napthyl</td>
</tr>
<tr>
<td>PPH</td>
<td>3-(Diphenylphosphino)propylphenylphosphine</td>
</tr>
<tr>
<td>cyPPH</td>
<td>3-(Dicyclohexylphosphino)propylphenylphosphine</td>
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Part I

A $^{195}\text{Pt}(^1\text{H})$ and $^{31}\text{P}(^1\text{H})$ NMR Investigation of

the Platinum(0)-Tetrathosphino Complexes, Pt(CH$_3$C(CH$_2$PPh$_2$)$_3$PR$_3$
CHAPTER I
Introduction and Statement of Research Problem

Fourier transform nmr spectroscopy, which was introduced to the scientific community in the 1970's, provides the necessary tool for the routine investigation of the $^{195}$Pt nucleus (spin = 1/2, natural abundance = 33.7%, relative sensitivity = $9.94 \times 10^{-3}$). Platinum-195 nmr spectroscopy is a useful method for qualitative and structural investigations of platinum complexes because the $^{195}$Pt chemical shift variation is large (range: $> 15,000$ ppm) and it is sensitive to the ligands present in the platinum coordination sphere.$^{1,2}$

The chemical shift of an nmr active nucleus depends on the net nuclear magnetic shielding, $\sigma_t$, which Ramsey$^3$ has shown to be the sum of a diamagnetic term, $\sigma_d$, and a paramagnetic term, $\sigma_p$ (Eq. 1). The main contribution to the nuclear magnetic shielding of a heavy nucleus, such as $^{195}$Pt, is the paramagnetic term, which has also been defined by Ramsey.$^3$ The equation for $\sigma_p$, which is often labeled the Ramsey equation, is given as follows:

$$\sigma_p = \frac{-e^2}{(2m^2c^2)} \sum_{n=0} \left( E_n - E_0 \right)^{-1} \left( \langle \psi_o | \Sigma_j \alpha_j | \psi_n \rangle \langle \psi_n | \Sigma_k r_3 \alpha_k | \psi_o \rangle \right) + \left( \langle \psi_o | \Sigma_j r_3 \alpha_j | \psi_n \rangle \langle \psi_n | \Sigma_k \alpha_k | \psi_o \rangle \right)$$

(2)
where $e$ is the charge on an electron, $m$ is the mass, $c$ is the speed of light, $\psi_o$ and $\psi_n$ are the wavefunctions of the ground and excited states and $E_o$ and $E_n$ are the corresponding energies, $l_\alpha$ is the angular momentum operator for the jth electron and $r_k$ is the distance of the kth electron from the nucleus under study.

Because of the $(E_n - E_o)^{-1}$ term, the paramagnetic term is often dominated by the lowest electronic excitation energy in a complex, provided the upper state has the correct symmetry to yield nonzero integrals in Equation 2. Therefore, by measuring the electronic excitation energy of a complex incorporating a heavy nmr active nucleus, the chemical shift of the heavy nucleus can be predicted theoretically. For example, the chemical shifts of the $^{59}$Co nucleus in a series of octahedral Co(III) complexes were found to be proportional to the wavelength of the $^1A_{1g} \rightarrow ^1T_{2g}$ transition in the electronic absorption spectra of the complexes. Thus, using a modification the Ramsey equation based on ligand field theory, theoretical chemical shift predictions for cobalt complexes have been made.4-6

Pidcock and co-workers7 attempted to predict theoretically the $^{195}$Pt chemical shift of a series of Pt(II) complexes, PtX$_2$L$_2$ ($X =$ anionic ligand, $L =$ neutral ligand) by using a simplified form of the Ramsey equation based on $D_{4h}$ symmetry and electronic absorption data. However, a correlation was not observed between the frequency of the $^1A_{1g} \rightarrow ^1E_g$ transition and the $^{195}$Pt chemical shift for the PtX$_2$L$_2$ complexes. Recent work relating UV-visible spectroscopic data8 and molecular orbital analyses9 to $^{195}$Pt chemical shifts has been more
successful. Saito, Shinoda and Koie\textsuperscript{10} have done a particularly
elegant analysis of the relationship between \( ^{195}\text{Pt} \) chemical shifts and
UV-visible spectroscopic data for a series of Pt(0)-acetylene
complexes, \([\text{Pt}(\text{RC} \equiv \text{CR}')(\text{PPh}_3)_2]\), based on molecular orbital theory.

The study conducted by Saito and co-workers\textsuperscript{10} provides a starting
point for theoretically predicting and calculating \( ^{195}\text{Pt} \) chemical
shifts; however, a more immediate method of relating \( ^{195}\text{Pt} \) nmr data to
molecular composition and structure is obtained by drawing empirical
relationships. In order to draw these relationships, a substantial
data base is required. Platinum(IV) and Pt(II) complexes have been
investigated extensively by \( ^{195}\text{Pt} \) nmr spectroscopy, usually by use of
INDOR techniques; in contrast, the amount of \( ^{195}\text{Pt} \) nmr data available
on mononuclear Pt(0) complexes is limited.\textsuperscript{1,2} In addition to the
Pt(0)-acetylene complexes investigated by Saito and co-workers,
approximately 41 additional mononuclear Pt(0) complexes have been
investigated by \( ^{195}\text{Pt} \) nmr spectroscopy.\textsuperscript{8,11,12-16} Included in these
investigations are Pt(0) monophosphine complexes, Pt\( L_n \) \( (L = \) monophosphine) and the available data for these complexes are given in
Table 1.

The available data concerning the magnitudes of Pt-P coupling
constants and \( ^{195}\text{Pt} \) and \( ^{31}\text{P} \) chemical shifts for Pt(0)-tetraphosphine
complexes are particularly limited due to the tendency of Pt(PR\textsubscript{3})\textsubscript{4}
compounds to dissociate in solution. The available \( ^{31}\text{P} \) and \( ^{195}\text{Pt} \) nmr
data for Pt(0)-tetraphosphine complexes are given in Tables 1 and
2.\textsuperscript{8,12,16-19} By use of the chelating triphosphine ligand,
Meek and co-workers\textsuperscript{20} prepared a series of dissociatively stable tetraphosphino complexes, Pt(tripod)PR\textsubscript{3} (PR\textsubscript{3} = PPh\textsubscript{3}, P(p-tol)\textsubscript{3}, PPh\textsubscript{2}Me, P(OCH\textsubscript{2})\textsubscript{3}CCH\textsubscript{3}, PF\textsubscript{2}NMe\textsubscript{2}, P(OPh)\textsubscript{3} and PF\textsubscript{3}) and investigated the one-bond platinum-phosphorus coupling constants by \textsuperscript{31}P(\textsuperscript{1}H) nmr spectroscopy. In the present investigation, an expanded series of Pt(tripod)PR\textsubscript{3} complexes are prepared, the \textsuperscript{31}P(\textsuperscript{1}H) and \textsuperscript{195}Pt(\textsuperscript{1}H) nmr spectra are recorded, the Pt-P and P-P coupling constants are reported and the \textsuperscript{31}P and \textsuperscript{195}Pt chemical shifts are reported for the first time. These data increase the data base available for Pt(0) complexes and they are used to draw empirical relationships based on the platinum and phosphorus chemical shifts and the Pt-P and P-P coupling constants.
Table 1. \( ^{195}\text{Pt}(^1\text{H}) \) NMR Data for Pt(0)-Monophosphine Complexes, PtLₙ

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<td>c</td>
<td></td>
<td></td>
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Chemical shifts are in ppm relative to H₂PtCl₆. Solvent: d-8 toluene, temperature: 213K.

a) d-8 THF solvent.
b) 310K.
c) 258K.
d) No temperature given.
e) 243K.
f) 193K.
g) CD₂Cl₂ solvent.
### Table 2. $^{31}\text{P}^{(1\text{H})}$ NMR Data for Pt(0)-Tetrathosphate Complexes

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<th>Complex</th>
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<th>$^1J(\text{Pt-P})$</th>
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<td>11</td>
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<td>Pt(PET$_3$)$_4$</td>
<td>-17</td>
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<td>Pt[P(OEt)$_3$]$_4$</td>
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<td>PPh$_3$</td>
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Chemical shifts are in ppm, coupling constants are in Hz.
CHAPTER II
Experimental

A. General Procedures

All reactions and sample preparations were carried out using standard Schlenk and inert atmosphere box techniques. Reagent grade solvents were dried by use of conventional methods and distilled under argon. Distilled water, absolute ethanol and 2,2,2-trifluoroethanol were purged with an Ar stream for 20 minutes prior to use. Deuterated THF, all phosphines and phosphites (all liquids were received under Ar) and NaBH₄ were used without further purification. The synthesis of the ligand P(3,5-(CF₃)₂C₆H₃)₃ is described in Part II of this dissertation. The K₂PtCl₄ was prepared using a literature procedure and it was recrystallized from a 5% HCl solution.

B. Instrumentation

Preliminary ³¹P(¹H) nmr spectra were recorded on an Bruker HX-90 FT nmr spectrometer operating at 36.43 MHz in 10 mm tubes fit with a coaxial insert containing d₆-acetone and trimethylphosphate or on a Bruker AM-250 FT nmr spectrometer in 5 mm tubes. The spectra were referenced to external 85% H₃PO₄. The infrared spectra were recorded on a Perkin-Elmer 283B grating spectrometer as Nujol mulls between KBr plates. The spectra were referenced to the sharp 1601 cm⁻¹ peak of a polystyrene film.
The $^{195}\text{Pt}(^1\text{H})$ and $^{31}\text{P}(^1\text{H})$ nmr spectra used for the data analyses were recorded at 296K on a Bruker MSL-300 FT nmr spectrometer operating at 64.386 MHz and 121.497 MHz, respectively. The $^{31}\text{P}(^1\text{H})$ nmr spectra are referenced to external $85\% \text{H}_3\text{PO}_4$ and the $^{195}\text{Pt}(^1\text{H})$ spectra are referenced to external $\text{H}_2\text{PtCl}_6$ in $\text{D}_2\text{O}/\text{HCl}$ with a correction made for the d8-THF solvent.

The samples were prepared in a 25% d8-THF/75% THF solvent mixture as 0.05M solutions. The samples were recorded in 10 mm nmr tubes fit with vortex plugs.

C. Synthesis of Pt(tripod)PR$_3$ Complexes

1. Synthesis of PtCl$_2$(tripod)

A solution of tripod, 1,1,1-tris(diphenylphosphinomethyl)ethane, (0.7012g, 1.122 mmol) in 25 ml of DMF was heated to 120°C. To the warm solution, $\text{K}_2\text{PtCl}_4$ (0.4662g, 1.123 mmol) in 2.5 mL of water was added. The red color due to the aqueous $\text{K}_2\text{PtCl}_4$ disappeared within minutes and the solution became clear. The solution was allowed to cool to 90°C and 5.0 mL of water were added. The solution was allowed to cool to room temperature and a white solid precipitated. The solid was collected by vacuum filtration, washed with water and dried in a dessicator. Yield: 0.9302, 93.2%.

2. Synthesis of Pt(tripod)PPh$_3$

A solution of $\text{P(C}_6\text{H}_5)_3$ (0.1213g, 0.4625 mmol) in 5.0 mL of absolute ethanol was added to a solution of PtCl$_2$(tripod) (0.4111g, 0.4616 mmol) in 23 mL of absolute ethanol and 6 mL of H$_2$O. The resulting slurry was refluxed for ten minutes, cooled to room temperature and stirred for one hour. Sodium borohydride (0.0524g,
1.38 mmol) dissolved in 10 mL of H₂O was added dropwise, over a 15 minute period, to the room temperature solution containing the platinum complex. A yellow solid precipitated and the resulting slurry was stirred for an additional 30 minutes. The yellow solid was collected on a Schlenk frit, washed with water and dried in vacuo. The yield was not recorded.

3. Synthesis of Pt(tripod)PPh₂Me

Diphenylmethylphosphine (0.55 mL, 3.0 mmol) was added to a slurry of PtCl₂(tripod) (2.6195 g, 2.9409 mmol) in 135 mL of absolute ethanol. The resulting slurry was stirred for one hour, during which most of the solid dissolved. Then, 33 mL of H₂O were added and the solution was warmed gently until all the solid dissolved. Sodium borohydride (0.3442g, 9.094 mmol) dissolved in 30 mL of H₂O was added, dropwise, over a 30 minute period, to the platinum solution. A yellow solid precipitated. The yellow solid was collected on a Schlenk frit, washed with water and dried in vacuo. The yield was not recorded.

4. Synthesis of Pt(tripod)PPhMe₂

Dimethylphenylphosphine (0.65 mL, 0.46 mmol) was added via a microsyringe to a slurry of PtCl₂(tripod) (0.40g, 0.45 mmol) in 25 mL of absolute ethanol. The resulting solution was refluxed for one hour, during which the solid dissolved. The solution was cooled to room temperature and 0.0536g (1.42 mmol) of NaBH₄ dissolved in 10 mL of H₂O was added, dropwise, over a 10 minute period. A yellow solid precipitated and the slurry was stirred for an additional 30 minutes. The bright yellow solid was collected on a Schlenk frit, washed with H₂O and dried in vacuo. The yield was not recorded.
5. Synthesis of Pt(tripod)P(CH$_2$CH$_2$CN)$_3$

Absolute ethanol (17 mL) was added to 0.4400g (0.4940 mmol) of PtCl$_2$(tripod) and 0.0952g (0.493 mmol) of P(CH$_2$CH$_2$CN)$_3$. The resulting slurry was refluxed for one hour, and then 4.0 mL of H$_2$O was added. Sodium borohydride (0.0571g, 1.51 mmol) dissolved in 6 mL of H$_2$O was added, dropwise, over a 20 minute period, to the platinum solution. A yellow solid precipitated. The yellow solid was collected on a Schlenk frit, washed with H$_2$O and dried in vacuo. The yield was not recorded.

6. Synthesis of Pt(tripod)P(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$

A solution containing 0.2499g (0.2806 mmol) of PtCl$_2$(tripod) and 0.1885g (0.2812 mmol) of P(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$ in 35 mL of THF was refluxed for one hour. The solution was concentrated to one-half its initial volume in vacuo followed by the dropwise addition of 0.0314g (0.830 mmol) of NaBH$_4$ dissolved in 10 mL of distilled water. The solvent was removed from the resulting orange slurry and 20 mL of absolute ethanol and 10 mL of distilled water were added to the orange paste. The orange solid was collected on a Schlenk frit, washed with 2 x 5 mL aliquots of distilled water and dried in vacuo. Yield: 0.30g, 71%.

7. Synthesis of Pt(tripod)P(p-FC$_6$H$_4$)$_3$

Absolute ethanol (35 mL) was added to 0.40g (0.46 mmol) of PtCl$_2$(tripod) and 0.18g (0.57 mmol) of P(p-FC$_6$H$_4$)$_3$. The resulting slurry was refluxed for one hour and then cooled to room temperature. Sodium borohydride (0.0663g, 1.75 mmol) dissolved in 10 mL of H$_2$O was added, dropwise, to the platinum solution. A yellow solid
precipitated and the slurry was stirred an additional 30 minutes. The yellow solid was collected on a Schlenk frit, washed with water and dried in vacuo. Yield: 0.33g, 52%.

8. Synthesis of Pt(tripod)P(OMe)$_3$

Trimethylphosphite (0.040 mL, 0.34 mmol) was added via a microsyringe to 0.30g (0.34 mmol) of PtCl$_2$(tripod) in 20 mL of distilled methanol. The resulting slurry was refluxed until all the solid dissolved. The solution was cooled to room temperature and NaBH$_4$ (0.0401g, 1.06 mmol) dissolved in 10 mL of H$_2$O was added dropwise. A yellow solid precipitated and the slurry was stirred until the evolution of gas (H$_2$) terminated. The yellow solid was collected on a Schlenk frit, washed with water and dried in vacuo. Yield: 0.20g, 63%.

9. Synthesis of Pt(tripod)P(OC$_6$H$_5$)$_3$

Triphenylphosphite (0.12 mL, 0.45 mmol) was added to a slurry of 0.40g (0.45 mmol) of PtCl$_2$(tripod) in 45 mL of ethanol. The resulting slurry was refluxed for 30 minutes, however, the solid did not dissolve. The slurry was concentrated in vacuo to 10 mL and 30 mL of THF were added. Again, the slurry was refluxed, but the solid did not dissolve completely. The solution was then cooled to room temperature and 0.0515g (1.363 mmol) of NaBH$_4$ dissolved in 15 mL of H$_2$O was added dropwise. The resulting yellow solution was filtered to remove remaining solids. The yellow filtrate was then concentrated to 10 mL in vacuo and 10 mL of H$_2$O were added. A yellow precipitate formed which was collected on a Schlenk frit, washed with water and dried in vacuo. Yield: 0.24g, 47%.
The solvent used should be THF, not absolute ethanol due to exchange reactions between the OPh\(^-\) groups on P(OPh\(_3\)) and OEt\(^-\).

10. Synthesis of Pt(tripod)P(OCH\(_2\)CF\(_3\))\(_3\)

Tris(2,2,2-trifluoroethyl)phosphite (0.075 mL, 0.34 mmol) was added, via a microsyringe, to a slurry containing 0.30g (0.34 mmol) of PtCl\(_2\)(tripod) in 15 mL of CF\(_3\)CH\(_2\)OH. The resulting slurry was refluxed gently for one hour whereupon all the solid dissolved. The solution was cooled to room temperature and 0.0380g (1.00 mmol) of NaBH\(_4\) dissolved in 10 mL of H\(_2\)O was added dropwise. A white precipitate formed and the resulting slurry was stirred for one hour. The white solid was collected on a Schlenk frit, washed with H\(_2\)O and dried in vacuo. Yield: 0.20g, 51%.

11. Synthesis of Pt(tripod)P(OMe)Ph\(_2\) and Pt(tripod)P(OMe)\(_2\)Ph

Equimolar amounts of P(OMe)Ph\(_2\) and P(OMe)\(_2\)Ph were added to 2 mL of 0.05M solutions of Pt(tripod)MePh\(_2\) in 10 mm nmr tubes. The more electronegative P(OMe)Ph\(_2\) and P(OMe)\(_2\)Ph molecules displaced the PMePh\(_2\) ligand from the Pt(tripod)PPh\(_2\)Me complex to form Pt(tripod)P(OMe)Ph\(_2\) and Pt(tripod)P(OMe)\(_2\)Ph, respectively. The \(^{31}P(^1H)\) and \(^{195}Pt(^1H)\) nmr spectra were recorded in situ.

12. Synthesis of Pt(tripod)[P(OMe)\(_2\)]\(_2\)

Trimethylphosphite (0.12 mL, 1.0 mmol) was added via a microsyringe to a suspension of 0.40g (0.45 mmol) of PtCl\(_2\)(tripod) in 30 mL of THF. The resulting slurry was refluxed until all the solid dissolved. The solution was cooled to room temperature and 0.0518g (1.37 mmol) of NaBH\(_4\) dissolved in 10 mL of distilled H\(_2\)O was added
dropwise. The resulting yellow solution was concentrated \textit{in vacuo} until a yellow solid formed. The yellow solid was collected on a Schlenk frit and dried \textit{in vacuo}. Yield: 0.30g, 63%.

13. Synthesis of Pt(tripod)(P(OC\textsubscript{H}\textsubscript{2}CF\textsubscript{3})\textsubscript{3})\textsubscript{2}

Tris(2,2,2-trifluoroethyl)phosphite (0.20 mL, 0.91 mmol) was added to a suspension of 0.40g (0.45 mmol) of PtCl\textsubscript{2}(tripod) in 20 mL of CF\textsubscript{3}CH\textsubscript{2}OH. The resulting slurry was refluxed gently for one hour while all the solid dissolved. The solution was cooled to room temperature and 0.0539g (1.42 mmol) dissolved in 10 mL of distilled H\textsubscript{2}O was added dropwise. A white solid formed and the slurry was stirred for one hour. The solid was collected on a Schlenk frit, washed with 5 mL of H\textsubscript{2}O and dried \textit{in vacuo}. Yield: 0.46g, 70%.
A. Synthesis of Pt(0)-Tetraphosphino Complexes

Platinum(0)-tetraphosphino complexes incorporating the chelating tridentate phosphine ligand, 1,1,1-tris(diphenylphosphinomethyl)ethane ("tripod"), Pt(tripod)PR$_3$, have been reported previously.$^{20,24,25}$ Three synthetic procedures have been used to prepare these complexes: 1) a one-flask procedure designed by Park$^{24}$ using K$_2$PtCl$_4$ as the starting material (PR$_3$ = PMePh$_2$, PPh$_3$, P(p-tolyl)$_3$, P(p-FC$_6$H$_4$)$_3$, PPh$_2$C$_6$F$_5$, P(CH$_2$CH$_2$CN)$_3$, Ph$_2$PC=CPPh$_2$); 2) a procedure described briefly by Meek and co-workers$^{20}$ using PtCl$_2$(tripod) as the starting material (PR$_3$ = P(p-tolyl)$_3$, PPh$_3$, P(OCH$_2$)$_3$CCH$_3$); and 3) an in situ displacement reaction between Pt(tripod)PMePh$_2$ or Pt(tripod)PPh$_3$ and a more electronegative monophosphine ligand (PR$_3$ = P(OMe)Ph$_2$,$^{24}$ PF$_2$(t-Bu),$^{24}$ PF$_2$NMe$_2$,$^{20,24}$ P(OMe)$_3$,$^{20,24}$ P(o-PC$_6$H$_4$Cl)$_3$,$^{24}$ PF$_3$,$^{20,24}$ PF$_2$(OPh),$^{25}$ PPhCl$_2$,$^{25}$ PCl$_3$,$^{25}$ PF(CF$_3$)$_2$,$^{25}$ PF$_2$CHCl$_2$)$^{25}$).

For this investigation, the Pt(tripod)PR$_3$ complexes (PR$_3$ = PPh$_3$, PMePh$_2$ and P(CH$_2$CH$_2$CN)$_3$) were prepared initially using the one-flask procedure of Park. This procedure is outlined in Equations 3-5. Based on the $^{31}$P($^1$H) nmr spectra and solubility tests, the
complexes prepared using this method were contaminated with uncharacterized impurities. Thus, an attempt was made to isolate PtCl₂(tripod) using the first step of Park’s procedure (Equation 3). This method consistently lead to an insoluble tan solid, which formed the desired complex, PtCl₂(tripod), when heated to 120°C in N,N-dimethylformamide (DMF). The tan precipitate is believed to be a Magnus-type salt of the formula [Pt(tripod)₂][PtCl₄]. The PtCl₂(tripod) complex can be easily prepared by adding an aqueous solution of K₂PtCl₄ to a solution containing the tripod ligand dissolved in DMF warmed to 120°C. Based on the $^{31}$P($^1$H) nmr spectrum of PtCl₂(tripod), I, (Figure 1), two of the PPh₂ groups of the tripod ligand are bound to the Pt center ($\delta$P₁ = -1.73 ppm, $^1$J(Pt-P₁) = 3428 Hz) and one PPh₂ group remains uncoordinated ($\delta$P₂ = -29.7 ppm, $^4$J(P₁-P₂) = 3.7 Hz).

$$\text{EtOH}$$
$$K_2\text{PtCl}_4 + \text{tripod} \rightarrow \text{PtCl}_2(\text{tripod}) + 2\text{KCl} \quad (3)$$

$$\text{EtOH}$$
$$\text{PtCl}_2(\text{tripod}) + \text{PR}_3 \rightarrow [\text{PtCl}(\text{tripod})\text{PR}_3]\text{Cl} \quad (4)$$

$$\text{NaBH}_4$$
$$[\text{PtCl}(\text{tripod})\text{PR}_3]\text{Cl} \rightarrow \text{Pt}(\text{tripod})\text{PR}_3$$

$\text{H}_2\text{O}$
Figure 1. 90 MHz $^{31}$P($^1$H) nmr spectrum of PtCl$_2$(tripod) in THF.
The Pt(tripod)PR₃ complexes used in this investigation (PR₃ = PMe₂Ph, PMePh₂, PPh₃, P(p-FC₆H₄)₃ and P(3,5-(CF₃)₂C₆H₃)₃) were prepared by refluxing solutions containing PtCl₂(tripod) and PR₃ in absolute ethanol or THF, followed by the addition of aqueous solutions of the reducing agent, NaBH₄. The yellow solids were characterized by their ³¹P(¹H) nmr spectra, and Pt(tripod)P(3,5-(CF₃)₂C₆H₃)₃ was further characterized by IR spectroscopy (Figure 2). A strong absorption band due to the CF₃ group is observed at 1120 cm⁻¹ and peaks due to the absorptions of the C=C stretching vibrations are observed at 1612 cm⁻¹, 1583 cm⁻¹ and 1571 cm⁻¹. Solid Pt(tripod)PMe₂Ph is very unstable, completely decomposing within a few days, even under an Ar atmosphere. Hence, it was prepared and its ³¹P(¹H) and ¹⁹⁵Pt(¹H) nmr spectra recorded immediately.

The phosphite complexes, Pt(tripod)P(OR)₃ (P(OR)₃ = P(OPh)₃, P(OME)₃ and P(OCH₂CF₃)₃) were prepared by refluxing solutions of PtCl₂(tripod) and P(OR)₃ in the appropriate alcohol (CF₃CH₂OH and MeOH) or THF (for the preparation of Pt(tripod)P(OPh)₃) followed by the addition of aqueous solutions of the reducing agent, NaBH₄. The isolated solids were characterized by their ³¹P(¹H) nmr spectra and the new complexes, Pt(tripod)P(OME)₃ and Pt(tripod)P(OCH₂CF₃)₃, were further characterized by IR spectroscopy (Figure 3). Strong absorptions due to the P-O-C stretch are observed at 1100 cm⁻¹ for the trimethylphosphite group and 1090 cm⁻¹ for the tris(2,2,2-trifluoroethyl)phosphite ligand. In addition, a strong absorption due to the CF₃ group of the P(OCH₂CF₃)₃ ligand is observed at 1160 cm⁻¹.
Figure 2. The infrared spectrum of Pt(tripod)P[3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>

(Nujol mull).
Figure 3. The infrared spectrum of Pt(tripod)P(OCH$_2$CF$_3$)$_3$ (Nujol mull).
The complexes Pt(tripod)[P(OR)₃]₂, II (P(OR)₃ = P(OMe)₃ and P(OCH₂CF₃)₃), were prepared accidentally when two equivalents of P(OMe)₃ or P(OCH₂CF₃)₃ were reacted with one equivalent of PtCl₂(tripod). The $^{31}$P($^1$H) nmr spectrum of Pt(tripod)[P(OCH₂CF₃)₃]₂ is shown in Figure 4; traces of Pt(tripod)P(OCH₂CF₃)₃ are also observed. The $^{31}$P($^1$H) nmr spectra of Pt(tripod)[P(OCH₂CF₃)₃]₂ and Pt(tripod)[P(OMe)₃]₂ reveal four inequivalent phosphorus atoms. The two phosphite groups are magnetically inequivalent and appear as doublet of triplets with the corresponding $^{195}$Pt satellites. The two PPh₂ groups of the tripod ligand bound to the platinum center are coincidentally equivalent and appear as a doublet of doublets along with the corresponding $^{195}$Pt satellites. The third PPh₂ group of the tripod ligand remains uncoordinated and appears as a singlet in the $^{31}$P($^1$H) nmr spectrum. The $^{195}$Pt($^1$H) nmr spectrum of Pt(tripod)[P(OMe)₃]₂ appears as a doublet of doublet of triplets (Figure 5). The $^{31}$P($^1$H) and $^{195}$Pt($^1$H) nmr data are given in Table 3. The complexes were further characterized by IR spectroscopy. Once again, the IR spectrum of Pt(tripod)[P(OMe)₃]₂ (Figure 6) displays a
Figure 4. 250 MHz $^{31}$P($^1$H) nmr spectrum of Pt(tripod)[P(OCH$_2$CF$_3$)$_3$]$_2$ in THF/d$_6$-benzene.
Figure 5. 300 MHz $^{195}$Pt($^1$H) nmr spectrum of Pt(tripod)[P(OMe)$_3$]$_2$ in 25% d$_8$-THF/75% THF.
Table 3. $^{31}P(^{1}H)^a$ and $^{195}Pt(^{1}H)$ NMR Data for Pt(tripod)[P(OR)$_3$]$_2$

Complexes

<table>
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<tr>
<th>P(OR)$_3$</th>
<th>P(OMe)$_3$</th>
<th>P(OCH$_2$CF$_3$)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta P1^b$</td>
<td>137.4</td>
<td>129.7</td>
</tr>
<tr>
<td>$\delta P2^b$</td>
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<td>119.8</td>
</tr>
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<td>$\delta P4$</td>
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<td>$^1J(Pt-P3)$</td>
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<td>$^2J(P1-P2)$</td>
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<td>$^2J(P1-P3)$</td>
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<td>52</td>
</tr>
<tr>
<td>$^2J(P2-P3)$</td>
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</tr>
<tr>
<td>$\delta Pt^c$</td>
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<td>d</td>
</tr>
</tbody>
</table>

Chemical shifts are in ppm, Coupling Constants are in Hz.

a) THF/d-6 benzene.

b) The labels 1 and 2 are arbitrary. The P(OR)$_3$ groups cannot be differentiated from one another.

c) 25% d-8 THF/75% THF.

d) The $^{195}Pt(^{1}H)$ nmr spectrum was not recorded.
Figure 6. The infrared spectrum of Pt(tripod)[P(OMe)_3]_2 (Nujol mull).
strong absorption at 1020 cm\(^{-1}\) due to the P-O-C stretch, the same stretch is observed at 1090 cm\(^{-1}\) for Pt(tripod)[P(OCH\(_2\)CF\(_3\))]\(_2\). A strong absorption due to the CF\(_3\) group is observed at 1170 cm\(^{-1}\).

The remaining complexes, Pt(tripod)P(OMe)Ph\(_2\) and Pt(tripod)P(OMe)\(_2\)Ph, were prepared in an nmr tube by adding the more electronegative ligand P(OMe)Ph\(_2\) or P(OMe)\(_2\)Ph to Pt(tripod)PMePh\(_2\) and displacing PMePh\(_2\). Once again, the complexes were characterized based on the \(^{31}\)P(\(^1\)H) nmr spectra. A peak due to free PMePh\(_2\) (\(\delta P = -25 \text{ ppm}\)) is observed in the \(^{31}\)P(\(^1\)H) nmr spectra of both complexes. The \(^{31}\)P(\(^1\)H) spectrum of Pt(tripod)P(OMe)Ph\(_2\) is shown in Figure 7.

Unsuccessful attempts were made to prepare Pt(tripod)PET\(_3\) and Pt(tripod)PMe\(_3\). A solid product was not isolated in the reaction of PtCl\(_2\)(tripod) with PET\(_3\); however, a pale-yellow solid was isolated from the reaction of PtCl\(_2\)(tripod) with PMe\(_3\). Although the solid was found to be a mixture of products, the \(^{31}\)P(\(^1\)H) nmr data of the major compound matched the \(^{31}\)P(\(^1\)H) nmr data of an authentic sample of Pt(tripod)\(_2\) (III).\(^{24}\) The \(^{31}\)P(\(^1\)H) and \(^{195}\)Pt(\(^1\)H) nmr data are given in Table 4.
Figure 7. 250 MHz $^{31}$P($^1$H) nmr spectrum of Pt(tripod)P(OMe)Ph$_2$ in 25% d6-benzene/75% THF. Peak at -25.9 ppm is assigned to free PMePh$_2$. 
Table 4. $^{31}\text{P}(^1\text{H})$ and $^{195}\text{Pt}(^1\text{H})$ NMR Data for Pt(tripod)$_2$

<table>
<thead>
<tr>
<th>δP1$^a$</th>
<th>δP2$^a$</th>
<th>δP3</th>
<th>δPt</th>
<th>$^1\text{J}(\text{Pt-P1})^b$</th>
<th>$^1\text{J}(\text{Pt-P2})^b$</th>
<th>$^2\text{J}(\text{P1-P2})$</th>
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<td>3570</td>
<td>3725</td>
<td>50</td>
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</tbody>
</table>

25% d-8 THF/75% THF. Chemical shifts are in ppm, coupling constants are in Hz.

a) The labels 1 and 2 are arbitrary since the position of the uncoordinated PPh$_2$ group is unknown.

b) $^1\text{J}(\text{Pt-P})$ values are from $^{195}\text{Pt}(^1\text{H})$ spectrum and have a resolution of ± 5 Hz.
Park \textsuperscript{24} made an unsuccessful attempt to prepare Pt(tripod)PCy\textsubscript{3}; the product isolated from the reaction mixture was Pt(tripod)\textsubscript{2}. The inability to synthesize Pt(tripod)PCy\textsubscript{3} was attributed to the large steric requirements of the PCy\textsubscript{3} ligand (\( \theta = 170^\circ \)). However, PEt\textsubscript{3} (\( \theta = 132^\circ \)) and PMe\textsubscript{3} (\( \theta = 118^\circ \)), which have smaller cone angles than many of the PR\textsubscript{3} ligands used in this investigation, also failed to react with PtCl\textsubscript{2}(tripod), the preferred product being Pt(tripod)\textsubscript{2}. All three phosphines are electron-rich, \( \sigma \)-donors, as evidenced by their small net substituent contributions: 1) PCy\textsubscript{3}, \( \Sigma \chi_1 = 0.3 \); 2) PEt\textsubscript{3}, \( \Sigma \chi_1 = 5.4 \); and 3) PMe\textsubscript{3}, \( \Sigma \chi_1 = 7.8 \).\textsuperscript{26} Hence, the platinum metal center may be too electron-rich to accept the electron-donation from these ligands, preferentially bonding to a second tripod ligand. Thus, the failure of these phosphines to react with PtCl\textsubscript{2}(tripod) may be due to an electronic effect.

B. \textsuperscript{195}Pt\textsuperscript{(1H)} and \textsuperscript{31}P\textsuperscript{(1H)} Chemical Shifts

The Fourier transform \textsuperscript{31}P\textsuperscript{(1H)} nmr spectra for the Pt(tripod)PR\textsubscript{3} (IV) complexes are the first order spectra characteristic of an \( A_3PX \) spin system, and consist of a doublet with the corresponding \textsuperscript{195}Pt satellites and a quartet with the corresponding \textsuperscript{195}Pt satellites.

\[
\begin{array}{c}
\text{Ph}_2 \quad \text{P}_3 \\
\text{Ph}_2 & \text{P}_3 & \text{Pt} & \text{P}_1 \text{R}_3 \\
\text{CH}_3 \text{C} & \text{P}_3 \\
\text{Ph}_2 & \text{P}_3 \\
\end{array}
\]

IV
The $^{31}$P($^1$H) nmr spectra of Pt(tripod)P(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$ and Pt(tripod)PMePh$_2$ are shown in Figures 8 and 9, respectively. Several of the complexes, including Pt(tripod)PMePh$_2$, were stored under an Ar atmosphere for two years; only slight decomposition was observed to have occurred on the basis of the $^{31}$P($^1$H) nmr spectra. The $^{31}$P($^1$H) chemical shifts of the phosphite groups of the Pt(tripod)P(OR)$_3$ complexes are shifted to considerably higher field than the monophosphine ligands of the Pt(tripod)PR$_3$ analogs. The $^{31}$P($^1$H) nmr spectrum for Pt(tripod)P(OPh)$_3$ is shown in Figure 10. The minor set of peaks is assigned to Pt(tripod)P(OEt)(OPh)$_2$. The synthesis of Pt(tripod)P(OPh)$_3$ was carried out initially in absolute ethanol, resulting in an exchange reaction between the OPh$^-$ group on the monophosphine ligand and OEt$^-$ groups from the solvent. The preferred solvent for the synthesis of Pt(tripod)P(OPh)$_3$ is THF.

The $^{195}$Pt($^1$H) nmr spectra for the Pt(tripod)PR$_3$ complexes consist of overlapping doublet of quartets. The $^{195}$Pt($^1$H) nmr spectra for Pt(tripod)P(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$ and Pt(tripod)PMePh$_2$ are given in Figures 11 and 12 respectively. As the PR$_3$ group is changed from a phosphine to a phosphite (P(OR)$_3$ groups), the doublet of quartets no longer overlap in the $^{195}$Pt($^1$H) spectra. This is a result of the larger $^1$J(Pt-P1) coupling constants observed for the phosphite complexes. The $^{195}$Pt($^1$H) nmr spectra for Pt(tripod)P(OPh)$_3$ is shown in Figure 13. The $^{31}$P($^1$H) and $^{195}$P($^1$H) nmr data for the Pt(tripod)PR$_3$ complexes are compiled in Table 5.
Figure 8. 300 MHz $^{31}\text{P}^{1\text{H}}$ nmr spectrum of Pt(tripod)(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$ in 25% d8-THF/75% THF (i = OP(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$).
Figure 9. 300 MHz $^{31}$P($^1$H) nmr spectrum of Pt(tripod)PMePh$_2$ in 25% d8-THF/75% THF (i = impurities).
Figure 10. 300 MHz $^{31}$P($^1$H) nmr spectrum of Pt(tripod)P(OEt)(OEt) in 25% d8-THF/75% THF. The minor set of peaks are assigned to Pt(tripod)P(OEt)(OEt).
Figure 11. 300 MHz $^{195}\text{Pt}^{1\text{H}}$ nmr spectrum of

\[ \text{Pt(tripod)P(3,5-(CF}_3)_2\text{C}_6\text{H}_3)_3} \] in 25% d8-THF/75% THF.
Figure 12. 300 MHz $^{195}$Pt($^1$H) nmr spectrum of Pt(tripod)PMePh$_2$ in 25\% d8-THF/75\% THF.
Figure 13. 300 MHz $^{195}\text{Pt}(^1\text{H})$ nmr spectrum of Pt(tripod)P(OPh)$_3$ in 25\% d8-THF/75\% THF.
Table 5. $^{31}P(^1H)$ and $^{195}Pt(^1H)$ NMR Data for the Pt(tripod)PR$_3$ Complexes$^a$

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<th>PR$_3$</th>
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<th>$\delta P3$</th>
<th>$\delta Pt$</th>
<th>$^1J_{Pt-P1}$</th>
<th>$^1J_{Pt-P3}$</th>
<th>$^2J_{P1-P3}$</th>
<th>$\Sigma X$</th>
<th>Cone Angle</th>
<th>$\sigma^*$</th>
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</tr>
<tr>
<td>10. P(OCH$_2$CF$_3$)$_3$</td>
<td>148.5</td>
<td>-16.5</td>
<td>-5372</td>
<td>8785</td>
<td>2805</td>
<td>85</td>
<td>NA</td>
<td>NA</td>
<td>NA$^c$</td>
</tr>
<tr>
<td>11. P(OPh)$_3$</td>
<td>116.4</td>
<td>-17.2</td>
<td>-5254</td>
<td>9128</td>
<td>2887</td>
<td>86</td>
<td>29.1</td>
<td>128</td>
<td>7.14</td>
</tr>
</tbody>
</table>

a) Chemical shifts are in ppm. Coupling constants are in Hz. The numeric labels (1 - 11) are used in place of molecular formulas of in Figures 15-21.

b) Saturated solutions, less than 0.05M

c) NA - not available.
The main contribution to the nuclear magnetic shielding of a heavy nucleus is the paramagnetic shielding term, \( \sigma_p \), which is defined by the Ramsey equation (Equation 2).\(^3\) Based on the Ramsey equation, the \(^{195}\)Pt chemical shift is affected by: (1) the asymmetry of the electronic distribution within the 5d orbital of the platinum atom; (2) the mean inverse cube of the distance between these electrons and the platinum nucleus \( (r^{-3}) \); and (3) the inverse energy separations between the ground and excited states for the complex \( ([E_n-E_0]^{-1}) \).\(^11\)

The results of x-ray structural studies on Fe, Ni and the Pt tripod complex, Pt(tripod)P(p-FC\(_6\)H\(_4\))\(_3\), show that the tripod ligand constrains the P-Pt-P angles to the range 93-99°;\(^24\),\(^28\),\(^30\) hence, the Pt(tripod)PR\(_3\) complexes possess pseudo-tetrahedral geometries. From the three factors listed that affect the \(^{195}\)Pt chemical shift, both the symmetry of the electronic distribution within the 5d orbital and the mean inverse cube of the distance between these electrons and the Pt nucleus should remain fairly constant because the pseudo-tetrahedral geometry is maintained as the monodentate phosphine is varied. This means that the variation of the \(^{195}\)Pt chemical shift for these complexes should depend on the contribution of the lowest available excitation energy \( ([E_n-E_0]^{-1}) \) to the paramagnetic shielding. If this term were negligible also, the \(^{195}\)Pt chemical shift for zerovalent platinum complexes would therefore depend on the diamagnetic shielding term (Equation 1). The diamagnetic shielding term, the main factor affecting \(^1H\) nmr chemical shifts, gives rise to chemical shift variations of approximately 10 ppm. Experimentally,
the Pt(tripod)PR₃ complexes show a surprisingly large chemical shift variation (range = 591 ppm), hence the \((E_n - E_o)^{-1}\) term must be contributing significantly to the observed chemical shifts.

This can be explained by analogy to tetrahedral Pt(PR₃)₄ complexes. A qualitative MO diagram for Pt(PR₃)₄ complexes under \(C_{3v}\) symmetry is shown in Figure 14. Although the energetic ordering of the molecular orbitals is subjective in Figure 14, the symmetry characteristics of the \(C_{3v}\) point group dictate that the d-orbitals will transform as 2e and \(a_1\) symmetries. Further, it is expected that these orbitals will comprise the highest occupied orbitals in the complex. Additionally, the symmetry characteristics of the lowest unoccupied molecular orbitals will be either \(a_1\) or e. Since the angular momentum operator transforms as \(a_2\) and e under \(C_{3v}\) symmetry, the integrals of equation 2 will be nonzero and hence contribute to \(\sigma_P\). Since the \(\sigma\)-lone pair of electrons on the monodentate phosphine ligand in the complexes possesses \(a_1\) symmetry, its variation should affect the \((E_n - E_o)^{-1}\) term and subsequently give rise to the observed changes in the nmr chemical shifts. Thus, the large variation of the \(^{195}\)Pt chemical shifts for the Pt(tripod)PR₃ complexes is due to a significant contribution to the overall shielding from \(\sigma_P\).

Indeed, a rough linear correlation \((\rho = -0.905)\) is observed between the \(^{195}\)Pt chemical shift and the sum of Tolman's substituent contributions \((\Sigma X_i)^{26}\) of the groups bound to the monodentate phosphine ligand (Figure 15). The linear expression is given in Equation 6 \((a = \Sigma X_i, b = \delta Pt)\). As the substituents bound to phosphorus become more

\[
a = -2.97 \times 10^{-2} b - 130
\]
Figure 14. Molecular orbital diagram for the tetrahedral Pt(PR$_3$)$_4$ complex under $C_3v$ symmetry.
Figure 15. A plot of the sum of $\delta_{\text{Pt}}$ versus $\Sigma X_1$ of the PR$_3$ ligands.
electron-withdrawing (larger $\Sigma X_i$) and the donor-acceptor ratio of the PR$_3$ ligands decrease, $\delta$Pt moves upfield; the apparent shielding becomes greater. This can be attributed to the stronger Pt-P bond as the monodentate phosphine ligands become better $\pi$-acceptors. It should be noted that $\Sigma X_i$ takes into account only the electronic effect of the monophosphine ligand, however, the chemical shift of the platinum nucleus has been shown to shift downfield due to the increased steric requirements of a phosphine ligand.$^{1,2}$ Therefore, an exact correlation is not observed. However, a much better linear correlation ($\rho = -0.989$) is observed between the $^{195}$Pt chemical shift and the sum of the substituent constant ($\Sigma X_i$) as the monophosphine ligand is changed from PPh$_3$ to P(OMe)$_3$, (PPh$_3$, P(OMe)Ph, P(OMe)$_2$Ph, P(OMe)$_3$). This is because the electronic effects outweigh the steric effects as the phosphine ligand is changed to a phosphite ligand. A graph of $\delta$Pt versus $\Sigma X_i$ for these complexes is given in Figure 16.

A linear correlation, given in Equation 7 (Figure 17), is also observed between $\delta$Pt and the one bond coupling constant, $^1J$(Pt-Pl), ($\rho = -0.949$, $c = ^1J$(Pt-Pl), $b = \delta$Pt). It has been shown that the magnitude of the Pt-Pl coupling constant depends primarily on the percent s-character present in the orbital containing the lone pair of electrons on phosphorus, $\alpha_p$, and the valence s electron density at the nucleus, $|\psi_{3s}(0)|^2$. The upfield shift of $\delta$Pt with an
Figure 16. A plot of $\delta_{Pt}$ versus $\Sigma x_1$ for Pt(tripod)PR$_3$ complexes where PR$_3$ is PPh$_3$, P(OMe)Ph$_2$, P(OMe)$_2$Ph and P(OMe)$_3$. 
Figure 17. A plot of $\delta Pt$ versus $^{1}J(Pt-P1)$. 
increase in the magnitude of $^1J(Pt-Pl)$ reflects the greater s-character used by the phosphorus orbital in bonding to platinum, imparting greater strength to the Pt-P bond. The point for Pt(tripod)P(CH$_2$CH$_2$CN)$_3$ (#5) falls off the line in the plot of $\delta$Pt versus $^1J(Pt-Pl)$ in Figure 17. The monodentate ligand, P(CH$_2$CH$_2$CN)$_3$, is an unusual phosphine because its effective net substituent constant, $\Sigma \chi_1 = 21.9$, is closer to the net substituent constants of phosphites. The anomalous behavior of P(CH$_2$CH$_2$CN)$_3$ has been observed previously, and it has been suggested that its cone angle (\(\Theta = 132^\circ\)) has been greatly underestimated.

The chemical shifts of Pt(II) complexes have been observed empirically at higher field than Pt(IV) complexes, and resonances for Pt(0) complexes have been found in the same region as Pt(II) complexes. However, by combining the data reported previously for Pt(0) complexes with that from other recent reports of Pt(0) chemical shifts and the data obtained in this study, it can be stated that Pt(0) resonances occur at higher fields than for Pt(II) complexes. Although Pt(II) complexes have $^{195}$Pt resonances as high as -5500 ppm (range for Pt(II) complexes: -1600 to -5500 ppm), the resonances of Pt(0) complexes range as high as -6596 ppm for Pt[P(i-Pr)$_3$]$_2$ (range for Pt(0) complexes: -4500 to -6600 ppm).

A linear relationship does not exist between $\delta$Pt and $\delta$Pl (Figure 18). This is not surprising since $\delta$Pl should not be affected by the electronic environment of the $^{195}$Pt nucleus to the same extent as $\delta$Pt. However, in general, the chemical shift of Pl shifts downfield as $\delta$Pt shifts upfield. The chemical shift of P3 remains fairly constant as
Figure 18. A plot of $\delta P_t$ versus $\delta P_l$. 
the monodentate phosphine ligand, P₁, is varied; it moves upfield by about 5 ppm as Σₓ₁ for the monodentate phosphine ligands increases (Figure 19).

C. Coupling Constants, ¹J(Pt-P₁), ¹J(Pt-P₃) and ²J(P₁-P₃)

The variation in the magnitude of the Pt-P coupling constant for the tripod ligand, ¹J(Pt-P₃), is relatively small as the monodentate phosphine ligand changes from PMe₂Ph to P(OPh)₃; however, the magnitude of the Pt-P coupling constant for the monodentate phosphine ligands, ¹J(Pt-P₁) increases dramatically from 5342 Hz to 9128 Hz. The platinum-phosphorus coupling constants for the monodentate phosphine ligands are approximately double the ¹J(Pt-P) values observed for trans-Pt(II) complexes and 55% larger than ¹J(Pt-P) values in cis-PtCl₂(PR₃)₂ complexes. In addition, the magnitude of ¹J(Pt-P₃) values for the tripod ligand are smaller than those of the Pt(PR₃)₄ complexes (Table 2). These changes reflect the increased p-character of the Pt-P₃ bonds of the tripod ligand due to the restricted P₃-Pt-P₃ bond angles (93-99°). This constrained bonding geometry of the tripod ligand imposes more s-character in the Pt-P₁ bond, which results in the unusually large Pt-P₁ coupling constants. As mentioned previously, the magnitude of one-bond coupling constants between platinum and phosphorus depend primarily on αₚ² and |ψ₃ₓ(0)|². The alteration of the groups bound to one of the coupled phosphorus atoms (i.e., P₁) can have a large effect on αₚ² and |ψ₃ₓ(0)|² for that atom, but it will have only a small effect on the corresponding terms for another magnetically inequivalent phosphorus atom (i.e., P₃).
Figure 19. A plot of $\delta P_1$ versus $\delta P_3$. 
The magnitude of $^{2}J(P-P)$ coupling constants for Pt(II) complexes are affected by the electronegativity of the substituents bound to phosphorus.\footnote{This also holds true for the Pt(0) complexes, Pt(tripod)PR$_3$.} A linear correlation ($\rho = 0.978$) is observed between $^{2}J(Pl-P3)$ and Taft's constant, $\sigma^*$ ($y = \sigma^*$, $x = ^{2}J(Pl-P3)$, Figure 20).

$$y = 1.57 \times 10^{-1}x - 7.10$$ \hspace{1cm} (8)

This constant is dependent only upon the net polar effect of the substituent $R$ bound to an ester molecule, RCOOR', and its effect is additive. A similar relationship has been observed for the one-bond, metal-phosphorus coupling constants, $^{1}J(Pt-Pl)$, in related Pt(tripod)PR$_3$ complexes.\footnote{In fact, a linear correlation ($\rho = 0.993$), shown in Figure 21, exists between $^{2}J(Pl-P3)$ and $^{1}J(Pt-Pl)$ for the Pt(tripod)PR$_3$ complexes ($x = ^{2}J(Pl-P3)$, $z = ^{1}J(Pt-Pl)$). This}

$$x = 9.02 \times 10^{-2}z + 3.85$$ \hspace{1cm} (9)

similarity between $^{2}J(Pl-P3)$ and $^{1}J(Pt-Pl)$ is not surprising since the two-bond, phosphorus-phosphorus coupling constants are transmitted through the metal center.
Figure 20. A plot of $^2J(P_1-P_3)$ versus $\sigma^*$. 
Figure 21. A plot of $^1J(P_t-P_l)$ versus $^2J(P_1-P_3)$. 
PART II

Synthesis, Characterization and Reactivity of
Group VIII Metal Phosphine Complexes Coordinated to
Alkoxide and Hydroxide Ligands
CHAPTER IV
Statement of Research Problem

Although the first hydroxide compounds of the late transition metals have been known for over one-hundred years, it is generally believed that compounds containing soft Lewis acids, such as second and third row group VIII metals in low oxidation states, and hard Lewis bases (OH⁻ and OR⁻) are inherently unstable. However, the first alkoxide complex of a group VIII metal in a low oxidation state, [Rh(OMe)(C₈H₁₂)]₂, was reported in 1957, since that time group VIII metal alkoxide and hydroxide complexes have been postulated as intermediates in a number of important reactions. For example, metal alkoxide intermediates have been postulated in the formation of metal hydrides from alcohols (Scheme 1), the Pd(II) catalyzed vinyl interchange reaction (Scheme 2), the metal catalyzed hydroformylation reaction and the metal-catalyzed hydrogenation of CO. Metal alkoxy carbonyl intermediates are proposed in the palladium catalyzed hydrocarboxylation of olefins and acetylene and in the water-gas shift reaction, also, there is precedence for hydroxymethyl, alkoxyalkyl and alkoxide intermediates in metal formyl chemistry. Metal hydroxide complexes have been postulated as intermediates in the Wacker process and platinum and rhodium hydroxides catalyze the hydration of nitriles to carboxamides (Scheme 3). In addition, platinum(II) hydroxide complexes catalyze the
Scheme 1

\[
\text{M} + \text{RCH}_2\text{OH} \rightarrow \text{M-O-C-R}
\]

↓

\[
\text{M-H} + \text{HC(O)R}
\]

Scheme 2

\[
\text{Pd-OEt} + \text{H-OPr} \rightarrow \text{H-C-C} \rightarrow \text{H-OEt} + \text{OPr}
\]

↓ rotation

Scheme 3

\[
\text{M-OH} + \text{RCN} \rightarrow \text{MN-C(OH)R}
\]

↓

\[
\text{H}_2\text{O} \rightarrow \text{RC(O)NH}_2 \rightarrow \text{MN(H)COR}
\]

Scheme 1

\[
\text{H} \quad \text{M} + \text{RCH}_2\text{OH} \rightarrow \text{M-O-C-R} \quad \text{H}
\]

↓

\[
\text{M-H} + \text{HC(O)R}
\]

PrOH fast

EtOH

Scheme 2

Pd-OEt + H-OPr = H-C-C = H-PrO + OPr

↓ rotation

Scheme 3

M-OH + RCN → MN-C(OH)R

↓

H2O

RC(O)NH2 → MN(H)COR
Despite the possibility for rich and fruitful chemistry, few direct studies of the syntheses, physical properties and chemical reactivities of the group VIII metal alkoxide and hydroxide complexes have been undertaken. In fact, most of the hydroxide and alkoxide complexes of the group VIII metals have been discovered fortuitously during the course of other investigations. The goal of this research is to prepare, isolate and characterize a series of group VIII metal phosphine complexes of the general formula \([M(P3)(OR)]^{n+}\) (V; M = Pt, Rh and Ir; P3 = chelating triphosphine ligand, R'P(CH₂CH₂CH₂PR")₂; R = H, alkyl or aryl group; n = 0, 1). The chelating triphosphine ligand offers several advantages: first, the chelate effect reduces the tendency of the ligand from dissociating from the metal, which restricts the number of sites for further reaction chemistry; second, the ligands can be tailored to donate different amounts of electron density to the metal center by changing the groups bound to phosphorus; and third, the four coordinate geometry imposed by the triphosphine ligand leaves the molecules sterically and electronically unsaturated. The proposed complexes will be the most electron rich group VIII metal alkoxide and hydroxide compounds prepared to date, hence, it is predicted that the metal-oxygen bond will be very reactive. In addition, the restrictions imposed by the chelating triphosphine ligands should allow these complexes to be used as models for important reactions involving metal-alkoxide and hydroxide complexes.
The strength and reactivity of the metal-oxygen bond will be examined chemically by varying the electron donating ability of the chelating triphosphine ligand, by varying the metal, by insertion reactions involving small molecules (i.e., CO, SO$_2$ and CH$_2$CH$_2$) and by reactions with weak organic acids. The metal-oxygen bond will also be investigated by physical methods such as nmr and IR spectroscopies.
CHAPTER V

Synthesis of Polyphosphine Ligands

Introduction

Following the pioneering work of F. G. Mann\textsuperscript{66-68} on the syntheses of trivalent phosphorus derivatives, many tertiary phosphines have become available and these compounds have become important ligands in coordination and organometallic chemistry and catalysis. Tertiary phosphine ligands are able to accommodate a wide range of properties in transition metal complexes, in part, because it is relatively easy to tailor the electronic and steric properties of the ligands by varying the groups bound to phosphorus. For example, these ligands are useful for stabilizing both high- and low-transition metal oxidation states.\textsuperscript{69} In addition, transition-metal complexes of tertiary phosphine ligands have been used extensively for stabilizing metal-hydrogen, metal-carbon, metal-olefin and metal-acetylene bonds,\textsuperscript{70} for activating small molecules,\textsuperscript{71} for oxidative-addition to metal centers\textsuperscript{72} and for asymmetric synthesis, in which optically active metal phosphine catalysts are employed.\textsuperscript{73,74} Finally, the ability to probe the structure and reactivity of transition metal-tertiary phosphine complexes by phosphorus-31 \textit{nmr} spectroscopy has increased the popularity of these ligands.\textsuperscript{35}
The chemistry of ligands containing two or more phosphorus atoms has been slower to evolve than the monophosphine analogs, primarily because the synthetic procedures for their preparation are more complicated. However, a properly designed chelating polyphosphine ligand can accentuate the special effects of phosphine ligands as it simultaneously provides: (1) more control on the coordination number, stoichiometry and stereochemistry of the resulting metal complexes; (2) an increased basicity (or nucleophilicity) at the metal center; (3) slower intra- and intermolecular exchange processes; and (4) detailed structural and bonding information in the form of metal-phosphorus and phosphorus-phosphorus coupling constants. For example, chelating polyphosphine ligands may be used to change the magnetic states and coordination geometries of complexes by carefully selecting parameters such as (1) the donor ability of the groups bound to phosphorus, (2) the "chelate bite angle", and (3) sterically demanding substituent groups.

One of the first bidentate phosphine ligands incorporating a methylene linkage between the phosphorus atoms, \( \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \), was reported by Chatt and Hart in 1960, and in 1962, the tridentate ligands, \( \text{PhP(CH}_2\text{CH}_2\text{PPh}_2)_2 \) and \( \text{CH}_3\text{C(CH}_2\text{PPh}_2)_3 \), were reported by Hewerton and Watson. The preparation of these ligands involved the reaction of a metal phosphide with alkyl halides (Eq. 10). However,

\[
\text{R}_2\text{PM} + \text{X(CH}_2\text{)}_2\text{X} \rightarrow \text{R}_2\text{P(CH}_2\text{)}_2\text{PR}_2 + 2\text{MX}
\]

the synthesis of ligands containing three or more phosphorus atoms was limited due to the lack of appropriate alkyl halides. The discovery
of the base-catalyzed\textsuperscript{79} and free radical-catalyzed\textsuperscript{75} addition of a secondary phosphine to the double bond of a vinyl phosphine have given rise to many new ligands incorporating from 2 to 6 phosphorus atoms. However, these methods are limited to multidentate phosphine ligands containing ethylene (-CH\textsubscript{2}CH\textsubscript{2}-) linkages or ligands containing both ethylene and trimethylene (-CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}-) linkages, respectively.

The first multidentate phosphine ligand incorporating flexible trimethylene linkages exclusively, PhP[CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2}]\textsubscript{2} (ttp), was reported by Meek and co-workers in 1973\textsuperscript{80}. The synthetic procedure required the following reactions:

\begin{align*}
\text{PhPPh}_2 + 2n\text{-C}_4\text{H}_9\text{Li} &\rightarrow \text{PhPLi}_2 + 2n\text{-C}_4\text{H}_{10} \quad (11) \\
\text{PhPLi}_2 + 2\text{CH}_2\text{CH}_2\text{OH} &\rightarrow \text{PhP(Ch}_2\text{CH}_2\text{CH}_2\text{OH})_2 \quad (12) \\
\text{PhP(Ch}_2\text{CH}_2\text{CH}_2\text{OH})_2 + \text{H}_2\text{O}_2 &\rightarrow \text{PhP(O)(CH}_2\text{CH}_2\text{CH}_2\text{OH})_2 \quad (13) \\
\text{PhP(O)(CH}_2\text{CH}_2\text{CH}_2\text{OH})_2 + \text{PCl}_5 &\rightarrow \text{PhP(O)(CH}_2\text{CH}_2\text{CH}_2\text{Cl})_2 \quad (14) \\
\text{Ph}_2\text{PH} + n\text{-C}_4\text{H}_9\text{Li} &\rightarrow \text{Ph}_2\text{PLi} + n\text{-C}_4\text{H}_{10} \quad (15) \\
\text{PhP(O)(CH}_2\text{CH}_2\text{CH}_2\text{Cl})_2 + 2\text{Ph}_2\text{PLi} &\rightarrow \text{PhP(O)(CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)\text{2} \quad (16) \\
\text{Ph(O)(CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)\text{2} + \text{Si}_2\text{Cl}_6 &\rightarrow \text{PhP(Ch}_2\text{CH}_2\text{CH}_2\text{PPh}_2)\text{2} \quad (17)
\end{align*}

In 1975, Grim\textsuperscript{81} published a procedure for the straight-forward, high-yield synthesis of chloroalkyldiphenylphosphines (Eqs. 18-20), Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{n}Cl (n = 1, 2, 3). Prompted by this report, Meek and co-workers\textsuperscript{82} successfully modified this method to develop a new procedure:

\begin{align*}
2\text{Na} + \text{Ph}_3\text{P} &\rightarrow \text{Ph}_2\text{PNa} + \text{NaPh} \quad (18) \\
\text{NaPh} + \text{NH}_4\text{Cl} &\rightarrow \text{NaCl} + \text{NH}_3 + \text{C}_6\text{H}_6 \quad (19) \\
\text{Ph}_2\text{PNa} + \text{Cl(CH}_2\text{)}\text{2n}\text{Cl} &\rightarrow \text{Ph}_2\text{P(CH}_2\text{)}\text{2n}\text{Cl} + \text{NaCl} \quad (20)
\end{align*}
for the synthesis of ttp involving a coupling reaction between 3-chloropropylphosphine intermediates and phosphide nucleophiles (Eqs. 21-24). This method has been extended to a new ligand containing trimethylene linkages, PhP[CH₂CH₂CH₂PCy₂]₂ (cyttP).

\[
\begin{align*}
R_2PH + n-C_4H_9Li & \rightarrow R_2PLi + n-C_4H_{10} \\
R_2PLi + xC_1(CH_2)_3Cl & \rightarrow R_2P(CH_2)_3Cl + LiCl \\
PhPH₂ + 2n-C_4H_9Li & \rightarrow PhPLi₂ + 2n-C_4H_10 \\
PhPLi₂ + 2R_2P(CH_2)_3Cl & \rightarrow PhP[CH₂CH₂CH₂PR₂]₂ + 2LiCl
\end{align*}
\] (21-24)

Several additional strategies for the synthesis of tridentate phosphine ligands containing trimethylene linkages have begun to emerge. A rapid, high-yield synthesis involves the platinum or rhodium assisted base-catalyzed condensation of simpler phosphine units onto a coordinated secondary phosphine or a coordinated 3-chloropropylphosphine intermediate (Eqs. 25 and 26). A second

\[
\begin{align*}
NEt_3PtCl₂[Ph₂P(CH₂)_3P(H)Ph] + R₂P(CH₂)_3Cl & \rightarrow \\
& PtCl[PhP(CH₂CH₂CH₂PR₂)₂] \\
NEt_3RhCl(COD)(Cy₂CH₂CH₂CH₂Cl) + Cy₂PCH₂CH₂CH₂P(H)Ph & \rightarrow \\
& RhCl[PhP(CH₂CH₂CH₂PCy₂)₂]
\end{align*}
\] (25-26)

method involves free-radical P-H addition to allyl derivatives of P(V), H₂C=CHCH₂P(O)(O-i-Pr)(2-n)Rₙ (n = 0, 1), followed by LiAlH₄ reduction (Eqs. 27 and 28). Finally, the UV/AIBN (AIBN =

\[
\begin{align*}
PhPH₂ + 2CH₂=CHCH₂P(O)(O-i-Pr)(2-n)Rₙ & \rightarrow \\
& PhP[CH₂CH₂CH₂P(O)(O-i-Pr)(2-n)Rₙ]₂
\end{align*}
\] (27)
\[
\text{PhP[(CH}_2\text{)}_3\text{P(O)(0-i-Pr)}(2-n)\text{R}_n]_2 + \text{LiAlH}_4 \rightarrow \text{PhP[(CH}_2\text{)}_3\text{PR}_n]_2
\] (28)

2,2'-azobis(isobutyronitrile) initiated free-radical addition of P-H groups across the double bonds of allylphosphines containing two or three CH\text{=CHCH}_2- functions has been exploited for the high-yield synthesis of chelating phosphines containing trimethylene linkages (Eq. 29). 87-89

\[
\text{UV/AIBN}
\]

\[
P(\text{CH}_2\text{CH}=\text{CH}_2)_3 + 2\text{HPEt}_2 \rightarrow P(\text{CH}_2\text{CH}_2\text{CH}_2\text{PEt}_2)_3
\] (29)

The straightforward coupling reactions between 3-chloropropylphosphines, R\text{}_2\text{P(CH}_2\text{)}_3\text{Cl}, and phosphide nucleophiles is still the most common method for preparing ttp and cyttp. However, the range of application of this method has been limited by the stability of the 3-chloropropylphosphine intermediates which have been available only with bulky substituents such as phenyl or cyclohexyl on phosphorus. In addition, this method involves a number of disadvantages: (1) a 10-fold excess of 1,3-dichloropropane is required to inhibit subsequent substitution of both Cl atoms to form R\text{}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PR}_2; (2) 1,3-dichloropropane is expensive; (3) impurities, such as phosphine oxides, disubstituted species, R\text{}_2\text{P(CH}_2\text{)}_3\text{PR}_2, and R\text{}_2\text{P(CH}_2\text{)}_3\text{P(H)Ph}, are generated; (4) the ligands require purification by column chromatography and vacuum distillation; and (5) the method is time consuming.
The goal of the author’s research was to develop a new, general method for the synthesis of 3-chloropropylphosphine intermediates, ttp and cyttp. In addition, this method was to be extended to the synthesis of new chelating phosphine ligands and ligand intermediates.
Experimental

A. General Procedures

Reagent grade chemicals were used without further purification where possible. 1-Bromo-3-chloropropane was purified by distillation from anhydrous MgSO₄ under Ar and diisopropylamine was purified by distillation from anhydrous BaO under Ar. All phosphines were purchased under an Ar atmosphere and were used without further purification. Stock solutions of lithium diisopropylamide were prepared in hexane and titrated using published procedures. Reagent grade solvents were purified by distillation under N₂ over the appropriate drying agents. Distilled water and absolute ethanol were purged with an Ar stream for 20 minutes prior to use. General procedures for the manipulation of air-sensitive compounds, under an Ar atmosphere, were used in the following synthetic procedures.

The phosphorus-31 nmr spectra were recorded on a Bruker HX-90 FT nmr spectrometer operating at 36.43 MHz in 10 mm tubes fit with co-axial inserts containing trimethylphosphate in d₆-acetone or on a Bruker AM-250 FT nmr spectrometer operating at 101.256 in 5 mm tubes. The ³¹P(¹H) nmr spectra are referenced to external 85% phosphoric acid. The proton nmr spectra were recorded on a Bruker WP-80 FT nmr spectrometer operating at 80.07 MHz or on a Bruker AM-250 FT nmr spectrometer operating at 250.134 in 5 mm tubes. The proton spectra are referenced to external TMS. The carbon-13 nmr spectra were recorded on a Bruker MSL-300 FT nmr spectrometer operating at 75.479 MHz in 10 mm tubes or on a Bruker AM-250 FT nmr spectrometer operating at 62.896 in 5 mm tubes. The ¹³C(¹H) nmr spectra are referenced to
external TMS. Infrared spectra were recorded neat or as Nujol mulls between KBr or CsI plates on a Perkin-Elmer model 283B grating spectrometer and the spectra were referenced to the sharp 1601 cm⁻¹ peak of a polystyrene film.

B. Synthesis of Polyphosphine Ligands and Ligand Intermediates

1. Synthesis of \((p-CF_3C_6H_4)gPH\)

A Grignard solution of 4-bromobenzotrifluoride was prepared by the dropwise addition of a solution containing 31.0 mL (221 mmol) of 4-bromobenzotrifluoride in 100 mL of diethylether to 5.83 g (240 mmol) of Mg turnings and a crystal of I₂ in 50 mL of diethylether. Gentle heat was applied to initiate the reaction and 100 mL of additional diethylether were added. The resulting Grignard solution was filtered through celite on a frit and the filtrate was cooled to 0°C. A solution of 10.0 mL (77.6 mmol) of diethyl phosphite in 100 mL of diethylether was added dropwise to the Grignard solution. The resulting viscous solution was refluxed for 2 hours (40-50°C) during which it became thick and waxy. The waxy mixture was cooled to 0°C and it was slowly hydrolyzed with 150 mL of an aqueous 10% HCl solution. The hydrolyzed solution was warmed to room temperature, the layers were allowed to separate and the deep-red organic layer was transferred to a flask containing anhydrous MgSO₄. The aqueous layer was extracted 6 times with 50 mL aliquots of benzene. The organic layers were combined over anhydrous MgSO₄ and dried overnight. The red solution was filtered to remove the MgSO₄ and the solvent was removed \textit{in vacuo}. The resulting red oil was dissolved in 200 mL of diethylether and the solution was cooled to 0°C. Solid lithium
aluminum hydride (3.03g, 79.8 mmol) was added very slowly, via a solid addition funnel, to the cold red solution; gas bubbles evolved. The cold slurry was stirred for one hour and then hydrolyzed slowly with 6 mL of water, 6 mL of an aqueous 10% NaOH solution, and then by 12 mL of water. The slurry was warmed to room temperature and the orange phosphine solution was filtered into a flask containing anhydrous MgSO₄. The remaining salts were washed 6 times with 30 mL aliquots of benzene and the aliquots were combined over anhydrous MgSO₄ and dried. The orange solution was filtered through a Schlenk frit to remove the MgSO₄ and the solvent was removed from the filtrate in vacuo to yield an orange oil. The clear liquid product, (p-CF₃C₆H₄)₂PH, was extracted from the orange oil by Kugelrohr distillation. Yield: 13.92g, 58.63%. ³¹P nmr data: δP = -42.2 ppm, ¹J(P-H) = 227 Hz.

2. Synthesis of 3,5-(CF₃)₂C₆H₃PCl₂, 3,5-(CF₃)₂C₆H₃l₂PCl and [(3,5-(CF₃)₂C₆H₃]₃P

a) A Grignard solution of 3,5-bis(trifluoromethyl)bromobenzene was prepared by the dropwise addition of a solution containing 15.0 mL (186 mmol) of 3,5-bis(trifluoromethyl)bromobenzene in 50 mL of diethylether to 2.20g (90.5 mmol) of Mg turnings in 25 mL of diethylether. The reaction occurred spontaneously and an additional 50 mL of diethylether were added. The resulting mixture was heated to reflux (50°C) to complete the reaction and the Grignard was filtered through a frit into a clean flask. It was then added dropwise to a solution containing 7.6 mL of 98% PCl₃ (85 mmol) in 60 mL of diethylether. A solid precipitated immediately and the solution became yellow-brown. The resulting slurry was refluxed for 1 hour at
60°C and stirred overnight. The slurry was filtered through a Schlenk frit to remove the Mg salts and the salts were washed 3 times with 30 mL aliquots of diethylether. The volume of the filtrate was reduced in vacuo to 50 mL and the remaining diethylether was removed by distillation at ambient pressure to yield a brown oil. The products were obtained from the brown oil by fractional vacuum distillation. Three fractions were obtained: 0.5-1.5 mm Hg, 55-65°C, 3,5-(CF₃)₂C₆H₃PCl₂ (δP = 149.9 ppm), 3,5-(CF₃)₂C₆H₃PBrCl (δP = 144.0 ppm) and 3,5-(CF₃)₂C₆H₃PBr₂ (δP = 136.3 ppm), 1.53g; 1.5-2.5 mm Hg, 120-130°C, [3,5-(CF₃)₂C₆H₃]₂PCl (δP = 56.6 ppm), 5.50g; and 2.5 mm Hg, 130°C, P[3,5-(CF₃)₂C₆H₃]₃ (δP = -6.0 ppm), 3.56g.

b) A Grignard solution of 3,5-bis(trifluoromethyl)bromobenzene was prepared by the dropwise addition of a solution containing 14.5 mL (84.1 mmol) of 3,5-bis(trifluoromethyl)bromobenzene in 60 mL of diethylether to 2.23g (91.8 mmol) of Mg turnings in 30 mL of diethylether. Gentle heat was applied to initiate the reaction and an additional 50 mL of diethylether were added. The resulting Grignard solution was filtered into a clean flask and it was diluted with 90 mL of diethylether. It was added slowly, dropwise to a solution of PCl₃ (8.0 mL, 92 mmol) in 150 mL of diethylether which had been cooled to -63°C in a chloroform/liquid nitrogen bath. A white solid precipitated. The resulting slurry was filtered through celite on a Schlenk frit and the Mg salts were washed four times with 20 mL aliquots of diethylether. The filtrate was concentrated in vacuo by 1/2 and the remaining diethylether was removed by distillation at ambient pressure. The products were collected from the resulting
brown residue by Kugelrohr distillation. Two fractions were obtained: the first fraction contained \([3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_2\text{PCl}\), which was distilled a second time to remove residual impurities (yield 8.07g); and the second fraction contained \(\text{P}[3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_3\) (yield 2.35g).

3. Synthesis of \([3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_2\text{PH}\)

Lithium aluminum hydride (0.62g, 16.3 mmol) was added slowly, via a solid addition funnel, to a solution of 8.07g (16.4 mmol) of \([3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_2\text{PCl}\) in 100 mL of diethylether which had been cooled to 0°C. The resulting yellow-green slurry was stirred for 1 hour and then the cold solution was hydrolyzed with 1.0 mL of \(\text{H}_2\text{O}\), 1.0 mL of an aqueous 10% NaOH solution followed by 2.0 mL of \(\text{H}_2\text{O}\). The resulting slurry was warmed to room temperature and filtered through a Schlenk frit. The remaining solids were washed with benzene and the filtrate was dried over anhydrous MgSO\(_4\). The solution was filtered to remove the MgSO\(_4\) and the solvent was removed from the filtrate \textit{in vacuo} to give a white solid. Yield: 3.70g, 49.3%. \(^{31}\text{P} \text{nmr data: } \delta\text{P} = -42.3 \text{ ppm, } \^1\text{J}(\text{P-H}) = 230 \text{ Hz.}

4. Synthesis of \((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}\)

A stock solution of 0.547 M LDA (22.5 mL, 12.3 mmol) was added dropwise to a solution of \((\text{C}_6\text{H}_5)_2\text{PH}\) (2.00 mL, 11.5 mmol) and \(\text{Br(CH}_2)_3\text{Cl}\) (1.20 mL, 12.0 mmol) in 40 mL of THF cooled to -78°C in a Dry Ice/isopropanol bath over a 15 minute period. The solution was warmed to room temperature and the solvent was removed \textit{in vacuo}. The yellow-orange oil was dissolved in 30 mL of toluene and hydrolyzed with 30 mL of water. After 10 minutes of rapid stirring, the organic layer was transferred to a flask containing anhydrous MgSO\(_4\). The
aqueous layer was extracted three times with 15 mL aliquots of toluene and the extracts were combined over anhydrous MgSO₄ and dried overnight. The solution was filtered through neutral alumina (60 mesh) on a Schlenk frit to remove the MgSO₄ and the solvent was removed in vacuo to give a clear pale-yellow oil. Yield: 2.86 g, 95.0%. ³¹P(¹H) nmr data: δP = -17.4 ppm.

5. Synthesis of (p-CF₃C₆H₄)₂PCH₂CH₂Cl

A stock solution of 0.2398 M LDA (83.0 mL, 19.9 mmol) was added dropwise, over a 3.5 hour period, to a solution of 6.08 g (18.9 mmol) of (p-CF₃C₆H₄)₂PH and 1.90 mL (19.2 mmol) of Br(CH₂)₃Cl in 150 mL of THF cooled to -78°C in a Dry Ice/isopropanol bath. The resulting solution was allowed to warm slowly in the Dry Ice/isopropanol bath and it was stirred overnight at room temperature. The solvent was removed in vacuo, and the resulting yellow oil was redissolved in 100 mL of toluene and hydrolyzed with 120 mL of water. The organic layer was transferred to a flask containing anhydrous MgSO₄. The aqueous layer was extracted four times with 50 mL aliquots of toluene. The extracts were combined over anhydrous MgSO₄ and dried overnight. The solution was filtered through a small amount of neutral alumina (60 mesh) on a Schlenk frit to remove the MgSO₄. The solvent was removed from the clear, colorless filtrate in vacuo to give a clear oil. The oil was warmed in vacuo to remove all volatile materials. Yield: 7.54 g, 100%. ³¹P(¹H) nmr data: δP = -16.7 ppm.

6. Synthesis of [3,5-(CF₃)₂C₆H₃]₂PCH₂CH₂Cl

A stock solution of 0.523 M LDA (20.0 mL, 10.5 mmol) diluted with 40 mL of hexane was added slowly, dropwise to a solution of 4.65 g
(10.1 mmol) of [3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}]\textsubscript{2}PH and 1.00 mL (10.1 mmol) of Br(CH\textsubscript{2})\textsubscript{3}Cl in 250 mL of THF cooled to -78°C in a Dry Ice/isopropanol bath. The resulting purple solution was allowed to warm slowly to room temperature and then it was stirred overnight. The solvent was removed in vacuo, and the purple residue was redissolved in 200 mL of toluene and hydrolyzed with 200 mL of water. The organic layer was transferred to a flask containing anhydrous MgSO\textsubscript{4}. The aqueous layer was extracted three times with 50 mL aliquots of toluene and one 50 mL aliquot of THF. An uncharacterized brown solid remained in the aqueous layer. The extracts were combined over anhydrous MgSO\textsubscript{4} and dried overnight. The solution was filtered through neutral alumina (60 mesh) on a Schlenk frit to remove the MgSO\textsubscript{4} and the solvent was removed from the filtrate in vacuo to give a brown oil. The product was extracted from the brown oil by Kugelrohr distillation to give a clear liquid which formed a white solid upon cooling. Yield: 3.52g, 64.8%. \textsuperscript{31}P\textsuperscript{(1H)} nmr data: \delta P = -14.4 ppm.

7. Synthesis of (CH\textsubscript{3}CH\textsubscript{2})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}Cl

A stock solution of 0.2398 M LDA (34.0 mL, 8.15 mmol) was added dropwise to a solution of 0.70g (7.8 mmol) of (CH\textsubscript{3}CH\textsubscript{2})\textsubscript{2}PH and 0.80 mL (8.1 mmol) of Br(CH\textsubscript{2})\textsubscript{3}Cl in 20 mL of THF cooled to -78°C in a Dry Ice/isopropanol bath. The resulting solution was stirred for one hour and then warmed to room temperature. The solvent was removed in vacuo and the resulting yellow oil was redissolved in 25 mL of toluene. The solution was hydrolyzed with 25 mL of water, the layers were allowed to separate and the organic layer was transferred to a flask containing anhydrous MgSO\textsubscript{4}. The aqueous layer was extracted with one
20 mL aliquot and two 10 mL aliquots of toluene and the extracts were combined over anhydrous MgSO₄ and dried. The solution was filtered through neutral alumina (60 mesh) on a Schlenk frit to remove the MgSO₄ and the solvent was removed from the filtrate in vacuo to give a clear, colorless liquid. Yield: 0.62g, 48%. ³¹P{(H)} nmr data: δP = -24.6 ppm.

8. Synthesis of C₆H₅P(CH₂CH₂CH₂Cl)₂

A stock solution of 0.654 M LDA (65.0 mL, 42.5 mmol) was added dropwise, over a one hour period, to a solution of 2.30 mL (20.9 mmol) of C₆H₅PH₂ and 4.10 mL (41.5 mmol) of Br(CH₂)₃Cl in 150 mL of THF cooled to -78°C in a Dry Ice/isopropanol bath. The solvent was removed in vacuo, and the resulting yellow oil was redissolved in 150 mL of toluene and hydrolyzed with 150 mL of water. The organic layer was transferred to a flask containing anhydrous MgSO₄. The aqueous layer was extracted three times with 40 mL aliquots of toluene and the extracts were combined over anhydrous MgSO₄ and dried overnight. The solution was filtered through a small amount of neutral alumina (60 mesh) on a Schlenk frit to remove the MgSO₄ and the solvent was removed from the filtrate in vacuo to give a clear oil. The oil was heated in vacuo for several hours at 45°C to remove all volatile materials. Yield: 5.40g, 100%. ³¹P{(H)} nmr data: δP = -26.6 ppm.

9. Synthesis of (C₆H₅)(H)PCH₂CH₂CH₂Cl

A stock solution of 0.654 M LDA (29.0 mL, 18.7 mmol) was added slowly, dropwise to a solution of 2.00 mL (18.2 mmol) of (C₆H₅)PH₂ and 1.80 mL (18.2 mmol) of Br(CH₂)₃Cl in 40 mL of THF cooled to -78°C in a Dry Ice/isopropanol bath. The resulting solution was allowed to warm
to room temperature and the solvent was removed in vacuo. The white residue was redissolved in 30 mL of toluene and the resulting solution was hydrolyzed with 30 mL of water. The layers were allowed to separate and the organic layer was transferred to a flask containing anhydrous MgSO₄. The aqueous layer was extracted four times with 10 mL aliquots of toluene and the extracts were combined over anhydrous MgSO₄ and dried overnight. The solution was filtered through neutral alumina (60 mesh) on a Schlenk frit to remove the MgSO₄ and the solvent was removed from the filtrate in vacuo to give a clear, colorless liquid. The liquid was purified by Kugelrohr distillation. Yield: 3.40g, 100 %. ³¹P nmr data: δP = -53.9 ppm, ¹J(P-H) = 208 Hz.

10. Synthesis of (C₆H₁₁)(H)PCH₂CH₂CH₂Cl

A stock solution of 0.645 M LDA (24.0 mL, 15.5 mmol) was added dropwise, over a one hour period, to a solution of 2.00 mL (15.1 mmol) of (C₆H₁₁)PH₂ and 1.50 mL (15.1 mmol) of Br(CH₂)₃Cl in 40 mL of THF cooled to -78°C in a Dry Ice/isopropanol bath. The resulting solution was warmed to room temperature and the solvent was removed in vacuo to give a yellow oil. The oil was redissolved in 30 mL of toluene and the resulting solution was hydrolyzed with 30 mL of water. The organic layer was transferred to a flask containing anhydrous MgSO₄. The aqueous layer was extracted three times with 10 mL aliquots of toluene and the extracts were combined over anhydrous MgSO₄ and dried overnight. The solution was filtered through a small amount of neutral alumina (60 mesh) on a Schlenk frit to remove the MgSO₄ and the solvent was removed from the filtrate to give a clear, colorless liquid. The liquid was purified by Kugelrohr distillation. Yield:
2.35g, 81%. $^{31}$P nmr data: $\delta P = -51.9$ ppm, $^{1}J(P-H) = 193$ Hz.

11. Synthesis of $C_{6}H_{5}P(CH_{2}CH_{2}CH_{2}P(C_{6}H_{5})_{2})_2$, ttp

A stock solution of 1.6 M n-BuLi (120 mL, 192 mmol) was added dropwise, over a one hour period, to a solution of $(C_{6}H_{5})_{2}PH$ (31.6 mL, 182 mmol) in 800 mL of THF cooled to 0°C. The red solution was stirred for an additional 30 minutes and then it was added dropwise, over a 2.5 hour period, to a solution of $C_{6}H_{5}P(CH_{2}CH_{2}CH_{2}Cl)$_2 (23.88g, 90.75 mmol) in 200 mL of diethylether. The resulting bright orange solution was stirred overnight and then refluxed for 6 hours. The solvent was removed in vacuo, and the resulting yellow-orange oil was dissolved in 300 mL of toluene and hydrolyzed with 100 mL of absolute ethanol followed by 400 mL of water. After 30 minutes of rapid stirring, the organic layer was transferred to a flask containing anhydrous MgSO$_4$. The aqueous layer was extracted three times with 150 mL aliquots of toluene, and the extracts were combined over anhydrous MgSO$_4$ and dried overnight. The solution was filtered through neutral alumina (60 mesh) on a Schlenk frit to remove the MgSO$_4$ and the solvent was removed in vacuo to give a white oil. Yield: 51.0g, 100%.

$^{31}$P($^1$H) nmr data: $\delta PPh = -28.7$ ppm, $\delta PPh$_2 = -18.1$ ppm.

12. Synthesis of $C_{6}H_{5}P(CH_{2}CH_{2}CH_{2}P(C_{6}H_{11})_{2})_2$, cyttpp

A stock solution of 1.6 M n-BuLi (100 mL, 160 mmol) was added dropwise, over a 1 hour period, to a solution of $(C_{6}H_{11})_{2}PH$ (33.5 mL, 153 mmol) in 600 mL of THF cooled to 0°C. The yellow solution was stirred an additional hour and then it was added dropwise, over a 2.5 hour period, to a solution of $C_{6}H_{5}P(CH_{2}CH_{2}CH_{2}Cl)$_2 (20.00g, 76.0 mmol) in 230 mL of diethylether cooled to 0°C. The solution was refluxed
for one hour and the solvent was removed \textit{in vacuo}. The resulting yellow oil was dissolved in 300 mL of toluene and hydrolyzed with 100 mL of absolute ethanol followed by 300 mL of water. After one hour of rapid stirring, the organic layer was transferred to a flask containing anhydrous MgSO$_4$. The aqueous layer was extracted three times with 150 mL aliquots of toluene, and the extracts were combined over anhydrous MgSO$_4$ and dried overnight. The solution was filtered through neutral alumina (60 mesh) on a Schlenk frit to remove the MgSO$_4$ and the solvent was removed from the filtrate \textit{in vacuo} to give a clear, pale-yellow oil. Yield: 40.47 g, 90.74%. $^{31}$P($^1$H) nmr data: $\delta$PPh = -27.7 ppm, $\delta$PCy$_2$ = -7.2 ppm.

13. Synthesis of (p-CF$_3$C$_6$H$_4$)$_2$PCH$_2$CH$_2$P(H)C$_6$H$_5$. CF$_3$PPH

A stock solution of 0.523 M LDA (38.0 mL, 19.9 mmol) diluted with 40 mL of hexane was added slowly, dropwise to a solution of 7.54 g (18.9 mmol) of (p-CF$_3$C$_6$H$_4$)$_2$PCH$_2$CH$_2$CH$_2$Cl and 2.10 mL (18.9 mmol) of C$_6$H$_5$PH$_2$ in 200 mL of THF cooled to -78°C in a Dry Ice/isopropanol bath. The resulting red solution was allowed to warm to room temperature and it was stirred overnight. The solution was refluxed for three hours (80°C) and then the solvent was removed \textit{in vacuo} to give a light orange oil. The oil was dissolved in 200 mL of toluene and hydrolyzed with 200 mL of water. The yellow organic layer was transferred to a flask containing anhydrous MgSO$_4$. The aqueous layer was extracted four times with 50 mL aliquots of toluene and the extracts were combined over MgSO$_4$ and dried overnight. The solution was filtered through neutral alumina (60 mesh) on a Schlenk frit to remove the MgSO$_4$ and the solvent was removed from the filtrate \textit{in...
vacuo to give a white oil. The oil was heated in vacuo for one hour to remove volatile materials. Yield: 7.13g, 79.8%. $^{31}P$ nmr data: $\delta$PPh = -54.5 ppm, $^1J(P-H) = 207$ Hz, $\delta$P(p-CF$_3$C$_6$H$_4$)$_2$ = -16.6 ppm.

14. Synthesis of C$_6$H$_5$P(CH$_2$CH$_2$CH$_2$)P(p-CF$_3$C$_6$H$_4$)$_2$CF$_3$PPP

A stock solution of 0.525 M LDA (34.0 mL, 17.8 mmol) diluted with 40 mL of hexane was added, over a 5.5 hour period, to a solution containing 6.34g (15.9 mmol) of (p-CF$_3$C$_6$H$_4$)$_2$PCH$_2$CH$_2$CH$_2$Cl and 0.90 mL (8.2 mmol) of C$_6$H$_5$PH$_2$ in 300 mL of THF cooled to -78°C in a Dry Ice/isopropanol bath. The resulting deep red solution was stirred overnight and then refluxed for 3.5 hours (70°C) during which the solution became pale orange in color. The solvent was removed in vacuo to give an orange oil. The oil was dissolved in 200 mL of benzene and then hydrolyzed with 200 mL of water. The resulting solution was stirred vigorously for 30 minutes, then the layers were allowed to separate and the pale-yellow organic layer was transferred to a flask containing anhydrous MgSO$_4$. The aqueous layer was extracted four times with 50 mL aliquots of benzene. The extracts were combined over anhydrous MgSO$_4$ and dried overnight. The solution was filtered through neutral alumina (60 mesh) on a Schlenk frit to remove the MgSO$_4$ and the solvent was removed from the filtrate in vacuo to give a yellow oil. The oil was gently heated in vacuo to remove remaining volatile materials. Yield: 5.47g, 82.4%. $^{31}(^1H)$P nmr data: $\delta$Ph = -28.0 ppm, $\delta$P(p-CF$_3$C$_6$H$_4$)$_2$ = -16.9 ppm.

C. Synthesis of Platinum Complexes of CF$_3$PPP and CF$_3$PPP

1. Synthesis of PtCl$_2$(CF$_3$PPP)

A solution of 0.30 M CF$_3$PPP ligand in benzene (1.8 mL, 0.54 mmol)
was added to a slurry containing 0.2032 g (0.5431 mmol) of PtCl₂COD and 1 drop of a 6 M HCl solution in 20 mL of benzene. A yellow color was observed which quickly disappeared and a white solid precipitated. The solution was concentrated under an Ar stream to 1 mL and then 10 mL of hexane were added to complete the precipitation of the white solid. The white solid was collected on a Schlenk frit, washed two times with 2.0 mL aliquots of hexane and dried in vacuo. Yield: 0.37 g, 92%.

Elemental analysis:

Theory: %C %H %Cl %F %P
37.42 2.73 9.60 15.44 8.39

Found: %C %H %Cl %F %P
37.39 3.00 9.41 15.16 8.22

2. Synthesis of [PtCl(CF₃ttp)]Cl

A stock solution of 0.10 M CF₃ttp ligand (14.0 mL, 1.40 mmol) in benzene was added to a slurry containing 0.52 g (1.40 mmol) of PtCl₂COD in 40 mL of benzene via a syringe. A faint yellow color appeared and then a fine white solid precipitated. The slurry was refluxed for 3 hours and then it was concentrated in vacuo to one-half its initial volume. The white solid was collected by vacuum filtration, washed with benzene and diethylether and dried in a dessicator. Yield: 1.54 g, 62.3%.

Elemental Analysis:

Theory: %C %H %Cl %P
43.65 3.02 6.44 8.44

Found: %C %H %Cl %P
43.14 3.44 6.79 7.96
RESULTS AND DISCUSSION

A. Synthesis of 3-Chloropropylphosphines

The most direct method for preparation of triphosphine ligands containing trimethylene linkages is the coupling reaction between 3-chloropropylphosphines and organophosphide nucleophiles (Eq. 30).

\[ R'PLi_2 + 2R_2P(CH_2)_3Cl \rightarrow R'[CH_2CH_2CH_2PR_2]_2 + 2LiCl \] (30)

Traditionally, the 3-chloropropylphosphines were prepared by adding the lithium salt of the appropriate phosphine (Cy₂PH or Ph₂PH) to an excess of 1,3-dichloropropane (1:10 molar ratio) over a period of 15-24 hours (Eqs. 31 and 32). However, the author has developed a new method for the synthesis of 3-chloropropylphosphines which is less expensive, requires less operator time and results in high-yield, high-purity products.

Two modifications of the original procedure have been implemented by the author. First, 1-bromo-3-chloropropane has been substituted for 1,3-dichloropropane. The advantage is obvious; the bromine end of 1-bromo-3-chloropropane undergoes nucleophilic substitution reactions faster than the chlorine end of the molecule. This allows for a more selective substitution reaction and eliminates the disubstitution reaction (Eq. 33), which is a competition reaction that commonly

\[ 2R_2PLi + Cl(CH_2)_3Cl \rightarrow R_2PCH_2CH_2CH_2PR_2 + 2LiCl \] (33)
occurs in the original method. Kyba and co-workers\textsuperscript{93} used a 4\% excess of 1-bromo-3-chloropropane for the synthesis of $C_6H_5P(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})_2$ in the presence of $C_6H_5PH_2$ by the addition of n-butyllithium. However, they generated only a 36\% yield of the product via Equation 34. In the reactions carried out in this work, the 1-bromo-3-chloropropane

$$C_6H_5PH_2 + xs\text{Br(\text{CH}_2)_3Cl} + 2n-\text{BuLi} \rightarrow C_6H_5P(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})_2$$ (34)

is used in stoichiometric amounts with the phosphine molecule, preventing the need to remove excess starting materials (ie. excess Cl(\text{CH}_2)_3Cl or Br(\text{CH}_2)_3Cl) from the final products.

Replacing n-butyllithium with lithium diisopropylamide (LDA) is the second modification of the original method to be implemented in this study. Kyba and co-workers\textsuperscript{94} used LDA to prepare bis(3-chloropropyl)(1-naphthylmethyl)phosphine (Eq. 35) in 83\% yield.

$$\text{NphCH}_2\text{PH}_2 + 2\text{Br(\text{CH}_2)_3Cl} + 2\text{LDA} \rightarrow \text{NphCH}_2\text{P(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})}_2$$ (35)

Because LDA is a weaker base than n-butyllithium, it can be used to generate the lithium phosphides (ie. R\textsubscript{2}PLi) \textit{in situ} at colder temperatures in the presence of 1-bromo-3-chloropropane. Hence, the reaction used to generate 3-chloropropylphosphines is now a one-step, one-flask reaction (Eqs. 36 and 37). Addition of LDA to a mixture of

$$\text{R}_2\text{PH} + \text{Br(\text{CH}_2)_3Cl} + \text{LDA} \rightarrow \text{R}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{LiBr} + \text{HN(i-Pr)}_2$$ (36)
$$\text{RPH}_2 + 2\text{Br(\text{CH}_2)_3Cl} + 2\text{LDA} \rightarrow \text{RP(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})}_2 + 2\text{LiBr} + 2\text{HN(i-Pr)}_2$$ (37)

the appropriate primary or secondary phosphine and Br(\text{CH}_2)_3Cl in THF cooled to -78\celsius requires only one hour (on a 20-50 gram scale) as
compared to the 15-24 hours required in the original method.

The new method of preparing 3-chloropropylphosphines (Eq. 36) works extremely well for the preparation of \((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}\) from diphenylphosphine, \((\text{C}_6\text{H}_5)_2\text{PH}\), in near quantitative yield. The 3-chloropropyldiphenylphosphine was characterized by \(^{31}\text{P}(^1\text{H}), ^1\text{H}\) and \(^{13}\text{C}(^1\text{H})\) nmr spectroscopy and infrared spectroscopy. The data are compiled in Tables 6, 7 and 8. The carbon-13 nmr spectrum is particularly useful for determining the composition and purity of the product as each carbon atom or sets of equivalent carbon atoms are clearly delineated (Figures 22 and 23). The \(^{13}\text{C}(^1\text{H})\) peak assignments for \((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}\) matched the assignments made by Dahlenburg and Arpac for this compound.\(^95\) The purity of \((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}\) was also tested using thin layer chromatography; no trace impurities were observed. The compound has an \(R_f\) value of 1.4 in 1:1 toluene/hexane solvent mixtures. Equation 36 was also used to prepare 3-chloropropyldiethylphosphine, \((\text{CH}_3\text{CH}_2)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}\) from diethylphosphine, \((\text{CH}_3\text{CH}_2)_2\text{PH}\). The 3-chloropropyldiethylphosphine was characterized based on its \(^{31}\text{P}(^1\text{H})\) nmr chemical shift, -24.6 ppm, versus the chemical shift of diethylphosphine, -55.0 ppm. The product has not been further characterized because it is a very volatile liquid, and it could not be obtained free of reaction solvents.

Reaction of dicyclohexylphosphine, \((\text{C}_6\text{H}_{11})_2\text{PH}\), and \(\text{Br(CH}_2)_3\text{Cl}\) with LDA was unsuccessful as determined by \(^{31}\text{P}\) nmr spectroscopy. Only a peak at -28.3 was observed in the \(^{31}\text{P}(^1\text{H})\) nmr spectrum of the reaction mixture, which is assigned to the starting material,
Figure 22. The aliphatic region of a 250 MHz \(^{13}C\)(\(^1\)H) nmr spectrum of \((C_6H_5)_2PCH_2CH_2CH_2Cl\) in d6-acetone. S = residual acetone.
Figure 23. The aromatic region of a 250 MHz $^{13}\text{C}(^1\text{H})$ nmr spectrum of $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ in d6-acetone.
dicyclopenthyl phosphine. The known 3-chloropropyl-
dicyclohexylphosphine, (C₆H₁₁)₂PCH₂CH₂CH₂Cl, has a $^{31}P(¹H)$ nmr
chemical shift at -6.2 ppm⁸² (Table 6). A similar reaction involving
diisopropylphosphine, [(CH₃)₂CH]₂PH, was also unsuccessful as
determined by $^{31}P(¹H)$ nmr spectroscopy. The diisopropylphosphine,
which was prepared from the reduction of [(CH₃)₂CH]₂PCl with LiAlH₄,
has a $^{31}P$ chemical shift of -16.6 ppm ($¹J(P-H) = 184$ Hz); whereas the
known 3-chloropropyldiisopropylphosphine,⁹⁶ [(CH₃)₂CH]₂PCH₂CH₂CH₂Cl
has a $^{31}P(¹H)$ nmr chemical shift of 1.4 ppm. The $^{31}P(¹H)$ nmr spectrum
of the mixture resulting from the reaction of [(CH₃)₂CH]₂PH and
Br(CH₂)₃Cl with LDA displayed only a peak due to the starting
material, [(CH₃)₂CH]₂PH (-16.6 ppm).

The reaction of phenylphosphine, C₆H₅PH₂, and Br(CH₂)₃Cl with LDA
(Eq. 37) gives rise to nearly quantitative yields of pure bis(3-
chloro-propyl)phenylphosphine, C₆H₅P(CH₂CH₂CH₂Cl)₂. This compound has
been characterized by $^{31}P(¹H)$, $¹H$ and $¹³C(¹H)$ nmr spectroscopy and
infrared spectroscopy (Tables 6-8) and the data corroborates that
reported by Kyba and co-workers.⁹³ The bis(3-chloropropyl)-
phenylphosphine was tested for trace impurities by thin layer
chromatography, and it was pure. The compound has an $R_f$ value of 2.0
in a 1:1 toluene/hexane solvent mixture. Equation 37 was also used to
prepare bis(3-chloropropyl)cyclohexylphosphine, C₆H₁₁P(CH₂CH₂CH₂Cl)₂
from cyclohexylphosphine, C₆H₁₁PH₂. However, only 17% (based on $^{31}P$
nmr intensities) of the desired product was formed ($δ^{31}P = -20.8$ ppm);
the major product was the monoalkylated species, C₆H₁₁(H)PCH₂CH₂CH₂Cl
($δ^{31}P = -51.9$ ppm).
Table 6. $^{31}$P($^1$H) NMR Data for Primary and Secondary Phosphines and the Corresponding 3-Chloropropylphosphines

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>$\delta$P</th>
<th>$^1$J(P-H)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{C}_6\text{H}_5)_2\text{PH}$</td>
<td>-41.1</td>
<td>214</td>
<td>THF</td>
</tr>
<tr>
<td>$(\text{C}_6\text{H}_5)_2\text{P(CH}_2)_3\text{Cl}$</td>
<td>-17.4</td>
<td></td>
<td>THF</td>
</tr>
<tr>
<td>$(\text{CH}_3\text{CH}_2)_2\text{PH}$</td>
<td>-55.0</td>
<td>190</td>
<td>(CD$_3$)$_2$CO</td>
</tr>
<tr>
<td>$(\text{CH}_3\text{CH}_2)_2\text{P(CH}_2)_3\text{Cl}$</td>
<td>-24.6</td>
<td></td>
<td>(CD$_3$)$_2$CO</td>
</tr>
<tr>
<td>$(\text{C}_6\text{H}_11)_2\text{PH}$</td>
<td>-28.3</td>
<td>197</td>
<td>THF</td>
</tr>
<tr>
<td>$(\text{C}_6\text{H}_11)_2\text{P(CH}_2)_3\text{Cl}$</td>
<td>-6.2</td>
<td></td>
<td>C$_6$H$_6$</td>
</tr>
<tr>
<td>[$(\text{CH}_3)_2\text{CH}]_2\text{PH}$</td>
<td>-16.6</td>
<td>184</td>
<td>(CD$_3$)$_2$CO</td>
</tr>
<tr>
<td>[$(\text{CH}_3)_2\text{CH}]_2\text{P(CH}_2)_3\text{Cl}$</td>
<td>1.4</td>
<td></td>
<td>CD$_2$Cl$_2$</td>
</tr>
<tr>
<td>C$_6$H$_5$PH$_2$</td>
<td>-126.0</td>
<td>196</td>
<td>Et$_2$O</td>
</tr>
<tr>
<td>C$_6$H$_5$(H)PCH$_2$CH$_2$CH$_2$Cl</td>
<td>-53.9</td>
<td>208</td>
<td>(CD$_3$)$_2$CO</td>
</tr>
<tr>
<td>C$_6$H$_5$P(CH$_2$CH$_2$CH$_2$Cl)$_2$</td>
<td>-26.6</td>
<td></td>
<td>THF</td>
</tr>
<tr>
<td>C$_6$H$_11$PH$_2$</td>
<td>-113.6</td>
<td>162</td>
<td>THF</td>
</tr>
<tr>
<td>C$_6$H$_11$(H)PCH$_2$CH$_2$CH$_2$Cl</td>
<td>-51.9</td>
<td>193</td>
<td>(CD$_3$)$_2$CO</td>
</tr>
<tr>
<td>C$_6$H$_11$P(CH$_2$CH$_2$CH$_2$Cl)$_2$</td>
<td>-20.8</td>
<td></td>
<td>THF</td>
</tr>
<tr>
<td>(p-CF$_3$C$_6$H$_4$)$_2$PH</td>
<td>-42.2</td>
<td>227</td>
<td>(CD$_3$)$_2$CO</td>
</tr>
<tr>
<td>(p-CF$_3$C$_6$H$_4$)$_2$P(CH$_2)_3$Cl</td>
<td>-16.7</td>
<td></td>
<td>(CD$_3$)$_2$CO</td>
</tr>
<tr>
<td>[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_2$PH</td>
<td>-42.3</td>
<td>230</td>
<td>(CD$_3$)$_2$CO</td>
</tr>
<tr>
<td>[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_2$P(CH$_2)_3$Cl</td>
<td>-14.4</td>
<td></td>
<td>CD$_3$Cl</td>
</tr>
</tbody>
</table>

Chemical shifts are in ppm, coupling constants are in Hz.

a) Ref. 44.

b) Ref. 60.
Table 7. Proton NMR and Diagnostic Infrared Data for 3-Chloropropylphosphines

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>$^1$H (ppm)</th>
<th>IR (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(C_6H_5)_2P(CH_2)_3Cl^a$</td>
<td>7.35 (m) 10H</td>
<td>1589 (C=C)</td>
</tr>
<tr>
<td></td>
<td>3.58 (t) 2H</td>
<td>1572 (C=C)</td>
</tr>
<tr>
<td></td>
<td>J(H-H) = 6.2Hz</td>
<td>1485 (Ph-P)</td>
</tr>
<tr>
<td></td>
<td>2.04 (m) 4H</td>
<td>649 (C-Cl)</td>
</tr>
<tr>
<td>$C_6H_5(H)P(CH_2)_3Cl^b$</td>
<td>7.52 (m)</td>
<td>2290 (P-H)</td>
</tr>
<tr>
<td></td>
<td>7.34 (m)</td>
<td>1590 (C-C)</td>
</tr>
<tr>
<td></td>
<td>4.15 (d) 1H</td>
<td>1488 (Ph-P)</td>
</tr>
<tr>
<td></td>
<td>J(P-H) = 207Hz</td>
<td>648 (C-Cl)</td>
</tr>
<tr>
<td></td>
<td>3.60 (t) 2H</td>
<td></td>
</tr>
<tr>
<td></td>
<td>J(H-H) = 6.3Hz</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.89 (m) 4H</td>
<td></td>
</tr>
<tr>
<td>$C_6H_5P(CH_2CH_2CH_2Cl)_2^a$</td>
<td>7.42 (m) 5H</td>
<td>1588 (C=C)</td>
</tr>
<tr>
<td></td>
<td>3.55 (m) 4H</td>
<td>1560 (C-C)</td>
</tr>
<tr>
<td></td>
<td>1.79 (m) 8H</td>
<td>1488 (Ph-P)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>648 (C-Cl)</td>
</tr>
<tr>
<td>$C_6H_{11}(H)P(CH_2)_3Cl^b$</td>
<td>3.64 (t) 2H</td>
<td>2270 (P-H)</td>
</tr>
<tr>
<td></td>
<td>J(H-H) = 6.4Hz</td>
<td>645 (C-Cl)</td>
</tr>
<tr>
<td></td>
<td>2.94 (d) 1H</td>
<td></td>
</tr>
<tr>
<td></td>
<td>J(P-H) = 194Hz</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.77 (m) 10H</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.26 (m) 5H</td>
<td></td>
</tr>
</tbody>
</table>

d = doublet, m = multiplet, t = triplet.

a) CD$_2$Cl$_2$ solvent.
b) (CD$_3$)$_2$CO solvent.
Table 8. $^{13}$C($^1$H) NMR Data for 3-Chloropropylphosphines

<table>
<thead>
<tr>
<th></th>
<th>$(\text{C}_6\text{H}_5)_2\text{P(CH}_2\text{)}_3\text{Cl}$</th>
<th>$\text{C}_6\text{H}_5\text{P(CH}_2\text{CH}_2\text{CH}_2\text{Cl})_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Phenyl rings</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C</td>
<td>138.1 d (13)</td>
<td>137.0 d (13)</td>
</tr>
<tr>
<td>o-C</td>
<td>132.6 d (19)</td>
<td>132.4 d (20)</td>
</tr>
<tr>
<td>m-C</td>
<td>128.5 d (7.2)</td>
<td>128.6 d (6.4)</td>
</tr>
<tr>
<td>p-C</td>
<td>128.7 s</td>
<td>129.3 s</td>
</tr>
<tr>
<td><strong>Trimethylene chain</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C</td>
<td>28.1 d (18)</td>
<td>29.1 d (15)</td>
</tr>
<tr>
<td>-C-</td>
<td>25.4 d (12)</td>
<td>25.4 d (11)</td>
</tr>
<tr>
<td>C-Cl</td>
<td>45.7 d (15)</td>
<td>45.7 d (13)</td>
</tr>
</tbody>
</table>

Chemical shifts are in ppm, Coupling constants (in parentheses) are in Hz. $s$ - singlet, $d$ - doublet. Solvent: CD$_3$Cl.
A deliberate attempt was made to prepare the monoalkylated species of phenylphosphine and cyclohexylphosphine using Equation 38.

\[
\text{RPH}_2 + \text{Br(CH}_2\text{)}_3\text{Cl} + \text{LDA} \rightarrow \text{R(H)PCH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{LiBr} + \text{HN(i-Pr)}_2
\]  \tag{38}

Both 3-chloropropylphenylphosphine, \(\text{C}_6\text{H}_5(\text{H})\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}\), and 3-chloropropylcyclohexylphosphine, \(\text{C}_6\text{H}_{11}(\text{H})\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}\) were prepared successfully. These phosphines are useful intermediates for the synthesis of chelating polydentate ligands because they incorporate reactive P-H and C-Cl bonds. Once again, the compounds were characterized by \(\text{^31P}^{(1H)}\), \(^1\text{H}\) and \(^{13}\text{C}^{(1H)}\) nmr spectroscopy and infrared spectroscopy (Tables 6, 7 and 9). The \(\text{^31P}^{(1H)}\) nmr and the \(^1\text{H}\) spectra of \(\text{C}_6\text{H}_{11}(\text{H})\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}\) are shown in Figure 24 and the infrared spectrum of \(\text{C}_6\text{H}_5(\text{H})\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}\) is shown in Figure 25. The infrared spectra for both species exhibit characteristic P-H stretching bands, and the doublets due to the hydrogen bound to phosphorus in the \(^1\text{H}\) nmr spectra also confirm the presence of the P-H bond.

B. Synthesis of ttp and cyttp

By use of the new method developed for the synthesis of 3-chloropropylphosphines, two schemes can be envisioned for the synthesis of the chelating triphosphine ligands ttp and cyttp (Schemes 4 and 5).

\[
\text{R}_2\text{PH} + \text{Br(CH}_2\text{)}_3\text{Cl} + \text{LDA} \rightarrow \text{R}_2\text{P(CH}_2\text{)}_3\text{Cl} + \text{LiBr} + \text{HN(i-Pr)}_2
\]  \tag{39}

\[
\text{R'}\text{PH}_2 + 2\text{n-BuLi} \rightarrow \text{R'}\text{PLi}_2 + 2\text{n-C}_4\text{H}_{10}
\]  \tag{40}

\[
\text{R'}\text{PLi}_2 + 2\text{R}_2\text{P(CH}_2\text{)}_3\text{Cl} \rightarrow \text{R'}\text{P(CH}_2\text{CH}_2\text{CH}_2\text{PR}_2)_2
\]  \tag{41}

Scheme 4
Table 9. $^{13}\text{C}^{(1)}\text{H}$ NMR Data for C$_6$H$_5$(H)P(CH$_2$)$_3$Cl and C$_6$H$_{11}$(H)P(CH$_2$)$_3$Cl

<table>
<thead>
<tr>
<th>Data</th>
<th>C$_6$H$_5$(H)P(CH$_2$)$_3$Cl</th>
<th>C$<em>6$H$</em>{11}$(H)P(CH$_2$)$_3$Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl ring</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C</td>
<td>135.6 d (11)</td>
<td></td>
</tr>
<tr>
<td>o-C</td>
<td>134.0 d (16)</td>
<td></td>
</tr>
<tr>
<td>m-C</td>
<td>129.1 d (5.8)</td>
<td></td>
</tr>
<tr>
<td>p-C</td>
<td>128.8 s</td>
<td></td>
</tr>
<tr>
<td>Cyclohexyl ring</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C</td>
<td></td>
<td>32.4 br</td>
</tr>
<tr>
<td>o-C</td>
<td></td>
<td>31.5 d (7.2)</td>
</tr>
<tr>
<td>m-C</td>
<td></td>
<td>27.4 d (9.5)</td>
</tr>
<tr>
<td>p-C</td>
<td></td>
<td>26.7 s</td>
</tr>
<tr>
<td>Trimethylene chain</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C</td>
<td>32.1 d (7.9)</td>
<td>32.3 d (12)</td>
</tr>
<tr>
<td>-C-</td>
<td>20.9 d (13)</td>
<td>16.0 d (13)</td>
</tr>
<tr>
<td>C-Cl</td>
<td>45.9 d (9.3)</td>
<td>46.1 d (11)</td>
</tr>
</tbody>
</table>

Chemical shifts are in ppm. Coupling constants (in parentheses) are in Hz. s = singlet, d = doublet, br = broad. Solvent: (CD$_3$)$_2$CO.
Figure 24. a) 250 MHz $^1H$ nmr spectrum of $C_6H_{11}(H)PCH_2CH_2CH_2Cl$ in d$_6$-acetone. b) 250 MHz $^{31}P^{(1)}H$ nmr spectrum of $C_6H_{11}(H)PCH_2CH_2CH_2Cl$ in d$_6$-acetone; the inset is the proton-decoupled spectrum.
Figure 25. The infrared spectrum of \( \text{C}_6\text{H}_5\text{(H)PCH}_2\text{CH}_2\text{CH}_2\text{Cl}. \) (Neat)
Scheme 5 has been used successfully for preparation of cyttpp, and both methods have been used successfully for the preparation of ttp. However, Scheme 5 is preferred for the synthesis of ttp because the lithium salts of secondary phosphines are easy to prepare and transfer whereas lithium phenylphosphide (C₆H₅PLi₂, Scheme 4) is an insoluble, pyrophoric salt which must be transferred as a slurry.

By use of Scheme 5, pure samples of ttp and cyttpp have been made in high-yield. The $^{31}$P($^1$H) nmr spectrum of ttp (Figure 26) displays the expected peaks at -18.1 ppm (Ph₂P, intensity 2) and -28.7 ppm (PhP, intensity 1) and the $^{31}$P($^1$H) nmr spectrum of cyttpp (Figure 27) displays the expected peaks at -7.25 ppm (Cy₂P, intensity 2) and -27.7 ppm (PhP, intensity 1). The ligands were also characterized by $^1$H nmr and infrared spectroscopies (Table 10) and $^{13}$C($^1$H) nmr spectroscopy (Table 11). The $^{13}$C($^1$H) nmr assignments for ttp corroborated those reported by Arpac and Dahlenburg. The purity of cyttpp and ttp were also tested by thin layer chromatography. The $R_f$ value of cyttpp is 6.2 in a 1:1 toluene/hexane solvent mixture, and the $R_f$ value of ttp is 8.1 in a 1:1 toluene/hexane solvent mixture. Both ligands were found to be pure, based on thin layer chromatography.
Figure 26. 90 MHz $^{31}$P($^1$H) nmr spectrum of $C_6H_5P(CH_2CH_2CH_2P(C_6H_5)_2)_2$ (ttp) in toluene.
Figure 27. 90 MHz $^{31}$P($^1$H) nmr spectrum of $C_6H_5P\text{[CH}_2\text{CH}_2\text{CH}_2P(C_6H_{11})_2]$ (cytpp) in toluene.
Table 10. Proton NMR and Diagnostic Infrared Spectroscopic Data for ttp and cytpp

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\delta_{\text{Ph}}$</th>
<th>$\delta_{\text{-CH}_2}$</th>
<th>$\nu_{\text{C=C}}$</th>
<th>$\nu_{\text{P-Ph}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ttp</td>
<td>7.32(m)</td>
<td>1.74(m)</td>
<td>1588</td>
<td>1482</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1572</td>
</tr>
<tr>
<td>cytpp</td>
<td>7.35(m)</td>
<td>Cy, CH$_2$</td>
<td>1590</td>
<td>1485</td>
</tr>
<tr>
<td></td>
<td>1.14-1.72</td>
<td></td>
<td>1570</td>
<td></td>
</tr>
</tbody>
</table>

Chemical shifts are in ppm, the solvent is CD$_2$Cl$_2$. IR frequencies are in cm$^{-1}$. m = multiplet.
Table 11. $^{13}\text{C}(^1\text{H})$ NMR Data for ttp and cyttp

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$(\text{C}_6\text{H}_5)_2\text{P}$</th>
<th>$(\text{C}_6\text{H}_5)\text{P}$</th>
<th>$(\text{C}<em>6\text{H}</em>{11})_2\text{P}$</th>
<th>Trimethylene-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ttp</td>
<td>C-P 138.7 d (12)</td>
<td>138.6 d (12)</td>
<td>C-P 29.6 t (17)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>o-C 132.7 d (19)</td>
<td>132.6 d (19)</td>
<td>-C- 22.4 t (31)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>m-C 128.4 s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>p-C 128.3 s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyttp</td>
<td>C-P 138.6 d (15)</td>
<td>33.3 d (12)</td>
<td>C-P 30.3 t (23)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>o-C 132.5 d (19)</td>
<td>29.0 d (7.2)</td>
<td>-C- 24.8 t (33)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>m-C 128.2 d (5.3)</td>
<td>27.3 d</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>p-C 128.6 s</td>
<td>26.5 s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Chemical shifts are in ppm; coupling constants (in parentheses) are in Hz. d = doublet, s = singlet, t = pseudo triplet (overlapping doublet of doublets) and coupling constants for the pseudo triplets are $^1J(\text{P-C}) + ^3J(\text{P-C})$. The trimethylene carbons bound to phosphorus are coincidentally equivalent.

a. The ortho and meta carbon atoms of the phenyl rings on Ph$_2$P and PhP are coincidentally equivalent.
C. Synthesis of CF$_3$PPH, CF$_3$ttp and [3,5-(CF$_3$)$_2$C$_6$H$_3$]$_2$PCH$_2$CH$_2$CH$_2$Cl

In order to vary the electron density at the metal center of proposed metal-alkoxide or hydroxide complexes of the type, [M(OR)P$_3$]$_n$+, the electron donating ability of the chelating triphosphine ligands, P$_3$, needs to be changed. New chelating triphosphine ligands, more electronegative than ttp and the very strong electron-donor cyttp, should provide an interesting comparison.

The first new ligands to be developed, (p-CF$_3$C$_6$H$_4$)$_2$-P(CH$_2$)$_3$P(H)C$_6$H$_5$ ("CF$_3$PPH") and C$_6$H$_5$P[CH$_2$CH$_2$CH$_2$P(p-CF$_3$C$_6$H$_4$)$_2$]$_2$ ("CF$_3$ttp"), incorporate an electron withdrawing CF$_3$ group onto the para position of the phenyl rings bound to the terminal phosphorus atom. The ability of the CF$_3$ group to withdraw electron density from the phenyl rings should result in a decrease in the electron-donating ability of the phosphorus atom to which the p-CF$_3$C$_6$H$_4$ groups are bound.

The first step in preparing these new ligands is the synthesis of a new secondary phosphine, bis[4-(trifluoromethyl)phenyl]phosphine, (p-CF$_3$C$_6$H$_4$)$_2$PH. Kapoor and co-workers$^{97-99}$ have been successful in generating secondary phosphines containing electron-withdrawing groups (ie. (p-FC$_6$H$_4$)$_2$PH, (m-FC$_6$H$_4$)$_2$PH and (m-CF$_3$C$_6$H$_4$)$_2$PH) and incorporating these phosphines into bidentate ligands; however, they have not prepared (p-CF$_3$C$_6$H$_4$)$_2$PH. Based on Hammett substituent constants, a CF$_3$ group in the para position of a benzene ring is more electron attracting ($\sigma = 0.54$) than the same group in the meta position of a
benzene ring ($\sigma = 0.43$). Thus, the (p-CF$_3$C$_6$H$_4$)$_2$P group incorporated into a chelating triphosphine ligand will provide the greatest contrast to ttp.

The method Kapoor and co-workers$^{97-99}$ developed for preparing secondary phosphines involves isolation of the secondary phosphine oxides (ie. (p-FC$_6$H$_4$)$_2$P(O)H, (m-FC$_6$H$_4$)$_2$P(O)H and (m-CF$_3$C$_6$H$_4$)$_2$P(O)H). Although the oxide of bis[4-(trifluoromethyl)phenyl]phosphine has been reported,$^{101}$ the synthetic details provided were very vague. The method reported here for the synthesis of (p-CF$_3$C$_6$H$_4$)$_2$PH does not rely on the isolation of the phosphine oxide, but incorporates an in situ reduction of the oxide to form the desired secondary phosphine (Scheme 6).

\[
\begin{align*}
\text{p-CF}_3\text{C}_6\text{H}_4\text{Br} + \text{Mg} & \rightarrow \text{p-CF}_3\text{C}_6\text{H}_4\text{MgBr} \quad (45) \\
3\text{p-CF}_3\text{C}_6\text{H}_4\text{MgBr} + (\text{EtO})_2\text{P(O)H} & \rightarrow (\text{p-CF}_3\text{C}_6\text{H}_4)_2\text{P(O)MgBr} \quad (46) \\
(\text{p-CF}_3\text{C}_6\text{H}_4)_2\text{P(O)MgBr} + \text{HCl} & \rightarrow (\text{p-CF}_3\text{C}_6\text{H}_4)_2\text{P(O)H} + \text{MgBrCl} \quad (47) \\
4(\text{p-CF}_3\text{C}_6\text{H}_4)_2\text{P(O)H} + \text{LiAlH}_4 & \rightarrow 4(\text{p-CF}_3\text{C}_6\text{H}_4)_2\text{PH} + \text{LiAl(OH)}_4 \quad (48)
\end{align*}
\]

Scheme 6

The first three steps of Scheme 6; the formation of a Grignard, followed by addition of diethyl phosphite to the Grignard solution and subsequent reaction with a strong acid, comprise a well documented procedure for the synthesis of secondary phosphine oxides.$^{102,103}$ The presence of the phosphine oxide, (p-CF$_3$C$_6$H$_4$)$_2$P(O)H, can be detected in situ by $^{31}$P nmr spectroscopy ($\delta P = 16.4$ ppm, $^1J(\text{P-H}) = 495$ Hz). The final step of the scheme involves an in situ reduction of the phosphine oxide with LiAlH$_4$$^{104}$ to form the secondary phosphine. The
clear liquid product, \((p-CF_3C_6H_4)_2PH\), has been characterized by \(^{31}P\) and \(^1H\) nmr and infrared spectroscopies (Tables 6 and 12) and \(^{13}C\left(^1H\right)\) nmr spectroscopy (Table 13).

The second step in preparing the chelating phosphine ligands, CF\(_3\)PPH and CF\(_3\)tttp, is the synthesis of the 3-chloropropylphosphine intermediate, \((p-CF_3C_6H_4)_2PCH_2CH_2CH_2Cl\). Reactions involving the secondary phosphine, \((p-CF_3C_6H_4)_2PH\), are complicated by side reactions which involve the CF\(_3\) group and n-butyl lithium or LDA to give uncharacterized products. These complications have also been observed by Levason and Higgins.\(^{105}\) It is possible to prepare the 3-chloropropylphosphine intermediate of \((p-CF_3C_6H_4)_2PH\) by use of the new method depicted in Equation 36. By use of dilute solutions of LDA and by adding LDA very slowly to a solution of \((p-CF_3C_6H_4)_2PH\) and \(Br(CH_2)_3Cl\), these side reactions can be eliminated and high yields of \((p-CF_3C_6H_4)_2PCH_2CH_2CH_2Cl\) are obtained. The nmr and infrared spectroscopic data for \((p-CF_3C_6H_4)_2PCH_2CH_2CH_2Cl\) are given in Tables 6, 12 and 13.

The synthesis of \((p-CF_3C_6H_4)_2PCH_2CH_2P(H)C_6H_5\) (CF\(_3\)PPH) can be carried out using Scheme 7. The final step of this procedure involves

\[
(CF_3C_6H_4)_2PH + Br(CH_2)_3Cl + LDA \rightarrow (p-CF_3C_6H_4)_2PCH_2CH_2CH_2Cl
\]

\[
(p-CF_3C_6H_4)_2P(CH_2)_3Cl + C_6H_5PH_2 + LDA \rightarrow (p-CF_3C_6H_4)_2PCH_2CH_2CH_2P(H)C_6H_5
\]

*Scheme 7*

a one-step, one-flask reaction in which LDA is added slowly to a solution of \((p-CF_3C_6H_4)_2P(CH_2)_3Cl\) and \(C_6H_5PH_2\) cooled to \(-78°C\). The
Table 12. Proton NMR and Diagnostic Infrared Data for \((\text{p-CF}_3\text{C}_6\text{H}_4)_2\text{PH}\), \((\text{p-CF}_3\text{C}_6\text{H}_4)_2\text{P(\text{CH}_2)_3\text{Cl}}\), \(\text{CF}_3\text{PPH}\) and \(\text{CF}_3\text{ttp}\)

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>(^1\text{H} \text{ (ppm)})</th>
<th>IR (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{p-CF}_3\text{C}_6\text{H}_4)_2\text{PH})</td>
<td>7.45 (m) 8H</td>
<td>2290 (P-H)</td>
</tr>
<tr>
<td></td>
<td>5.15 (d) 1H</td>
<td>1610 (C=C)</td>
</tr>
<tr>
<td></td>
<td>(^1\text{J}(\text{P-H}) = 222\text{Hz})</td>
<td>1499 (P-Ph)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1125 (CF(_3))</td>
</tr>
<tr>
<td>((\text{p-CF}_3\text{C}_6\text{H}_4)_2\text{P(\text{CH}_2)_3\text{Cl}})</td>
<td>7.72 (m) 8H</td>
<td>1611 (C=C)</td>
</tr>
<tr>
<td></td>
<td>3.71 (m) 2H</td>
<td>1500 (P-Ph)</td>
</tr>
<tr>
<td></td>
<td>2.38 (m) 2H</td>
<td>1150 (CF(_3))</td>
</tr>
<tr>
<td></td>
<td>1.92 (m) 2H</td>
<td>650 (C-Cl)</td>
</tr>
<tr>
<td>(\text{CF}_3\text{PPH}^a)</td>
<td>7.68 (m)</td>
<td>2280 (P-H)</td>
</tr>
<tr>
<td></td>
<td>7.45 (m)</td>
<td>1608 (C=C)</td>
</tr>
<tr>
<td></td>
<td>7.31 (m)</td>
<td>1150 (CF(_3))</td>
</tr>
<tr>
<td></td>
<td>(^1\text{J}(\text{P-H}) = 207\text{ Hz})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(^3\text{J}(\text{H-H}) = 5.9\text{ Hz})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(^3\text{J}(\text{H-H}) = 7.8\text{ Hz})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.31 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.00 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.59 (m)</td>
<td></td>
</tr>
<tr>
<td>(\text{CF}_3\text{ttp})</td>
<td>7.47 (m) 20H</td>
<td>1609 (C=C)</td>
</tr>
<tr>
<td></td>
<td>2.17 (m) 4H</td>
<td>1120 (CF(_3))</td>
</tr>
<tr>
<td></td>
<td>1.81 (m) 4H</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.48 (m) 4H</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\text{H}\) nmr spectra were recorded in \((\text{CD}_3)_2\text{CO}\). m = multiplet; d = doublet.

a) Poor integration due to small residual impurities.
Table 13. $^{13}$C($^1$H) NMR Data for (p-CF$_3$C$_6$H$_4$)$_2$PH and (p-CF$_3$C$_6$H$_4$)$_2$PCH$_2$CH$_2$CH$_2$Cl

<table>
<thead>
<tr>
<th>Data</th>
<th>(p-CF$_3$C$_6$H$_4$)$_2$PH</th>
<th>(p-CF$_3$C$_6$H$_4$)$_2$P(CH$_2$)$_3$Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl ring</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C</td>
<td>140.4 d (13)</td>
<td>143.8 d (17)</td>
</tr>
<tr>
<td>o-C</td>
<td>135.3 d (17)</td>
<td>133.4 d (19)</td>
</tr>
<tr>
<td>m-C</td>
<td>126.3 s</td>
<td>125.8 m</td>
</tr>
<tr>
<td>p-C</td>
<td>131.5 q (33)$^a$</td>
<td>131.0 q (32)$^a$</td>
</tr>
<tr>
<td>CF$_3$ Group</td>
<td>125.2 q (272)$^a$</td>
<td>125.5 q (272)$^a$</td>
</tr>
<tr>
<td>Methylene chain</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C</td>
<td></td>
<td>29.6 d (18)</td>
</tr>
<tr>
<td>-C-</td>
<td></td>
<td>24.9 d (13)</td>
</tr>
<tr>
<td>C-Cl</td>
<td></td>
<td>45.8 d (16)</td>
</tr>
</tbody>
</table>

Chemical shifts are in ppm, coupling constants (in parentheses) are in Hz. s - singlet, d - doublet, m - multiplet, q - quartet.
Solvent: (CD$_3$)$_2$CO. $^a$ Coupling due to fluorines on CF$_3$ group.
$^{31}$P nmr spectrum of CF$_3$PPH displays a peak at -54.5 ppm due to the
-P(H)C$_6$H$_5$ group ($^1$J(P-H) = 207 Hz) and a peak at -16.6 ppm due to the
-P(p-CF$_3$C$_6$H$_4$)$_2$ group (Figure 28). The $^1$H nmr and infrared data are
given in Table 12. The $^{13}$C($^1$H) nmr data are given in Table 15. The
infrared spectrum is shown in Figure 29.

The synthesis of C$_6$H$_5$P(CH$_2$CH$_2$CH$_2$P(p-CF$_3$C$_6$H$_5$)$_2$)$_2$ similar to the
procedure used to prepare CF$_3$PPH, however, two equivalents of phenyl-
phosphine and two equivalents of LDA are used (Scheme 8). The product

\[
(p$-$p$-$CF$_3$C$_6$H$_4$)$_2$PH + Br(CH$_2$)$_3$Cl + LDA \rightarrow (p$-$p$-$CF$_3$C$_6$H$_4$)$_2$P(CH$_2$)$_3$Cl
\]

(51)

\[
(p$-$p$-$CF$_3$C$_6$H$_4$)$_2$P(CH$_2$)$_3$Cl + 2C$_6$H$_5$PH$_2$ + 2LDA \rightarrow
C$_6$H$_5$P(CH$_2$CH$_2$CH$_2$P(p$-$p$-$CF$_3$C$_6$H$_4$)$_2$)$_2$
\]

(52)

Scheme 8

has been characterized by $^{31}$P($^1$H) nmr spectroscopy. The spectrum
displays a peak at -16.6 ppm due to the -p(p-CF$_3$C$_6$H$_4$)$_2$ group
(intensity 2) and a peak at -28.0 ppm due to the -PC$_6$H$_5$ group
(intensity 1). The spectrum is shown in Figure 30. The $^1$H nmr and
infrared spectroscopic data are given in Table 12. The $^{13}$C($^1$H) nmr
spectrum is shown in Figures 31 and 32. The quartet due to the CF$_3$
group is located in the phenyl region at 124.6 ppm ($^1$J(C-F) = 262 Hz).
Two sets of peaks are observed for the p-CF$_3$C$_6$H$_4$ groups bound to
phosphorus; this suggests that the conformation of the CF$_3$tpp ligand
causes these groups to be magnetically inequivalent. A quartet is
observed for the para carbon ring in the p-CF$_3$C$_6$H$_4$ group due to
coupling to the fluorine atoms in the CF$_3$ group ($^2$J(C-F) = 32 Hz).
The trimethylene region displays three sets of pseudo triplets which
Table 14. $^{31}\text{P}({}^1\text{H})$ NMR Data for CF$_3$PPH and CF$_3$ttp

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\delta\text{P}$ (ppm)</th>
<th>$^{1}J(\text{P-H})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$PPH$^a$</td>
<td>-P(H)C$_6$H$_5$</td>
<td>-54.5</td>
</tr>
<tr>
<td></td>
<td>-P(p-CF$_3$C$_6$H$_4$)$_2$</td>
<td>-16.6</td>
</tr>
<tr>
<td>CF$_3$ttp$^b$</td>
<td>-PC$_6$H$_5$-</td>
<td>-28.0</td>
</tr>
<tr>
<td></td>
<td>-P(p-CF$_3$C$_6$H$_4$)$_2$</td>
<td>-16.9</td>
</tr>
</tbody>
</table>

a) (CD$_3$)$_2$CO solvent.
b) CD$_2$Cl$_2$ solvent.
Figure 28. 250 MHz $^{31}P(^{1}H)$ nmr spectrum of $C_{6}H_{5}(H)PCH_{2}CH_{2}CH_{2}$-P(p-CF$_{3}$C$_{6}$H$_{4}$)$_{2}$ (CF$_{3}$PPh) in d$_{6}$-acetone. The minor peaks are due to CF$_{3}$ttp and unreacted (p-CF$_{3}$C$_{6}$H$_{4}$)$_{2}$P(CH$_{2}$)$_{3}$Cl.
Figure 29. The infrared spectrum of CF$_3$PPH. (Neat).
Figure 30. 250 MHz $^{31}\text{P}({}^1\text{H})$ nmr spectrum of $\text{C}_6\text{H}_5\text{P}([\text{CH}_2\text{CH}_2\text{CH}_2-\text{P(p-CF}_3\text{C}_6\text{H}_4)_2])_2$ (CF$_3$ttp) in CD$_2$Cl$_2$. 
Figure 31. The alphatic region of a 250 MHz $^{13}$C($^1$H) nmr spectrum of CF$_3$ttp in CD$_2$Cl$_2$. 
Figure 32. The aromatic region of a 250 MHz $^{13}\text{C}^{1}\text{H}$ nmr spectrum of CF$_3$ttp in CD$_2$Cl$_2$. 
Table 15. $^{13}$C($^1$H) NMR Data for CF$_3$PPH and CF$_3$ttp

<table>
<thead>
<tr>
<th>Data</th>
<th>CF$_3$PPH</th>
<th>CF$_3$ttp</th>
</tr>
</thead>
<tbody>
<tr>
<td>-PC$_6$H$_5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C</td>
<td>135.1 d (12)</td>
<td>138.4 d (16)</td>
</tr>
<tr>
<td>o-C</td>
<td>133.5 d (16)</td>
<td>132.9 d (19)</td>
</tr>
<tr>
<td>m-C</td>
<td>128.3 d (5.8)</td>
<td>128.8 d (7.3)</td>
</tr>
<tr>
<td>p-C</td>
<td>128.0 s</td>
<td>129.4 s</td>
</tr>
<tr>
<td>-P(p-CF$_3$C$_6$H$_4$)$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C</td>
<td>143.0 d (18)</td>
<td>143.7 t (30)$^a,b$</td>
</tr>
<tr>
<td>o-C</td>
<td>132.8 d (19)</td>
<td>133.6 d (11)</td>
</tr>
<tr>
<td>m-C</td>
<td>125.0 m</td>
<td>125.6 m</td>
</tr>
<tr>
<td>p-C$^c$</td>
<td>130.5 q (32)</td>
<td>131.1 q (32)</td>
</tr>
<tr>
<td>-CF$_3$</td>
<td>128.6 q (272)</td>
<td>124.6 q (272)</td>
</tr>
<tr>
<td>Methylene-C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PhP-C</td>
<td>24.2 dd (16, 9.0)$^d$</td>
<td>29.4 t (24)$^b$</td>
</tr>
<tr>
<td>-C-</td>
<td>24.4 t (25)$^b$</td>
<td>22.7 t (32)$^b$</td>
</tr>
<tr>
<td>CF$_3$PhP-C</td>
<td>28.4 dd (14, 7.2)$^d$</td>
<td>30.0 t (25)$^b$</td>
</tr>
</tbody>
</table>

$d$ - doublet, $dd$ - doublet of doublets, $m$ - multiplet $q$ - quartet, $s$ - singlet, $t$ - pseudo triplet. Solvent: CF$_3$PPH, (CD$_3$)$_2$CO; CF$_3$ttp, CD$_2$Cl$_2$.

a) The two phenyl rings on P are inequivalent.

b) Coupling constant (in brackets) is $^1$J(C-P) + $^3$J(P-C).

c) Coupling is due to the fluorine atoms on the CF$_3$ group.

d) ($^1$J(P-C), $^3$J(P-C)).
are assigned to each of the three carbons in the propylene chain. The downfield triplet (30.0 ppm, $^{1}J(C-P) + ^{3}J(C-P) = 25$ Hz) is assigned to the carbon atoms bound to the phosphorus containing the p-CF$_3$C$_6$H$_4$ groups, the next triplet (29.4 ppm, $^{1}J(C-P) + ^{3}J(C-P) = 24$ Hz) is assigned to the carbon atoms bound to the phosphorus atom containing the C$_6$H$_5$ group and the upfield triplet (22.7 ppm, $^{1}J(C-P) + ^{3}J(C-P) = 32$ Hz) is assigned to the central carbon atoms of the propylene chain. A complete listing of the data is given in Table 15.

A new chelating triphosphine ligand which would incorporate an electron-withdrawing group bound to the central phosphorus atom would also provide an interesting contrast to ttp and ctytp. Thus, an attempt has been made to prepare a new primary phosphine containing two CF$_3$ groups in the meta positions of a phenyl ring, [3,5-(CF$_3$)$_2$C$_6$H$_3$]PH$_2$. The first step in the synthesis of this new phosphine involves the preparation of bis(3,5-trifluoromethyl)phenylphosphonous dichloride (Eq. 53). The synthetic procedure used was based on the synthesis of C$_6$F$_5$PCl$_2$ developed by Peterson. In this procedure,

$$PCl_3 + 3,5-(CF_3)_2C_6H_3MgBr \rightarrow 3,5-(CF_3)_2C_6H_3PCl_2 + MgBrCl$$

the Grignard solution of 3,5-(CF$_3$)$_2$C$_6$H$_3$MgBr was added to PCl$_3$ and the resulting solution was refluxed for one hour. Three fractions were collected by vacuum distillation of the resulting reaction mixture. The fractions were characterized by $^{31}$P($^1$H) nmr spectroscopy and the assignments were based on the known chemical shifts of phenylphosphine chlorides (Table 16). The first fraction (1.53g) displayed peaks at 136.3, 144.0 and 149.9 ppm which are assigned to 3,5-(CF$_3$)$_2$C$_6$H$_3$PBr$_2$,
Table 16. $^{31}P(\text{H})$ NMR Data for Chlorophosphines

<table>
<thead>
<tr>
<th>Phosphine&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$\delta$&lt;sup&gt;P&lt;/sup&gt;</th>
<th>Phosphine&lt;sup&gt;b&lt;/sup&gt;</th>
<th>$\delta$&lt;sup&gt;P&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(C$_6$H$_5$)Cl$_2$</td>
<td>162.0</td>
<td>P[3,5-(CF$_3$)$_2$C$_6$H$_3$]Cl$_2$</td>
<td>149.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P[3,5-(CF$_3$)$_2$C$_6$H$_3$]BrCl</td>
<td>144.0</td>
</tr>
<tr>
<td>P(C$_6$H$_5$)Br$_2$</td>
<td>152.0</td>
<td>P[3,5-(CF$_3$)$_2$C$_6$H$_3$]Br$_2$</td>
<td>136.3</td>
</tr>
<tr>
<td>P(C$_6$H$_5$)$_2$Cl</td>
<td>80.5</td>
<td>P[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_2$PCl</td>
<td>56.6</td>
</tr>
<tr>
<td>P(C$_6$H$_5$)$_3$</td>
<td>-5.9</td>
<td>P[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_3$</td>
<td>-6.0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Ref. 108.

<sup>b</sup> Solvent: Et$_2$O/CD$_3$Cl.
3,5-(CF3)2C6H3PBrCl and 3,5-(CF3)2C6H3PCl2, respectively. The second fraction (5.50g) displayed a peak at 56.6 ppm which is assigned to [3,5-(CF3)2C6H3]2PCl and the third fraction displayed a peak at -6.0 ppm which is assigned to the tertiary phosphine, [3,5-(CF3)2C6H3]3P. The tertiary phosphine was further characterized by 1H nmr and infrared spectroscopies (Table 17) and 13C(1H) nmr spectroscopy (Table 18). The 13C(1H) nmr spectrum is shown in Figure 33. The quartet due to the equivalent carbon atoms of the CF3 groups is located in the phenyl region of the 13C(1H) nmr spectrum (124.1 ppm, 1J(C-F) = 272 Hz). A quartet of doublets is observed at 132.0 ppm which is assigned to the meta carbon atoms of the phenyl rings which are split into a quartet by the fluorines of the CF3 groups (1J(C-F) = 33 Hz) and into doublets by phosphorus (3J(C-P) = 6.6 Hz). The carbon atoms directly bound to phosphorus are split into a doublet (1J(C-P) = 18 Hz) centered at 139.7 ppm. The ortho carbons are also split into a doublet (2J(C-P) = 21 Hz) centered at 135.2 ppm and the para carbon atoms appear as a singlet at 124.7 ppm.

In order to improve the yield of 3,5-bis(trifluoromethyl)-phenylphosphonous dichloride, [3,5-(CF3)2C6H3]PCl2, a second procedure was attempted based on the synthesis of t-butylphosphonous dichloride. In this procedure, a dilute Grignard solution of 3,5-(CF3)2C6H3MgBr is added to a dilute solution of PCl3 at -63°C. The primary product of this reaction was bis[3,5-bis(trifluoromethyl)-phenyl]phosphinous chloride; a small amount of the tertiary phosphine was also formed. Unfortunately, the 3,5-bis(trifluoromethyl)-phenylphosphonous dichloride was not produced by this method. Since
Table 17. Proton NMR and Diagnostic Infrared Data for Chlorophosphines

<table>
<thead>
<tr>
<th>Chlorophosphine</th>
<th>$^1$H (ppm)</th>
<th>IR (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[3,5-(CF_3)_2C_6H_3]_3P$(^a)</td>
<td>8.20 (m)</td>
<td>1621 (C=C) 1100 (CF$_3$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[3,5-(CF_3)_2C_6H_3]_2PH$(^a)</td>
<td>5.81 (d) 1H</td>
<td>2301 (P-H)</td>
</tr>
<tr>
<td></td>
<td>8.33 (d) 4H</td>
<td>1615 (C=C) 1140 (CF$_3$)</td>
</tr>
<tr>
<td></td>
<td>J(H-H) = 6.2 Hz</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.05 s 2H</td>
<td></td>
</tr>
<tr>
<td>$[3,5-(CF_3)_2C_6H_3]_2P(CH_2)_3Cl$(^b)</td>
<td>7.90 (m) 6H</td>
<td>1610 (C=C)</td>
</tr>
<tr>
<td></td>
<td>3.65 (t) 1H</td>
<td>1120 (CF$_3$)</td>
</tr>
<tr>
<td></td>
<td>J(H-H) = 6.2 Hz</td>
<td>661 (C-Cl)</td>
</tr>
<tr>
<td></td>
<td>2.34 (m) 4H</td>
<td></td>
</tr>
</tbody>
</table>

m = multiplet, s = singlet, d = doublet, t = triplet.

a) (CD$_3$)$_2$CO solvent.

b) CD$_2$Cl$_2$ solvent.
Figure 33. 250 MHz $^{13}\text{C}(^1\text{H})$ nmr spectrum of [3,5-$(\text{CF}_3)\text{C}_6\text{H}_3]_3\text{P}$ in d$_6$-acetone.
significant yields of 3,5-bis(trifluoromethyl)phenylphosphonous dichloride were not produced in either procedure, the desired primary phosphine could not be synthesized.

Since good yields of the bis[3,5-bis(trifluoromethyl)phenyl]-phosphinous chloride were synthesized, the secondary phosphine was prepared by the reduction of [3,5-(CF₃)₂C₆H₃]₂PCl with LiAlH₄ to yield bis[3,5-bis(trifluoromethyl)phenyl]phosphine, [3,5-(CF₃)₂C₆H₃]₂PH (Equation 54). This phosphine has a ³¹P nmr chemical shift of -42.3 ppm and a phosphorus-hydrogen coupling constant of 230 Hz (Table 6). The phosphine has also been characterized by ¹H and ¹³C(¹H) nmr spectroscopy and infrared spectroscopy. The data are compiled in Tables 17 and 18.

The 3-chloropropylphosphine intermediate, [3,5-(CF₃)₂C₆H₃]₂-PCH₂CH₂CH₂Cl, was prepared according to Equation 36 by use of a procedure similar to the method used to prepare (p-CF₃C₆H₄)₂-PCH₂CH₂CH₂Cl. The product was not obtained in high-yield, and an uncharacterized solid was formed in addition to the expected product. Once again, a side reaction involving the CF₃ group may be reducing the yield of the desired product. The 3-chloropropylphosphine, [3,5-(CF₃)₂C₆H₃]₂PCH₂CH₂CH₂Cl, has a ³¹P(¹H) nmr chemical shift of -14.4 ppm (Table 6). It has also been characterized by ¹H nmr and infrared spectroscopies (Table 17) and ¹³C(¹H) nmr spectroscopy (Table 18). An attempt to prepare the chelating triphosphine ligand, C₆H₅P(CH₂CH₂CH₂P[3,5-(CF₃)₂C₆H₃]₂)₂, by reacting
Table 18. $^{13}\text{C}^{1}\text{H}$ NMR Data for $[3,5-(\text{CF}_3)2\text{C}_6\text{H}_3]_3\text{P}$, $[3,5-(\text{CF}_3)2\text{C}_6\text{H}_3]_2\text{PH}$ and $[3,5-(\text{CF}_3)2\text{C}_6\text{H}_3]_2\text{P(CH}_2)_3\text{C}_1$

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>$3,5-(\text{CF}_3)2\text{C}_6\text{H}_3$-</th>
<th>Methylene-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[3,5-(\text{CF}_3)2\text{C}_6\text{H}_3]_3\text{P}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C</td>
<td>139.7 d (18)</td>
<td>P-C</td>
</tr>
<tr>
<td>o-C</td>
<td>135.2 d (21)</td>
<td>-C-</td>
</tr>
<tr>
<td>m-C</td>
<td>132.7 qd (33, 6.6)$^a$</td>
<td>m-C</td>
</tr>
<tr>
<td>p-C</td>
<td>124.7 s</td>
<td>p-C</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>124.1 q (272)</td>
<td>CF$_3$</td>
</tr>
<tr>
<td>$[3,5-(\text{CF}_3)2\text{C}_6\text{H}_3]_2\text{PH}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C</td>
<td>138.6 d (17)</td>
<td></td>
</tr>
<tr>
<td>o-C</td>
<td>134.9 d (17)</td>
<td></td>
</tr>
<tr>
<td>m-C</td>
<td>132.0 qd (33, 5.5)$^a$</td>
<td></td>
</tr>
<tr>
<td>p-C</td>
<td>123.4 s</td>
<td></td>
</tr>
<tr>
<td>CF$_3$</td>
<td>123.9 q (272)</td>
<td></td>
</tr>
<tr>
<td>$[3,5-(\text{CF}_3)2\text{C}_6\text{H}_3]_2\text{P(CH}_2)_3\text{C}_1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C</td>
<td>141.5 d (21)</td>
<td>P-C</td>
</tr>
<tr>
<td>o-C</td>
<td>133.6 d (18)</td>
<td>-C-</td>
</tr>
<tr>
<td>m-C</td>
<td>132.9 qd (33, 6.4)$^a$</td>
<td>C-Cl</td>
</tr>
<tr>
<td>p-C</td>
<td>124.3 (m)</td>
<td></td>
</tr>
<tr>
<td>CF$_3$</td>
<td>124.1 q (273)</td>
<td></td>
</tr>
</tbody>
</table>

d = doublet, m = multiplet, q = quartet, qd = quartet of doublets
s = singlet. Chemical shifts are in ppm, coupling constants (in parentheses) are in Hz. Solvent: (CD$_3$)$_2$CO.

a) Coupling constants are $^2J(C-F)$, $^3J(C-P)$. 
[3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl with Li<sub>2</sub>PC<sub>6</sub>H<sub>5</sub> was unsuccessful, probably due to reactions of the CF<sub>3</sub> group with the lithium phosphide. The only characterized product obtained from the reaction mixture was the starting material, [3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl.

D. Generality of the Procedure to Prepare 3-Chloropropylphosphines

The observation that the new method, which has been developed for the syntheses of 3-chloropropylphosphines (Equations 36, 37 and 38), works for some primary and secondary phosphines, but not others, is interesting. The primary driving force behind these reactions appears to be the ease with which the primary or secondary phosphines are deprotonated. Unfortunately, pKa data are not available for primary or secondary phosphines. By analogy to amines, it can be stated that phosphines bound to aryl groups are less basic; hence, they are more easily deprotonated, than phosphines bound to alkyl groups. This may explain the ease with which phenylphosphines and substituted phenylphosphines react with LDA, whereas cyclohexylphosphines and diisopropylphosphine react with LDA with difficulty. However, diethylphosphine appears to be an exception based on its pKa, because it does react with LDA to form (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>Cl. Thus, a more inclusive rule for predicting phosphine reactivity with LDA would be useful to make the predictions of reactivity more general.

Reactions mechanisms involving phosphines and metal-phosphine complexes are often interpreted on the basis of the steric and electronic properties of the phosphines. Tolman's cone angle, θ, and substituent contribution χ<sub>i</sub>, (where χ<sub>i</sub> is additive and χ<sub>t-Bu</sub> = 0 for t-Bu) are measures of the steric and electronic (σ-donor and π-donor
or π-acceptor) properties of phosphines. The author has made an attempt to correlate the cone angle and substituent contribution of phosphines to the ability of the primary or secondary phosphines to react with LDA in the presence of Br(CH₂)₃Cl to form the 3-chloropropylphosphines.

A comparison of the reactions attempted (Equations 36, 37 and 38) with the electronic and steric properties of the primary and secondary phosphines, compiled in Table 19, suggests that successful reactions between phosphines and LDA are favored when the sum of the substituent contributions, Σ_iX_i, is large. Cyclohexylphosphine, has a net substituent contribution (Σ_iX_i = 16.7) similar to the net substituent contribution (Σ_iX_i = 16.9) of diphenylphosphine; like diphenylphosphine, it reacts with one equivalent of LDA to give C₆H₁₁(H)PCH₂CH₂CH₂Cl. However, cyclohexylphosphine fails to react with two equivalents of LDA, perhaps because its net substituent contribution is too small for the substitution of both P-H bonds. In contrast, phenylphosphine, which has a larger net substituent contribution (Σ_iX_i = 20.9) than cyclohexylphosphine, reacts rapidly with two equivalents of LDA.

Despite its small net substituent contribution (Σ_iX_i = 11.9), diethylphosphine reacts with LDA and Br(CH₂)₃Cl to form (CH₃CH₂)₂P(CH₂)₃Cl. Thus, the reactions of phosphines with LDA in the presence of Br(CH₂)₃Cl must also be controlled by steric factors.
Table 19. A Survey of the Reactions Used to Generate 3-Chloropropylphosphines

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>Cone &lt;</th>
<th>$\sum \chi_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_5PH_2$</td>
<td></td>
<td>Yes</td>
<td>Yes</td>
<td>101</td>
<td>20.9</td>
</tr>
<tr>
<td>$C_6H_{11}PH_2$</td>
<td></td>
<td>N.R.</td>
<td>Yes</td>
<td>115$^a$</td>
<td>16.7</td>
</tr>
<tr>
<td>$(C_6H_5)_2PH$</td>
<td>Yes</td>
<td>-</td>
<td>-</td>
<td>128</td>
<td>16.9</td>
</tr>
<tr>
<td>$(p-CF_3C_6H_4)_2PH$</td>
<td>Yes</td>
<td>-</td>
<td>-</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>$[3,5-(CF_3)_2C_6H_3]_2PH$</td>
<td>Yes</td>
<td>-</td>
<td>-</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>$(CH_3CH_2)_2PH$</td>
<td>Yes</td>
<td>-</td>
<td>-</td>
<td>117$^a$</td>
<td>11.9</td>
</tr>
<tr>
<td>$[(CH_3)_2CH]_2PH$</td>
<td>N.R.</td>
<td>-</td>
<td>-</td>
<td>136$^a$</td>
<td>10.3</td>
</tr>
<tr>
<td>$(C_6H_{11})_2PH$</td>
<td>N.R.</td>
<td>-</td>
<td>-</td>
<td>142$^a$</td>
<td>8.5</td>
</tr>
</tbody>
</table>

N.R. = no reaction, N.A. = not available

a) These cone angles are approximated using the equation

$$\theta = (2/3)\Sigma(\theta_i/2).^{109}$$
The cone angle of diethylphosphine ($\Theta = 117^\circ, \Sigma_1 \chi_1 = 11.9$) is much smaller than diisopropylphosphine ($\Theta = 136^\circ, \Sigma_1 \chi_1 = 10.3$) and dicyclohexylphosphine ($\Theta = 142^\circ, \Sigma_1 \chi_1 = 8.5$), which have similar net substituent contributions but fail to react with LDA. The small size of diethylphosphine may explain the ease with which it reacts with LDA. The remaining phosphines, which do react with LDA, also have relatively small cone angles ($101-128^\circ$). The new phosphines, which have phenyl rings substituted with CF$_3$ groups, should possess cone angles similar to diphenylphosphine since the CF$_3$ groups are removed from the area of the phosphorus atom (meta and para positions of the phenyl rings). In conclusion, reactions of primary and secondary phosphines with LDA appear to be favored when the net substituent contributions of the phosphines are large and the cone angles are small.

E. Synthesis of Platinum Complexes of CF$_3$PPH and CF$_3$ttp

In order to investigate the physical properties of metal-complexes coordinated to the new chelating phosphine ligands that contain bis(4-trifluorormethylphenyl)phosphine groups, (p-CF$_3$C$_6$H$_4$)$_2$P-, platinum complexes of CF$_3$PPH and CF$_3$ttp were prepared (VI, VII). The platinum complex of CF$_3$PPH, PtCl$_2$(CF$_3$PPH), was prepared from

VI \quad VII
PtCl$_2$COD$^{92}$ (Eq. 55) using a procedure similar to the method used to prepare PtCl$_2$(PPH) (PPH = (C$_6$H$_5$)CH$_2$CH$_2$CH$_2$P(H)C$_6$H$_5$) and PtCl$_2$(cyPPH) (cyPPH = (C$_6$H$_{11}$)$_2$PCH$_2$CH$_2$CH$_2$P(H)C$_6$H$_5$). The infrared spectrum of PtCl$_2$(CF$_3$PPH) is shown in Figure 34. The $^{31}$P($^1$H) nmr spectrum of PtCl$_2$(CF$_3$PPH) is a first-order AB spin system, and it consists of two doublets with the corresponding $^{195}$Pt satellites (Figure 35). In order to evaluate the inductive effect of the (p-CF$_3$C$_6$H$_4$)$_2$P- groups, the $^{31}$P nmr data obtained for PtCl$_2$(CF$_3$PPH) are compared to the data obtained by Waid$^{110}$ for PtCl$_2$(PPH) and PtCl$_2$(cyPPH). The data are summarized in Table 20. The $^{31}$P chemical shift of the (p-CF$_3$C$_6$H$_4$)$_2$P-group (-5.2 ppm) shifts to slightly higher field than the (C$_6$H$_5$)$_2$P-group (-5.7 ppm) of PtCl$_2$(PPH) due to the increased deshielding of the phosphorus nucleus from the inductive effect of the more electronegative p-CF$_3$C$_6$H$_4$- groups. However, the effect is minimal. The inductive effect of the p-CF$_3$C$_6$H$_4$- groups is also observed in the one-bond coupling constant, $^1$J(Pt-P2), which is slightly larger for the (p-CF$_3$C$_6$H$_4$)$_2$P- group of PtCl$_2$(CF$_3$PPH) ($^1$J(Pt-P2) = 3422 Hz) than for the (C$_6$H$_5$)$_2$P- group of PtCl$_2$(PPH) ($^1$J(Pt-P2) = 3403 Hz). However, the effect is not as dramatic as the difference in $^1$J(Pt-P2) between PtCl$_2$(cyPPH) ($^1$J(Pt-P2) = 3303 Hz) and PtCl$_2$(PPH) ($^1$J(Pt-P2) = 3403 Hz). It was thought that the CF$_3$ substituted groups on the CF$_3$PPH ligand would convey increased solubility on the resultant metal complexes, compared to the PPH analogs. However, the solubility of PtCl$_2$(CF$_3$PPH) and PtCl$_2$(PPH) in organic solvents appear to be similar.
Figure 34. The infrared spectrum of PtCl$_2$(CF$_3$PPH). (Nujol mull).
Figure 35. 250 MHz $^{31}\text{P}^{(1}\text{H})$ nmr spectrum of PtCl$_2$(CF$_3$PPH) in d$_6$-acetone.
Table 20. $^{31}$P NMR Data for PtCl$_2$(L-L') Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta$P$_1$</th>
<th>$\delta$P$_2$</th>
<th>$^1$J(Pt-P$_1$)</th>
<th>$^1$J(Pt-P$_2$)</th>
<th>$^1$J(P$_1$-H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtCl$_2$(CF$_3$PPH)$^a$</td>
<td>-29.0</td>
<td>-5.2</td>
<td>3199</td>
<td>3422</td>
<td>480</td>
</tr>
<tr>
<td>PtCl$_2$(PPH)$^b$</td>
<td>-28.8</td>
<td>-5.7</td>
<td>3256</td>
<td>3403</td>
<td>460</td>
</tr>
<tr>
<td>PtCl$_2$(cyPPH)$^c$</td>
<td>-28.8</td>
<td>7.5</td>
<td>3390</td>
<td>3303</td>
<td>430</td>
</tr>
</tbody>
</table>

Chemical shifts are in ppm, coupling constants are in Hz. The HPPh groups are labeled P1, The R$_2$P groups are labeled P2.

a) Solvent = (CD$_3$)$_2$CO.

b) Solvent not reported, PPH = C$_6$H$_5$(H)P(CH$_2$)$_3$P(C$_6$H$_5$)$_2$.

c) Solvent = CH$_2$Cl$_2$, cyPPH = C$_6$H$_5$(H)P(CH$_2$)$_3$P(C$_6$H$_{11}$)$_2$. 
The platinum complex of the triphosphine ligand CF₃ttp,

\[ \text{[PtCl(CF₃ttp)]Cl} \]

was prepared also from PtCl₂COD (Eq. 56) by use of a procedure similar to the method used by Tau¹¹¹ for the synthesis of

\[ \text{PtCl₂COD + CF₃ttp} \rightarrow \text{[PtCl(CF₃ttp)]Cl + COD} \quad (56) \]

\[ \text{[PtCl(ttp)]Cl} \]. The infrared spectrum is shown in Figure 36. The ³¹P(¹H) nmr spectrum of [PtCl(CF₃ttp)]Cl is a first-order A₂B spin system, and it consists of a triplet and the corresponding ¹⁹⁵Pt satellites and a doublet and the corresponding ¹⁹⁵Pt satellites (Figure 37). The data are compiled in Table 21, and the data obtained by Tau¹¹¹ for [PtCl(ttp)]Cl and Yang¹¹² for [PtCl(cyttpp)]Cl have been included for comparison. Once again, the ³¹P chemical shift of the (p-CF₃C₆H₄)₂P- groups (-2.8 ppm) is slightly downfield from the chemical shift of the (C₆H₅)₂P- groups (-3.9 ppm) of [PtCl(ttp)]Cl due to the electron-withdrawing effect of the p-CF₃C₆H₄- groups. In addition, the ¹J(Pt-P2) coupling constant for [PtCl(CF₃ttp)]Cl (¹J(Pt-P2) = 2264 Hz) is larger than the same coupling constant for [PtCl(ttp)]Cl (¹J(Pt-P2) = 2229 Hz). However, like PtCl₂(CF₃PPH), the difference between the ¹J(Pt-P2) coupling constants of [PtCl(CF₃ttp)]Cl and [PtCl(ttp)]Cl is not as dramatic as the difference between [PtCl(ttp)]Cl (¹J(Pt-P2) = 2229 Hz) and [PtCl(cyttpp)]Cl (¹J(Pt-P2) = 2016 Hz).

The CF₃ groups on the phenyl rings of CF₃ttp do not markedly increase the solubility of the metal complex, [PtCl(CF₃ttp)]Cl. The complex is slightly soluble in nitromethane and it is insoluble in all other common solvents.
Figure 36. The infrared spectrum of [PtCl(CF₃ttp)]Cl. (Nujol mull).
Figure 37. 250 MHz $^{31}$P($^1$H) nmr spectrum of [PtCl(CF$_3$ttp)]Cl in CD$_3$NO$_2$. 
Table 21. $^{31}\{}^1\text{H}\text{)}$ NMR Data for [PtCl(L-L'-L)]Cl Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta P_1$</th>
<th>$\delta P_2$</th>
<th>$^1J(Pt-P_1)$</th>
<th>$^1J(Pt-P_2)$</th>
<th>$^2J(P_1-P_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PtCl(CF$_2$ttt)]Cl$^a$</td>
<td>-20.9</td>
<td>-2.8</td>
<td>3025</td>
<td>2264</td>
<td>27</td>
</tr>
<tr>
<td>[PtCl(ttt)]Cl$^a$</td>
<td>-20.7</td>
<td>-3.9</td>
<td>3134</td>
<td>2229</td>
<td>27</td>
</tr>
<tr>
<td>[PtCl(cyttoo)]Cl$^{b,c}$</td>
<td>-14.5</td>
<td>1.8</td>
<td>3234</td>
<td>2106</td>
<td>24</td>
</tr>
</tbody>
</table>

Chemical shifts are in ppm, coupling constants are in Hz. The terminal phosphorus atoms are labeled P2, the central phosphorus atoms are labeled P1.

a) Solvent = CD$_3$NO$_2$.

b) Ref 112.

c) Solvent was not reported.
Although the p-CF₃ group does impart electron-withdrawing character to the \((p\text{-CF}_3\text{C}_6\text{H}_4)_2\text{P}\) groups of the CF₃PPH and CF₃ttp ligands, the effect is very (disappointingly) small. In addition, the CF₃ group on the phenyl rings does not impart increased solubility to the platinum complexes of CF₃PPH and CF₃ttp, relative to the platinum complexes of PPH and ttp. Therefore, the CF₃ group on the phenyl rings of CF₃PPH and CF₃ttp does not impart properties to these ligands that are significantly different from PPH and ttp.
CHAPTER VI

Synthesis, Characterization and Reactivity of
Group VIII Metal Alkoxide and Hydroxide Complexes

Introduction

Although extensive work has been published on alkoxide derivatives of early and inner transition metals and of main group metals, until recently, relatively few investigations of group VIII metal-alkoxide and hydroxide complexes have been undertaken. In fact, this topic has been reviewed in the literature only once. However, current interest in second and third row group VIII metal complexes is increasing rapidly and numerous papers on this topic have been published during the past two years.

The focus of this investigation is the chemistry of mononuclear platinum, rhodium and iridium triphosphine complexes incorporating alkoxide and hydroxide ligands, \([\text{M(OR)P}_3]^n+\) \((\text{P}_3 = \text{ttp or cyttp, } n = 0, 1)\). In order to illustrate the importance of group VIII metal-alkoxide and hydroxide complexes, a brief review of the reported complexes, the synthetic procedures used to prepare these complexes and the catalytic activity of platinum, rhodium and iridium alkoxide and hydroxide complexes will be presented.
A. Group VIII Metal Alkoxide and Hydroxide Complexes

The group VIII metal alkoxide and hydroxide complexes which have been investigated most comprehensively are the methoxide and hydroxide complexes of platinum(II). The monomeric platinum(II) complexes reported in the literature have the general formula \( \text{Pt} \left( \text{OR} \right) \left( \text{R}' \right) \text{L}_2 \) where OR is OH or OCH\(_3\), R' is an alkyl, aryl or hydride group, L is a monodentate phosphine ligand; and in some cases, L\(_2\) is a bidentate phosphine ligand.\(^{47,57,61,62,117-125}\) These complexes exhibit interesting chemistry, which includes condensation reactions with organic acids,\(^{117-120,122}\) and insertion reactions with small molecules, such as: CO\(^{120,125}\) (Scheme 9), SO\(_2\), COS, CS\(_2\)\(^{120}\) (Scheme 10) and isocyanides\(^{121}\) (Scheme 11). One of the most exciting discoveries in this area of chemistry was the insertion of tetrafluoroethylene into a Pt-OR bond, which was recently reported by Bryndza.\(^{123,124}\) The platinum complex, \( \text{Pt} \left( \text{OCH}_3 \right) \left( \text{CH}_3 \right) \text{dppe} \) (dppe = 1,2-bis(diphenylphosphino)ethane), was reacted with CF\(_2\)CF\(_2\) (2 atm) in THF at 25°C for four hours to yield \( \text{Pt} \left( \text{CF}_2\text{CF}_2\text{OCH}_3 \right) \left( \text{CH}_3 \right) \text{dppe} \) in quantitative yield. It was determined that coordination of CF\(_2\)CF\(_2\) to the metal center preceded the insertion reaction and that the methoxide group did not dissociate from the metal center. Bryndza also noted that the insertion reaction occurred at least three orders of magnitude faster than the comparable insertion into a metal-carbon bond.

A particularly interesting series of \( \text{Pt} \left( \text{OR} \right) \left( \text{R}' \right) \text{L}_2 \) complexes are the Pt(II)-cyclohexenyl complexes, \( \text{Pt} \left( \text{C}_6\text{H}_9 \right) \left( \text{OR} \right) \text{dppe} \).\(^{126-129}\) These complexes are prepared by the reaction of \( \text{(C}_6\text{H}_8)\text{Ptdppe} \) with \( \text{H}_2\text{O} \) or
Scheme 9

Scheme 10
\[
\text{Pt} - \text{OCH}_3 \quad \xrightarrow{\text{CNR}} \quad \text{Pt} - \text{OCH}_3
\]

\[
\text{Pt} - \text{OH} \quad \xrightarrow{\text{CNR}} \quad \text{Pt} - \text{HN}=\text{O}
\]

\[R = \text{CF}_3, \text{CH}_2\text{CN}; \quad \text{P} - \text{P} = \text{c-Ph}_2\text{PCH-CHPPh}_2\]

\[R = \text{methyl, p-methoxyphenyl, 2,6-dimethylphenyl group}\]

Scheme 11
CH$_3$OH (Eq. 57) and insert CO to give hydroxy- and methoxycarbonyl complexes.

\[
(C_6H_8)Pt(dppe + ROH \rightarrow (C_6H_9)Pt(OR)dppe \quad (57)
\]

Platinum(II) complexes incorporating two methoxide ligands, Pt(OCH$_3$)$_2$dppe have also been reported. These complexes are capable of inserting two molecules of CO to give Pt(CO$_2$CH$_3$)$_2$dppe.

Several binuclear platinum(II) hydroxide and methoxide complexes have been prepared. These complexes incorporate bridging hydroxide and alkoxide ligands that are less reactive than the singly bound OR ligands. Relatively few investigations of palladium alkoxide and hydroxide complexes have been undertaken. The palladium complexes reported include monomeric species as well as alkoxide and hydroxide bridged dimers.

In contrast to the chemistry of platinum, rhodium(I) hydroxide and alkoxide chemistry is dominated by binuclear complexes bridged by alkoxide and hydroxide ligands. The first mononuclear complex, Rh(OPh)(PPh$_3$)$_3$, was reported in 1968. It was prepared by the reaction of PhOH with Rh(R)(PPh$_3$)$_3$ (R = Me, Ph) (Eq. 58), and was reported to undergo facile loss of one PPh$_3$ ligand to form

\[
Rh(R)(PPh$_3$)$_3$ + PhOH \rightarrow Rh(OPh)(PPh$_3$)$_3$ + RH \quad (58)
\]

Rh(OPh)(PPh$_3$)$_2$. Unfortunately, the details of the synthesis and characterization of these compounds are vague. The complexes were reported again in 1976, along with the $\eta^6$-Ph0 analogs, Rh($\eta^6$-PhO)(PPh$_3$)$_2$.PhOH.0.5C$_6$H$_5$Me and Rh($\eta^6$-PhO)(PPh$_3$)$_2$.3PhOH.C$_6$H$_5$Me.
Once again, experimental details are vague and further reaction chemistry was not mentioned. The hydroxide and phenoxide complexes of rhodium and iridium, $M(OR)(CO)(PPh_3)_2$, have been prepared by the reaction of $M'OR$ ($M' = Li, Na$ or $K$) with $trans$-$MF(CO)(PPh_3)_2$ (Eq. 59), however the data for the characterization of these complexes were not given. In a later communication, the hydroxide complexes, $M(OH)(CO)(PPh_3)_2$ ($M = Rh, Ir$), were reported to insert $CO_2$ and $COS$ to give $M(OCO_2H)(CO)(PPh_3)_2$ and $M(OCOSH)(CO)(PPh_3)_2$, respectively.

The alkoxide and hydroxide chemistry of iridium(I) has shown tremendous growth during the past two years. The bulk of the work has been conducted by Atwood and co-workers on $Ir(OR)(CO)(PPh_3)_2$ complexes ($OR = OH, OMe, n$-$PrO, i$-$PrO, OPh, t$-$BuO$ and $C_6F_5O$). These complexes, with the exception of $Ir(OC_6F_5)(CO)(PPh_3)_2$, react with $CO$ to form the alkoxycarbonyl complexes, $Ir(C(0)OR)(CO)_2(PPh_3)_2$. Initially, $CO$ adds associatively to the iridium(I) center, using a mechanism similar to that of platinum(II) complexes; however, these systems show dissociation of the $OR^-$ group to give $Ir(CO)_3(PPh_3)_2^{+OR^−}$ intermediates. The proven mechanism is depicted in Equations 60-62.
When the OR group contains β-hydrogens (OR = OMe, i-PrO and n-PrO), the Ir(OR)(CO)(PPh\(_3\))\(_2\) complexes form the hydride complex, Ir(H)(CO)(PPh\(_3\))\(_2\), upon decomposition.\(^{156}\) The decomposition mechanism has not been firmly established; however, complexes containing OR groups which do not contain β-hydrogens (OR = OH, OPh and t-BuO) do not form the hydride complexes. Therefore, decomposition is believed to occur by β-hydrogen elimination from the OR group. The methoxide complex reacts with two equivalents of acetyl chloride to yield Ir(C(O)CH\(_3\))(CO)(PPh\(_3\))\(_2\)Cl\(_2\)^\(^{157}\) and with tetracyanoethylene (TCNE) to yield Ir(OMe)(CO)(PPh\(_3\))\(_2\)(TCNE).^\(^{158}\)

Several additional monomeric Ir(I) complexes have been reported. These include nitrosyl complexes, [Ir(OH)(NO)(PPh\(_3\))\(_2\)]ClO\(_4\), [Ir(OEt)(NO)(AsPh\(_3\))\(_2\)]ClO\(_4\) and [Ir(OEt)(NO)(PPh\(_3\))\(_2\)]X (X = ClO\(_4\), BF\(_4\) and BPh\(_4\)),\(^{159}\) a dioxygen complex Ir(O\(_2\))(OEt)(CO)(PPh\(_3\))\(_2\),\(^{160}\) and a hydridoalkoxyiridium complex, C\(_5\)Me\(_5\)Ir(OEt)(H)PPh\(_3\).\(^{161}\) The hydridoalkoxyiridium complex did not undergo insertion reactions when reacted with ligands L (L = CO, C\(_2\)H\(_4\) and PPh\(_3\)), but rather eliminated EtOH to yield C\(_5\)Me\(_5\)Ir(L)PPh\(_3\). However, the hydridoalkoxyiridium complex was found to insert CO\(_2\) and CS\(_2\) to give C\(_5\)Me\(_5\)Ir(XC(X)OEt)(H)PPh\(_3\) (X = S, O). In addition, the binuclear complexes, Ir\(_2\)(CO)\(_2\)(μ-OH•Cl)(Ph\(_2\)PCH\(_2\)PPh\(_2\))\(_2\) and [Ir\(_2\)(CO)\(_2\)(μ-OH)(Ph\(_2\)PCH\(_2\)PPh\(_2\))\(_2\)]BF\(_4\), have been prepared and their chemistry has been related to a model water-gas shift cycle.\(^{58}\)

The alkoxide and hydroxide complexes of ruthenium and osmium include both mononuclear and polynuclear species. Only a few
mononuclear complexes have been reported. These include the nitrosyl complexes, \([\text{Ru(OH)(NO)}_2(\text{PPh}_3)_2]\text{BF}_4\) and \([\text{Os(OH)(NO)}_2(\text{PPh}_3)_2]\text{BF}_4\),\(^{162}\) hydridohydroxo ruthenium(II) complexes, \(\text{Ru(H)(OH)(PPh}_3)_2(\text{Sol})\) (Sol = H\(_2\)O, THF) and chlorohydroxo ruthenium(II) complexes \(\text{Ru(Cl)(OH)(PPh}_3)_2(\text{Sol})_2\) (Sol = H\(_2\)O, THF).\(^{42}\) Binuclear ruthenium complexes are more prevalent and include complexes containing a single hydroxide bridge, for example, \(\text{Ru}_2(\mu-\text{H})(\mu-\text{OH})(\text{PMMe}_3)_6\),\(^{163}\) complexes bridged by two hydroxide ligands, \((\text{Rh}(\mu-\text{OH})(\text{OH})(\text{PMMe}_3)_3)_2\),\(^{163}\) and \((\text{Ru}(\mu-\text{OH})(\text{H})(\text{PPh}_3)_2(\text{Sol}))_2\),\(^{42}\) and complexes bridged by three hydroxide or methoxide ligands, \([\eta^6-\text{C}_6\text{H}_6]\text{Rh}(\mu-\text{OH})_3\text{Ru}(\eta^6-\text{C}_6\text{H}_6)]\text{BPh}_4\)\(^{164}\) and \([(\eta^6-\text{C}_6\text{H}_6)]\text{Ru}(\mu-\text{OMe})_3\text{Ru}(\eta^6-\text{C}_6\text{H}_6)]\text{BPh}_4\).\(^{165}\) Several polynuclear hydroxide and methoxide ruthenium and osmium complexes in which the OR groups bridge two metal centers have also been reported.\(^{166-168}\)

B. Preparation of Group VIII Metal Alkoxide and Hydroxide Complexes

Synthesis of second and third row group VIII metal alkoxide or hydroxide complexes involves five general procedures, although some of the reported complexes have been synthesized by less ubiquitous methods. The five procedures are: (1) displacement of a chloride ion by OR\(^-\); (2) other types of substitution reactions; (3) hydrolysis and alkoxide exchange reactions; (4) addition of O\(_2\) to a metal hydride and (5) \(\beta\)-elimination of an OR\(^-\) group from a metal alkylalkoxide.

The displacement of chloride ion by OR\(^-\) is the most common synthetic procedure for preparing metal hydroxide and alkoxide complexes. Examples of this type of reaction can be found for most of the group VIII metals (Eqs. 63 to 66).\(^{42,152,142,117}\) Often, a
\[
\text{RuHCl(PPh}_3\text{)}_3 + \text{NaOH} \rightarrow \text{RuH(OH)(PPh}_3\text{)}_2(\text{H}_2\text{O}) + \text{NaCl} \quad (63)
\]

\[
\text{trans-IrCl(CO)(PPh}_3\text{)}_2 + \text{NaOMe} \rightarrow \text{trans-Ir(OMe)(CO)(PPh}_3\text{)}_2 + \text{NaCl} \quad (64)
\]

\[
\text{(C}_5\text{Me}_5\text{)Rh}_2\text{Cl}_2 + 3\text{NaOH} \rightarrow [(\text{C}_5\text{Me}_5\text{)Rh(μ-OH)}_3\text{]}\text{BPh}_4\text{2} \quad (65)
\]

\[
\text{cis-PtCl(C}_6\text{F}_5\text{)(PPh}_3\text{)}_2 + \text{NaOMe} \rightarrow \text{cis-Pt(OMe)(C}_6\text{F}_5\text{)(PPh}_3\text{)}_2 \quad (66)
\]

chloride abstractor is necessary to promote substitution by OR\(^{-}\).

Silver salts are commonly employed as the abstractor (Eqs. 67 and 68; Sol = Solvent).

\[
\text{PtCl(CH}_3\text{)dppe + AgBF}_4 \rightarrow \text{Pt(CH}_3\text{)(Sol)dppe}^+ \\
\text{Pt(CH}_3\text{)(Sol)dppe}^+ + \text{NaOH} \rightarrow \text{Pt(OH)(CH}_3\text{)dppe} \quad (67)
\]

\[
\text{IrCl}_2(\text{NO})(\text{PPh}_3\text{)}_2 + 2\text{AgClO}_4 + \text{ROH} \rightarrow [\text{Ir(OR)(NO)(PPh}_3\text{)}_2]\text{ClO}_4 \quad (68)
\]

Substitution reactions in which OR\(^{-}\) replaces a ligand other than Cl\(^{-}\)
are rare, but examples can be found (Eqs. 59, 69 and 70).

\[
\{(\text{η}^6-\text{C}_6\text{H}_6\text{)}_2\text{Ru}_2(μ-\text{OH})_3\text{]}\text{BPh}_4 + \text{ROH} \rightarrow \{(\text{η}^6-\text{C}_6\text{H}_6\text{)}_2\text{Ru}_2(μ-\text{OR})_3\}\text{BPh}_4 \quad (69)
\]

\[
[\text{Ir(CO)(CH}_3\text{CN)(PPh}_3\text{)}_2]^+ + \text{OH}^- \rightarrow \text{Ir(OH)(CO)(PPh}_3\text{)}_2 \quad (70)
\]

Metal hydroxide complexes are often prepared by simple hydrolysis reactions (Eqs. 71 and 72).

\[
\text{Os}_3(\text{CO})_{12} + \text{H}_2\text{O} \rightarrow \text{Os}_3(\text{CO})_{10}\text{H(OH)} + \text{other compounds} \quad (71)
\]

\[
[[\text{C}_5\text{Me}_5\text{Ir}_2(μ-\text{OC(O)CH}_3)_2(μ-\text{H})]]\text{PF}_6 + \text{H}_2\text{O} \rightarrow \\
[[\text{C}_5\text{Me}_5\text{Ir}_2(μ-\text{OC(O)CH}_3)(μ-\text{OH})(μ-\text{H})]]\text{PF}_6 \quad (72)
\]

hydroxide complexes were discovered unintentionally. Many metal
hydroxides were prepared during attempts to prepare alkoxide compounds due to facile hydrolysis of many metal alkoxides (Eqs. 73 and 74). Reactions in which an alkoxide complex is formed from a hydroxide complex (Eq. 75) or another alkoxide complex in the presence of an alcohol are also known. (Eq. 76)

$$\text{cis-Pt(C(Cl)-CCl}_2)(\text{OMe})(\text{PPh}_3)_2 + \text{H}_2\text{O} \rightarrow \text{cis-Pt(C(Cl)-CCl}_2)(\text{OH})(\text{PPh}_3)_2$$ (73)

$$\text{trans-IrCl(CO)[P(n-Pr)}_2\text{t-Bu]}_2 + \text{NaO-i-Pr} \rightarrow \text{Ir(OH)(CO)[P(n-Pr)}_2\text{t-Bu]}_2$$ (74)

Addition of oxygen to a metal hydride complex has provided an interesting synthetic route to metal hydroxides. In 1970, Roper reported the first examples of group VIII metal hydroxides prepared by this method (Eqs. 77-79). Roper postulated that the reactions of ruthenium and osmium proceeded via a hydroperoxy species, $[\text{M(OOH)(NO)}_2(\text{PPh}_3)_2]^+$; however, he did not speculate on the mechanism of the iridium reaction, except to state that it must differ from that of ruthenium and osmium due to the occurrence of OPPh3. In 1973, he postulated the following mechanism for the iridium reaction (Scheme
He also suggested that an alternate mechanism involving a hydroperoxid intermediate might be possible, which upon solvolysis with traces of water in the solvent, could yield the requisite cation, together with hydrogen peroxide. The hydrogen peroxide could then oxidize free triphenylphosphine. In 1970, Gillard also reported the use of this synthetic procedure to prepare a rhodium compound, trans-[Rh(en)$_2$(OH)$_2$]$^+$ (en = ethylenediamine) (Eq. 80). He was able to isolate a rhodium hydroperoxo species trans-[Rh(en)$_2$(OH)(OOH)]$^+$. 

$$\text{trans-}[\text{Rh(en)}_2(\text{OH})_2]^+ + \text{O}_2 \rightarrow \text{trans-}[\text{Rh(en)}_2(\text{OH})(\text{OOH})]^+$$ (80)

Alkoxide and hydroxide complexes of group VIII metals can also be prepared by $\beta$-elimination of an OR$^-$ group from a metal alkylalkoxide.
This type of reaction is very interesting because relatively few examples of $\beta$-elimination of groups other than hydrogen are known.\textsuperscript{173-176}

\[
\text{PhCH-CHPh + PdL}_4 \rightarrow \text{PhCH-CHPh} \rightarrow \text{PhCH-CHPh} + L\text{Pd(OCH}_3\text{)Br} \\
\text{Br OCH}_3 \quad L\text{BrPd OCH}_3
\]

\[\text{L} = \text{PPh}_3\]

\[
\text{Pt(PPh}_3\text{)_4 + Br(CH}_2\text{)_3OPh} \rightarrow (\text{Ph}_3\text{P})_2\text{PtBrCH}_2\text{CH}_2\text{OPh} \\
(\text{Ph}_3\text{P})_2\text{PtBr(OPh)} + \text{CH}_2\text{CH}_2
\]

\[\text{(Equations 81 and 82).}\]

C. Catalytic Chemistry of Group VIII Hydroxides

The generally high reactivity of group VIII metal-alkoxide and metal-hydroxide bonds allows for insertion of small molecules into M-OR bonds. In addition, a facile displacement of the OR\textsuperscript{-} group by other ligands often occurs, which in turn can be followed by the possible subsequent attack of free OR\textsuperscript{-} on the coordinated ligand. It is the potent reactivity of the M-OR bond that has made group VIII metal alkoxide and hydroxide complexes attractive for the catalytic generation of numerous organic compounds.

Perhaps the best understood catalytic cycle is the hydration of nitriles to carboxamides by rhodium and platinum hydroxide complexes. Bennett and Yoshida have reported a catalytic hydration of acetonitrile to acetamide employing Pt(C\textsubscript{6}H\textsubscript{9})(OH)dppe (producing 6.8 moles of CH\textsubscript{3}CONH\textsubscript{2} per mole of catalyst in one hour), trans-Ir(OH)(CO)(PPh\textsubscript{3})\textsubscript{2} (producing 25 moles of CH\textsubscript{3}CONH\textsubscript{2} per mole of catalyst in 20 hours), and trans-Rh(OH)(CO)(PPh\textsubscript{3})\textsubscript{2} (producing 150
moles of CH$_3$CONH$_2$ per mole of catalyst in 3 hours) as catalysts. In addition, Pt(C$_6$H$_8$)dppe and Pt(C$_6$H$_8$)(PPh$_3$)$_2$ function as catalysts. The rhodium complex also catalyzed the hydration of phenylacetonitrile, acrylonitrile and crotonitrile to the corresponding carboxamides; however, it was ineffective for benzonitrile. All of the catalytic reactions were carried out in the presence of water. In fact, the presence of water was essential for the Pt-cyclohexyne complexes to act as catalysts. Isolation of the N-amido metal complexes from the catalytic reactions led to the development of the catalytic cycle depicted in Scheme 3 in Chapter IV.

In 1980, Bennett and Appleton published a more extensive investigation of the catalytic hydration of nitriles by platinum hydroxide complexes, Pt(OH)RL$_2$ (R = Me, Ph; L = phosphine ligand). They found that the isolable intermediates in the catalytic hydration of acetonitrile, Pt(NHC$_0$Me)RL$_2$, were also hydration catalysts in the presence of water. In fact, the catalytic activities of Pt(OH)Ph(PEt$_3$)$_2$ and Pt(NHCOMe)Ph(PEt$_3$)$_2$ were identical within experimental error. In addition, they found that catalytic activities were dependent on the phosphine ligands. Phosphine ligands of high basicity and low steric requirements, ie. PEt$_3$, promoted the reaction. The catalytic cycle in Scheme 13 has been proposed. The key step in the cycle is believed to be attack of OH$^-$ on a cationic platinum(II)-nitrile complex to form an imino-enol complex; however, the possibility of R'CN inserting into the Pt-O bond has not been eliminated. The N-carboxamide complex may react directly with water.
to give a hydroxo complex, or with a nitrile to give an ion-paired species, $[\text{Pt}(R)(R'\text{CN})L_2]OH$. These reactions are limited by the insolubility of higher nitriles in water.

It is interesting to note that hydration of acrylamide ($\text{CH}_2=\text{CHCN}$) by Pt(II) hydroxide catalysts, which was developed by Bennett and Appleton, gives a mixture of acrylamide, $\beta$-cyanoethanol and $\beta,\beta$-dicyanoethyl ether. The $\beta$-cyanoethanol arises from addition of water to the double bond of acrylonitrile, and the $\beta,\beta$-dicyanoethyl ether arises from base catalyzed addition of $\beta$-cyanoethanol to acrylonitrile. A catalytic cycle was not proposed.

Platinum(0) hydroxide complexes also catalyze hydration of nitriles to carboxamides, as well as hydration of the double bond in acrylonitrile and crotonitrile ($\text{CH}_3\text{CH}=\text{CHCN}$). These Pt(0) complexes are also efficient catalysts for H-D exchange of activated C-H bonds of organic compounds. The Pt(0) complexes are formed by oxidative-addition of H$_2$O to PtL$_2$ complexes ($L = \text{PPh(t-Bu)}_2$, P(i-
The complex Pt[PPh(t-Bu)$_2$]$_2$ in the presence of H$_2$O and CH$_3$CN at 80°C for 20 hours gave 99 moles of acetamide per mole of catalyst, with recovery of the catalyst. The reaction mechanism shown in Scheme 14 has been proposed. Once again, hydration of nitriles occurs by insertion of RCN into the Pt-OH bond or by nucleophilic attack of OH$^-$ on the coordinated nitrile. In this case, detailed studies of the reaction in solution favor the latter mechanism.$^62$

Formation of $\beta$-hydroxybutyronitrile from CH$_3$C=CHCN can be drastically reduced compared to formation of $\beta$-hydroxypropionitrile from CH$_2$=CHCN, if Pt[PPh(t-Bu)$_2$]$_2$ or Pt[P(i-Pr)$_3$]$_3$ is used as a catalyst. The best catalyst for hydration of olefinic bonds is Pt(PEt$_3$)$_3$. These results suggest that the steric requirements of the

$$\text{PtL}_3 = \text{PtL}_2 + \text{L}$$  \hspace{1cm} (83)

$$\text{H}_2\text{O} + \text{PtL}_2 = \text{PtH(OH)L}_2$$  \hspace{1cm} (84)
catalyst ligands and the incoming olefinic nitrile affect the hydration of the olefinic bond. Thus, Yoshida and co-workers explained hydration of the double bond based on an $\eta^2$-coordination of the olefin (versus $\sigma$-N coordination of the nitrile group in nitrile hydration), and proposed the following catalytic cycle (Scheme 15).

The most potent catalyst for hydration of acetonitrile and hydration of the olefinic bond of acrylonitrile is a hydridohydroxy platinum(II) complex, $\text{PtH(OH)(PR}_3)_2$ ($R = \text{Me, Et}$), investigated by Trogler. The rate of nitrile hydration by $\text{PtH(OH)(PMe}_3)_2$ at 80°C was 25 times greater than that of the most active platinum catalyst and 4 times faster for hydration of the olefinic group. In addition, at room temperature, the catalyst showed a remarkable selectivity (97%) for production of acrylamide. The catalytic cycle for
generation of acetamide is given in Scheme 16.

Insertion of tetrafluoroethylene into the Pt-OR bond of Pt(OCH\textsubscript{3})(CH\textsubscript{3})dppe,\textsuperscript{123,124} discussed earlier, gives precedence for catalytic hydration of olefins. Direct and inexpensive catalytic hydration of terminal olefins to primary alcohols would be important industrially and would provide a convenient synthetic route for the synthesis of terminal alcohols and ethers in general. Only one report of direct, catalytic hydration of olefins has appeared in the literature.\textsuperscript{65} That catalyst is the hydridohydroxy complex, PtH(OH)(PMe\textsubscript{3})\textsubscript{2}, investigated by Trogler for hydration of nitriles. At 60°C, selective hydration of 1-hexene to 1-hexanol occurs at a rate of 6.9 turnovers per hour; at 100°C, 1-dodecene was converted to 1-dodecanol at 8.3 turnovers per hour. Less than 0.5% of the branched alcohols were observed. The proposed catalytic cycle is shown in Scheme 17.
One of the key steps in catalytic cycles for hydration of nitriles and olefins is the activation of water, usually to give a hydridohydroxy complex. These complexes are typically generated in situ\textsuperscript{64,65} and only a few, such as trans-PtH(OH)[P(i-Pr)\textsubscript{3}]\textsubscript{2}\textsuperscript{62} have been isolated. The first crystallographically characterized complex, generated by addition of excess purified water to [Ir(PMe\textsubscript{3})\textsubscript{4}]PF\textsubscript{6}, is cis-[IrH(OH)(PMe\textsubscript{3})\textsubscript{4}]PF\textsubscript{6}.\textsuperscript{180} However, the solution chemistry of the activation of water by low-valent group VIII metal complexes has been examined in depth by Yoshida and co-workers.\textsuperscript{56,57,62,177-179}
Experimental

A. General Procedures

All reactions were carried out by use of standard Schlenk and inert atmosphere box techniques. Reagent grade solvents were dried by use of conventional methods and distilled under Ar. Absolute ethanol, distilled water, acetone and 2,2,2-trifluoroethanol were purged with an Ar stream for 20 minutes prior to use. Trifluoroacetic acid (99.9%+) was degassed three times using the freeze-thaw method. Methanol and absolute ethanol were dried over magnesium turnings and distilled under Ar. Reagent chemicals were purchased in the highest purity possible and used directly. The [PtCl(ttp)]Cl and [Ir(OCH₃)COD]₂ complexes were prepared by use of literature procedures.

The ³¹P(¹H) nmr spectra were recorded on a Bruker HX-90 FT nmr spectrometer operating at 36.43 MHz or on a Bruker 200 MHz FT nmr spectrometer operating at 81.016 MHz. The samples were placed in 10 mm nmr tubes fit with a coaxial insert containing d₆-acetone and trimethylphosphate. Many of the ³¹P(¹H) nmr spectra were recorded on a Bruker AM-250 FT nmr spectrometer operating at 101.256 MHz in 5 mm nmr tubes. The ³¹P(¹H) nmr spectra are referenced to external 85% H₃PO₄. Proton nmr spectra were recorded on a Bruker WP-80 FT nmr spectrometer in 5 mm nmr tubes. The ¹H spectra are referenced to external tetramethylsilane (TMS). Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrometer. The samples were prepared as either Nujol mulls between KBr or CsI plates or as KBr pellets and the
spectra are referenced to the sharp 1601 cm^{-1} peak of a polystyrene film. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

B. Synthesis of Metal Complexes

1. Metathesis Reaction Between [PtCl(ttp)]Cl, NaOCH₃ and H₂O

A 0.0625 M volumetric solution of NaOCH₃ and an equivalent amount of 18-Crown-6 in methanol was prepared. An 8.0 mL aliquot (0.50 mmol, 50% excess) of the NaOCH₃ solution was added to 0.831g (0.100 mmol) of [PtCl(ttp)]Cl dissolved in 5.0 mL of methanol. The resulting solution was stirred overnight. The ³¹P(¹H) nmr spectrum was recorded. A 28 molar excess of distilled water was added to the reaction solution. The resulting solution was stirred overnight. The ³¹P(¹H) nmr spectrum was recorded a second time. A solid product could not be isolated.

2. Synthesis of [Pt(OH)ttp]AsF₆

A solution containing 0.78g (4.6 mmol) of AgNO₃ in 20 mL of distilled water was added to a solution containing 1.88g (2.27 mmol) of [PtCl(ttp)]Cl in 100 mL of acetone. The reaction flask was wrapped in aluminum foil and the resulting solution was stirred for two hours. The AgCl, which precipitated from solution, was removed by filtration through celite dampened with acetone on a Schlenk frit. The solvent was removed from the filtrate in vacuo and the resulting white solid was dissolved in 100 mL of methanol. The solution was cooled to 0°C in an ice/water bath and a solution of 0.16g (2.9 mmol) of KOH in 10 mL of distilled water was added. Silver metal precipitated from
solution, and it was removed by filtration through celite dampened with methanol on a Schlenk frit. The filtrate was concentrated to 1/2 volume in vacuo and a solution containing 0.50g (2.4 mmol) of NaAsF6 in 20 mL of methanol was added to it. A white solid precipitated immediately. The solvent was then removed from the resulting white slurry in vacuo and the resulting white solid was dissolved in 150 mL of THF. The resulting slurry was stirred for one hour and then the slurry was filtered through celite dampened with THF on a Schlenk frit. The filtrate was concentrated to 5 mL in vacuo and the resulting gray solid was collected by vacuum filtration and dried in a desiccator. Yield: 1.00g, 45.7%. 31P(1H) nmr data:
\[
\delta{}_{\text{PPh}} = -26.1 \text{ ppm}; \quad \delta{}_{\text{PPh}_2} = -0.9 \text{ ppm}; \quad J(\text{Pt-PPh}) = 2598 \text{ Hz}; \quad J(\text{Pt-PPh}_2) = 2386 \text{ Hz}; \quad J(\text{PPh-PPh}_2) = 28 \text{ Hz}.
\]

3. Synthesis of [Pt(OC\text{H}_3)\text{ttp}]AsF6

A solution containing 0.0699g (0.411 mmol) of AgNO3 in 3.0 mL of methanol was added to a solution containing 0.1695g (0.2046 mmol) of [PtCl(\text{ttp})]Cl in 5.0 mL of methanol. A white solid, AgCl, precipitated immediately. The slurry was stirred for two hours and then the AgCl was removed by filtration through a cannula wrapped in glass wool and filter paper. A 1.0 mL (0.20 mmol) aliquot of a 0.2 M NaOCH3 solution in methanol was added to the filtrate. Silver metal precipitated and the slurry was stirred for 30 minutes. The silver was removed by filtration through celite dampened with methanol on a Schlenk frit. The filtrate was concentrated to 1/2 volume in vacuo. A solution containing 0.0472g (0.223 mmol) of NaAsF6 in 2.0 mL of
methanol was added to the filtrate. A white solid precipitated immediately and the slurry was cooled in a freezer. The white solid was collected on a Schlenk frit, washed with methanol and dried in vacuo. Yield: 0.050g, 25%. 31P(1H) nmr data: δPPh = -20.8 ppm; δPPh2 = -3.4 ppm; 1J(Pt-PPh) = 3094 Hz; 1J(Pt-PPh2) = 2207 Hz; 2J(PPh-PPh2) = 27 Hz.

4. Synthesis of [Rh(OH)COD]2

A solution of 0.98g (18 mmol) of KOH in 60 mL of distilled water was added to an orange suspension of 4.3223g (8.769 mmol) of [RhCl(COD)]2 in 480 mL of acetone. The slurry immediately became yellow and it was stirred for 3 hours. The slurry was concentrated to 2/3 volume in vacuo and then 150 mL of distilled water was added. The yellow solid was collected by vacuum filtration and washed with water until all traces of Cl- were gone from the filtrate (as tested with aqueous solutions of AgNO3). The solid was dried in a dessicator and then stored under Ar. Yield: 3.06g, 76.5%. The infrared and 1H nmr spectra matched that of an authentic sample. 1H nmr data: δ3.82 (8H), δ2.45 (10H), δ1.67 (8H). Infrared data: ν(O-H) = 3580 cm⁻¹.

5. Synthesis of [Rh(OCH3)COD]2

A solution of 0.70g (12 mmol) of KOH in 90 mL of methanol was added to 3.0482g (6.184 mmol) of [RhCl(COD)]2 in 250 mL of CH2Cl2. The solution immediately became a light yellow-orange color and it was stirred for 1 hour. The solvent was removed in vacuo and 150 mL of methanol followed by 200 mL of distilled water were added to the yellow solid. The yellow solid was collected on a Schlenk frit,
washed 10 times with 25 mL aliquots of distilled water and dried in vacuo. Yield: 2.79g, 93.3%. The infrared and $^1$H nmr spectra matched that of an authentic sample. $^1$H nmr data: $\delta_{3.55}$ (8H), $\delta_{2.67}$ (6H), $\delta_{2.47}$ (8H), $\delta_{1.63}$ (8H). Infrared data: 
$\nu$(C-O) = 1070 cm$^{-1}$.

6. Synthesis of [Rh(OC$_6$H$_5$)COD]$_2$

A mixture of 10.4g (111 mmol) of phenol and 0.63g (11 mmol) of KOH was heated with a heat gun until the phenol melted and the KOH dissolved. This solution was added to 2.6802g (5.438 mmol) of [RhCl(COD)]$_2$ in 250 mL of CH$_2$Cl$_2$. A pale-yellow solid precipitated immediately and the slurry was stirred for 3 hours. The solvent was removed in vacuo to give a yellow paste to which was added 150 mL of distilled water followed by 100 mL of CH$_2$Cl$_2$. The solution was stirred vigorously for several minutes, the layers were allowed to separate, and the water layer was removed with a cannula. The solid remaining in the methylene chloride layer was washed 4 times with 100 mL aliquots of distilled water. The yellow solid was collected on a Schlenk frit, and dried in vacuo. Yield: 2.48g, 74.9%.

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7. Synthesis of [Rh(OCH$_2$CF$_3$)COD]$_2$

A solution of 0.50g (8.9 mmol) of KOH in 40 mL of CF$_3$CH$_2$OH was added to a solution of 2.00g (4.06 mmol) of [RhCl(COD)]$_2$ in 200 mL
of CH₂Cl₂. A yellow slurry formed immediately and it was stirred for one hour. The solvent was removed in vacuo and 60 mL of CF₃CH₂OH was added to the solid residue followed by 150 mL of distilled water. The yellow solid was collected by vacuum filtration and it was washed with water until all traces of Cl⁻ were gone from the filtrate (as tested with aqueous AgNO₃). The solid was dried in a dessicator and then stored under Ar. Yield: 2.37g, 94.0%.

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8. Synthesis of [Rh(OCH₂CH₃)COD]₂·2H₂O

A solution of 2.41g (43.0 mmol) of KOH in a minimum amount of absolute ethanol was added to 4.2399g (8.602 mmol) of [RhCl(COD)]₂ suspended in 180 mL of acetone. The slurry immediately became yellow and it was stirred for 2 hours. The solution was concentrated to 1/3 volume in vacuo and the yellow solid was collected on a Schlenk frit. The solid was washed 2 times with 10 mL aliquots of acetone and dried in vacuo. Yield: 4.66g, 98.7%. The analytically pure sample was obtained by recrystallization from a hot 1:1 CH₂Cl₂:hexane mixture. The infrared spectrum displayed peaks due to coordinated water, perhaps due to wet solvents.
Elemental Analysis:

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Found: %C %H
   43.73  6.09

9. Synthesis of Rh(OH)ttp

A 39.0 mL (7.07 mmol) aliquot of 0.1813 M ttp in toluene was added to a suspension of 1.50g (3.29 mmol) of [Rh(OH)COD]₂ in 125 mL of toluene. The slurry immediately became yellow-red and it was stirred overnight. The solution was concentrated in vacuo to 30 mL and 20 mL of cold hexane were added. The yellow solid was collected on a Schlenk frit, washed 3 times with 4.0 mL aliquots of cold toluene and 4 times with 4.0 mL aliquots of cold hexane and dried in vacuo. Yield: 3.06g, 68.2%.

Elemental Analysis:

Theory: %C %H %P
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Found: %C %H %P
   63.28  5.73  13.48

10. Synthesis of Rh(OC₆H₅)ttp

A 15.3 mL (2.77 mmol) aliquot of a 0.1813 M solution of ttp in toluene was diluted with 60 mL of toluene and then added in small aliquots over several minutes to a suspension of 0.7081g (1.164 mmol) of [Rh(OC₆H₅)COD]₂ in 30 mL of toluene. The resulting clear magenta colored solution was stirred overnight. The solution was concentrated to 30 mL in vacuo and 20 mL of hexane were added. The solid was collected on a Schlenk frit, washed 2 times with 5.0 mL aliquots of hexane, followed by 5.0 mL of cold toluene and 5.0 mL of hexane and
dried in vacuo. The solid turned orange when it was dried. Yield: 1.36g, 76.8%.

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11. Synthesis of Rh(OCH<sub>2</sub>CF<sub>3</sub>)ttp

A 9.60 mL (1.74 mmol) aliquot of a 0.1813 M solution of ttp in toluene was added to a solution containing 0.5162g (0.8322 mmol) of [Rh(OCH<sub>2</sub>CF<sub>3</sub>)COD]₂ in 40 mL of toluene. The resulting solution was stirred for three hours and then it was concentrated to 5 mL in vacuo and 5.0 mL of cold hexane was added. The yellow solid which formed was collected on a Schlenk frit, washed 3 times with 2.0 mL aliquots of cold toluene and 2 times with 2.0 mL aliquots of cold hexane and dried in vacuo. Yield: 1.13g, 89.0%.

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12. Synthesis of [Ir(OH)COD]<sub>2</sub>

A solution of 0.35g (6.2 mmol) of KOH in 15 mL of distilled water was added to a red suspension of [IrCl(COD)]₂<sup>183</sup> in 100 mL of acetone. After a few minutes of stirring, the solution began to lighten and a yellow solid began to precipitate. The solution was stirred until the red color disappeared. The solution was concentrated in vacuo to 40
mL and 100 mL of distilled water was added. The yellow solid was collected on a Schlenk frit, washed 8 times with 20 mL aliquots of distilled water and dried in vacuo. Yield: 1.80g, 90.0%.

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13. Synthesis of [Ir(OC₆H₅)COD]₂

Dichloromethane (50 mL) was added to a mixture of 0.37g (6.0 mmol) of 87% KOH and 0.57g (6.0 mmol) of phenol and a heavy white solid formed. The slurry was transferred to 2.00g (2.98 mmol) of [IrCl(COD)]₂ in 100 mL of CH₂Cl₂ and an additional 50 mL of CH₂Cl₂ was added. A yellow solid began to precipitate immediately and the resulting yellow-brown slurry was stirred for 2 hours. The yellow solid was collected on a Schlenk frit, washed 4 times with 10 mL aliquots of distilled water and dried in vacuo. Yield: 1.87g, 79.9%.

The infrared spectrum matches that of an authentic sample.\(^{170}\)

Infrared data: $\nu(OC₆H₅) = 1581 \text{ cm}^{-1}$, $\nu(C-O) = 1060 \text{ cm}^{-1}$.

14. Synthesis of Ir(C₈H₁₂OCH₃)ttp

A 3.60 mL (0.652 mmol) aliquot of 0.1813 M ttp in toluene was added to a suspension containing 0.2037g (0.3072 mmol) of [Ir(OCH₃)COD]₂ in 30 mL of toluene. The solid dissolved immediately and a red-orange solution formed. The solution was stirred overnight and then concentrated to 3 mL in vacuo. Hexane (10 mL) was added to the concentrated solution and a yellow solid precipitated. The solid
was collected on a Schlenk frit, washed with 2 mL of hexane and dried in vacuo. Yield: 0.50g, 91%. $^{31}\text{P}^{(1\text{H})}$ nmr data: $\delta_{\text{P}1} = -51.74$ ppm, $\delta_{\text{P}2} = -34.95$ ppm, $\delta_{\text{P}3} = -29.87$ ppm, $^{2}J(\text{P}1-\text{P}2) = 14.5$ Hz, $^{2}J(\text{P}1-\text{P}3) = 16.2$ Hz, $^{2}J(\text{P}2-\text{P}3) = 72.0$ Hz.

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15. Synthesis of Ir(C₈H₁₀OH)ttp

A 5.50 mL (1.00 mmol) aliquot of 0.1813 M ttp in toluene was added to a suspension containing 0.30g (0.47 mmol) of [Ir(OH)COD]₂ in 30 mL of toluene. The slurry became orange and it was stirred for two days. The solution was then concentrated in vacuo to 10 mL and 15 mL of hexane were added; a yellow solid precipitated. The solid was collected on a Schlenk frit, washed three times with 2.0 mL aliquots of hexane and dried in vacuo. Yield: 0.39g, 50%. $^{31}\text{P}^{(1\text{H})}$ nmr data: $\delta_{\text{P}1} = -50.23$ ppm, $\delta_{\text{P}2} = -34.95$ ppm, $\delta_{\text{P}3} = -29.87$ ppm, $^{2}J(\text{P}1-\text{P}2) = 17.3$ Hz, $^{2}J(\text{P}1-\text{P}3) = 16.8$ Hz, $^{2}J(\text{P}2-\text{P}3) = 72.0$ Hz.

16. Synthesis of Ir(C₈H₁₀OC₆H₅)ttp

A 4.40 mL (0.798 mmol) aliquot of 0.1813 M ttp in toluene was added to a suspension containing 0.30g (0.38 mmol) of [Ir(OC₆H₅)COD]₂ in 30 mL of toluene. The solid immediately dissolved and an orange solution formed. The solution was stirred for two days and then concentrated in vacuo to 10 mL. Hexane (15 mL) was added to the paste and the resulting orange-yellow precipitate was collected on
a Schlenk frit and dried in vacuo. Yield: 0.45g, 62%. $^{31}$P($^1$H) nmr
data: $\delta$P$_1$ -50.24 ppm, $\delta$P$_2$ -30.04 ppm, $\delta$P$_3$ -29.05 ppm, $^2$J(P$_1$-P$_2$) = 16.4 Hz, $^2$J(P$_1$-P$_3$) = 17.8 Hz, $^2$J(P$_2$-P$_3$) = 71.0 Hz.

17. Synthesis of Ir(C$_8$H$_{12}$OH)cyttp

A 6.20 mL (0.83 mmol) of 0.1338 M cyttp in toluene was added to a
suspension containing 0.25g (0.39 mmol) of [Ir(OH)COD)$_2$ in 30 mL of
toluene. The solid immediately dissolved and a rose-colored solution
formed. The solution was stirred overnight and then concentrated to 5
mL in vacuo. Hexane (20 mL) was added to the concentrated solution
and a yellow solid precipitated. The solid was collected on a Schlenk
frit, washed three times with 2.0 mL aliquots of hexane and dried in vacuo.
Yield: 0.38g, 89%. $^{31}$P($^1$H) nmr data: $\delta$P$_1$ -52.63 ppm, $\delta$P$_2$
-41.37 ppm, $\delta$P$_3$ -29.76 ppm, $^2$J(P$_1$-P$_2$) = 17.3 Hz, $^2$J(P$_1$-P$_3$) = 14.0
Hz, $^2$J(P$_2$-P$_3$) = 52.6 Hz.

18. Synthesis of Ir(OC$_6$H$_5$)ttp

A 6.80 mL (1.2 mmol) aliquot of 0.1883 M ttp in toluene was
added to a suspension of 0.4602g (0.5847 mmol) of [Ir(OC$_6$H$_5$)COD)$_2$
in 40 mL of toluene. After stirring the mixture a few minutes, the solid
dissolved and a clear orange solution formed. The solution was
refluxed for 18 hours and then cooled to room temperature. The orange
solution was then concentrated in vacuo to 5 mL and 20 mL of hexane
were added, whereupon an orange solid precipitated. The solid was
collected on a Schlenk frit, washed 3 times with 5 mL aliquots of
hexane and dried in vacuo. Yield: 1.0 g, 100%.
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19. Synthesis of Ir(OC6H5)cyttpp

A 3.50 mL (0.468 mmol) aliquot of 0.1338 M cyttpp in toluene was added to a suspension containing 0.1804g (0.2271 mmol) of [Ir(OC6H5)COD]2 in 20 mL of toluene. The solid dissolved immediately and an orange solution formed. The orange solution was stirred overnight and then concentrated in vacuo to a paste. Hexane (10 mL) was added to the paste and a small amount of red solid precipitated. The solid was collected on a Schlenk frit and the filtrate was concentrated in vacuo. The desired complex remained in the filtrate, but it could not be isolated from solution. \(^{31}P\)\(^{(1}H\) nmr data: \(\delta_{\text{PhP}} = -19.63\) ppm, \(\delta_{\text{Cy}_2\text{P}} = 5.16\) ppm, \(J(\text{PhP-Cy}_2\text{P}) = 29.1\) Hz.

20. Synthesis of Ir(OH)cyttpp

A 8.20 mL (1.10 mmol) aliquot of 0.1338 M cyttpp in toluene was added to a suspension containing 0.3336g (0.5255 mmol) of [Ir(OH)COD]2 in 30 mL of toluene. The solid dissolved immediately and an orange solution formed. The solution was refluxed for 17.5 hours, cooled to room temperature and then concentrated in vacuo to 3 mL. Hexane (15 mL) was added and a small amount of precipitate formed. The solution was then cooled in an ice/water bath for 30 minutes and the solid was collected on a Schlenk frit. The desired complex remained in the filtrate, but it could not be isolated from solution.
$^{31}\text{P}(^1\text{H})$ nmr data: $\delta_{\text{PhP}} = -0.90$ ppm, $\delta_{\text{Cy}_2\text{P}} = -17.96$ ppm, $^2J(\text{PhP-Cy}_2\text{P}) = 31.1$ Hz. Several isomers are also observed in low concentration.

21. **Synthesis of Rh(OC(0)CF$_3$)tp**

a) **From Rh(OH)ttp**

Trifluoroacetic acid (0.10 mL, 1.3 mmol) was added to a suspension containing 0.2424g (0.3551 mmol) of Rh(OH)ttp in 30 mL of benzene. The solid dissolved immediately to give a yellow solution. The solution was stirred for 3 hours, concentrated *in vacuo* to 2 mL, and then 10 mL of hexane were added. The resulting cream-colored precipitate was collected on a Schlenk frit, washed 2 times with 1.0 mL aliquots of hexane and dried *in vacuo*. Yield: 0.12g, 43%.

b) **From Rh(OC$_6$H$_5$)ttp**

Trifluoroacetic acid (0.10 mL, 1.3 mmol) was added to a solution containing 0.2843g (0.3747 mmol) of Rh(OC$_6$H$_5$)ttp in 20 mL of benzene. The solution color lightened immediately and it was stirred for 2 hours. The solution was then concentrated *in vacuo* to 5 mL and 15 mL of hexane were added, whereupon a cream-colored solid precipitated. The solid was collected on a Schlenk frit, washed 3 times with 10 mL aliquots of hexane and dried *in vacuo*. Yield: 0.24g, 83%.

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22. Synthesis of Rh(O(C(0)C_6H_4Br))ttp

a) From Rh(OH)ttp

A solution containing 0.0770g (0.383 mmol) of para-bromobenzoic acid in 10 mL of diethylether was added to a suspension containing 0.2599g (0.3808 mmol) of Rh(OH)ttp in 30 mL of toluene. The solid disappeared and a clear orange solution formed. The solution was stirred for 2.5 hours and then concentrated in vacuo to 5 mL. A yellow solid precipitated when 20 mL of hexane were added to the concentrated solution. The solid was collected on a Schlenk frit, washed with 5 mL of hexane and dried in vacuo. Yield: 0.25g, 76%.

b) From Rh(O(C_6H_5)ttp

A solution containing 0.0601g (0.299 mmol) of para-bromobenzoic acid in 15 mL of diethylether was added to a solution containing 0.2173g (0.2864 mmol) of Rh(O(C_6H_5)ttp in 20 mL of benzene. The resulting solution was stirred for 2.5 hours and then it was concentrated in vacuo to 3 mL. A yellow solid precipitated when 30 mL of hexane was added to the concentrated solution. The solid was collected on a Schlenk frit, washed with 2 mL of hexane and dried in vacuo. Yield: 0.19g, 76%.

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23. Synthesis of Rh(OC(O)C₆H₅)ttp

a) From Rh(OH)ttp

A solution of 0.0500g (0.410 mmol) of benzoic acid in 10 mL of benzene was added to a suspension containing 0.2000g (0.2930 mmol) of Rh(OH)ttp in 20 mL of benzene. The solid dissolved and a clear orange solution formed. The solution was stirred for 1 hour and then concentrated in vacuo to 5 mL. A pale-orange-yellow solid precipitated when 20 mL of hexane were added to the concentrated solution. The solid was collected on a Schlenk frit, washed 2 times with 2.0 mL aliquots of hexane and dried in vacuo. Yield: 0.18g, 78%.

b) From Rh(OC₆H₅)ttp

A solution containing 0.0365g (0.299 mmol) of benzoic acid in 10 mL of benzene was added to a solution containing 0.1970g (0.2596 mmol) of Rh(OC₆H₅)ttp in 20 mL of benzene. The resulting solution was stirred for 1.5 hours and then the solvent was removed in vacuo. Hexane (15 mL) was added to the yellow solid and the solid was collected on a Schlenk frit, washed with 2.0 mL of hexane and dried in vacuo. Yield: 0.19g, 95%.

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24. Synthesis of \( \text{Rh(SO}_2\text{OH)}^{\text{ttp-SO}_2} \)

Anhydrous \( \text{SO}_2 \) gas was bubbled through a solution of \( \text{Rh(OH)}^{\text{ttp}} \) (0.25g, 0.37 mmol) in 60 mL of THF for 1 hour. The color of the solution immediately lightened to yellow. The resulting yellow solution was concentrated \textit{in vacuo} to 10 mL. Addition of 4 mL of cyclohexane caused the precipitation of a yellow solid, which was collected on a Schlenk frit and dried \textit{in vacuo}. Yield: 0.23g, 77%.

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</tbody>
</table>

25. Synthesis of \( \text{Rh(SO}_2\text{OC}_6\text{H}_5)^{\text{ttp-SO}_2} \)

Anhydrous \( \text{SO}_2 \) gas was bubbled through a solution of \( \text{Rh(OC}_6\text{H}_5)^{\text{ttp}} \) (0.34g, 0.45 mmol) in 20 mL of THF for one hour. A yellow solid precipitated. The slurry was concentrated to 2/3 volume \textit{in vacuo} and 4 mL of cyclohexane were added. The solid was collected on a Schlenk frit, washed with 2.0 mL of cyclohexane and dried \textit{in vacuo}. Yield: 0.27g, 73%.

Elemental Analysis:

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<td>56.65</td>
<td>4.94</td>
<td>10.57</td>
<td>7.23</td>
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</table>

26. Synthesis of \( \text{Rh(SO}_2\text{OC}_6\text{H}_5)^{\text{cyttp-SO}_2} \)

A 5.6 mL (0.76 mmol) aliquot of 0.1338 M cyttp in toluene was added to 0.1865g (0.3065 mmol) of \( \text{[Rh(OC}_6\text{H}_5)^{\text{COD}}]_2 \) in 20 mL of toluene.
The yellow solution was stirred for 3 hours and was then allowed to stand, under Ar, for 20 days, while an SO₂ tank was located. Upon location of an SO₂ tank, anhydrous SO₂ gas was bubbled through the yellow solution for 10 minutes. The solution immediately turned orange and then a yellow solid precipitated. The resulting slurry was concentrated in vacuo to 5 mL and 5 mL of hexane were added. The lemon-yellow solid was collected on a Schlenk frit and dried in vacuo. Yield: 0.25g, 45%.

Elemental Analysis:

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<td>7.47</td>
<td>10.14</td>
<td>6.80</td>
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</table>

27. Synthesis of Ir(SO₂OC₆H₅)ttp•SO₂

Anhydrous SO₂ gas was bubbled through a solution of 0.1616g (0.1905 mmol) of Ir(OC₆H₅)ttp in 20 mL of THF for 10 minutes. The solution immediately lightened in color, became a cloudy yellow-green slurry and then a clear yellow solution. The yellow solution was concentrated in vacuo to 5 mL and 10 mL of hexane were added. A yellow solid precipitated and it was collected on a Schlenk frit, washed with 2.0 mL of hexane and dried in vacuo. Yield: 0.15g, 79%.

Elemental Analysis:

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<tr>
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<td>4.60</td>
<td>9.37</td>
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</table>
28. Reaction of Rh(OH)ttp with CO

Carbon monoxide gas was bubbled through an orange solution of 0.20g (0.29 mmol) of Rh(OH)ttp in 65 mL of benzene for several minutes. The solution immediately became deep-red in color and then yellow. The yellow solution was concentrated in vacuo, whereupon it became red again. The solvent was completely removed in vacuo to give a brick-red solid. The solid decomposed after two days under an Ar atmosphere. Yield: 0.25g.

29. Reaction of Rh(OC₆H₅)ttp with CO

Carbon monoxide gas was bubbled through an orange solution containing 0.30g (0.39 mmol) of Rh(OC₆H₅)ttp in 30 mL of benzene. The solution immediately became red in color and, after several minutes of CO addition, the solution turned yellow. The yellow solution was concentrated in vacuo, whereupon it became red again. The solvent was completely removed in vacuo to give a red microcrystalline solid. The solid decomposed after two days under an Ar atmosphere. The yield was not reported.

30. Synthesis of [Rh(CO)ttp]AsF₆

a) From Rh(OH)ttp

Carbon monoxide gas was bubbled through a slurry containing 0.1823g (0.2671 mmol) of Rh(OH)ttp in 15 mL of toluene for a few minutes until the solid dissolved and a red solution formed. A solution containing 0.6g (0.3 mmol) of NaAsF₆ in 7 mL of THF was added to the red solution, whereupon a solid precipitated. The slurry was concentrated in vacuo to 3 mL and 10 mL of hexane were added. The
yellow solid was collected on a Schlenk frit, washed with hexane and dried in vacuo. Yield: 0.16g, 67%.

b) From Rh(OC₆H₅)ttp

Carbon monoxide gas was bubbled through a slurry containing 0.2200g (0.2900 mmol) of Rh(OC₆H₅)ttp in 15 mL of toluene for a few minutes until the solid dissolved and a red solution formed. A solution containing 0.6g (0.3 mmol) of NaAsF₆ in 7 mL of THF was added to the red solution, whereupon a solid precipitated. The slurry was concentrated in vacuo to 3 mL and 10 mL of hexane were added. The yellow solid was collected on a Schlenk frit, washed with hexane and dried in vacuo. Yield: 0.18g, 69%. The ³¹P(¹H) nmr data matches that for an authentic sample of [Rh(CO)ttp]PF₆: δPPh = -13.74 ppm, δPPh₂ = 5.82 ppm, ¹J(Rh-PhP) = 113.8 Hz, ¹J(Rh-PPh₂) = 115.2 Hz, ²J(PPh-PPh₂) = 52.2 ppm.
RESULTS AND DISCUSSION

A. Synthesis and Characterization of Group VIII Metal Alkoxide and Hydroxide Complexes

1. Platinum(II) Complexes

Initial preparations of the platinum-methoxide complex, [Pt(OCH₃)ttp]⁺, involved a simple metathesis reaction between [PtCl(ttp)]Cl and NaOCH₃ in methanol. The ³¹P(¹H) nmr spectrum of the resulting solution displayed two sets of peaks each characteristic of a first order A₂BX spin system for a [PtX(ttp)]⁺ complex (Figure 38). Both complexes displayed a doublet due to splitting of the two terminal phosphorus atoms (P2 = PPh₂) of ttp by the central phosphorus atom (P1 = PPh) along with the corresponding satellites due to coupling with the ¹⁹⁵Pt nucleus (I = 1/2, natural abundance = 33.7%). The complexes also exhibit a triplet due to the splitting of the central phosphorus atom (P1) by the two equivalent terminal phosphorus atoms (P2), along with the corresponding satellites. The satellites due to the ¹⁹⁵Pt nucleus are not well resolved in Figure 38. One set of peaks is assigned to the starting material, [PtCl(ttp)]⁺. The second set of peaks is assigned to the methoxide complex, [Pt(OCH₃)ttp]⁺. Addition of excess NaOCH₃ did not dramatically increase the concentration of [Pt(OCH₃)ttp]⁺ in solution, and a ratio better than 1:1 of [PtCl(ttp)]⁺ to [Pt(OCH₃)ttp]⁺ was not achieved. Since alkoxide complexes of the group VIII metals are known to hydrolyze in water¹¹⁷, an aliquot of water was added to the reaction mixture containing both [PtCl(ttp)]⁺ and [Pt(OCH₃)ttp]⁺. The ³¹P(¹H)
Figure 38. 90 MHz $^{31}\text{P}^{1\text{H}}$ nmr spectrum of a mixture of

1) $[\text{PtCl(ttp)}]^+$ and 2) $[\text{Pt(OCH}_3\text{ttt)}]^+$ in THF.
spectrum of the reaction solution was recorded a second time; a strong third set of peaks was observed (Figure 39). The third set of peaks is assigned to the hydroxide complex, $[\text{Pt(OH)}\text{ttp}]^+$. However, addition of a 28 molar excess of water did not completely convert $[\text{Pt(OCH}_3\text{)}\text{ttp}]^+$ to the hydroxide complex.

Because a mixture of the chloride, methoxide and hydroxide complexes exists in solution, silver salts are employed to extract the chloride ligand and to facilitate substitution by the methoxide or hydroxide ligand. The author developed reaction Scheme 18 for the synthesis of $[\text{Pt(OR)}\text{ttp}]\text{AsF}_6$ (OR = OH, OCH$_3$; M' = Na, K; Sol = solvent). The use of AsF$_6^-$ as the counter-anion results in precipitation of the desired complexes, $[\text{Pt(OR)}\text{ttp}]\text{AsF}_6$, from solution, while the inorganic salts, NaNO$_3$ and KNO$_3$, remain soluble. Two other counter-anions, BF$_4^-$ and BPh$_4^-$, were also employed; however, $[\text{Pt(OR)}\text{ttp}]\text{BF}_4$ complexes were too soluble to be isolated from solution, whereas, $[\text{Pt(OR)}\text{ttp}]\text{BPh}_4$ complexes were completely insoluble in common organic solvents and co-precipitated with the inorganic salts present in the reaction solution.

Complexes $[\text{Pt(OH)}\text{ttp}]\text{AsF}_6$ and $[\text{Pt(OCH}_3\text{)}\text{ttp}]\text{AsF}_6$ (VIII) were isolated as off-white solids in low yield due to decomposition of the
Figure 39. 90 MHz $^{31}\text{P}^{1}\text{H}$ nmr spectrum of a mixture of 1) [PtCl(ttp)]$^+$, 2) [Pt(OCH$_3$)ttp]$^+$ and 3) [Pt(OH)ttp]$^+$ in THF.
platinum complex. Attempts to recrystallize [PtOH(ttp)]AsF$_6$ and [PtOCH$_3$(ttp)]AsF$_6$ from mixtures of THF and hexane or CH$_2$Cl$_2$ and hexane resulted in further decomposition of the complexes. An attempt was made to prepare the t-butoxide complex, [Pt(OCH$_3$)$_3$(ttp)]AsF$_6$, using Scheme 18; however, addition of KOC(CH$_3$)$_3$ to the reaction mixture (Eq. 86) caused complete decomposition of the platinum complex to platinum metal.

The [Pt(OR)ttp]AsF$_6$ complexes (OR = OH, OCH$_3$) were characterized by $^{31}$P($^1$H) nmr and infrared spectroscopy. The experimental $^{31}$P($^1$H) nmr spectra matched the original peak assignments made for [Pt(OH)ttp]Cl and [Pt(OCH$_3$)ttp]Cl prepared from the metathesis reaction. The $^{31}$P($^1$H) nmr spectra for [Pt(OH)ttp]AsF$_6$ and for [Pt(OCH$_3$)ttp]AsF$_6$ are shown in Figures 40 and 41, respectively. The data are compiled in Table 22 along with data acquired by K. Taum for other [PtX(ttp)]AsF$_6$ complexes. The infrared spectrum of [Pt(OH)ttp]AsF$_6$ displays a sharp peak at 3590 cm$^{-1}$ which is characteristic of an OH group bound to a metal center.\textsuperscript{117,119,120}

\[
\begin{align*}
\text{VIII}
\end{align*}
\]
Figure 40. 250 MHz $^{31}$P($^1$H) nmr spectrum of [Pt(OH)ttp]AsF$_6$ in THF.
Figure 41. 200 MHz $^{31}\text{P}^{(1\text{H})}$ nmr spectrum of [Pt(OCH$_3$)$_3$ttp]AsF$_6$ in THF.
<table>
<thead>
<tr>
<th>Complex</th>
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<th>( \delta P1 )</th>
<th>( ^{1}J_{Pt-P2} )</th>
<th>( ^{1}J_{Pt-P1} )</th>
<th>( ^{2}J_{P1-P2} )</th>
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<td>2722</td>
<td>1541</td>
<td>34</td>
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</table>

The data reported by K. Tau\(^{111}\) were acquired in CH\(_3\)NO\(_2\). The data obtained by the author for the hydroxide and alkoxide complexes were acquired in CH\(_2\)Cl\(_2\). Chemical shifts are reported in ppm. Coupling constants are reported in Hz. The numeric labels given to the triphosphine ligand in complex VIII will be used throughout the dissertation.
The one-bond coupling constant between platinum and the central phosphorus atom of ttp, $^1J(Pt-P1)$, can be used as a measure of the trans influence. The trans effect is defined as the ability of a ligand to facilitate substitution of the ligand trans to itself in the ground state of the metal complex. A typical trans influence series given in terms of increasing trans influence ability is as follows: $H_2O$, $OH^-$, $NH_3$, pyridine $< Cl^-$, $Br^-$ $< SCN^-$, $I^-$, $NO_2^-$, $C_6H_5^-$ $< SC(NH_2)_2$, $CH_3^-$ $< H^-$, $PR_3$ $< C_2H_4$, CO. The magnitude of one-bond metal ligand coupling constants decreases when the trans ligand forms a strong interaction with the metal (ie. it lies high in the trans influence series). An examination of the magnitudes of $^1J(Pt-P1)$ values in Table 22 shows that the $OH^-$ complex, $[Pt(OH)t tp]AsF_6$ ($^1J(Pt-P1)$ $= 2598$ Hz), and the $OCH_3^-$ complex, $[Pt(OCH_3)t tp]AsF_6$ ($^1J(Pt-P1)$ $= 3094$ Hz), have smaller $^1J(Pt-P1)$ values than the corresponding $Cl^-$ complex ($^1J(Pt-P1)$ $= 3109$ Hz). This suggests that the $OH^-$ and $OCH_3^-$ ligands form a stronger interaction to the metal center than does the $Cl^-$ ligand, which is directly opposite to the trend predicted by the trans influence series. This result is surprising, because the Pt-OR bond was expected to be relatively weak due to the electron-rich metal center created by the coordinated chelating triphosphine ligand. Although comparisons of the trans influence of chloride and hydroxide ligands have not been reported previously for platinum(II) hydroxide complexes, the hydroxide ligand in $Pt(OH)(CH_3)dppe$ has a trans influence similar to that of typical sulfur donors (ie. $SCN^-$ and $SPh^-$) and greater than that of other anionic oxygen donors (ie. $CH_3CO_2^-$ and
2. Rhodium(I) Complexes

Initially, RhCl(ttp)\(^80\) was treated with KOH in an attempt to synthesize Rh(OH)ttp (Eq. 88) by substitution of Cl\(^-\) with OH\(^-\).

\[
\text{RhCl(ttp) + KOH} \rightarrow \text{Rh(OH)ttp + KCl} \quad (88)
\]

However, direct substitution did not lead to the desired product; only unreacted RhCl(ttp) was detected in the reaction mixture by \(^{31}\text{P}(\text{\textsuperscript{1}H})\) nmr spectroscopy. Hence, TlNO\(_3\) was added to solutions of RhCl(ttp) in THF to abstract Cl\(^-\) from the rhodium complex in order to promote substitution by OH\(^-\) (Eq. 89). The only characterized product obtained from the reaction mixture was oxidized ttp ligand. Since traces of peroxides in THF were subsequently found to promote decomposition of RhCl(ttp) and formation of the trioxide of ttp, \((\text{C}_6\text{H}_5\text{P(O)[CH}_2\text{CH}_2\text{CH}_2\text{P(O)(C}_6\text{H}_5)_2]}\)\(_2\)), a hypothesis was advanced that OH\(^-\) might promote a similar decomposition. Thus, a simple hydrolysis reaction in the presence of TlNO\(_3\) was attempted (Eq. 90). Once again,

\[
\text{RhCl(ttp) + TlNO}_3 + \text{H}_2\text{O} \rightarrow \text{Rh(OH)ttp + TlCl + H}^+ + \text{NO}_3^- \quad (90)
\]

the only characterized product was the trioxide of ttp. The author proposed that the nitrate anion was perhaps causing the decomposition; hence, hydrated TlAsF\(_6\) was employed (Eq. 91). Once again, decomposition of the rhodium complex occurred.
\[ \text{RhCl(ttp)} + \text{TlAsF}_6 \cdot 3\text{H}_2\text{O} \rightarrow \text{Rh(OH)ttp} + \text{TlCl} + 2\text{H}^+ + \text{AsF}_6^- + 2\text{H}_2\text{O} \]  

(91)

Since the simple metathesis reaction (Eq. 88) did not yield the desired complex, even when using halide abstracting agents (Eqs. 89 - 91), a completely new approach was used for synthesis of the Rh(OR)ttp complexes. It was decided to attach the OR ligand to rhodium before treating the rhodium complex with a chelating triphosphine ligand. The reported synthesis of RhCl(ttp) involved the reaction of \([\text{RhCl(COD)}]_2\) with 2 equivalents of ttp (Eq. 92).\(^8\)

\[ [\text{RhCl(COD)}]_2 + 2\text{ttp} \rightarrow 2\text{RhCl(ttp)} + 2\text{COD} \]  

(92)

Thus, an analogous starting material for a Rh(OR)ttp complex would be \([\text{Rh(OR)COD]}_2\) (IX). The synthesis of \([\text{Rh(OR)COD)}]_2\) complexes involves the reaction of KOH and an alcohol or water with \([\text{RhCl(COD)}]_2\) (Eq. 93). It is important to wash the yellow solid products extensively with water in order to dissolve all traces of KCl. The hydroxide bridged bimetallic complex was prepared initially by the author; however, syntheses of \([\text{Rh(OH)COD)}]_2\) and \([\text{Rh(OCH}_3\text{)COD)}]_2\) were published
recently by use of the procedure depicted in Equation 93. The author has extended this method to the synthesis of [Rh(OCH2CH3)COD]2, [Rh(OCH2CF3)COD]2, and [Rh(OCH2CH3)COD]2•2H2O. The ethoxide complex, [Rh(OCH2CH3)COD]2, was prepared previously by the reaction of ethanol with the oxygen bridged dimer, [RhO(COD)]2.185

The rhodium alkoxide and hydroxide bridged bimetallic complexes were characterized by proton nmr and infrared spectroscopy. The proton nmr spectrum of [Rh(OCH2CH3)COD]2 is shown in Figure 42 and proton nmr data for all of the complexes are given in Table 23. The three sets of inequivalent hydrogen atoms of the 1,5-cyclooctadiene ligand appear as three broad peaks in the proton nmr spectra due to coupling with the 103Rh nucleus. The infrared spectra of [Rh(OCH2CH3)COD]2 and [Rh(OCH2CF3)COD]2 are shown in Figures 43 and 44, respectively. The infrared spectra display peaks characteristic of the alkoxide or hydroxide ligands. For example, the O-H stretch of the hydroxide group bound to rhodium for [Rh(OH)COD]2 shows a sharp absorption at 3580 cm⁻¹. The C-O stretch of alkoxide ligands bound to a group VIII metals exhibit infrared absorptions between 1000 cm⁻¹ and 1100 cm⁻¹.170 The C-O stretching vibration occurs at 1065 cm⁻¹ for [Rh(OCH2CH3)COD]2, 1070 cm⁻¹ for [Rh(OCH3)COD]2, 1082 cm⁻¹ for [Rh(OCH2CF3)COD]2 and 1093 cm⁻¹ and 1057 cm⁻¹ for [Rh(OCH2CH3)COD]2•2H2O. Despite recrystallization from CH2Cl2/hexane mixtures, the ethoxide complex retains two molecules of water, based on the elemental analysis and the infrared spectrum. The O-H stretching vibration occurs at 3330 cm⁻¹. The CF3 group of
Figure 42. 80 MHz $^1$H nmr spectrum of [Rh(OCH$_5$)$_2$COD]$_2$ in CD$_2$Cl$_2$. 
Table 23. Proton NMR Data for [Rh(OR)COD]₂ Complexes

<table>
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<tr>
<th></th>
<th>OH</th>
<th>OCH₃</th>
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<th>OC₆H₅</th>
<th>OCH₂CF₃⁻a</th>
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<td>3.82</td>
<td>8H (br)</td>
<td>3.55 8H (br)</td>
<td>3.8 8H (br)</td>
<td>6.86 10H (br)</td>
<td>1.73 (br)</td>
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<tr>
<td>2.45</td>
<td>10H (br)</td>
<td>2.67 6H (s)</td>
<td>2.4 10H (br)</td>
<td>3.08 8H (br)</td>
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<td>1.67</td>
<td>8H (br)</td>
<td>2.47 8H (br)</td>
<td>1.6 10H (br)</td>
<td>2.16 8H (br)</td>
<td>3.57 (br)</td>
</tr>
<tr>
<td></td>
<td>1.63 8H (br)</td>
<td>0.99 4H (t)</td>
<td>1.26 8H (br)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ J_{H-H} = 7.1 \text{ Hz} \]

The spectra were recorded in CD₂Cl₂. Chemical shifts are reported in ppm.

a) The OCH₂CF₃ protons could not be located in the proton nmr spectrum. Poor integration suggest that it is buried under the peaks due to the protons of the COD ligand.
Figure 43. The infrared spectrum of \([\text{Rh(OC}_6\text{H}_5\text{COD)]}_2\). (Nujol mull).
Figure 44. The infrared spectrum of $\text{[Rh(OCH}_2\text{CF}_3\text{)COD]}_2$. (Nujol mull).
[Rh(OCH$_2$CF$_3$)COD]$_2$ exhibits a distinctive absorption in the infrared spectrum at 1150 cm$^{-1}$ and the C=C groups of the phenoxide ligand in [Rh(OC$_6$H$_5$)COD]$_2$ exhibits a distinctive absorption at 1582 cm$^{-1}$.

The hydroxide and alkoxide bridged dimers, [Rh(OR)COD]$_2$, were used successfully for the synthesis of monomeric four-coordinate hydroxide and alkoxide rhodium complexes incorporating a chelating triphosphine ligand, (Eq. 94, $P_3$ = chelating triphosphine ligand).

$$[\text{Rh(OR)COD}]_2 + 2P_3 \rightarrow 2\text{Rh(OR)P}_3 + 2\text{COD} \quad (94)$$

The reactions involved addition of an aliquot of a known concentration solution of the chelating triphosphine ligand to a suspension of the [Rh(OR)COD]$_2$ complexes in toluene.

The reaction procedure described above has been used for successful preparation and isolation of Rh(OH)ttp, Rh(OC$_6$H$_5$)ttp and Rh(OCH$_2$CF$_3$)ttp ($X$). The complexes are air and moisture sensitive yellow solids that are unstable thermally; decomposing at temperatures above 130°C. Numerous attempts were made to prepare the methoxide complex, Rh(OCH$_3$)ttp; however, all of the reactions failed. Proton-decoupled phosphorus nmr spectra of reaction mixtures that combined
[Rh(OCH$_3$)COD]$_2$ and ttp exhibited over 80 unidentified peaks.

The $^{31}$P($^1$H) nmr spectra of the Rh(OR)ttp complexes are consistent with an $A_2B_1X$ spin system. The spectra exhibit a doublet of doublets due to splitting of the two equivalent PPh$_2$ groups (P2) of the ttp ligand by the $^{103}$Rh nucleus and then by the central phosphorus atom of the ttp ligand (PhP = P1). The central phosphorus atom (P1) exhibits a doublet of triplets due to splitting by the $^{103}$Rh nucleus and then by the two equivalent terminal phosphorus atoms of the ttp ligand (P2). The $^{31}$P($^1$H) spectra of Rh(OC$_6$H$_5$)ttp and Rh(OH)ttp are shown in Figures 45 and 46, respectively. The spectrum of Rh(OH)ttp exhibits second order effects characteristic of an $A_2B_1X$ spin system.$^{186}$

Phosphorus-31 nmr data of the Rh(OR)ttp complexes (OR = OH, OC$_6$H$_5$, OCH$_2$CF$_3$) are given in Table 24. Data for RhCl(ttp)$^{187}$ are given for comparison. The magnitudes of $^1J$(Rh-P1) for Rh(OH)ttp ($^1J$(Rh-P1) = 136.1 Hz), Rh(OC$_2$CF$_3$)ttp ($^1J$(Rh-P1) = 145.1) and Rh(OC$_6$H$_5$)ttp ($^1J$(Rh-P1) = 147.0) and are smaller than the magnitude of $^1J$(Rh-P1) for RhCl(ttp) ($^1J$(Rh-P1) = 162.3). Analogous to [Pt(OR)ttp]AsF$_6$ complexes, the above trend is opposite to the accepted trans influence series. The Rh-OR bonds were expected to be weak due to the electron-rich metal center. Therefore, it is surprising that the hydroxide and alkoxide ligands apparently form a stronger interaction with rhodium than does the chloride ligand.

The Rh(OR)ttp complexes (OR = OH, OC$_6$H$_5$, OCH$_2$CF$_3$) were also characterized by infrared spectroscopy; the spectra of Rh(OH)ttp and Rh(OC$_6$H$_5$)ttp are shown in Figures 47 and 48, respectively.
Figure 45. 250 MHz $^{31P}{^1H}$ nmr spectrum of Rh(OC$_6$H$_5$)$_{tt}$ in THF with C$_6$D$_6$ added as an internal lock.
Figure 46. 250 MHz $^{31}$P($^1$H) nmr spectrum of Rh(OH)ttt in THF with C$_6$D$_6$ added as an internal lock. The minor set of peaks is assigned to a small amount of RhCl(tt) impurity.
Table 24. $^{31}\text{P}(^{1}\text{H})$ NMR Data for RhX(ttp) Complexes

<table>
<thead>
<tr>
<th>X</th>
<th>Cl$^a$</th>
<th>OH</th>
<th>OC$_6$H$_5$</th>
<th>OCH$_2$CF$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$P1</td>
<td>15.48</td>
<td>16.57</td>
<td>18.04</td>
<td>18.76</td>
</tr>
<tr>
<td>$\delta$P2</td>
<td>8.20</td>
<td>7.87</td>
<td>3.31</td>
<td>3.92</td>
</tr>
<tr>
<td>$^1J$(Rh-P1)</td>
<td>162.3</td>
<td>136.1</td>
<td>147.0</td>
<td>145.1</td>
</tr>
<tr>
<td>$^1J$(Rh-P2)</td>
<td>128.8</td>
<td>141.6</td>
<td>137.0</td>
<td>140.2</td>
</tr>
<tr>
<td>$^2J$(P1-P2)</td>
<td>52.5</td>
<td>54.0</td>
<td>54.0</td>
<td>55.0</td>
</tr>
</tbody>
</table>

Chemical shifts are reported in ppm; coupling constants are reported in Hz. Spectra were recorded in THF with C$_6$D$_6$ added as an internal lock.

$^a$) Ref. 187.
Figure 47. The infrared spectrum of Rh(OH)ttp. (Nujol mull).
Figure 48. The infrared spectrum of Rh(OC₆H₅)ttp. (Nujol mull).
The O-H stretching vibration of the hydroxide complex, Rh(OH)ttp, exhibits a very weak, but sharp absorption at 3600 cm\(^{-1}\), characteristic of a hydroxide group bound to a group VIII metal.\(^{144,160}\) The phenoxide group of Rh(OC\(_6\)H\(_5\))ttp shows absorptions due to the C-C ring stretching vibration at 1590 cm\(^{-1}\) and 1581 cm\(^{-1}\) and the 2,2,2-trifluoroethoxide complex, Rh(OCH\(_2\)CF\(_3\))ttp, exhibits a strong, broad peak centered at 1108 cm\(^{-1}\), characteristic of the CF\(_3\) group. The C-O stretching vibration of the alkoxide complexes (OR = OC\(_6\)H\(_5\), OCH\(_2\)CF\(_3\)), cannot be identified due to numerous peaks from coordinated ttp in the 1000 cm\(^{-1}\) to 1100 cm\(^{-1}\) region.

Several attempts were made to synthesize the hydroxide and alkoxide complexes of the chelating ligand cyttp, Rh(OR)cyttp, XI (OH, OC\(_6\)H\(_5\), OCH\(_2\)CH\(_3\)), using the procedure employed for the synthesis of Rh(OR)ttp complexes (Eq. 94). However, solid products could not be isolated from the reaction mixtures. Removal of the reaction solvent under vacuum lead to formation of oils. However, evidence for the hydroxide and phenoxide complexes is present in the \(^{31}\)P\(^{(1)H}\) nmr spectra of the reaction mixtures. For example, the \(^{31}\)P\(^{(1)H}\) nmr spectrum of Rh(OC\(_6\)H\(_5\))cyttp, which is shown in Figure 49, exhibits a pattern consistent with an \(A_2BX\) spin system. The data for
Figure 49. 200 MHz $^{31}$p$^1$H nmr spectrum of Rh$(\text{OC}_6\text{H}_5)$cyttp in THF.

a. Unreacted cyttp.
Rh(OH)cyttp and Rh(OC₆H₅)cyttp are given in Table 25; also, data for RhCl(cyttp)¹⁸⁸ are given for comparison. It should be noted that identification of Rh(OC₆H₅)cyttp and Rh(OH)cyttp is tentative, since only ³¹P(¹H) nmr spectroscopy was used to characterize these complexes.

3. Iridium(I) Complexes

The syntheses of monomeric, four coordinate iridium complexes, Ir(OR)P₃ (P₃ = chelating triphosphine ligand), were approached in a manner analogous to those of the rhodium complexes. Alkoxide bridged bimetallic complexes of iridium, [Ir(OR)COD]₂, XII (OR = OCH₃, OCH₂CH₃, OC₆H₅, O(CH₂)₂CH₃, O(CH₂)₃CH₃, and O(CH₂)₇CH₃), were reported previously.¹⁷⁰ The synthesis of the methoxiide bridged complex, [Ir(OCH₃)COD]₂, has been reported a second time by use of a method similar to the procedure by use of the synthesis of [Rh(OR)COD]₂ complexes (Eq. 95).¹⁸² The author extended this method to the

\[
[IrCl(COD)]₂ + 2KOH + 2ROH \rightarrow [Ir(OR)COD]₂ + 2KCl + 2H₂O \quad (95)
\]

synthesis of the hydroxide complex, [Ir(OH)COD]₂, which has not been reported previously. In addition, the reaction depicted in Equation
Table 25. $^{31}P(^1H)$ NMR Data for RhX(cyttp) Complexes

<table>
<thead>
<tr>
<th>X</th>
<th>Cl$^a$</th>
<th>OH</th>
<th>OC$_6$H$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta P_1$</td>
<td>20.6</td>
<td>24.7</td>
<td>24.1</td>
</tr>
<tr>
<td>$\delta P_2$</td>
<td>9.2</td>
<td>11.2</td>
<td>8.6</td>
</tr>
<tr>
<td>$^1J(Rh-P1)$</td>
<td>174</td>
<td>164</td>
<td>159</td>
</tr>
<tr>
<td>$^1J(Rh-P2)$</td>
<td>126</td>
<td>132</td>
<td>134</td>
</tr>
<tr>
<td>$^2J(P1-P2)$</td>
<td>49</td>
<td>53</td>
<td>50</td>
</tr>
</tbody>
</table>

Chemical shifts are reported in ppm. Coupling constants are reported in Hz. The spectra were recorded in toluene.

a) Ref. 188.
95 has been used to synthesize [Ir(OC₆H₅)COD]₂. This complex was reported previously; however, it was prepared from a reaction between [Ir(OCH₃)COD]₂ and C₆H₅OH.¹⁷⁰

The [Ir(OR)COD]₂ complexes (OR = OH, OCH₃, OC₆H₅) have been characterized by infrared spectroscopy. The infrared spectrum of [Ir(OH)COD]₂ is shown in Figure 50. The O-H stretching frequency of the [Ir(OH)COD]₂ complex exhibits a strong, sharp absorption at 3542 cm⁻¹. The alkoxide complexes show strong absorptions due to the C-O stretching vibration at 1068 cm⁻¹ and 1060 cm⁻¹ for the phenoxide complex, [Ir(OC₆H₅)COD]₂ and for the methoxide complex, [Ir(OCH₃)COD]₂, respectively. In addition, the phenoxide group of [Ir(OC₆H₅)COD]₂ exhibits a strong absorption at 1581 cm⁻¹ due to the C=C ring stretching frequency.

Treatment of [Ir(OR)COD]₂ complexes (OR = OH, OCH₃, OC₆H₅) with chelating triphosphine ligands (ttp and cytpp) produces different products, depending on the duration and temperature of the experiment. Reactions between [Ir(OR)COD]₂ (OR = OH, OCH₃, OC₆H₅) and two equivalents of ttp or cytpp in toluene at room temperature over an 18 to 42 hour period results in the formation of yellow to pale-orange solids. However, these compounds decompose to gray solids after several days under an argon atmosphere, even when kept cold (0°C) and in the dark. This rapid decomposition of the complexes prevented successful elemental analyses from being performed on most of the complexes. However, based on the successful elemental analysis of the methoxide complex of ttp, the complexes are tentatively assigned as
Figure 50. The infrared spectrum of [Ir(OH)COD]₂. (Nujol mull).
the 18-electron, five-coordinate iridium(I) complexes, \( \text{Ir}(\text{C}_8\text{H}_{12}\text{OR})_3 \), in which an OR group has attacked the coordinated 1,5-cyclooctadiene ligand (Eq. 96). The following products were obtained from the general reaction depicted in Equation 96: (1) \( \text{Ir}(\text{C}_8\text{H}_{12}\text{OH})_3 \); (2) \( \text{Ir}(\text{C}_8\text{H}_{12}\text{OCH}_3)_3 \); (3) \( \text{Ir}(\text{C}_8\text{H}_{12}\text{OC}_6\text{H}_5)_3 \); and (4) \( \text{Ir}(\text{C}_8\text{H}_{12}\text{OH})_3 \). An attempt will be made to prove these assignments using available spectroscopic data.

The reaction between \([\text{Ir(OCH}_3]\text{COD})_2 \) and cytpp was not successful; a characterized product was not isolated. A similar reaction between \([\text{Ir(OC}_6\text{H}_5]\text{COD})_2 \) and cytpp leads to a four-coordinate complex \( \text{Ir}(\text{OC}_6\text{H}_5)_3 \). This complex will be discussed in more detail in a later section.

The \( \text{^{31}P} (\text{^1H}) \) nmr spectra of the \( \text{Ir}(\text{C}_8\text{H}_{12}\text{OR})_3 \) complexes are characteristic of an ABP spin system in which three magnetically inequivalent phosphorus atoms are coordinated to iridium. The spectra for \( \text{Ir}(\text{C}_8\text{H}_{12}\text{OCH}_3)_3 \) (Figure 51) and \( \text{Ir}(\text{C}_8\text{H}_{12}\text{OH})_3 \) (Figure 52) are first order; however, the remaining spectra are characteristic of a second order ABP spin system.\(^{186}\) The second order \( \text{^{31}P} (\text{^1H}) \) nmr spectrum for \( \text{Ir}(\text{C}_8\text{H}_{12}\text{OC}_6\text{H}_5)_3 \) is shown in Figure 53 and the data for these complexes are compiled in Table 26. Several of the complexes show one major set of peaks and one or two minor sets of peaks, indicative of two or three compounds or isomers.
Figure 51. 250 MHz $^{31}\text{P}^{(1\text{H})}$ nmr spectrum of Ir(C$_8$H$_2$OCH$_3$)ttp in THF with C$_6$D$_6$ added as an internal lock.
Figure 52. 250 MHz $^{31}$P($^1$H) nmr spectrum of Ir(C$_8$H$_{12}$OH)cyttpp in THF with C$_6$D$_6$ added as an internal lock.
Figure 53. 250 MHz $^{31}$P($^1$H) nmr spectrum of Ir(C$_8$H$_{12}$OC$_6$H$_5$)ttp in THF with C$_6$D$_6$ added as an internal lock.
Table 26. $^{31}P(\text{H})$ NMR Data for Ir(C$_8$H$_{12}$OR)$_{ttp}$ and Ir(C$_8$H$_{12}$OH)$_{cyttp}$ Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>$2J(P1-P2)$</th>
<th>$2J(P1-P3)$</th>
<th>$2J(P2-P3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir(C$<em>8$H$</em>{12}$OH)$_{ttp}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Major isomer</td>
<td>-50.23</td>
<td>-41.37</td>
<td>-29.76</td>
<td>17.3</td>
<td>16.8</td>
<td>72.0</td>
</tr>
<tr>
<td>Minor isomer</td>
<td>-50.61</td>
<td>-35.27</td>
<td>-30.83</td>
<td>16.4</td>
<td>10.0</td>
<td>75.0</td>
</tr>
<tr>
<td>Ir(C$<em>8$H$</em>{12}$OCH$<em>3$)$</em>{ttp}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Major isomer</td>
<td>-51.74</td>
<td>-34.95</td>
<td>-29.87</td>
<td>14.5</td>
<td>16.2</td>
<td>72.0</td>
</tr>
<tr>
<td>Minor isomer</td>
<td>-37.61</td>
<td>-41.91</td>
<td>-30.78</td>
<td>16.2</td>
<td>13.6</td>
<td>57.7</td>
</tr>
<tr>
<td>Ir(C$<em>8$H$</em>{12}$OC$_6$H$<em>5$)$</em>{ttp}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Major isomer</td>
<td>-50.24</td>
<td>-30.04</td>
<td>-29.05</td>
<td>16.4</td>
<td>17.8</td>
<td>71.0</td>
</tr>
<tr>
<td>Ir(C$<em>8$H$</em>{12}$OH)$_{cyttp}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Major isomer</td>
<td>-52.63</td>
<td>-41.37</td>
<td>-29.76</td>
<td>17.3</td>
<td>14.0</td>
<td>52.6</td>
</tr>
<tr>
<td>Minor isomer</td>
<td>-54.30</td>
<td>-38.27</td>
<td>-35.01</td>
<td>15.7</td>
<td>21.6</td>
<td>44.0</td>
</tr>
</tbody>
</table>

Chemical shifts are reported in ppm, coupling constants are reported in Hz. The spectra were recorded in toluene with C$_6$D$_6$ added as an internal lock.
Typically, the $^{31}\text{P}(^1\text{H})$ nmr spectra of four-coordinate, planar complexes of iridium(I), $\text{IrX}(\text{P}_3)^{n+}$ ($X = \text{anionic or neutral ligand; } \text{P}_3 = \text{ttp or cytpp; } n = 0, 1$) are characteristic of a first-order $A_2B$ spin system. The ABP spin system of the $\text{Ir}(\text{C}_8\text{H}_{12}\text{OR})\text{P}_3$ complexes suggests that these systems are either five- or six-coordinate. Thus, it is suggested that the 1,5-cyclooctadiene molecule remains coordinated to iridium. There is literature precedence for 1,5-cyclooctadiene remaining bound to products isolated from reactions similar to that depicted in Equation 96. For example, the reaction between $[\text{IrCl(COD)}]^2$ and two equivalents of cytpp lead to the formation of a five coordinate species, $\text{IrCl(COD)cytpp}$ (XIII), in which one of the terminal phosphorus atoms ($\text{Cy}_2\text{P}$- group) of the cytpp ligand remains uncoordinated. The 1,5-cyclooctadiene ligand remained coordinated to iridium by both olefinic groups. A similar five coordinate complex, $\text{IrCl(COD)PPN}$, was prepared by the reaction of $[\text{IrCl(COD)}]^2$ with two equivalents of PPN ($\text{PPN} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{P(Ph)(CH}_2)_2\text{N(CH}_3)_2$). Based on the $^1\text{H}$ nmr spectrum of this complex, the nitrogen group of the PPN ligand remains
uncoordinated; however, the 1,5-cyclooctadiene complex remains coordinated through both olefinic groups. A similar complex, \( \text{IrCl(COD)ppol} \cdot \text{C}_6\text{H}_6 \), is obtained when \( [\text{IrCl(COD)}]_2 \) is reacted with two equivalents of ppol in benzene (ppol = Ph\(_2\)P(CH\(_2\))\(_3\)P(Ph)-CH\(_2\)CH\(_2\)CH-CH\(_2\))\(^{62}\). In this case, the olefinic group of the ppol ligand remains uncoordinated, while the 1,5-cyclooctadiene ligand remains coordinated through both olefinic groups.

The iridium(I) complexes prepared in this investigation (Eq. 96) differ from the three cases discussed above, because all three phosphorus atoms of the ligand are coordinated to iridium. If both olefinic groups of 1,5-cyclooctadiene also remain coordinated to iridium, the resulting complexes would be formulated as a 20-electron, six-coordinated complexes, i.e. \( \text{Ir(OR)(COD)P}_3 \). This formulation is unlikely and probably incorrect.

The presence of coordinated 1,5-cyclooctadiene can be confirmed usually by \(^1\text{H} \) nmr spectroscopy. The chemical shift of olefins shifts downfield by about 1 ppm upon coordination to a metal.\(^{193}\) Unfortunately, the \(^1\text{H} \) nmr spectra of the complexes prepared in this investigation exhibit a broad peak from approximately 1 ppm to 3.5 ppm. This is the same region in which coordinated 1,5-cyclooctadiene is found. However, infrared spectra of these iridium complexes do not exhibit a peak due to a free olefinic group from 1,5-cyclooctadiene. The infrared spectrum of uncoordinated 1,5-cyclooctadiene exhibits a strong peak at 1650 cm\(^{-1}\) due to the C=C stretch.\(^{192}\) The absorption of the C=C stretch shifts to lower energy when an olefin coordinates to a
metal. Although the infrared spectra of Ir(C₈H₁₂OR)P₃ complexes are rather unremarkable, strong peaks at 1650 cm⁻¹ are not observed. The presence of the phenoxide group in the complex formulated as Ir(C₈H₁₂OC₆H₅)ttp is confirmed by a peak at 1595 cm⁻¹ in the infrared spectrum due to the C=C ring stretching vibration (Figure 54). However, strong absorptions due to the C-O stretch of the coordinated alkoxide are not observed in the infrared spectra of Ir(C₈H₁₂OC₆H₅)ttp and Ir(C₈H₁₂OCH₃)P₃ (Figure 55). Absorption peaks due to the O-H stretch of the hydroxide complexes, Ir(C₈H₁₂OH)cyttp and Ir(C₈H₁₂OH)ttp (Figure 56), are not observed. The spectra of these two complexes do exhibit very weak peaks in the absorption region of uncoordinated carbon-carbon double bonds. The ³¹P(¹H) nmr spectra of these complexes also show the presence of a small concentration of a four coordinate species, presumably the Ir(OH)P₃ complexes. Therefore, the weak peaks around 1650 cm⁻¹ in the infrared spectra are assigned to trace amounts of free 1,5-cyclooctadiene.

Based on the data given above, one of the olefinic groups of 1,5-cyclooctadiene does not dissociate from iridium to yield 18-electron, five-coordinate complexes formulated as Ir(OR)(η⁴-COD)P₃. The spectroscopic data suggest that: (1) the chelating triphosphine ligand is coordinated to iridium through all three phosphorus atoms; (2) the OR group is probably no longer coordinated to iridium, but it is present in the complex; and (3) the 1,5-cyclooctadiene does not dissociate from iridium, but its formula may be altered. Thus, it is suggested that the coordinated alkoxide or hydroxide ligands
Figure 54. The infrared spectrum of $\text{Ir(C}_8\text{H}_{12}\text{O}_2\text{C}_6\text{H}_5)\text{ttp}$.
Figure 55. The infrared spectrum of Ir($C_8H_{12}OCH_3$)ttp.
Figure 56. The infrared spectrum of Ir(C$_8$H$_{12}$OH)$_{2}$ttp. (Nujol mull).
attack the coordinated 1,5-cyclooctadiene ligand to give an iridium-carbon bond and a carbon-alkoxide or hydroxide bond (Eq. 96). This reaction would result in 18-electron, five-coordinate iridium(I) complexes, which are formulated as Ir(C8H12OR)P3. There is precedence for the alkoxidation of coordinated 1,5-cyclooctadiene in the literature. For example, PtCl2COD reacts with silver ions in the presence of methanol to give [Pt(μ-OCH3)(C8H12OCH3)]2.135,136 Eight possible geometric isomers (XIVa-XIVh) for the Ir(C8H12OR)P3 complexes are shown in Scheme 19. Unfortunately, the major geometric isomer formed for the Ir(C8H12OR)P3 complexes cannot be determined based on the spectroscopic data. It should be noted that the assignment of the complexes prepared using the reaction depicted in Equation 96 as Ir(C8H12OR)P3 is not definitive, but rapid decomposition and insolubility of the complexes prevent further characterization.

In order to displace the 1,5-cyclooctadiene ligand from [Ir(OR)COD]2 complexes in the presence of the chelating triphosphine ligands to form the iridium(I) alkoxide or hydroxide complexes, the reactions were carried out in refluxing toluene over an 18 hour period (Eq. 97). This reaction lead to the successful isolation

\[
[\text{Ir(OR)COD}]_2 + 2\text{P}_3 \rightarrow 2\text{Ir(OR)P}_3 + 2\text{COD}
\]  

(97)

of Ir(OC6H5)ttp from [Ir(OC6H5)COD]2 and two equivalents of ttp. Treatment of [Ir(OH)COD]2 with two equivalents of ttp gave only the five-coordinate complex, Ir(C8H12OH)ttp; the 1,5-cyclooctadiene ligand could not be displaced. Treatment of [Ir(OCH3)COD]2 with two
Scheme 19
equivalents of ttp in refluxing toluene lead to an uncharacterized dihydride complex of iridium. The reaction of \([\text{Ir(OH)COD}]_2\) with cyttpp lead to formation of \(\text{Ir(OH)cyttpp}\); however, the complex could not be isolated as a solid. As mentioned previously, \([\text{Ir(OCH}_3\text{)COD}]_2\) does not react cleanly with cyttpp. The \([\text{Ir(OC}_6\text{H}_5\text{)COD}]_2\) complex does react with cyttpp at room temperature to give \(\text{Ir(OC}_6\text{H}_5\text{)cyttpp}\); however, the Ir(OC6H5)cyttpp complex could not be isolated as a solid and it was subsequently characterized in solution.

The \(^{31}P\)\(^{(1)H}\) nmr spectra of \(\text{Ir(OC}_6\text{H}_5\text{)ttp}\), \(\text{Ir(OH)cyttpp}\) and \(\text{Ir(OC}_6\text{H}_5\text{)cyttpp}\) (Figure 57) are characteristic of a first order \(A_2B\) spin system. The spectra exhibit a doublet due to splitting of two equivalent terminal phosphorus atoms, Ph\(_2\)P (ttp) or Cy\(_2\)P (cyttpp) (P2) by the central phosphorus atom PhP (P1); also, there is a triplet due to coupling of the central phosphorus atom by the two equivalent terminal phosphorus atoms (P2). The data are compiled in Table 27, and the data for \(\text{IrCl(ttp)}\) and \(\text{IrCl(cyttpp)}\) are given for comparison. The \(^{31}P\)\(^{(1)H}\) nmr spectrum of \(\text{Ir(OC}_6\text{H}_5\text{)ttp}\) exhibits a minor set of peaks, which can be assigned to \(\text{IrCl(ttp)}\) (Figure 58). The chloride complexes of ttp and cyttpp are observed occasionally in the \(^{31}P\)\(^{(1)H}\) nmr spectra of the \(\text{Ir(OR)P}_3\) and \(\text{Rh(OR)P}_3\) complexes. The chloride impurity is believed to arise from traces of LiCl dissolved in the chelating triphosphine ligands or from traces of KCl which may have co-precipitated with the \([\text{Rh(OR)COD}]_2\) and \([\text{Ir(OR)COD}]_2\) starting materials. The \(^{31}P\)\(^{(1)H}\) nmr spectrum of \(\text{Ir(OH)cyttpp}\) exhibits peaks due to several impurities which also possess \(A_2B\) spin systems.
Figure 57. 250 MHz $^{31}$P($^1$H) nmr spectrum of Ir(OC$_6$H$_5$)cytpp in THF with C$_6$D$_6$ added as an internal lock.
Table 27. $^{31}P(^1H)$ NMR Data for IrX(ttp) and IrX(cytttp) Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta$P1</th>
<th>$\delta$P2</th>
<th>$^2J$(P1-P2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrCl(ttp)$^a$</td>
<td>-19.9</td>
<td>2.7</td>
<td>32.8</td>
</tr>
<tr>
<td>Ir(OC$_6$H$_5$)ttp$^b$</td>
<td>-42.17</td>
<td>-28.83</td>
<td>26.3</td>
</tr>
<tr>
<td>IrCl(cytttp)$^c$</td>
<td>-16.8</td>
<td>1.98</td>
<td>30.5</td>
</tr>
<tr>
<td>Ir(OH)cyttyp$^d$</td>
<td>-17.96</td>
<td>0.90</td>
<td>31.1</td>
</tr>
<tr>
<td>Ir(OC$_6$H$_5$)cyttyp$^d$</td>
<td>-19.63</td>
<td>5.15</td>
<td>29.1</td>
</tr>
</tbody>
</table>

Chemical shifts are reported in ppm. Coupling constants are reported in Hz.

a) Ref. 189.

b) Ref. 112.

c) THF/C$_6$D$_6$.

d) Toluene/C$_6$D$_6$
Figure 58. 250 MHz $^{31}P(\text{H})$ nmr spectrum of Ir($\text{OC}_6\text{H}_5$)ttp in THF with $\text{C}_6\text{D}_6$ added as an internal lock. a. Ir(Cl)ttp.

b. Unreacted Ir($\text{OC}_6\text{H}_5$)(COD)ttp.
The infrared spectrum of Ir(O\textsubscript{6}H\textsubscript{5})ttp (Figure 59) exhibits a peak at 1585 cm\textsuperscript{-1} due to the C=C ring stretching vibration of the phenoxide group. The cttt complexes, Ir(OH)ctt and Ir(O\textsubscript{6}H\textsubscript{5})ctt were not characterized further, since the complexes could not be isolated as solids.

B. Reaction Chemistry

1. Reactions with Organic Acids

Although condensation reactions between platinum(II) hydroxide complexes have been investigated extensively\textsuperscript{117-120,122}, condensation reactions with monomeric rhodium(I) alkoxide and hydroxide complexes have not been examined. A general condensation reaction is depicted in Equation 98 (M = group VIII metal, HA = acid, OR = hydroxide or alkoxide group). The Rh(OH)ttp and Rh(O\textsubscript{6}H\textsubscript{5})ttp complexes prepared in this investigation have been reacted with a series of organic acids. The organic acids and their pK\textsubscript{a} values are listed in Table 28.

\[ M\text{-OR} + HA \rightarrow M\text{-A} + HOR \] (98)

Reactions between Rh(OR)ttp (OR = OH, O\textsubscript{6}H\textsubscript{5}) and trifluoroacetic acid (Eq. 99), p-bromobenzoic acid (Eq. 100) and benzoic acid
Figure 59. The infrared spectrum of Ir(O\textsubscript{5}H\textsubscript{5})ttp. (Nujol mull).
### Table 28. Organic Acids and pK\textsubscript{a} Values\textsuperscript{a}

<table>
<thead>
<tr>
<th>Acid</th>
<th>pK\textsubscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF\textsubscript{3}CO\textsubscript{2}H</td>
<td>0.2</td>
</tr>
<tr>
<td>p-BrC\textsubscript{6}H\textsubscript{4}CO\textsubscript{2}H</td>
<td>3.97</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{5}CO\textsubscript{2}H</td>
<td>4.20</td>
</tr>
<tr>
<td>CH\textsubscript{3}CO\textsubscript{2}H</td>
<td>4.74</td>
</tr>
<tr>
<td>p-NO\textsubscript{2}C\textsubscript{6}H\textsubscript{4}OH</td>
<td>7.15</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{5}OH</td>
<td>10.00</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>15.7</td>
</tr>
<tr>
<td>CH\textsubscript{3}C(O)CH\textsubscript{3}</td>
<td>20</td>
</tr>
<tr>
<td>CH\textsubscript{3}CN</td>
<td>25</td>
</tr>
</tbody>
</table>

\textsuperscript{a) Data taken from reference 100.}
(Eq. 101) in benzene proceeded smoothly to give the metal-carboxylates and water or phenol, respectively. The $^{31}$P($^1$H) nmr spectra of these carboxylate complexes exhibit peaks characteristic of an $A_2BX$ spin system. The $^{31}$P($^1$H) nmr spectrum of Rh(OC(O)C$_6$H$_5$)ttp exhibits second-order effects (Figure 60). The $^{31}$P($^1$H) nmr data for Rh(OC(O)CF$_3$)ttp, Rh(OC(O)C$_6$H$_4$Br)ttp and Rh(OC(O)C$_6$H$_5$)ttp are given in Table 29. Since the $^{31}$P($^1$H) nmr data for Rh(OC(O)C$_6$H$_4$Br)ttp and Rh(OC(O)C$_6$H$_5$)ttp are nearly identical, the bromine atom in the para position of the phenyl ring exhibits only a small effect on the $^{31}$P($^1$H) nmr spectra. However, the infrared spectra of these metal-condensate is unique. The spectra for Rh(OC(O)C$_6$H$_4$Br)ttp and Rh(OC(O)C$_6$H$_5$)ttp are shown in Figures 61 and 62, respectively.

Metal-acetate complexes are known to coordinate through one or both oxygen atoms (XVIa and XVIb). However, the two coordination geometries can be differentiated by use of infrared spectroscopy. In complexes coordinated to a single oxygen atom, XVIa, one of the C-O bonds shows enhanced double bond character and is often observed in
Figure 60. 250 MHz $^{31}\text{P}^{1\text{H}}$ nmr spectrum of Rh(OC(O)C$_6$H$_5$)ttp in THF with C$_6$D$_6$ added as an internal lock.
Table 29. $^{31}\text{P}^{1\text{H}}$ NMR Data for Rh(OC(O)R)ttp Complexes

<table>
<thead>
<tr>
<th>-OC(O)R</th>
<th>$\delta$P1</th>
<th>$\delta$P2</th>
<th>$^1J$(Rh-P1)</th>
<th>$^1J$(Rh-P2)</th>
<th>$^2J$(P1-P2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OC(O)CF$_3$</td>
<td>26.01</td>
<td>10.84</td>
<td>123.2</td>
<td>95.4</td>
<td>38.4</td>
</tr>
<tr>
<td>-OC(O)C$_6$H$_4$Br</td>
<td>18.10</td>
<td>9.38</td>
<td>155.3</td>
<td>135.7</td>
<td>54.0</td>
</tr>
<tr>
<td>-OC(O)C$_6$H$_5$</td>
<td>18.22</td>
<td>9.03</td>
<td>155.1</td>
<td>135.9</td>
<td>54.1</td>
</tr>
</tbody>
</table>

The chemical shifts are reported in ppm, the coupling constants are reported in Hz. The spectra were recorded in THF with C$_6$D$_6$ added as an internal lock.
Figure 61. The infrared spectrum of Rh(O(O)C₆H₄Br)ttt.

(Nujol mull).
Figure 62. The infrared spectrum of Rh(OC(O)C₆H₅)tp. (Nujol mull).
the 1590 to 1650 cm⁻¹ region. In contrast, acetate complexes coordinated through both oxygen atoms, XVIb, often exhibit peaks between 1400 cm⁻¹ and 1550 cm⁻¹.¹⁸⁴ A peak at 1778 cm⁻¹ is observed in the infrared spectrum of Rh(OC(0)CF₃)ttp¹⁹² which is assigned to a C=O stretching vibration; hence, the complex possesses coordination geometry XVIa. Likewise, peaks observed at 1609 cm⁻¹ in the spectrum of Rh(OC(0)C₆H₄Br)ttp¹⁹² (Figure 61) and at 1710 cm⁻¹ in the spectrum of Rh(OC(0)C₆H₅)ttp¹⁹² (Figure 62) are indicative of geometry XVIa.

Reactions of acetic acid (pKₐ = 4.74) with Rh(OH)ttp and Rh(OR)ttp lead consistently to decomposition of the metal complexes. The only identified product from these reactions was ligand oxide. In addition, reactions of p-nitrophenol (p-NO₂C₆H₄OH, pKₐ = 7.15) also lead to decomposition of the metal complexes; however, the decomposition products from these reactions were not identified. The hydroxide complex, Rh(OH)ttp, was reacted overnight with an equivalent amount of phenol (pKₐ = 10.00) in toluene at room temperature. However, on the basis of ³¹P(¹H) nmr data, no reaction occurred; only starting material was recovered from the reaction mixture. Likewise, Rh(OC₆H₅)ttp did not react with distilled water (pKₐ = 15.7).

Four-coordinate platinum(II) hydroxide complexes are very reactive toward organic acids, including very weak organic acids such as acetone (pKₐ = 20) and acetonitrile (pKₐ = 25). In contrast, the Rh(OR)ttp complexes (OR = OH, OC₆H₅) react only with organic acids with pKₐ values less than or equal to 4.20. Platinum(II) complexes are more reactive towards organic acids as the Pt-OH bond becomes more
This suggests that the lack of reactivity of Rh(OH)ttp and Rh(OR)ttp is due to the lack of ionic character of the Rh-OR bond (OR = OH, OC₆H₅), although rhodium(I) complexes are not as polarizable as platinum(II) complexes. Hence, the Rh-OR bonds may possess stronger covalent character than was originally predicted. This is supported by the lack of reactivity toward organic acids and the unexpectedly high position of the OC₆H₅⁻ and OH⁻ ligands in the trans influence series.

2. Reactions with SO₂ and CO

Anhydrous sulfur dioxide gas reacts with Rh(OH)ttp and Rh(OC₆H₅)ttp to yield a rhodium sulfonic acid, Rh(S(O)₂OH)ttp·SO₂, and a rhodium sulfonate, Rh(S(O)₂OC₆H₅)ttp·SO₂. This is the first report of SO₂ insertions into a Rh-OR bond to yield rhodium sulfonates and sulfonic acids. Based on elemental analyses, the complexes incorporate two molecules of SO₂. Analysis of the infrared spectrum (Nujol mull) of Rh(S(O)₂OC₆H₅)ttp·SO₂ (Figure 63) shows the presence of six peaks not present in the infrared spectrum of Rh(OC₆H₅)ttp. Four of the peaks are assigned based on assignments for platinum and palladium sulfonates.¹⁹⁴-¹⁹⁷ The asymmetric S-O stretching frequency for the platinum and palladium sulfonates absorbs between 1260 and 1270 cm⁻¹, the symmetric S-O stretching frequency absorbs between 1100 and 1110 cm⁻¹, the S-O stretching frequency absorbs between 900 and 1000 cm⁻¹ and the O-S-O bending vibration absorbs between 595-650 cm⁻¹. The peaks at 1260 cm⁻¹, 1150 cm⁻¹, 1015 cm⁻¹ and 590 cm⁻¹
Figure 63. The infrared spectrum of \( \text{Rh(S(O)}_2\text{OC}_6\text{H}_5)\text{ttp} \cdot \text{SO}_2 \).

(Nujol mull).
in the infrared spectrum of Rh(S(O)₂OC₆H₅)ttp·SO₂ are assigned to the asymmetric S=O stretch, symmetric S=O stretch, S-O stretch and O-S-O bend, respectively, of an SO₂ molecule inserted into the Rh-OC₆H₅ bond. The two remaining peaks at 1250 cm⁻¹ and 1085 cm⁻¹ are assigned to a second molecule of SO₂, which forms an adduct with the rhodium complex. This assignment is based on assignments made for a series of RhX(ttp)·SO₂ complexes for which the asymmetric S=O stretching vibration absorbs in the region of 1200 cm⁻¹ and symmetric S=O stretching vibration absorbs in the region of 1050 cm⁻¹.  The infrared assignments for the inserted SO₂ molecule and the SO₂ molecule which forms an adduct with the rhodium complex are characteristic of SO₂ molecules coordinated to the metal through the sulfur atom. The asymmetric S=O stretching frequency for a sulfur bound SO₂ molecule is in the range 1250-1100 cm⁻¹ and the symmetric S=O stretching frequency is in the range 1100-1000 cm⁻¹; the stretching frequencies for SO₂ molecules coordinated through oxygen absorb at lower energy. The infrared spectrum of Rh(S(O)₂OH)ttp·SO₂ is shown in Figure 64. Six peaks, in addition to those observed in the infrared spectrum of Rh(OH)ttp, are observed; similar assignments to those described above are made. Diagnostic infrared data are given in Table 30. The proposed structure of the Rh(S(O)₂OR)ttp·SO₂ complexes (XVII, OR = OH, OC₆H₅) is shown below.
Figure 64. The infrared spectrum of Rh(S(O)₂OH)ttp•SO₂.

(Nujol mull).
Table 30. Infrared Data for Rhodium and Iridium Sulfonates

<table>
<thead>
<tr>
<th>Complex</th>
<th>(S=O)$_{as}$</th>
<th>(S=O)$_{s}$</th>
<th>S-O</th>
<th>0-S-0</th>
<th>(S=O)$_{as}^a$</th>
<th>(S=O)$_{s}^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(S(O)$<em>2$OPh)$</em>{ttt}$•SO$_2$</td>
<td>1260</td>
<td>1150</td>
<td>1015</td>
<td>590</td>
<td>1250</td>
<td>1085</td>
</tr>
<tr>
<td>Rh(S(O)$<em>2$OH)$</em>{ttt}$•SO$_2$</td>
<td>1260</td>
<td>1148</td>
<td>1015</td>
<td>589</td>
<td>1250</td>
<td>1085</td>
</tr>
<tr>
<td>Rh(S(O)$<em>2$OPh)$</em>{cytt}$•SO$_2$</td>
<td>1271</td>
<td>1148</td>
<td>1009</td>
<td>582</td>
<td>1259</td>
<td>1095</td>
</tr>
<tr>
<td>Ir(S(O)$<em>2$OPh)$</em>{ttt}$•SO$_2$</td>
<td>1280</td>
<td>1155</td>
<td>1018</td>
<td>596</td>
<td>1260</td>
<td>1095</td>
</tr>
</tbody>
</table>

Stretching frequencies are reported in cm$^{-1}$. The spectra were recorded in the solid state as Nujol mulls or KBr pellets.

a) SO$_2$ adduct
The $^{31}\text{P}^{(1)}\text{H}$ nmr spectra of Rh(S(O)$_2$OC$_6$H$_5$)ttp•SO$_2$ and Rh(S(O)$_2$OH)ttp•SO$_2$ exhibit two sets of peaks characteristic of an $A_2B_1X$ spin system. Thus, a variable temperature $^{31}\text{P}^{(1)}\text{H}$ nmr experiment was performed to examine these complexes for fluxional behavior. The peaks observed in the $^{31}\text{P}^{(1)}\text{H}$ nmr spectrum of Rh(S(O)$_2$OC$_6$H$_5$)ttp•SO$_2$ moved apart as the temperature was cooled to 183K (Figure 65). One of the two sets of peaks in the $^{31}\text{P}^{(1)}\text{H}$ nmr spectrum of Rh(S(O)$_2$OH)ttp•SO$_2$ broadened as the temperature was cooled to 183K, the second set of peaks remained sharp. The $^{31}\text{P}^{(1)}\text{H}$ nmr data are compiled in Table 31. Proton-decoupled phosphorus nmr spectra recorded at temperatures above 303K exhibited many unidentified peaks; indicating that the complexes decompose at higher temperatures. The two sets of peaks in the $^{31}\text{P}^{(1)}\text{H}$ nmr spectra of these complexes are not a result of dissociation of the SO$_2$ adduct. Argon gas was bubbled through solutions of Rh(S(O)$_2$OR)ttp•SO$_2$ (OR = OH, OC$_6$H$_5$) in an attempt to displace the SO$_2$ molecule, but $^{31}\text{P}^{(1)}\text{H}$ nmr spectra of the reaction solutions still displayed two sets of peaks. In addition, RhCl(ttp)•SO$_2$ has been found to be stable with respect to dissociation of SO$_2$.\textsuperscript{187} One possible explanation for the two sets of
Figure 65. 250 MHz $^{31}$P($^1$H) nmr spectra of Rh(S(0)$_2$)OC$_6$H$_5$ttp$\cdot$SO$_2$ in CD$_2$Cl$_2$ at a) 303K and b) 183K.
Table 31. $^{31}P^{(1)}H$ NMR Data for Rhodium and Iridium Sulfonates

<table>
<thead>
<tr>
<th>Complex</th>
<th>δP1</th>
<th>δP2</th>
<th>$^1J$(Rh-P1)</th>
<th>$^1J$(Rh-P2)</th>
<th>$^2J$(P1-P2)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(S(0)2OH)ttp•SO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Major</td>
<td>14.87</td>
<td>1.98</td>
<td>147</td>
<td>114</td>
<td>39</td>
<td>303</td>
</tr>
<tr>
<td>Minor</td>
<td>-4.18</td>
<td>1.46</td>
<td>115</td>
<td>124</td>
<td>45</td>
<td>303</td>
</tr>
<tr>
<td>Major</td>
<td>15.97</td>
<td>2.01</td>
<td>146</td>
<td>113</td>
<td>39</td>
<td>183</td>
</tr>
<tr>
<td>Rh(S(0)2Ph)ttp•SO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Major</td>
<td>-4.02</td>
<td>1.43</td>
<td>115</td>
<td>125</td>
<td>45</td>
<td>303</td>
</tr>
<tr>
<td>Minor</td>
<td>21.86</td>
<td>-0.06</td>
<td>161</td>
<td>114</td>
<td>40</td>
<td>303</td>
</tr>
<tr>
<td>Major</td>
<td>-4.59</td>
<td>2.19</td>
<td>112</td>
<td>122</td>
<td>44</td>
<td>183</td>
</tr>
<tr>
<td>Minor</td>
<td>23.43</td>
<td>-0.06</td>
<td>158</td>
<td>112</td>
<td>39</td>
<td>183</td>
</tr>
<tr>
<td>Ir(S(0)2Ph)ttp•SO₂</td>
<td>-34.38</td>
<td>-16.84</td>
<td></td>
<td></td>
<td></td>
<td>31.7</td>
</tr>
<tr>
<td>Major</td>
<td>-42.97</td>
<td>-24.93</td>
<td></td>
<td></td>
<td></td>
<td>24.2</td>
</tr>
<tr>
<td>Rh(S(0)2Ph)cyp•SO₂</td>
<td>18.45</td>
<td>2.92</td>
<td>156</td>
<td>107</td>
<td>37</td>
<td>303</td>
</tr>
</tbody>
</table>

Chemical shifts are reported in ppm, coupling constants are reported in Hz. Spectra were recorded in CD$_2$Cl$_2$. K = Kelvin, P1 = PhP, P2 = Ph$_2$P.
peaks in the $^{31}\text{P}^{(1}\text{H})$ nmr spectra is that an equilibrium exists in solution between an $S(O)_{2}OR$ group coordinated through sulfur and an $OS(O)OR$ group coordinated through oxygen (Scheme 20). Evidence for this equilibrium was sought using infrared spectroscopy; unfortunately, the complexes are not soluble enough to record satisfactory solution infrared spectra. Nevertheless, linkage isomerization, as depicted in Scheme 20, is documented in the literature.197

Anhydrous sulfur dioxide gas also reacts with Ir$(\text{OC}_{6}\text{H}_{5})\text{ttp}$ to give an iridium sulfonate, Ir$(S(O)_{2}\text{OC}_{6}\text{H}_{5})\text{ttp} \cdot \text{SO}_{2}$. This complex has a structure similar to the rhodium sulfonates (XVII), based on the infrared data (Table 30). The $^{31}\text{P}^{(1}\text{H})$ nmr spectrum exhibits two sets of peaks, of nearly equivalent intensity, characteristic of an $A_{2}B$ spin system (Table 31). Once again, the two sets of peaks may be attributed to a linkage isomerism similar to the mechanism depicted in Scheme 20.

Since the rhodium sulfonate and sulfonic acid complexes of ttp are very insoluble in common organic solvents, an attempt was made to confirm the identification of Rh$(\text{OR})\text{cyttp}$ complexes by preparing the sulfonate analogues, Rh$(S(O)_{2}\text{OR})\text{cyttp} \cdot \text{SO}_{2}$ (Eq. 102). The reaction
[Rh(OR)COD]₂ + 2cyttp + 2SO₂ → 2Rh(S(O)₂OR)cyttp·SO₂ + 2COD (102)

depicted in Equation 102 was used successfully for the synthesis of Rh(S(O)₂OC₆H₅)cyttp·SO₂. The structure of this complex is similar to the ttp analogues (XVII) based on infrared spectroscopy (Table 30). The ³¹P(¹H) nmr spectrum exhibits one set of sharp peaks and one set of very broad peaks (Figure 66). The data are compiled in Table 31. Once again, the two sets of peaks are believed to be due to the linkage isomerism described above (Scheme 20). The reaction depicted in Equation 102 employing [Rh(OH)COD]₂ resulted in a complex which could not be characterized based on its infrared or ³¹P(¹H) nmr spectra.

Complexes Rh(OH)ttp and Rh(OC₆H₅)ttp were reacted with carbon monoxide gas. When carbon monoxide gas is bubbled through benzene solutions of Rh(OR)ttp (OR = OH, OC₆H₅) a red color forms immediately. After several minutes of CO addition, the solutions turn yellow. Concentration of the yellow solutions causes these solutions to turn red once again. In order to isolate solids from the reaction of Rh(OH)ttp and Rh(OC₆H₅)ttp with CO, the reaction solvent had to be removed completely from the red solutions under vacuum. The resulting red solids were unstable and decomposed within two days under an Ar atmosphere.

The infrared spectrum (KBr pellet) of the red solid isolated from the Rh(OH)ttp reaction exhibited a very broad, very weak peak at 3380 cm⁻¹ (O-H stretching vibration), and peaks at 2010 and 1955 cm⁻¹ indicative of coordinated CO molecules. In addition, the infrared
Figure 66. 250 MHz $^{31}$P($^1$H) nmr spectrum of Rh($S(0)$)$_2$OC$_6$H$_5$)cyttp in CD$_2$Cl$_2$ at 303K.
The infrared spectrum (Nujol mull) of the red solid isolated from the reaction of Rh(OC₆H₅)ttt with CO exhibits peaks at 2015 cm⁻¹ and 1905 cm⁻¹ in the carbon monoxide region, a peak at 1585 cm⁻¹, which is assigned to the C=C ring stretching vibration of the OC₆H₅ group, and a peak at 1690 cm⁻¹ characteristic of an inserted CO molecule. Based on these data, the red solids are believed to be mixtures of two rhodium complexes. The first complex is a monocarbonyl complex in which the previously coordinated phenoxide and hydroxide groups act as counter-ions, [Rh(CO)ttt]OC₆H₅ (ν(CO) = 2010 cm⁻¹) and [Rh(CO)ttt]OH (ν(CO) = 2015 cm⁻¹). A similar complex, [Rh(CO)ttt]PF₆, has been reported, and it exhibits a peak at 2026 cm⁻¹. The second complex incorporates a second molecule of carbon monoxide which has been attacked by the OR⁻ counter-anion, Rh(C(O)OH)(CO)ttt (ν(CO) = 1955 cm⁻¹, ν(C(O)OR) = 1655 cm⁻¹, ν(OH) = 3380 cm⁻¹) and Rh(C(O)OC₆H₅)(CO)ttt (ν(CO) = 1905 cm⁻¹, ν(C(O)OR) = 1690 cm⁻¹, ν(C=C) = 1585 cm⁻¹).

The ³¹P(¹H) nmr spectrum of the red solid isolated from the phenoxide complex consists of two sets of peaks. One set of peaks is resolved, but the resonance of the PhP group of the second set of peaks is very broad (Figure 67). The data for the resolved set of peaks are as follows: δPhP = -14.8 ppm; δPh₂P = 8.57 ppm; ¹J(Rh-PhP) = 112 Hz; ¹J(Rh-Ph₂P) = 115 Hz; and ²J(PPh-PPh₂) = 52 Hz. This data is consistent with the data observed for [Rh(CO)ttt]PF₆.
Figure 67. 250 MHz $^{31}$P($^1$H) nmr spectrum of the red solid isolated from the reaction of Rh(OC$_6$H$_5$)ttt with CO in C$_6$D$_6$. 
solid isolated from the hydroxide complex is very insoluble, and the $^{31}$P($^1$H) nmr spectrum displays only very weak, poorly resolved peaks. The second set of broad peaks observed in the $^{31}$P($^1$H) spectrum of the phenoxide complex is believed to be due to the attack of the OC$_6$H$_5^-$ group on one of the coordinated CO ligands to give Rh(C(O)OC$_6$H$_5$)(CO)ttp. A similar reaction is believed to be operating in the hydroxide reaction. The proposed mechanism is given in Scheme 21 and is similar to the proven mechanism for the insertion of CO into an iridium alkoxide bond (Eqs. 60-62).\textsuperscript{152,153}

\begin{align*}
\text{Rh(OR)ttp} + \text{CO} &\rightarrow [\text{Rh(CO)ttp}]\text{OR} \\
[\text{Rh(CO)ttp}]\text{OR} + \text{CO} &\rightarrow [\text{Rh(CO)}_2\text{ttp}]\text{OR} \\
[\text{Rh(CO)}_2\text{ttp}]\text{OR} &\rightarrow \text{Rh(C(O)OR)(CO)ttp}
\end{align*}

\textbf{Scheme 21}

In an attempt to establish the above mechanism, several experiments were carried out beginning with a variable temperature $^{31}$P($^1$H) nmr experiment. The nmr spectra were recorded in toluene (CD$_3$C$_6$D$_5$ added as an internal lock) on the red and yellow solutions resulting from reaction of Rh(OC$_6$H$_5$)ttp with CO. The nmr sample of the yellow solution was prepared under a CO atmosphere. The red and yellow solutions appeared to equilibrate to orange solutions after several minutes; however, for clarity, the solutions will still be referred to as red and yellow. Two sets of peaks are observed in both the red and yellow solutions at room temperature (303K); the major set of peaks are sharp and the second, minor set of peaks are broad.
(Figure 68). The broad set of peaks exhibited an increase in intensity in the yellow solution. The data are compiled in Table 32. The data of the minor set of peaks matches the data obtained on the red solid discussed above. The $^{31}$P($^1$H) nmr spectra of the red and yellow solutions were recorded at low temperatures (down to 195K) and high temperatures (375K) but the broad set of peaks simply became broader. The major set of peaks was not affected except for slight differences in the chemical shifts of P1 and P2, as the temperature was varied. Similar $^{31}$P($^1$H) nmr data for the hydroxide analogues could not be obtained because the solutions were too weakly concentrated.

The yellow solid of the phenoxide complex was isolated when carbon monoxide gas was bubbled through a solution of Rh(O$\text{C}_6\text{H}_5$)ttp in benzene until the solvent evaporated. The yellow solid was stable only under a carbon monoxide atmosphere. The $^{31}$P($^1$H) nmr spectrum of the yellow solid in benzene ($\text{C}_6\text{D}_6$ added as an internal lock) gave the following data: $\delta$PhP = 13.02 ppm; $\delta$Ph$_2$P = 3.35 ppm; $^1$J(Rh-PhP) = 99.0 Hz; $^1$J(Rh-Ph$_2$P) = 141.4 Hz; and $^2$J(PhP-Ph$_2$P) = 37.6 Hz. This matches the data for the major set of peaks given in Table 32 and confirms that this set of peaks is due to the yellow complex in solution.

The $^{31}$P($^1$H) nmr data suggest that an equilibrium exists between the red complex, which is assigned to the monocarbonyl complex, [Rh(CO)ttp]OR, and the yellow complex, which is assigned to Rh(C(0)OR)(CO)ttp. This equilibrium is dependent on the CO concentration, high CO concentration favoring the inserted product.
Figure 68. 250 MHz $^{31}P(^1H)$ nmr spectrum of the red solution containing the product from the reaction of Rh(OC$_6$H$_5$)ttp with CO in toluene with d$_8$-toluene added as an internal lock.
Table 32. $\text{^{31}P(^1H)}$ NMR Data for Rh(O\text{C}_6\text{H}_5)\text{ttp} + \text{CO} \text{Reaction Mixtures}$

<table>
<thead>
<tr>
<th>Set of Peaks</th>
<th>$\delta\text{P}_1$</th>
<th>$\delta\text{P}_2$</th>
<th>$^1J(\text{Rh-P}_1)$</th>
<th>$^1J(\text{Rh-P}_2)$</th>
<th>$^2J(\text{P}_1-\text{P}_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major</td>
<td>3.75</td>
<td>13.49</td>
<td>99.5</td>
<td>141.0</td>
<td>36</td>
</tr>
<tr>
<td>Minor</td>
<td>-14.73</td>
<td>3.75</td>
<td>112.6</td>
<td>115.3</td>
<td>52</td>
</tr>
</tbody>
</table>

Chemical shifts are reported in ppm, coupling constants are reported in Hz. The spectra were recorded in toluene with d-8 toluene added as an internal lock. $\text{P}_1 = \text{PhP}$, $\text{P}_2 = \text{Ph}_2\text{P}$.
The final experiment employed to test the mechanism suggested in Scheme 21 involved the addition of NaAsF$_5$ dissolved in THF to the red solutions of the phenoxide and hydroxide complexes in toluene. Solids immediately precipitated from the solutions. The $^{31}$P($^1$H) nmr data for the solids isolated from the phenoxide and hydroxide reactions are identical. The spectrum of the solid isolated from the phenoxide reaction is given in Figure 69. The $^{31}$P($^1$H) nmr data for the complex are as follows: $\delta$PhP = -13.74; $\delta$Ph$_2$P = 5.82; $^1$J(Rh-PhP) = 113.8 Hz; $^1$J(Rh-Ph$_2$P) = 115.2 Hz; and $^2$J(PhP-Ph$_2$P) = 52.2 Hz. This data matches the $^{31}$P($^1$H) nmr data for the known complex, [Rh(CO)ttt]PF$_6$, and the red solid isolated for the phenoxide complex. This complex is the monocarbonyl complex, [Rh(CO)ttt]AsF$_6$. The infrared spectrum of [Rh(CO)ttt]AsF$_6$ (Figure 70) exhibits a peak at 2020 cm$^{-1}$ due to the coordinated CO ligand and peaks at 700 cm$^{-1}$ and 396 cm$^{-1}$ due to the AsF$_6$ group. The CO ligand of the [Rh(CO)ttt]PF$_6$ complex exhibits a stretching frequency of 2026 cm$^{-1}$.198

Based on the data given above, the reactions of Rh(OR)ttt (OR = OH, OC$_6$H$_5$) with CO appear to proceed by the mechanism depicted in Scheme 21. The formation of [Rh(CO)ttt]AsF$_6$ from the red solutions suggest that [Rh(CO)ttt]OR is the correct formulation for the red monocarbonyl intermediate proposed in Scheme 21. The yellow complexes, Rh(C(O)OR)(CO)ttt, are stable only under a CO atmosphere, and the concentration of these complexes in solution depends on the CO concentration.
Figure 69. 250 MHz $^{31}\text{P}(^{1}\text{H})$ nmr spectrum of [Rh(CO)$_{2}$tpp]AsF$_{6}$ in THF with C$_{6}$D$_{6}$ added as an internal lock.
Figure 70. The infrared spectrum of [Rh(CO)ttp]AsF₆. (Nujol mull).
3. Reactions with Olefins

The report of platinum(II) hydroxide complexes acting as catalysts for olefin hydration\textsuperscript{65} makes the rhodium hydroxide and alkoxide complexes synthesized in this investigation candidates for olefin hydration catalysts. Two additional reports of reactions between group VIII metal alkoxide complexes and olefins have been published. As discussed in the introduction, Pt(OCH\textsubscript{3})(CH\textsubscript{3})dppe inserts tetrafluoroethylene to give Pt(CF\textsubscript{2}CF\textsubscript{2}OCH\textsubscript{3})(CH\textsubscript{3})dppe\textsuperscript{123,124} and the iridium complex, Ir(OCH\textsubscript{3})(CO)(PPh\textsubscript{3})\textsubscript{2}, reacts with tetracyanoethylene (TCNE) to give the adduct, Ir(OCH\textsubscript{3})(CO)(PPh\textsubscript{3})\textsubscript{2}TCNE.\textsuperscript{158}

The Rh(OH)ttp and Rh(OC\textsubscript{6}H\textsubscript{5})ttp complexes were treated with a series of olefins. The Rh(OR)ttp complexes (OR = OH, OC\textsubscript{6}H\textsubscript{5}) failed to react with ethylene gas (1 atm, 25°C); only starting material was recovered from the reaction mixtures. Similar results were obtained in reactions between Rh(OR)ttp (OR = OH, OC\textsubscript{6}H\textsubscript{5}) and trichloroethylene, even under refluxing conditions. Treatment of Rh(OH)ttp with tetracyanoethylene in benzene gives a purple solid which shows no evidence of phosphorus in the \textsuperscript{31}P(\textsuperscript{1}H) nmr spectrum. A phosphorus signal was not found also in \textsuperscript{31}P(\textsuperscript{1}H) nmr spectrum of the reaction filtrate. The reaction between Rh(OC\textsubscript{6}H\textsubscript{5})ttp and tetracyanoethylene in benzene yields a purple solution which gives only a few, weak unidentified peaks in the \textsuperscript{31}P(\textsuperscript{1}H) nmr spectrum. The reactions probably involve redox chemistry yielding a paramagnetic product; the absence of phosphorus signals in the \textsuperscript{31}P(\textsuperscript{1}H) spectra indicate that the
desired complexes (either an inserted product or an adduct) did not form.

It is unfortunate that these complexes fail to react with olefins, even activated olefins, to give inserted products or rhodium adducts. However, this result is not surprising based on earlier results which suggest that the rhodium-alkoxide and hydroxide bonds are stronger than originally predicted.
LIST OF REFERENCES


