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SYNTHESES, CHARACTERIZATION, AND REACTIVITY STUDIES OF IRIDIUM(III)-HYDRIDE AND IRIDIUM(I) COMPLEXES WITH TERTIARY TRIPHOSPHINE LIGANDS

The Ohio State University

Ph.D. 1984

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SYNTHESSES, CHARACTERIZATION, AND REACTIVITY STUDIES
OF IRIDIUM(III)-HYDRIDE AND IRIDIUM(I) COMPLEXES
WITH TERTIARY TRIPHOSPHINE 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
Chihae Yang, B.S., M.S.

* * * * *

The Ohio State University
1984

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Finally, I would like to dedicate this work to my parents, who provided me invaluable academic opportunities and inspiration as well as love and support.
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Studies in Coordination Chemistry and Organometallic
Chemistry, Dr. Devon W. Meek
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LIST OF ABBREVIATIONS

Ph = C$_6$H$_5^-$
Cy = C$_6$H$_{11}^-$
DMPE = Me$_2$PCH$_2$CH$_2$PMe$_2$
dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$
dppp = Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$
PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$
Cyttp = PhP(CH$_2$CH$_2$CH$_2$PCy$_2$)$_2$
ttp = PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$
PPN = Ph$_2$P(CH$_2$)$_3$P(Ph)(CH$_2$)$_3$N(CH$_3$)$_2$
ppol = Ph$_2$P(CH$_2$)$_3$P(Ph)(CH$_2$)$_2$CH=CH$_2$
COD = 1,5-cyclooctadiene, C$_8$H$_{12}$
COE = cyclooctene, C$_8$H$_{14}$
NBD = norbornadiene, C$_7$H$_8$
NBE = norbornene, C$_7$H$_{10}$
TBE = t-Butylethylene, C$_6$H$_{12}$
Cp = cyclopentadiene, C$_5$H$_5^-$
INTRODUCTION

A. General

Stabilization of transition metal complexes, ranging from low to high oxidation states, with poly-tertiary phosphines now plays an important role in synthetic organometallic chemistry, in addition to the catalytic aspects of phosphine complexes.¹,²,¹¹

Transition metal complexes containing the chelating tridentate phosphine ligands, ttp (PhP(CH₂CH₂CH₂PPh₂)₂) or Cyttp (PhP(CH₂CH₂CH₂PCy₂)₂), can offer several advantages over analogous complexes containing monodentate phosphines. Tridentate phosphine ligands provide (i) more control on the coordination number, stoichiometry, and stereochemistry of the resulting complex; (ii) an increased basicity (or nucleophilicity) of the metal, in particular, in the case of the ligand, Cyttp; (iii) decreased rates of intra and inter molecular exchange processes occurring via phosphine dissociation and (iv) detailed structural and bonding information in the form of phosphorus chemical shifts and phosphorus-phosphorus and metal-phosphorus (e.g., Rh, Pt) coupling constants.
Meek and coworkers have used $^{31}$P-NMR to investigate series of four-coordinate, planar Rh(I)-ttp or Cyttp complexes and activation of small molecules with these complexes.\(^3\text{-}^6\) Hydrogenation studies have also been reported for CoH\(_3\)(ttp), and RhH(ttp) with AlEt\(_3\) cocatalyst. J. Letts has demonstrated the fluxional behavior of BH\(_4^-\) in RuH(BH\(_4\))(ttp) by taking advantage of the fixed coordination environment created by ttp.\(^8\)

For compounds of the type MX\(_3\)P\(_3\), two possible isomers, facial (I) and meridional (II) can exist.

![Diagram](https://via.placeholder.com/150)

In the case of monodentate tertiary phosphines, the formation of mixtures containing both (I) and (II) is common. In a fac-isomer, the strong trans-influence of phosphorus labilizes all three M-X bonds; in a mer-isomer, only one M-X bond is affected by the phosphine ligand trans to the M-X. The chelating triphosphines, ttp and Cyttp, are designed to fit the metal coordination sphere so that a planar or octahedral complex can be formed as a stable complex. The complexes of ttp and Cyttp have been shown to exist only as the mer-isomers by $^{31}$P-NMR.\(^{135}\) The
mer-configuration of Cyttp in this study allows for the investigation of various chemical reactions without the complication of geometric isomers.

B. Iridium Polyhydrides and the Reactivity

Research in transition metal hydride chemistry currently attracts an intense interest. Hydride complexes are known to be intimately involved in catalytic hydrogenations, H/D exchange, hydroformylations, olefin isomerizations, and hydrosilations; they also have been shown to be important in some olefin oligomerization and polymerization reactions.\(^1\,2\,11\)

In 1931 Hieber discovered the first transition metal hydrides, \(\text{H}_2\text{Fe(CO)}_4\) and \(\text{HCo(CO)}_4\).\(^{12}\) It was not until 1955, however, that the first stable hydride, \(\text{ReH(}n^5\text{-Cp})_2\), was prepared by Wilkinson and Birmingham.\(^{13}\) Rapid advancement in the studies of metal-hydrides began after the characterization of trans-\(\text{PtHCl(PEt}_3\)\)\(_2\) by Chatt, Duncanson, and Shaw.\(^{14}\) During the 1960's Chatt, Shaw and their coworkers synthesized numerous mixed hydride-phosphine complexes of the third row transition metals, W, Re, Os, and Ir.\(^{13-15}\) These covalent compounds, called polyhydride complexes, were found to be remarkably stable and may contain up to seven hydride ligands per metal atom (e.g., \(\text{Re(PR}_3\)\(_2\text{H}_7\)).\(^{15}\) The topic of transition metal hydrides has been extensively
reviewed from 1965 to 1982. Three books on this topic are also available.

In this study, iridium hydrides are investigated; therefore, a literature review of the hydrides will be focused on the late transition metals.

a. Synthetic methods

Green and Jones have proposed five general categories for the synthesis of hydride complexes: direct hydrogenation, reduction of metal halide complexes, hydride transfer from solvent, reverse carbonylation, hydrolysis of alkali metal salts of complex carbonyls, and protonation.

Hydride complexes can be formed by addition of $\text{H}_2$ to coordinatively unsaturated metal complexes:

$$\text{trans } [\text{IrCl(CO)(PPh}_3)_2] + \text{H}_2 \rightarrow \text{IrH}_2\text{Cl(CO)(PPh}_3)_2$$ (1)

$$\text{IrCl(ttp) } + \text{H}_2 \rightarrow \text{IrH}_2\text{Cl(ttp)}$$ (2)

This activation of $\text{H}_2$ on the metal, forming metal hydrides in which the formal oxidation number is increased by two units, is termed oxidative addition. In a manner similar to $\text{H}_2$ activation on the metal, Group IVA-hydrogen bonds, e.g., $\text{Ph}_3\text{SiH}$, $\text{R}_3\text{SnH}$, or $\text{GeMe}_3\text{H}$ (eq. 3), can also be oxidatively added to electron-rich metals.
Orthometallation is an intramolecular activation of $\text{R}_3\text{C-H}$ (also Group IVA-hydrogen bond) to the metal; one of the substituents of $\text{CR}_3$ is one of the ligands of the complex.\textsuperscript{33,34}

\[
\text{(IrCl(COE)$_2$)$_2$} + (\text{tBu)$_2$P(CH}_2$_2$)$_2$P(\text{tBu)$^\prime$)}_2 \rightarrow \text{HC-Ir-Cl}
\]  \hspace{1cm} (4)

\[
\text{IrCl(PPh$_3$)$_3$} \xrightarrow{\Delta \text{or } \text{hv}} \text{Ir(PPh$_2$)}
\]  \hspace{1cm} (5)

Hydrogenolysis of transition metal-Group IV derivatives such as $\text{Rh(CH}_3)(\text{PPh}_3)_3$ or $\text{IrH}_2(\text{GePh}_3)(\text{CO})(\text{PPh}_3)_2$ give hydrido complexes, $\text{RhH(PPh}_3)_3$\textsuperscript{35} or $\text{IrH}_3(\text{CO})(\text{PPh}_3)_2$.\textsuperscript{32}

Reduction of metal-halide complexes with reducing agents such as $\text{NaBH}_4$,\textsuperscript{36} $\text{LiAlH}_4$,\textsuperscript{37} $\text{LiHBEt}_3$,\textsuperscript{38} $\text{LiBH}_4$,\textsuperscript{39} or $\text{N}_2\text{H}_4$-hydrate\textsuperscript{14,16} is another general route to metal hydride complexes. The following are examples:
\[
\text{In many syntheses of metal-hydride complexes, no external hydrogen source is required and hydrogen is abstracted from the solvent during the course of the reaction.}^{40}\text{ For example, the complex IrCl(PPh}_3\text{) in refluxing ethanol solution produces the cis-dihydride complex, IrH}_2\text{Cl(PPh}_3\text{), and CH}_3\text{CHO.}^{41}\text{ Displacement of the halide in metal halides by alkoxide ion, followed by the transfer of a hydrogen in boiling alcohol/alkoxide solution has been reported as in equations (9) and (10).}^{42}\]

\[
\text{Hydrolysis of metal carbonyl cations often forms hydrido metal complexes.}^{43}\text{ For example, treatment of}
\]
IrCl₂(CO)(PPh₃)₂⁺ with H₂O results in a carboxy derivative, IrCl₂(CO)(PPh₃)₂(COH), which undergoes pyrolysis at 160-180°C to give IrHCl₂(CO)(PPh₃)₂ and CO₂.44

Addition of a H⁺ to a coordinatively unsaturated metal complex can also produce a metal hydride. Protonation usually results in oxidative addition of a proton in the case of transition metal complexes with fewer than 18 electrons as in eq. (11).45

\[
\text{IrCl(CO)(PPh₃)₂} + \text{HBF₄} \rightarrow \text{Ir(Ph₃P)}H \quad (11)
\]

b. **Physical and Chemical Properties:**

**Spectroscopic Properties**

The transition metal-hydrogen bond exhibits proton magnetic resonances shifted to high field, e.g., in the range of -5 to -50 ppm,19 which is well separated from the resonances of hydrogens in the diamagnetic chemical environments of the usual organic hydrogens. These large chemical shifts result principally from paramagnetic shielding (δp). The isotropic values for the absolute shielding at the protons can be calculated from the following equation (12) used by Buckingham and Stephens46,47
\[ \sigma = \sigma_a + \sigma_p \]
\[ \sigma_a = \frac{e^2}{3mc^2} \langle 0 \left| \sum \frac{m_{ij}^3 + R_{ij}^3}{m_{ij}} \right| 0 \rangle \]
\[ \sigma_{px} = \frac{-e^2}{2m^2c^2} n_0 (E_n - E_o)^{-1} \{ \langle 0 \left| \sum m_{ij} \left| n \right\rangle < n \left| \sum \frac{r_{Hj}^3 H_{j\text{H}}}{r_{Hj}} \right| 0 \rangle \]
\[ + \langle 0 \left| \sum r_{Hj}^3 H_{j\text{H}} \right| n \rangle < n \left| \sum m_{ij} \right| 0 \rangle \} \]

\[ R = \text{distance of proton along the x-axis from a metal atom} \]
\[ m_{ij} = \text{one-electron angular momentum operator corresponding to motions about the metal} \]
\[ H_{j\text{He}} = \text{one-electron angular momentum operator of hydride} \]
\[ r_{Hj} = \text{distance of the electron i from the hydride} \]

The main contribution to \( \sigma_p \) arises from the influence of the metal d-electrons; it clearly depends on the metal to hydrogen distance, the properties of the metal d-orbitals defined by the radial exponent in the Slater d-orbital function, and excitation energies, \( \Delta E \). Variations in the Pt-H bond lengths in the series of square planar Pt-hydride complexes, trans-PtH(-RCO\(_2\))(PET\(_3\))\(_2\) (where \( R = \) a substituted benzene), were shown to be the main cause of the variations in \( \sigma_H \). An unusual amount of mixing in of an excited state under the influence of a magnetic field can also be a major contribution to \( \sigma_p \) as in the case of RhHCl\(_2\)(PtBuMe\(_2\))\(_2\) (\( \delta_H = -31.4 \text{ ppm} \)) whose electronic absorption maximum appears at a relatively low frequency (\( \lambda_{\text{max}} = 458 \text{ nm} \)).
### TABLE 1

Proton-NMR And Infrared Data Of Square Planar Pt(II)-Hydrido Complexes

<table>
<thead>
<tr>
<th>PtHX(PEt$_3$)$_2$</th>
<th>$v_{\text{Pt-H}}$</th>
<th>$\delta_{\text{Pt-H}}$</th>
<th>$\mu_{\text{Pt-H}}$</th>
<th>$\mu_{\text{t}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-PtH(NH$_3$)(PEt$_3$)$_2$</td>
<td>2242</td>
<td>-23.6</td>
<td>1322</td>
<td>51</td>
</tr>
<tr>
<td>trans-PtH(-NCS)(PEt$_3$)$_2$</td>
<td>2160</td>
<td>-17.6</td>
<td>1086</td>
<td>51</td>
</tr>
<tr>
<td>trans-PtH(N$_2$)(PEt$_3$)$_2$</td>
<td>2150</td>
<td>-19.4</td>
<td>1003</td>
<td>118</td>
</tr>
<tr>
<td>trans-PtH(Cl$_2$)(PEt$_3$)$_2$</td>
<td>2183</td>
<td>-16.8</td>
<td>1275</td>
<td>51</td>
</tr>
<tr>
<td>trans-PtHI(PEt$_3$)$_2$</td>
<td>2156</td>
<td>-12.65</td>
<td>1369</td>
<td>51</td>
</tr>
<tr>
<td>trans-PtH$_2$(PEt$_3$)$_2$</td>
<td>2105</td>
<td>-9.2</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>trans-PtH(P-NO$_2$-C$_6$H$_4$-CO$_2$)(PEt$_3$)$_2$</td>
<td>2235</td>
<td>-22.200</td>
<td>1209.6</td>
<td>48</td>
</tr>
<tr>
<td>trans-PtH(P-I-Cl$_6$H$_4$-CO$_2$)(PEt$_3$)$_2$</td>
<td>2231</td>
<td>-22.061</td>
<td>1193.2</td>
<td>48</td>
</tr>
<tr>
<td>trans-PtH(P-Cl-Cl$_6$H$_4$-CO$_2$)(PEt$_3$)$_2$</td>
<td>2231</td>
<td>-22.036</td>
<td>1109.1</td>
<td>48</td>
</tr>
<tr>
<td>trans-PtH(P-CH$_3$Cl$_6$H$_4$-CO$_2$)(PEt$_3$)$_2$</td>
<td>2226</td>
<td>-21.897</td>
<td>1176.2</td>
<td>48</td>
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<tr>
<td>trans-PtH(P-CH$_3$OC$_6$H$_4$-CO$_2$)(PEt$_3$)$_2$</td>
<td>2226</td>
<td>-21.869</td>
<td>1172.0</td>
<td>48</td>
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</table>

<table>
<thead>
<tr>
<th>PtHL(PEt$_3$)$_2^+$</th>
<th></th>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>trans-PtH(CU)(PEt$_3$)$_2$</td>
<td>2167</td>
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<td>119</td>
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</tr>
<tr>
<td>trans-PtH(C$_2$H$_4$)(PEt$_3$)$_2^+$</td>
<td>-</td>
<td>-7.2</td>
<td>120</td>
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<tr>
<td>PtH(PPh$_3$)$_3^+$</td>
<td>2102</td>
<td>-</td>
<td>121</td>
<td></td>
</tr>
<tr>
<td>trans-PtH(NCCMe$_3$)(PEt$_3$)$_2^+$</td>
<td>2104</td>
<td>-7.13</td>
<td>119</td>
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# TABLE 2

Proton-NMR And Infrared Data Of Iridium-Dihydride Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v_{\text{Ir-H}_1}$</th>
<th>$v_{\text{Ir-H}_2}$</th>
<th>$\delta_{\text{Ir-H}_1}$</th>
<th>$\delta_{\text{Ir-H}_2}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrH$_2$Cl(PPh$_2$)$_3$</td>
<td>2105</td>
<td>2193</td>
<td>-11.10</td>
<td>-20.20</td>
<td>95</td>
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<tr>
<td>IrH$_2$Br(PPh$_3$)$_3$</td>
<td>2090</td>
<td>2240</td>
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<td></td>
<td>17</td>
</tr>
<tr>
<td>IrH$_2$I(PPh$_3$)$_3$</td>
<td>2083</td>
<td>2222</td>
<td></td>
<td></td>
<td>32a</td>
</tr>
<tr>
<td>IrH$_2$(SnCl$_3$)(PPh$_3$)$_3$</td>
<td>2205</td>
<td>2262</td>
<td></td>
<td></td>
<td>95</td>
</tr>
<tr>
<td>[IrH$_2$(PPh$_3$)$_4$]ClO$_4$</td>
<td>2225</td>
<td>2250</td>
<td></td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>[IrH$_2$(CO)(PPh$_3$)$_3$]ClO$_4$</td>
<td>2110</td>
<td>1771/1750</td>
<td></td>
<td></td>
<td>37a</td>
</tr>
<tr>
<td>mer-IrH$_3$(PPh$_3$)$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fac-IrH$_3$(PPh$_3$)$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mer-IrH$_3$(PPh$_3$)$_3$</td>
<td>2030</td>
<td>1975</td>
<td></td>
<td></td>
<td>115</td>
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<tr>
<td>fac-IrH$_3$(PPh(CH$_2$CH$_2$PPh$_2$)$_2$</td>
<td>2118</td>
<td>2155</td>
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<tr>
<td>IrH$_2$Cl(CO)(PPh$_3$)$_2$</td>
<td>2098</td>
<td>2222</td>
<td>-7.30</td>
<td>-18.40</td>
<td>95</td>
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<tr>
<td>IrH$_2$Br(CO)(PPh$_3$)$_2$</td>
<td>2073</td>
<td>2232</td>
<td></td>
<td></td>
<td>32a</td>
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<tr>
<td>IrH$_2$I(CO)(PPh$_3$)$_2$</td>
<td>2045</td>
<td>2092</td>
<td></td>
<td></td>
<td>32a</td>
</tr>
<tr>
<td>IrH$_2$(SnCl$_3$)(CO)(PPh$_3$)$_2$</td>
<td>2014</td>
<td>2112</td>
<td>-9.90</td>
<td>-12.50</td>
<td>95</td>
</tr>
<tr>
<td>IrH$_2$(GeMe$_3$)(CO)(PPh$_3$)$_2$</td>
<td>2071</td>
<td>2123</td>
<td>-9.50</td>
<td>-10.50</td>
<td>32a</td>
</tr>
<tr>
<td>mer-IrH$_3$(CO)(PPh$_3$)$_2$</td>
<td>2080</td>
<td>1785</td>
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<td>116</td>
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<tr>
<td>IrH$_3$(CO)(PPh$_3$)$_2$</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>IrH$_3$(CO)(PPh$_3$)$_2$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IrH$_2$Cl(CO)(PPh$_2$)$_2$</td>
<td>2067</td>
<td>2169</td>
<td>-7.58</td>
<td>-18.36</td>
<td>44b</td>
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<tr>
<td>Trans ligand</td>
<td>$\nu_{\text{M-H}}$ (cm$^{-1}$)</td>
<td>$\delta_{\text{M-H}}$ (ppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------------</td>
<td>-------------------------------</td>
<td>-------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>1650 - 1750</td>
<td>-11.5 - -12.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO, PR$_3$</td>
<td>2000 - 2100</td>
<td>-7.5 - -13.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl, Br, I</td>
<td>2200 - 2250</td>
<td>-18 - -22.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bridging hydride</td>
<td>1000 - 1200</td>
<td>-8 - -10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnCl$_3$, SnMe$_3$, GeMe$_3$</td>
<td>2100 - 2200</td>
<td>-9.0 - -14.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Olefins</td>
<td></td>
<td>-10 - -14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-coordinated (-OSO$_2$CF$_3$)</td>
<td>~ 2300</td>
<td>-21.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-coordinated (-NCCH$_3$)</td>
<td>~ 2200</td>
<td>-16.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EtOH</td>
<td></td>
<td>-27 - -29</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Data compiled from References 20, 25, 53, 85, 160.*
The spin-spin coupling of hydride ligands with other hydrogen atoms or with other magnetically active nuclei in the complex (e.g., $^{31}\text{P}$, $^{13}\text{C}$, or $^{195}\text{Pt}$) provides direct structural information. The couplings between hydrogens in polyhydride complexes are usually small, in the order of 10 Hz or less. The coupling of hydrogen with a cis-phosphorus atom is generally in the range of 5-40 Hz; trans $^2J_{\text{P-H}}$ values are usually around 60-180 Hz.  

The metal-hydride infrared stretching frequencies generally occur in the 1650-2250 cm$^{-1}$ range. Bridging hydrides exhibit vibrational frequencies as low as 1000-1200 cm$^{-1}$. The magnitude of $\nu_{\text{M-H}}$ can be used as an aid to stereochemical determination, since the value is very sensitive to the nature of the ligand trans to hydride.

All these spectroscopic parameters, $\delta_{\text{MH}}$, $J_{\text{MH}}$, $\nu_{\text{MH}}$, are affected by the stereochemistry of the complex. The term trans-influence was defined by Pidcock, Richards and Venanzi in order to account for spectroscopic observations which involve the ground state of the complex. Hydride ligands exert an inductive effect such that the large component of s-character in the $\sigma$-bonds is directed toward the metal-hydride bond at the expense of the remaining $\sigma$-bonds, in particular, the position trans to the hydride ligand.

The effect of trans-influence has been investigated on square planar Pt(II)-hydride systems, trans-PtH(X)(PR$_3$)$_2$ (where X = anionic ligands) or trans-Pt(H)(L')(PR$_3$)$_2^+$.
(where \( L' = \text{neutral ligand, } \text{AsEt}_3, \text{PET}_3, t\text{BuN}=C, \text{etc.} \)).\textsuperscript{52} As the s-character in the Pt-H bond decreases by donation of charge on the Pt-metal, the \( \tau_{\text{Pt-H}} \) (= 10 - \( \delta_H \)), \( J_{\text{Pt-H}} \) and \( v_{\text{Pt-H}} \) also decrease together.\textsuperscript{53} Linear correlations have been observed for \( \tau_{\text{Pt-H}} \), \( J_{\text{Pt-H}} \) and \( v_{\text{Pt-H}} \).\textsuperscript{48,50-52} Selected Pt(II)-hydride complexes and their parameters are listed in Table 1.

Trans-influence studies were also extended to octahedral d\textsuperscript{6} systems, e.g., \( \text{IrH}_2(\text{PR}_3)_3X \), \( \text{IrHX}_2L_3 \), or \( \text{IrH}(\text{PR}_3)_3LX^+ \) (where X is the ligand trans to hydride and L are additional ligands) (Table 2). Weak trans-influence ligands give \( \delta_{\text{Ir-H}} = \sim -20 \text{ ppm} \) and \( v_{\text{Ir-H}} = 2195-2250 \text{ cm}^{-1} \); whereas, strong trans-influence ligands have \( \delta_{\text{Ir-H}} = \sim -10 \text{ ppm} \) and \( v_{\text{Ir-H}} = 2000-2100 \text{ cm}^{-1} \). The range of chemical shifts and stretching frequencies of Ir-hydride bonds according to the trans donor atoms are compared in Table 3. A linear correlation was reported for \( \text{IrHCl(CO)(PPh}_3)_2X \) complexes (where X = NCSe\textsuperscript{-}, OSO\textsubscript{2}CF\textsubscript{3}\textsuperscript{-}, etc.) (Table 4, Fig. 1).\textsuperscript{55}

The trans-influence of the hydride can also be studied from bond length data obtained by diffraction techniques.\textsuperscript{24,27} The metal to hydrogen bond lengths are usually in the range of 1.48-1.70 \text{ Å} (2.02 \text{ Å} for bridging hydrides).\textsuperscript{24} Due to the strong trans-influence of the hydride ligand, the metal-ligand bond lengths trans to hydrogen (d\textsubscript{t}) are slightly larger than the ones cis to hydrogen (d\textsubscript{c}).
Figure 1. Linear correlation plot of δ\textsubscript{Ir-H} and ν\textsubscript{Ir-H} in complexes of the type Ir\textsubscript{ClH(CO)}(PPh\textsubscript{3})\textsubscript{2}X\textsuperscript{n+}.

Table 4

<table>
<thead>
<tr>
<th>TABLE 4</th>
<th>Proton-NMR And Infrared Data Of Complexes Ir\textsubscript{ClH(CO)}(PPh\textsubscript{3})\textsubscript{2}X\textsuperscript{n+} (n= 0,1)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ(Ir-H) (CD\textsubscript{2}Cl\textsubscript{2})</td>
</tr>
<tr>
<td>(Ph\textsubscript{3}P\textsubscript{2})(Cu)ClIrF*</td>
<td>-26.5</td>
</tr>
<tr>
<td>(Ph\textsubscript{3}P\textsubscript{2})(Cu)ClIrF\textsubscript{2}C\textsubscript{6}H\textsubscript{5}</td>
<td>-21.86</td>
</tr>
<tr>
<td>(Ph\textsubscript{3}P\textsubscript{2})(Cu)ClIrF\textsubscript{2}CF\textsubscript{3}</td>
<td>-21.77</td>
</tr>
<tr>
<td>[(Ph\textsubscript{3}P\textsubscript{2})(Cu)ClIr(C6H\textsubscript{6})J\textsuperscript{BF\textsubscript{4}}</td>
<td>-22.24</td>
</tr>
<tr>
<td>[(Ph\textsubscript{3}P\textsubscript{2})(Cu)ClIr(C6H\textsubscript{6})J\textsuperscript{BF\textsubscript{4}}</td>
<td>-21.39</td>
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<td>[(Ph\textsubscript{3}P\textsubscript{2})(Cu)ClIr(UH\textsubscript{2})J\textsuperscript{BF\textsubscript{4}}</td>
<td>-21.13</td>
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<td>[(Ph\textsubscript{3}P\textsubscript{2})(Cu)ClIr(NC\textsubscript{6}H\textsubscript{5})J\textsuperscript{BF\textsubscript{4}}</td>
<td>-16.80</td>
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<td>(Ph\textsubscript{3}P\textsubscript{2})(Cu)ClIr(NC\textsubscript{6}H\textsubscript{5})</td>
<td>-16.44</td>
</tr>
<tr>
<td>(Ph\textsubscript{3}P\textsubscript{2})(Cu)ClIrCl</td>
<td>-16.1</td>
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<tr>
<td>[(Ph\textsubscript{3}P\textsubscript{2})(Cu)ClIr(CNC\textsubscript{6}H\textsubscript{5})J\textsuperscript{BF\textsubscript{4}}</td>
<td>-11.12</td>
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<tr>
<td>[(Ph\textsubscript{3}P\textsubscript{2})(Cu)ClIr(SeCN)J\textsuperscript{BF\textsubscript{4}}</td>
<td>-12.11</td>
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<td>(Ph\textsubscript{3}P\textsubscript{2})(Cu)ClIr(SeCN)</td>
<td>-11.4</td>
</tr>
<tr>
<td>[(Ph\textsubscript{3}P\textsubscript{2})(Cu)ClIr(PPh\textsubscript{3})J\textsuperscript{BF\textsubscript{4}}</td>
<td>-9.37</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reference, 55.
example [RhH(NH$_3$)$_2$](ClO$_4$)$_2$ has $d_L$(Rh-N) = 2.244 Å, whereas
$d_C$(Rh-N) = 2.079 Å ($d_L - d_C = 0.165$ Å).$^{56}$ In mer-
IrH$_3$(PPh$_3$)$_3$, $^{57}$ $d_L$(Ir-P) = 2.347 Å and $d_C$(Ir-P) = 2.287,
2.285 Å; this small difference, $d_L - d_C$ (= ~ 0.06 Å), compared
to that of RhH(NH$_3$)$_5^{2+}$ may be due to the comparatively strong
trans-influence of phosphorus. The fac-IrH$_3$(PET$_2$Ph)$_3$
complex shows almost the same Ir-P bond lengths (2.296 Å,
2.291 Å);$^{27}$ these data imply that phosphorus and hydride may
exert comparable influences on each other.

**Chemical Properties and Reactions**

Many transition metal hydrides react with halocarbon
solvents to yield metal halide derivatives. The order of
increasing reactivity is CH$_3$Cl<CH$_2$Cl$_2$<CHCl$_3$<CCl$_4$. $^{58}$ Halos-
gen$^{s}$ (eq. 13)$^{17,59}$ and hydrogen halides (eq. 14)$^{60}$ also
react with hydrides to produce a metal halide complex.

\[
(n^5\text{C}_5\text{Me}_5)\text{Os(CO)}_2\text{H} + I_2 \xrightarrow{\text{HI}} (n^5\text{C}_5\text{Me}_5)\text{Os(CO)}_2\text{I} \quad (13)
\]

\[
\text{IrHCl}_2(\text{PET}_2\text{Ph})_3 + \text{HCl} \xrightarrow{\text{H}_2} \text{IrCl}_3(\text{PET}_2\text{Ph})_3 \quad (14)
\]

Metal-hydrogen bonds react with strong hydride ab-
stractors, such as CPh$_3^+$ (eq. 15)$^{59}$ and C$_7$H$_7^+$ (eq. 16)$^{61}$, to
give either solvato- or $n^2$-complexes.
Hydridic metal-hydrogens of early transition metals, e.g., \((\eta^5{-}Cp)_2\text{Zr(Cl)H}\), \((\eta^5{-}Cp)_2\text{Nb(CO)H}\), and \((\eta^5{-}Cp)_2\text{MoH}_2\), react with \(\text{H}_2\text{O}\) and alcohol to evolve \(\text{H}_2\), and/or reduce \(\text{CO}\)-functional groups.\(^{62}\) Some late transition metal hydrides in ionic solvents show properties of Brønsted acids; \(\text{HCo(CO)}_4\) (\(K_a = 2.0\)), \(\text{H}_2\text{Fe(CO)}_4\), and \(\text{MnH(CO)}_4\) are known proton donors.\(^{63}\) Better \(\Pi\)-accepting and electron withdrawing ligands promote \(\text{H}^+\) dissociation by stabilizing \(\text{N}^-\), whereas phosphine ligands stabilize the hydridic character by donating electron density to metal.\(^{26}\)

Transfer of a hydride to another ligand in a complex is one of the key reaction steps in many catalytic cycles, including hydrogenations or hydroformylations.\(^{64}\) For example, the hydrido iridium(III) cation, \(\text{cis-IrH}_2(\text{diene})-(\text{PR}_3)_2^+\), can transfer a hydride to an olefin and eventually produce a monoene from diene.\(^{65,66}\)
Elimination of molecular hydrogen can occur from coordinatively saturated complexes containing cis-hydride ligands. For example, IrH$_2$Cl(CO)(PPh$_3$)$_2$ readily loses hydrogen if heated while purging with inert gas or when stirred under vacuum to give IrCl(CO)(PPh$_3$)$_2$.$^{67}$ Many stable polyhydrides do not lose H$_2$ under thermal conditions; however, photo-induced reductive elimination of H$_2$ from di- and polyhydrides has been reported for compounds of V, Mo, W, Re, Fe, Ru, Co, and Ir.$^{21}$

Elimination of hydrogen from the stable IrH$_2$Cl(PPh$_3$)$_3$ and mer- and fac-IrH$_3$(PPh$_3$)$_3$ by UV-irradiation or with sunlight was discovered by Geoffroy et al.$^{68,21}$

\[
\text{hv, } \phi = 0.6 \text{ (30 min)} \quad \text{IrH}_2\text{Cl(PPh}_3\text{)}_3 \xrightarrow{H_2} \text{IrCl(PPh}_3\text{)}_3 + H_2 \quad (19)
\]
Irradiation of a mixture of IrH$_2$Cl(PPh$_3$)$_3$ and IrD$_2$Cl(PPh$_3$)$_3$ gives only H$_2$ and D$_2$, which implies that photoelimination of H$_2$ occurs in a concerted intramolecular fashion. Prolonged photolysis of both IrH$_2$Cl(PPh$_3$)$_3$ and IrH$_3$(PPh$_3$)$_3$ results in products that are possibly orthometallated complexes; but these have not yet been completely understood.$^{68}$

\[
\text{hv, } H_2 \xrightarrow{} \text{IrH}_5\text{(PPh}_3\text{)}_2 + \text{PPh}_3
\] (20)

c. C-H Activation

Iridium hydrides show the capability of activating unreactive hydrocarbon bonds or CO/H$_2$ activation.$^{69,70}$

The C-H bonds in hydrocarbons are thought to be activated the same way as H-H bonds to give M-C.$^{71}$ Despite the intrinsic thermodynamic problems of C-M bonds,$^{82}$ significant advances have been made by choosing basic third-row transition metals to promote the oxidative addition step, and by using ligands which do not undergo an intramolecular activation.

G. Parshall proposed, for aromatic C-H bond activation, that arene coordination may take place prior to oxidative addition of the aromatic C-H bond as follows:$^{72}$
A recent observation on the isomerization of $(\eta^5\text{-Cp})\text{RhH(PMe}_3\text{)}(\text{CH}_3)$ to $(\eta^5\text{-Cp})\text{RhH(PMe}_3\text{)}(\text{CH}_3)$ also supports the possible $\eta^2$-arene intermediate, $(\eta^5\text{-Cp})\text{Rh(PMe}_3\text{)}(\text{CH}_3)$.

A number of transition metal complexes are known to facilitate the intermolecular oxidative addition of aromatic C-H bonds. For example, irradiation of $(\eta^5\text{-Cp})_2\text{WH}_2$ yields a reactive species "$(\eta^5\text{-Cp})_2\text{W}$", which subsequently reacts with benzene or THF to give $(\eta^5\text{-Cp})_2\text{W(C}_6\text{H}_5\text{)}(\text{H})$ or $(\eta^5\text{-Cp})_2\text{W(C}_4\text{H}_7\text{O})(\text{H})$ respectively. Photolysis is now one of the common methods to generate reactive species, i.e., coordinatively unsaturated basic metal complexes. Direct observation of C-H bond cleavage of a saturated alkane has been reported by Bergman et al. with Ir(III)-complexes.
When the ligand is \( \text{PPh}_3 \) instead of \( \text{PMe}_3 \), cyclometallation occurs as well as C-H activation under the same condition as in eq. (22). W. Jones and coworkers used a Rh-analog of Bergman's complex and observed alkylhydride complexes at low temperature.\(^\text{76}\)

Graham et al. suggested that irradiation of the Ir(I) (18 e\(^-\)) species, \((\eta^5-\text{Cp})\text{Ir(CO)}_2\), generates a reactive 16e\(^-\) intermediate, \((\eta^5-\text{Cp})\text{Ir(CO)}\), which then undergoes oxidative addition of neopentane.\(^\text{77}\)

A hydrogen catalyst was reversibly used for dehydrogenation of cycloalkanes by Crabtree and his coworkers. A stepwise dehydrogenation involving C-H bond cleavage was indicated. The active complex was generated by \( \text{H}_2 \) elimination of \( \text{IrH}_2(\text{solv})\text{L}_2^+ \) with TBE as a \( \text{H}_2 \) acceptor.\(^\text{78,79}\)

\[
\begin{align*}
\begin{array}{c}
\text{IrH}_2(\text{Me}_2\text{CO})(\text{P-FC}_6\text{H}_4)_2^+ \quad \text{TBE} \quad 80^\circ \\
\rightarrow \\
\text{IrHL}_2^+ + \text{CH}_4
\end{array}
\end{align*}
\tag{23}
\]

\[
\begin{align*}
\begin{array}{c}
\text{IrH}_2(\text{Me}_2\text{CO})(\text{P-FC}_6\text{H}_4)_2^+ \quad \text{TBE} \quad 85^\circ \\
\rightarrow \\
\text{IrHL}_2^+ + \text{IrL}_2^+
\end{array}
\end{align*}
\tag{24}
\]

The C-H bond of other functional groups such as \( \text{H}-\text{CH} \) is also activated to give \( \text{Ir} (\text{PMe}_3)_4\text{H}(\text{CH}) \).\(^\text{80}\) The concept of formaldehyde activation has been developed by Parshall, Thorn, and Tulip; lengthening of the aliphatic chain was
achieved from a formaldehyde complex by the following reaction (eq. 25).\(^7\)

\[
\begin{align*}
\text{CH}_3\text{M}-\text{C}^\text{O}_\text{H} & \xrightarrow{\text{H}_2} \text{M}-\text{CH}_2\text{OH} & \xrightarrow{-\text{H}_2\text{O}} \text{M}-\text{CH}_3 & \xrightarrow{\longrightarrow} \text{M}^*\text{CH}_2\text{CH}_3 \\
\text{25}
\end{align*}
\]

Carbon-hydrogen bond activation generally causes (or is deduced from) H-D exchange between C-H and M-H bond.

\[
\begin{align*}
\text{C-H} + \text{M-D} & \rightleftharpoons \text{C-M}^\text{H_D} & \rightleftharpoons \text{C-D} + \text{M-H} \\
\text{26}
\end{align*}
\]

Various transition metal complexes from high valent species \(((\eta^5-\text{C}_\text{p})_2\text{Ta}^\text{VH}_3\text{)}\text{ or }\text{IrH}_5(\text{PMe}_3)_2\text{)}\) to low valent species \((\text{Ru}^0(\text{dmpe}))\) are known to undergo H/D exchange as in eq. (26); however, only \(((\eta^5-\text{C}_\text{p})_2\text{TaH}_3\text{)}\text{ and }\text{IrH}_5(\text{PMe}_3)_2\text{)}\ catalyze the exchange of benzene with D\(_2\).\(^7\)

Recently, R. Eisenberg reported that the \(\text{IrH}_3(\text{CO})(\text{dppe})\) complex undergoes H/D exchange upon irradiation.\(^8\)

\[
\begin{align*}
\text{IrH}_3(\text{CO})(\text{dppe}) \xrightarrow{\text{hv}} \text{IrD}_3(\text{CO})(\text{dppe}) \\
\text{27}
\end{align*}
\]

When a benzene solution of the trihydride was irradiated under CO, a small amount of benzaldehyde formation was observed.
In conclusion, elucidation of C-H activation mechanism as well as isolation of the C-H activated complexes are currently being investigated actively. However, true catalytic functionalization of C-H bonds using transition metal complexes has not yet been achieved. ^0,82

In this study, series of iridium-dihydride and trihydride complexes with Cytpt ligand are prepared. The Ir-Cl and Ir-H bond reactivities of these octahedral complexes are investigated. The H/D exchange between Ir-deuterides and C-H bonds of organic solvents (or vice versa) is achieved by iridium(III) hydride complexes of the basic triphosphine ligand, Cytpt.
EXPERIMENTAL

A. Reagents and Chemicals

Rhodium trichloride trihydrate (RhCl₃·3H₂O) and iridium trichloride trihydrate (IrCl₃·3H₂O) were purchased from Engelhard Industries, Newark, NJ or Matthey Bishop, Inc., Malvern, PA. Diphenylphosphine (PPh₂H), dicyclohexylphosphine (P(C₆H₁₁)₂H), phenylphosphine (PPh₂H), 3-bis(diphenylphosphino)propane (Ph₂P(CH₂)₃PPh₂≡dppp), trifluorophosphine (PF₃), trimethylphosphite (P(OMe)₃), and dimethylphenylphosphine (PMe₂Ph) were obtained from either Pressure Chemical Co., Pittsburgh, PA, or Strem Chemical Co., Danvers, MA; these ligands were used as purchased except for trimethylphosphite, which was distilled from sodium under a nitrogen atmosphere prior to use. The reagents HBF₄·Et₂O and HAsF₆ were obtained from Cationics, Inc., Cleveland, OH (now part of Columbia Organic Chem. Co.), or Columbia Organic Chemical Co., Columbia, SC. Lithium triethylborohydride (LiBEt₃H) and potassium triisopropoxyborohydride [KB(O-iPr)₃H], n-butyl lithium (n-BuLi), and 1,3-dichloropropane were obtained from Aldrich Chemical Co., and used without further purification. Methyl lithium
was obtained either from Alfa Division, Ventron Corp., Danvers, MA or Aldrich Chemical Co.

Purification and distillation of solvents were performed according to literature methods. Tetrahydrofuran, benzene, toluene and hexane (hexanes of boiling point range of 65.1°-69°C) were distilled from sodium and benzophenone under nitrogen prior to use. Acetonitrile and dichloromethane were distilled from P4O10 prior to use. Acetone was distilled from Linde 4Å molecular sieves and/or from K2CO3. Methanol was distilled from Linde 4Å molecular sieves and from CaH2. Spectral grade absolute ethanol was used as received.

Deuterated solvents were purchased from Aldrich Chemical Co. except CD3CD2OD which was obtained from Stohler Isotope Chemicals, Waltham, MA.

All other chemicals, reagents, and solvents were reagent grade and were used without further purification unless stated otherwise.

B. Physical Measurements and Instrumentation

Infrared spectra were measured on a Perkin-Elmer 283B grating spectrophotometer from 200 to 4000 cm⁻¹ or on a 337 from 400 to 4000 cm⁻¹, as Nujol mulls, as pressed potassium bromide pellets or as solutions using a set of matched solution cells with path lengths of 0.522 and 0.526 mm. Sharp
polystyrene absorptions at 1601 and 906.7 cm$^{-1}$ were used for calibration of the infrared spectra.

Photolysis experiments were performed in the Rayonet Photolytic reactor (manufactured by the Southern New England Ultraviolet Company, Middletown, CT) with 16 UV lamps at 350 nm.

Conductivity data were obtained from approximately $10^{-3}$ M solutions with a Lab-line unbreakable type conductivity cell, Cat. No. 11200. An Industrial Instruments, Inc., conductivity bridge (model RC 16B2) was used to determine the resistance of the solutions at 1000 c.p.s.

Phosphorus-31 NMR spectra were routinely collected on a Bruker HX-90 or on a WM-300 spectrometer. The HX-90 was operated in the Fourier mode with or without quadrature phase detection at 36.43 MHz with a Bruker BNC-12 data system and the WM-300 was operated with the quadrature phase detection at 121.470 MHz with an Aspect 2000 data system. The $^{31}$P{$^1$H} spectra were in general obtained by use of 10 mm NMR tubes with 5 mm coaxial inserts (containing the deuterium lock and trimethylphosphate, (MeO)$_3$P=O, as a secondary standard). In some cases, deuterated solvents (20% of the sample volume) provided an internal deuterium lock; these spectra were standardized by external phosphoric acid. Positive $^{31}$P chemical shifts are assigned as being downfield from the external phosphorus standard, H$_3$PO$_4$ at 0.0 ppm. The phosphorus-31 spectra are generally
reproducible to ±0.1 ppm for chemical shifts. Major changes in concentration, solvent, or temperature can cause small differences in the ppm or Hz values.

Proton magnetic resonance spectra were collected on a Varian 90 (with TMS as the internal standard), on the HX-90, WP-200, WM-300 and Nicolet 500 (with Nic 1180E data system) instruments with TMS (Me$_4$Si) or the residual protons in the deuterated solvents (referenced back to TMS) as the internal standard. Deuterium magnetic resonance spectra were obtained for D-enriched samples in non-deuterated solvents in a 10 mm tube on Bruker WM-300 or Nicolet 500 operating in the Fourier mode with quadrature detection at 46.07 MHz or 76.76 MHz, respectively.

Selective decoupling experiments were performed on the WM-300 spectrometer. The absolute instrument frequency of the heteroatom that is to be decoupled should be given from a previous spectrum of the same sample.

Computer simulations of experimental spectra were performed with the PANIC Program provided by Bruker Instruments, Inc.

Mass spectra were measured by C. R. Weisenberger at The Ohio State University on a Kratos MS30 mass spectrometer either by E.I. or FAB techniques. The FT-ICR mass spectra were obtained from the Campus Instrument Center at The Ohio State University.
Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona or by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

C. General Experimental Procedures

Standard techniques for the manipulation of air-sensitive compounds were used for all reactions; Frank's manifold, Schlenk vessels, Schlenk filters with sintered glass frits, and gas inlets and outlets were employed. Solutions were transferred by the use of a nitrogen flushed syringe, a long stainless steel transfer needle, or a graduated dropping funnel with Teflon stopcock. Positive nitrogen pressure filtrations were performed by forcing the solutions through a stainless steel needle attached to a flared glass tube covered with a pad of glass wool and a layer of Whatman No. 1 filter paper (later on, it will be called a filter needle). Solvents were degassed by purging them with nitrogen for at least 20 min just prior to use, and the deuterated solvents were degassed by the freeze-pump-thaw method. High purity nitrogen was used to provide an inert atmosphere; the nitrogen was passed through a column of oxygen scavenger, Ridox (purchased from Fischer Scientific Company, Fairlawn, New Jersey), which was regenerated periodically by a 95:5 mixture of nitrogen and hydrogen. All reactions were carried out under a well-ventilated fume hood.
D. Ligand Preparations

1. Cytt₆, Bis(3-dicyclohexylphosphinopropyl)phenylphosphine.

\[(\text{C-C₆H₁₁})₂\text{P(CH₂)}₃\text{Cl} \]

Dicyclohexylphosphine (46 g, 0.233 mol) was dissolved in THF (650 mL) and methyl lithium (210 mL of a 1.2 M ether solution, 0.252 mol) was added to the phosphine solution at 0°C. The resultant reaction mixture was warmed to RT to give an orange-red solution and a small amount of yellow solid. This orange mixture was refluxed for 0.5 hr and resulted in a clear orange-red solution. This resulting solution was transferred to a solution of 1,3-dichloropropane (200 g, degassed previously) in ether (200 mL), the addition was performed dropwise through a graduated pressure equalizing funnel with a Teflon stopcock over a period of 24 hrs. The resulting white slurry was stirred for 2 hrs and then hydrolyzed with H₂O (200 mL, thoroughly degassed). The volatile solvents were evaporated under reduced pressure. The mixture of a pale yellow oil and a clear water layer was then extracted with 230 mL, and 2 x 100 mL of ether. The resultant pale yellow solution was dried over anhydrous Na₂SO₄ overnight. A pale yellow oil was obtained after removing all of the volatile component in vacuo (0.2 torr) at 60°C. The yield was 61.4 g (96%) and the purity was checked with \(^{31}\text{P}\) and \(^{1}\text{H}\) NMR; \(^{31}\text{P}\)-NMR, -6.99 ppm, (singlet, Cy₂P+H·Cl);
**Cytpp, [(C₆H₅)₂P(CH₂)₃]₂P(Ph)**

Phenylphosphine, PhPH₂, (11.8 mL, 0.107 mol) was dissolved in benzene (120 mL) and n-buLi (146 mL of a 1.6 M hexane solution, 0.233 mol) was added at 0°C. The resultant yellow slurry was refluxed for 0.5 hr and cooled to room temperature. This solution was then added dropwise to the solution of Cy₂P(CH₂)₃Cl (61.4 g, 0.212 mmol (assuming 95% purity), in 150 mL of benzene and 35 mL of ether) via a Teflon tube connected with a 2-way Teflon stopcock. The resulting yellow mixture was stirred overnight and then refluxed for 2 hrs; subsequently the yellow slurry was hydrolyzed with H₂O (200 mL) at 0°C. The organic layer was dried over anhydrous MgSO₄ and activated charcoal overnight. The pale yellow solution was then evaporated to an oil and heated at 60°C in vacuo overnight. The ³¹P-NMR spectrum of the resulting yellow oil showed the presence of Cytpp and a small amount of CyPPH (Cy₂P(CH₂)₃P(Ph)H). A Kugelrohr distillation was employed to remove the volatile diphosphine, CyPPH; the temperature was maintained at 150°C for 2 hrs. The resultant crude yield of Cytpp was 58.53 g (93%). The ligand was purified by a column chromatography eluting with benzene on a column packed with 8% deactivated alumina: ³¹P-NMR, -7.8 ppm (singlet, (Cy₂P⁺⁺⁺), -28.1 ppm (singlet, Ph-P⁺⁺⁺); ¹H-NMR, 7.2 ppm
(multiplet, 5H Ph-P) 1.0 ~ 1.9 ppm (multiplets, 56H CH₂ backbone and Cy₂P⁻). A 4 mL/m mole ligand solution was prepared in benzene for the stock solution.

2. ttp, Bis(3-diphenylphosphinopropyl)phenylphosphine

The ttp ligand was prepared according to the literature method except that the THF was used as the solvent for the synthesis of (Ph)₂P(CH₂)₃Cl as in the case of Cyttpp.

(Ph)₂P(CH₂)₃Cl: ³¹P-NMR, -17.7 ppm (singlet, Ph₂P⁻); ¹H-NMR, 7.1 ppm (Ph₂-P, 10H multiplet), 3.5 ppm (triplet, 2H -CH₂-Cl), 1.0 ~ 1.9 ppm (multiplets, 4H P-CH₂-CH₂).

(ttp): ³¹P-NMR, -18.1 ppm (singlet, Ph₂P⁻), -28.2 ppm (singlet, PhP⁻).

¹H-NMR, 7.1 ppm (multiplet, 25H Ph's), 1.0 ~ 1.9 ppm (multiplets, 12H CH₂ backbones).

E. Preparation of Iridium-Cyttpp Complexes

1. IrCl₂(H)(Cyttpp)

Method 1. A solution of [IrCl(COD)]₂ (500 mg, 0.745 mmol) in EtOH (50 mL) was treated with the ligand solution (6.0 mL, 1.50 mmol); the reaction mixture turned deep red immediately. The resulting red solution was refluxed for 2 hrs, and it gradually turned pale yellow. The solvent was removed completely under reduced pressure, and the resultant residue was dissolved in CH₂Cl₂ (15 mL); the solution then
was treated with EtOH (30 mL). The more volatile solvent, CH₂Cl₂, was removed by evaporation and a white precipitate formed in the remaining EtOH. The solid was isolated, washed with 10 mL of ether, and dried in vacuo overnight. M.P. decomposed at 250°C.

Analysis for C₃₆H₆₃ClIrP₃:

Calcd.: C, 52.97; H, 7.72; Cl, 4.34.

Found: C, 53.13; H, 7.67; Cl, 4.07.

**Method 2.** The same reaction as above was performed in MeOH. In MeOH, the discoloration of the red solution to pale yellow occurs rapidly, even at -78°C. The compound IrCl(H)₂(Cyttp) was isolated from the reaction mixture at room temperature, all the spectral data were identical with the authentic compound. When this same mixture was refluxed, the isolated product contained very little IrCl(H)₂(Cyttp) and several unidentifiable peaks in ³¹P and ¹H-NMR and infrared spectra.

Crystals for the X-ray structure determination were grown in CH₂Cl₂/EtOH mixture by a slow-diffusion method.

2. **IrI(H)₂(Cyttp)**

To a slurry of [IrI(COD)]₂ (90 mg, 0.118 mmol) in EtOH (15 mL) was added the ligand solution (0.95 mL, 0.118 mmol). The resulting orange solution was refluxed for 2 hrs and a pale yellow solid resulted. The solvent volume was reduced
to 5 mL and the resultant solid was collected on a frit, washed with 10 mL of ether, and dried in vacuo for 1 hr.

Analysis for C\textsubscript{3}H\textsubscript{6}I\textsubscript{3}IrP\textsubscript{3}:

Calcd.: C, 47.62; H, 6.99; I, 13.98.

Found: C, 47.55; H, 7.08; I, 13.76.

3. IrCl(D)(H)(Cyttpp)

The reaction vessel was stirred in D\textsubscript{2}O overnight and baked in the oven at 100°C for several hours. The reaction mixture of [IrCl(COD)]\textsubscript{2} (100 mg, 0.149 mmol) and the ligand in 8 mL of d\textsubscript{1}-EtOD was refluxed for 2 hrs and cooled to room temperature. Microcrystals were formed on the wall, and they were collected on a frit, and dried in vacuo for several hours. The mass spectrum showed a prominent one-deuteride molecular ion peak. Infrared and \textsuperscript{2}H-NMR spectra were employed to examine the deuteride analog.

4. IrCl(D)\textsubscript{2}(Cyttpp)

The reaction vessel and the syringe were exchanged with D\textsubscript{2}O as above (3). The ligand solution in benzene was evaporated to oil and combined with [IrCl(COD)]\textsubscript{2} (100 mg, 0.149 mmol); then the mixture was treated with 1 mL of d\textsubscript{6}-EtOD. The reaction mixture was stirred at room temperature for 1 day. The solvent was evaporated to dryness; it was recovered in a liquid N\textsubscript{2} trap under vacuum. The resulting yellow solid shows no bands at 1900-2300 cm\textsuperscript{-1} due to v\textsubscript{Ir-H}.
5. \textit{Ir(H)$_3$Cyt tp}

A deep red solution was generated by a mixture of [IrCl(COD)$_2$] (100 mg, 0.149 mmol) and Cyt tp ligand solution (1.2 mL, 0.300 mmol) in 10 mL of EtOH; it was treated with a solution of KOH (20 mg, 0.356 mmol) in 10 mL of EtOH. The reaction mixture gradually turned orange and cream-colored X-ray quality crystals formed overnight. The crystals were collected on a frit and dried in vacuo for 0.5 hr. M.P. decomposed at 180°C.

Analysis for C$_{36}$H$_{64}$IrP$_3$·2EtOH:

Calcd.: C, 54.96; H, 8.76; Cl, 0.00.

Found: C, 54.52; H, 8.88; Cl, trace.

6. Reaction of IrCl(H)$_2$(Cyt tp) with AgPF$_6$

A reaction mixture of IrCl(H)$_2$(Cyt tp) (80 mg, 0.0980 mmol) and AgPF$_6$ (30 mg, 0.118 mmol) in THF was prepared at -78°C in a $^{31}$P-NMR sample tube. Low temperature $^{31}$P($^1$H)-NMR spectra were obtained for the dark cream reaction mixture.

7. \textit{Ir(H)$_2$(SnCl$_2$)(Cyt tp)}

To a solution of IrCl(H)$_2$(Cyt tp) (100 mg, 0.123 mmol) in CH$_2$Cl$_2$ (25 mmol) was added anhydrous SnCl$_2$ (24 mg, 0.127 mmol). The resulting reaction mixture was stirred at room temperature for 3 hrs and the solution was filtered through a frit. The filtrate was evaporated to 5 mL and treated with 10 mL of hexane. The resultant solid was collected on
a frit, washed with 5 mL of acetone, and dried in vacuo for 2 hrs. The pale yellow filtrate was saved for $^{31}$P-NMR and $^1$H-NMR spectra; the spectra showed only one isomer. An off-white solid was isolated from this filtrate by adding 15 mL of ether. The solid which was originally isolated was recrystallized in acetone and CH$_2$Cl$_2$; its $^{31}$P and $^1$H-NMR spectra indicated the other isomer.

Analysis for C$_{36}$H$_{63}$Cl$_3$IrP$_3$Sn:
Calcd.: C, 42.97; H, 6.26; Cl, 10.57.
Found: C, 42.88; H, 6.10; Cl, 10.80.

8. [Ir(H)$_2$(CO)(Cyttp)]BF$_4$  
A solution of IrCl(H)$_2$(Cyttp) (400 mg, 0.490 mmol) was prepared in THF (40 mL) and TlBF$_4$ (160 mg, 0.590 mmol) was added to this solution. The reaction mixture was stirred for 10 min, then a slow stream of CO was bubbled into this solution for 1 hr; as soon as the CO was added, a heavy white solid, i.e. TlCl, precipitated. The solution was filtered through a filter needle and the filtrate was evaporated to dryness. To this resulting residue was added 30 mL of THF, and the solution was filtered again via a filter needle. The filtrate was evaporated under reduced pressure to ca 5 mL and then 15 mL of ether was added to cause precipitation. The resulting white solid was isolated, washed with 10 mL of ether and dried in vacuo for 2 hrs. $\Lambda_M = 120$ ohm$^{-1}$ mol$^{-1}$ cm$^{-2}$ (Acetone).
9. \([\text{Ir}(\text{H})_2(\text{Cytt})p(\text{PMe}_2\text{Ph})]\text{BF}_4\)

A solution of \(\text{IrCl}(\text{H})_2(\text{Cytt})p\) (200 mg, 0.245 mmol) and \(\text{TiBF}_4\) (90 mg, 0.309 mmol) in THF (30 mL) was treated with \(\text{PMe}_2\text{Ph}\) (0.04 mL, 0.290 mmol); a heavy white solid, \(\text{TiCl}\), precipitated. The reaction mixture was stirred for an hour and the solution was filtered via a filter needle. The resulting filtrate was evaporated to dryness and 10 mL of THF was added to dissolve this residue. The opaque solution was filtered again through celite and glass wool supported on a frit. The filtrate was reduced to \(\text{ca} \ 5 \text{ mL}\) and 15 mL of ether was added. The resultant white solid was collected on a frit, washed with \(3 \times 10 \text{ mL}\) of ether, and dried in vacuo for one day.

Analysis for \(\text{C}_{44}\text{H}_{74}\text{BF}_4\text{IrP}_4\):

Calcd.: \(\text{C}, 52.53; \text{H}, 7.41; \text{P}, 12.32.\)

Found: \(\text{C}, 52.46; \text{H}, 7.45; \text{P}, 12.09.\)

10. \(\text{IrClHI(Cytt)}\)

A solution of \(\text{IrCl}(\text{H})_2(\text{Cytt})p\) (100 mg, 0.123 mmol) and \(\text{I}_2\) crystals (40 mg, 0.157 mmol) in THF (20 mL) was stirred at room temperature; the solution gave a pale-red color due to \(\text{I}_2\). After 1 hr, the solvent was removed by evaporation.
under reduced pressure and a yellow residue resulted. Twenty mL of acetone was added to dissolve the excess I₂ and precipitate the product. The solid was collected on a frit, washed with 2 × 5 mL of acetone, and dried in vacuo for 1 hr.

Analysis for C₃₆H₆₂ClIrP₃:
Calcd.: C, 45.88; H, 6.63; I, 13.47.
Found: C, 45.76; H, 6.55; I, 13.29.

11. [IrClH(CH₃CN)(Cypttp)]BF₄

A solution of IrCl(H)₂(Cypttp) (150 mg, 0.184 mmol) in THF (5 mL) and a solution of C₇H₇BF₄ (35 mg, 0.197 mmol) in CH₃CN (20 mL) was combined through a stainless steel needle. The resulting solution was stirred at room temperature for 5 hrs, during which time some solid precipitated. The solvent was removed completely and 20 mL of CH₂Cl₂ was added to dissolve this residue. The resultant solution was filtered through a filter needle; at this point, the pale beige color due to the C₇H₇BF₄ disappeared. The filtrate was then reduced in volume to 5 mL and 20 mL of ether was added to isolate the product. A white solid was collected on a frit and washed with 2 × 10 mL of ether, and dried in vacuo overnight. $A_M = 118 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^{-2}$ (Acetone).

Analysis for C₃₈H₆₅BClF₄IrNP₃:
Calcd.: C, 48.38; H, 6.89; N, 1.48.
Found: C, 48.23; H, 6.68; N, 1.31.
12. \( \text{Ir}(\text{Cl}\cdot\text{SO}_2)\text{H}(\text{SO}_2\text{H})(\text{Cytpp}) \)

A solution of \( \text{SO}_2 \) in 15 mL of THF was prepared by bubbling \( \text{SO}_2 \) through the solvent for 5 min. The solution of \( \text{IrCl(H)}_2(\text{Cytpp}) \) (200 mg, 0.245 mmol) in THF (10 mL) was prepared and transferred to the \( \text{SO}_2 \) solution via a stainless steel needle. The excess \( \text{SO}_2 \) was purged with \( \text{N}_2 \) for 0.5 hr and a brownish green solution resulted. The solvent was reduced to \( \text{ca} \) 5 mL and 10 mL of hexane was added. The resulting dark green solid was isolated on a frit, washed with 10 mL of hexane, and dried in vacuo for 0.5 hr.

Analysis for \( \text{C}_{36}\text{H}_{63}\text{ClIrS}_2\text{O}_4\text{P}_3 \):

Calcd.: C, 45.76; H, 6.73; S, 6.79; Cl, 3.76.

Found: C, 45.65; H, 6.79; S, 5.80; Cl, 3.75

13. \( \text{IrCl(COD)(Cytpp)} \)

Into a red solution of \( [\text{IrCl(COD)}]_2 \) (300 mg, 0.447 mmol) in 50 mL of benzene was added the Cytpp ligand solution (3.6 mL, 0.900 mmol); the red solution turned deeper red momentarily and to pale yellow color as soon as the ligand solution was added. The resulting solution was stirred for 0.5 hr and then the solvent was removed completely under reduced pressure; a pale yellow solid resulted. To this solid was added 15 mL of hexane and the solid was isolated on a frit. The cream colored solid was washed with 10 mL of hexane and dried in vacuo for 2 hrs. The yield was 530 mg (64%).
Analysis for C_{44}H_{73}ClIrP_{3}:

Calcd.: C, 57.29; H, 7.92; Cl, 3.85.

Found: C, 56.88; H, 8.28; Cl, 4.05.

14. [Ir(COD)I]_{2}

A solution of [IrCl(COD)]_{2} (200 mg, 0.298 mmol) in 15 mL of acetone was treated with a solution of NaI (90 mg, 0.600 mmol) in 10 mL of acetone. The resulting solution was stirred at room temperature for 2 hrs to give a deep purple slurry. The solvent was removed by evaporation and 10 mL of benzene was added. The purple solution was filtered through a filter needle and the resultant filtrate was then evaporated to ca 5 mL and then 15 mL of ether was added to cause a complete precipitation. The purple solid was isolated on a frit, washed with 5 mL of acetone and 10 mL of ether, then dried in vacuo for several hours.

15. IrI(COD)(Cyttpp)

A purple solution of [IrI(COD)]_{2} (254 mg, 0.298 mmol) in benzene (30 mL) was treated with the ligand solution (2.4 mL, 0.800 mmol). After the resulting yellow solution was stirred for 20 min, the solvent was removed completely under vacuum, and 20 mL of hexane was added to the residue. The pale yellow solid was collected on a frit and dried in vacuo for 2 hrs. \( \lambda_{M} = 10 \text{ cm}^{-2} \text{ ohm}^{-1} \text{ mole}^{-1} (\text{CH}_{2}\text{Cl}_{2}) \).
Analysis for C_{44}H_{73}I_{1}IrP_{3}:

Calcd.: C, 52.11; H, 7.26; I, 12.51.

Found: C, 52.02; H, 7.28; I, 12.30.

16. IrCl(CO)_{2}(Cyttp)

A solution of IrCl(COD)(Cyttp) (200 mg, 0.216 mmol) in 15 mL of benzene was treated with a slow stream of CO for 20 min. Then 10 mL of hexane was added to cause a precipitation; the resultant pale yellow solid was collected on a frit, washed with 10 mL hexane, and dried in a N_{2} stream overnight. A ^{31}P-NMR spectrum will be discussed in the discussion. The infrared spectrum shows two CO stretches at 1980 (asymm) and 1925 cm^{-1} (sym).

17. [(Ir(CO)_{2}(Cyttp))BF_{4}]

A yellow slurry of IrCl(COD)(Cyttp) (400 mg, 0.433 mmol) in acetone (30 mL) was reacted with TlBF_{4} (160 mg, 0.550 mmol); a magenta color mixture resulted. The resulting reaction mixture was treated with a slow stream of CO for 3 hrs; the magenta color disappeared and a dark yellow solution and a heavy white precipitate resulted after ca 1 min of CO addition. The resultant solution was filtered through a filter needle and the filtrate was evaporated to dryness under reduced pressure. The resulting orange residue was dissolved in 20 mL of THF; the solution was filtered again through celite and glass wool supported on a
frit. The filtrate was evaporated to 5 mL and 20 mL of hexane was added to cause a precipitation. An orange-yellow solid was collected on a frit, washed with 10 mL of hexane, and dried in vacuo for 2 hrs. $A_M = 100 \text{ cm}^{-2} \text{ ohm}^{-1} \text{ mole}^{-1}$ (acetone).

Analysis for $C_{38}H_{61}BF_4IrO_2P$:

Calcd.: C, 49.51; H, 6.67; P, 10.08.

Found: C, 49.33; H, 6.87; P, 9.89.

18. $\text{[Ir}((\text{CH}_3)_2\text{CO})\text{(Cytpp)}\text{]}\text{AsF}_6$

A sample of $[\text{IrCl(COD)}]_2$ (80 mg, 0.119 mmol) and NaAsF$_6$ (60 mg, 0.283 mmol) was combined in 20 mL of acetone. The resulting yellow solution was stirred for 1 hr and was treated with the ligand solution (0.95 mL, 0.238 mmol) yielding a red color. The resulting solutions was filtered through a filter needle, a $^{31}$P-NMR spectrum was obtained on a 2 mL aliquot of the filtrate and it gave an $AB_2$ pattern.

The remaining solution was evaporated to dryness and 15 mL of ether was added. The red-orange solid was isolated; it gave acetone peaks in the infrared spectrum.

19. $\text{IrCl(Cytpp)}$

The solution of $[\text{IrCl(COD)}]_2$ (100 mg, 0.149 mmol) and the ligand solution (1.2 mL, 0.300 mmol) in 20 mL of toluene was stirred at room temperature for over 72 hours. The solvent was evaporated to ca 1 mL and 10 mL of hexane was added
to isolate the product. The resulting bright yellow solid was collected on a frit, washed with 5 mL of hexane and dried in vacuo for 1 hr.

Analysis for $\text{C}_3\text{H}_7\text{Cl}\text{IrP}_3$:

Calcd.: C, 53.09; H, 7.55; Cl, 4.35

Found: C, 52.77; H, 7.72; Cl, 4.57.

20. IrCl(Cyttp)

The solution of IrCl(COD)(Cyttp) (100 mg, 0.108 mmol) was refluxed in 15 mL of toluene for more than 4 hrs. The resulting solution was cooled at room temperature and stirred for another hour. The solvent was removed to dryness under vacuum and 15 mL of hexane was added to wash the residue. The resulting solid was isolated on a frit, washed with 5 mL of hexane, and dried in vacuo for 1 hr.

Analysis for $\text{C}_3\text{H}_7\text{Cl}\text{IrP}_3$:

Calcd.: C, 53.22; H, 7.32.

Found: C, 52.42; H, 7.37.

21. IrCl(Cyttp-OH)

The same procedure was performed as above for the case of IrCl(Cyttp) except that non-distilled hexane was used to precipitate the product.

Analysis for $\text{C}_3\text{H}_7\text{Cl}\text{IrOP}_3$:

Calcd.: C, 52.06; H, 7.40; Cl, 4.27.

Found: C, 50.22; H, 7.36; Cl, 4.25.
22. Ir(Cl)₂H(Cl-Cyttp)

A solution of IrCl(COD)(Cyttp) (100 mg, 0.108 mmol) was heated up to 70°C for 10 min and cooled to room temperature. To this yellow solution was added concentrated HClₐq (0.1 mL) and the solution turned white immediately. The resulting solution was evaporated to dryness and 10 mL of ether was added. A white precipitate was isolated, collected on a frit, washed with 2 x 10 mL of ether and dried in vacuo overnight.

Analysis for C₃₆H₆₂Cl₃IrP₃:
Calcld.: C, 48.84; H, 6.89; Cl, 12.01.
Found: C, 49.61; H, 6.97; Cl, 11.45.

F. Preparation of Rhodium Complexes

1. RhCl(Cyttp)

This compound was prepared according to the method of T.J. Mazanec; the ²¹P(¹H)-NMR spectrum of the pure compound was recorded in the discussion.

2. [Rh(Cyttp)(PPh₂H)]₅AsF₆

A solution of RhCl(Cyttp) (300 mg, 0.428 mmol) and TlAsF₆ (250 mg, 0.635 mmol) in 30 mL of THF was heated to 50°C for 5 min, during which time the solution turned orange. Into this solution was added approximately 0.09 mL (0.450 mmol) of PPh₂H, which caused a yellow slurry to form. This yellow slurry turned greenish yellow when ca 5
mg of HAsF₆ was added. The reaction mixture was stirred for 0.5 hr and it turned deep yellow. The solution was filtered through celite and glass wool supported on a frit. The filtrate was then evaporated completely and 10 mL of acetone was added to the solid. The resultant solution was filtered again through an airless frit, and then the filtrate was evaporated to dryness. To this resulting residue was added 5 mL of CH₂Cl₂ to give a red-orange solution. This solution was treated slowly with 25 mL of ether until it became cloudy, and was kept at 0°C in a freezer overnight. Yellow crystals separated by morning; 20 mL of ether was added to cause additional precipitation. The product was collected on a frit, washed with 2 x 20 mL of ether and dried in vacuo for one day. Aₘ = 140 cm⁻² ohm⁻¹ mol⁻¹ (acetone); m.p., decomposed at 150°C.

Analysis for C₄₈H₇₂AsF₆P₄Rh:

Calcd.: C, 54.14; H, 6.82; P, 11.63.

Found: C, 53.65; H, 6.79; P, 11.52.

3. [Rh(Cyttp)(PF₃(OMe))]AsF₆

A mixture of RhCl(Cyttp) (500 mg, 0.670 mmol) and NaAsF₆ (160 mg, 0.705 mmol) in 30 mL of MeOH was stirred for 5 min and then refluxed for 0.5 hr. A slow stream of PF₃(g) was added into this refluxing yellow slurry for 5 min; as soon as the gas touched the solvent, a thick cloud of white fumes, which presumably was HF, was evolved. The slurry
dissolved completely as the PF$_3$ was added, then the resulting yellow-orange solution was purged with N$_2$ for 5 min to remove the excess PF$_3$. The resultant solution was cooled to room temperature and filtered through a filter needle; this removed the unreacted NaAsF$_6$ and precipitated NaCl. The resulting filtrate was then evaporated to dryness and 15 mL of acetone was added. This slurry was filtered again through a filter needle to collect the acetone-soluble portion. The solvent was removed and 15 mL of hexane was added to precipitate the product. The resulting yellow solid was isolated on a frit, washed with 5 mL of hexane, and dried in vacuo for 3 hours. $\Lambda_M = 89 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$ (MeOH).

Analysis for C$_{37}$H$_{64}$AsF$_8$OP$_4$Rh:

Calcd.: C, 45.41; H, 6.59; P, 12.66.

Found: C, 43.88; H, 6.51; P, 11.98.

4. [Rh(Cyttp)(P(OMe)$_3$)]AsF$_6$

A reaction mixture of RhCl(Cyttp) (400 mg, 0.552 mmol) and NaAsF$_6$ (140 mg, 0.167 mmol) in 30 mL of MeOH was stirred for 15 min. No appreciable color change was observed, except that the yellow color of the mixture became lighter. To this slurry was added approximately 0.15 mL of P(OMe)$_3$; the slurry dissolved and turned orange immediately. The resulting solution was filtered through a filter needle and the orange filtrate was evaporated to dryness completely.
The resultant residue was then treated with 10 mL of acetone and the resulting solution was filtered again via a filter needle. The volume of the filtrate was reduced to 5 mL and then 50 mL of ether was added slowly; some of the solution separated as an oil, but most of the solution became cloudy. Orange crystals were isolated from the solution after an hour. The crystals were collected on a frit and dried in vacuo for 1 hr. The remaining solution was evaporated to dryness and hexane was added to precipitate the product. The solid was isolated, washed with 2 x 10 mL of hexane and dried in vacuo overnight. $\lambda_m = 100 \text{ cm}^{-2} \text{ ohm}^{-1} \text{ mol}^{-1}$ (MeOH).

Analysis for $C_{39}H_{70}AsF_6O_3P_4Rh$:

Calcd.: C, 46.48; H, 6.98; P, 12.36.

Found: C, 46.45; H, 6.90; P, 12.21.

5. $[\text{Rh(CO)(Cytpp)}]AsF_6$

Into a slurry of RhCl(Cytpp) (300 mg, 0.414 mmol) in methanol (30 mL) was bubbled a stream of CO. Over the period of an hour the slurry dissolved and a yellow solution was obtained. The resulting solution was treated with NaAsF$_6$ (140 mg, 0.617 mmol in 10 mL of MeOH) and a yellow solid precipitated immediately. The resultant slurry was stirred for 2 hrs, and the solvent volume was reduced to 10 mL by evaporation. The yellow solid was collected on a frit, washed with 2 x 10 mL of H$_2$O, 110 mL of MeOH, and
2 x 10 mL of ether, then it was dried in vacuo for 1 hr.

A_M = 140 cm^{-2} ohm^{-1} mol^{-1} (acetone).

Analysis for C_37H_61AsF_6OP_3Rh:

Calcd.: C, 49.02; H, 6.78; P, 10.25.

Found: C, 48.99; H, 6.71; P, 10.13.

6. Rh(NO_2)(Cyttp)

A reaction mixture of RhCl(Cyttp) (250 mg, 0.345 mmol) and NaNO_2 (30 mg, 0.435 mmol) in EtOH (20 mL) was stirred at room temperature. The solution became dark yellow after 0.5 hr and yielded a fluffy pale yellow solid. The volume of the solution was reduced to ca 15 mL and the resulting yellow solid was isolated, the infrared and ^{31}P NMR spectra indicated that this solid was RhCl(Cyttp)•O_2. The possible mechanism will be discussed later. The filtrate was evaporated to dryness and the residue was isolated in 15 mL of ether. The solid was collected on a frit, washed with 10 mL of EtOH, 10 mL of H_2O, 10 mL of EtOH, and then dried in vacuo overnight.

Analysis for C_{36}H_{61}NO_2P_3Rh:

Calcd.: C, 56.03; H, 7.91; N, 1.82.

Found: C, 56.38; H, 8.13; N, 1.82.

7. Attempted Synthesis of Rh(NO_2)(ttp)

The reaction mixture of RhCl(ttp) (300 mg, 0.414 mmol) and NaNO_2 (38 mg, 0.447 mmol) in 25 mL of THF was refluxed
for 1 hr. The color turned orange from yellow during the reaction time; a yellow solid precipitated when the mixture was cooled to room temperature. The yellow solid was isolated and washed with 10 mL of ether, 2 × 10 mL of H₂O, and 2 × 10 mL of ether, then it was dried in vacuo overnight. The resulting product was recrystallized in benzene and hexane.

Analysis for RhCl(ttp)O₂ (C₃₆H₃₇ClO₂P₃Rh):

Calcd.: C, 56.99; H, 5.05; N, 0.0.

Found: C, 56.94; H, 5.13; N, trace.

8. Rh(ttp)I·O₂

A slurry of [RhI(COD)]₂ (230 mg, 0.340 mmol) in 15 mL of ethanol was stirred, into which a ttp ligand solution (2.42 mL, 0.691 mmol) was added. The resulting red solution was refluxed for 1 hr; no significant change occurred. Ten mL of ether was added to cause precipitation and the solution was kept in the freezer overnight. The solution yielded a yellowish-green precipitate by morning. The solid was collected on a frit, washed with 2 × 10 mL of ether, and then dried in vacuo for several hours.

Analysis for C₃₆H₃₇IO₂P₃Rh:

Calcd.: C, 52.45; H, 4.52; I, 15.39.

Found: C, 52.50; H, 4.66; I, 15.22.
9. **Rh(SnCl<sub>3</sub>)(Cyttp)**

A reaction mixture of RhCl(Cyttp) (250 mg, 0.345 mmol) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and anhydrous SnCl<sub>2</sub> (68 mg, 0.358 mmol) was stirred at room temperature. The SnCl<sub>2</sub> was dried with acetic anhydride and ether, and the CH<sub>2</sub>Cl<sub>2</sub> was distilled over P<sub>2</sub>O<sub>5</sub> twice. As the SnCl<sub>2</sub> dissolved, the solution turned yellow, brownish-green, and eventually green. The solution was stirred overnight and yielded a green precipitate. The solvent was evaporated under a reduced pressure, and the residue was isolated with 20 mL of ether. The green solid was collected on a frit, washed with 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, and dried in vacuo for 1 hr.

Analysis for C<sub>36</sub>H<sub>61</sub>Cl<sub>3</sub>RhSn:

Calcd.: C, 47.27; H, 6.72; Cl, 11.63.

Found: C, 46.99; H, 6.48; Cl, 11.37.

10. **[Rh(CO)(Cyttp)(SO<sub>2</sub>)]AsF<sub>6</sub>**

Into a slurry of [Rh(CO)(Cyttp)]AsF<sub>6</sub> (200 mg, 0.237 mmol) in 25 mL of MeOH was added a slow stream of SO<sub>2</sub> gas for 10 min; at this point all the solid dissolved and yielded a yellow-orange solution. The resultant solution was purged for 5 min with N<sub>2</sub> to remove the excess SO<sub>2</sub>, and it was placed in a freezer overnight; orange crystals formed by morning. The crystals were collected on a frit and dried under N<sub>2</sub> for several hours (the <sup>31</sup>P-NMR spectrum showed only [Rh(CO)(Cyttp)(SO<sub>2</sub>)]AsF<sub>6</sub>). The remaining orange filtrate
was evaporated under reduced pressure (ca. 0.2 torr), which caused the color to change from orange to yellow. The $^{31}$P NMR spectrum of this solution indicated only the presence of $[\text{Rh(CO)}(\text{Cytpp})]\text{AsF}_6$. A stream of $\text{SO}_2$ was added again to this yellow solution for 10 min. Into the resultant yellow-orange solution was added 10 mL of hexane; a yellow-orange solid precipitated. The solid was isolated on a frit and dried under $\text{N}_2$ overnight (the $^{31}$P NMR spectrum of this solid showed a mixture of $[\text{Rh(CO)}(\text{Cytpp})]\text{AsF}_6$ and $[\text{Rh(CO)}(\text{Cytpp})-(\text{SO}_2)]\text{AsF}_6$.

Analysis for the orange crystals:

Calcd. for $\text{C}_{37}\text{H}_{61}\text{AsF}_6\text{O}_3\text{RhS}$:

- C, 45.78; H, 6.33; S, 3.65.
- Found: C, 45.57; H, 6.29; S, 3.38.

11. A Reaction of $\text{Rh(NO}_2)(\text{Cytpp})$ with CO

A solution of $\text{Rh(NO}_2)(\text{Cytpp})$ (200 mg, 0.272 mmol) in 20 mL of benzene was reacted with a slow stream of CO; the color turned orange. The resultant solution was evaporated to dryness under vacuum and the residue was isolated with 10 mL of ether. The solid was collected on a frit and dried in vacuo for 2 hrs. The $^{31}$P-NMR spectrum gave two different $\text{AB}_2\text{X}$ patterns and the infrared spectrum indicated the presence of CO, NO$_2$, NO and CO$_3$. $\nu_{\text{CO}}$, 1980 cm$^{-1}$; $\nu_{\text{NO}_2}$, 1320 cm$^{-1}$; $\nu_{\text{NO}^+}$, 1880 cm$^{-1}$; $\nu_{\text{CO}_3}$, 1660, 1640, 735 cm$^{-1}$, 620 cm$^{-1}$. 
12. \([\text{Rh}(\text{PPh}_2\text{H})_4] \text{AsF}_6\)

A solution of \([\text{RhCl(COD)}]_2\) (250 mg, 0.345 mmol) and \(\text{NaAsF}_6\) (230 mg, 1.01 mmol) in \(\text{CH}_2\text{Cl}_2\) (30 mL) was refluxed for 10 min; the \(\text{NaAsF}_6\) did not dissolve completely but the color of the solution turned darker. Into this hot solution was added approximately 0.38 mL of \(\text{PPh}_2\text{H}\); a reddish-orange solution resulted and a fluffy white solid, \(\text{NaCl}\), separated. The resultant mixture was refluxed for another 10 min and cooled to room temperature. The solution was filtered through a filter needle, and the filtrate was reduced to 5 mL. A bright yellow precipitate resulted; it was isolated on a frit, washed with 2 \(\times\) 10 mL of ether, and then dried in vacuum for one day. \(\Lambda_M = 125 \text{ cm}^{-2} \text{ ohm}^{-1} \text{ mol}^{-1}\) (acetone).

Analysis for \(\text{C}_{48}\text{H}_{44}\text{AsF}_{6}\text{P}_4\text{Rh}\):

Calcd.: C, 55.62; H, 4.23; P, 11.95.

Found: C, 55.39; H, 4.52; P, 11.79.

13. \([\text{Rh(}\text{dppp)}(\text{PPh}_2\text{H})_2\text{]} \text{AsF}_6\)

The reaction mixture of \([\text{Rh(PPh}_2\text{H}_4\text{AsF}_6\text{]}\) (200 mg, 0.193 mmol) and \(\text{dppp}\) (80 mg, 0.194 mmol) was stirred in acetone for 0.5 hr; no color change was observed. The solvent volume was then reduced to 5 mL and 20 mL of ether was added to precipitate a bright yellow solid. The solid was collected on a frit, washed with 2 \(\times\) 10 mL of ether, and dried in vacuo for 2 hrs. \(\Lambda_M = 140 \text{ cm}^{-2} \text{ ohm}^{-1} \text{ mol}^{-1}\) (acetone).
Analysis for C_{51}H_{48}AsF_{6}P_{4}Rh:
Calcd.: C, 55.89; H, 4.49; P, 11.51.
Found: C, 56.77; H, 4.52; P, 11.39.

14. [Rh(Cyttp)(PPh_{2})_{2}]Li

A red solution of LiPPh_{2} was generated by adding 0.13 mL of n-BuLi into the PPh_{2}H (0.04 mL) in THF (5 mL). The red solution was transferred via a transfer needle into the yellow solution of RhCl(Cyttp) (150 mg, 0.207 mmol) in 5 mL of THF. As soon as the LiPPh_{2} was introduced, the solution turned deep red. The resulting solution was stirred for 0.5 hr, and then 2 mL aliquot was taken for \textsuperscript{31}P{\textsuperscript{1}H}-NMR: 2 doublets of doublet of doublet at -35 ppm and multiplets at 12.5 \sim -7.65 ppm.

G. Preparation of Pt-Cyttp Complexes
1. [PtCl(Cyttp)]Cl

A reaction mixture of PtCl_{2}(COD) (100 mg, 0.267 mmol) and the ligand solution (1.08 mL, 0.270 mmol) in 20 mL of benzene was refluxed for 1 hr. The clear solution was evaporated to 5 mL and 10 mL of ether was added. The resulting white solid was isolated on a frit and dried in a water-aspirator.

Analysis for C_{36}H_{61}Cl_{2}P_{3}Pt:
Calcd.: C, 50.70; H, 7.21; Cl, 8.31.
Found: C, 50.87; H, 7.39; Cl, 8.16.
2. \([\text{PtCl(Cyttp) }]\text{NO}_3\)

The solution of \([\text{PtCl(Cyttp) }]\text{Cl}\) (80 mg, 0.0910 mmol) in 15 mL of EtOH was treated with \(\text{TlNO}_3\) (25 mg, 0.0939 mmol); the resulting solution was refluxed for 1 hr and cooled to room temperature. The solvent was removed completely and the resultant residue was washed in 15 mL of ether. The white solid was collected on a frit, washed with 10 mL of \(\text{H}_2\text{O}\) and 2 ~ 10 mL of ether. The product was characterized by \(^{31}\text{P}\) NMR spectrum (\(\text{AB}_2\text{X}\) pattern) and by infrared spectrum (\(\text{NO}_3\) stretching frequencies: 1260, 1050 cm\(^{-1}\) and 800 cm\(^{-1}\)).
RESULTS AND DISCUSSION

A. **Iridium(III) hydride complexes of Cytp**

**Synthesis and characterization**

The abstraction of hydride or carbonyl from a basic alcoholic mixture of heavy-metal complexes is quite well documented.\(^{17-20}\) The single stage syntheses of carbonyl or hydrido complexes, e.g., MCl(CO)(PCy\(_3\))\(_2\) (M = Rh, Ir),\(^{91}\) RhCl\(_2\)H(PCy\(_3\))\(_2\),\(^{83}\) IrClH\(_2\)(PPh\(_3\))\(_3\),\(^{40}\) are advantageous, since the carbonyl synthesis does not require the use of carbon monoxide and the hydride does not involve addition H\(_2\) or HCl.

Alcoholic solutions (e.g., EtOH, 2-methoxyethanol) of iridium complexes can give mixtures of Ir(III)-hydrides or carbonyl complexes depending on the refluxing temperature of the alcohol.\(^{36,41}\) In addition, \(\delta^6\)-octahedral complexes with monodentate phosphine ligands can yield geometric isomers such as mer- and fac-configurations; hence the clean synthesis of one pure isomeric form of metal-hydride has always been an issue in the preparation of metal-hydrides from reactions with the solvent.

In this study, a reaction mixture of [IrX(COD)]\(_2\) (X = Cl, I), Cytp ligand and EtOH gives a complex of
composition, $\text{IrXH}_2(\text{Cytpp})$ ($X = \text{Cl, I}$); it appears to have one configuration. The mer-$\text{IrH}_3(\text{Cytpp})$ complex is also obtained by treating the same mixture with KOH/EtOH. The $\text{IrClH}_2(\text{Cytpp})$ complex was used to investigate the Ir-Cl bond reactivity, reactivity patterns of the Ir-hydride bonds with electrophiles, and the H/D exchange with hydrocarbon solvents. The $\text{IrXH}_2(\text{Cytpp})^{n+}$ complexes were also prepared from $\text{IrClH}_2(\text{Cytpp})$ to study the effect of the ligand $X$ trans to the hydride. Scheme I summarizes the reactions prepared during this study.

\begin{center}
\textbf{SCHEME I}
\end{center}
The complexes in Scheme I were isolated and characterized by $^{31}$P($^1$H)-NMR, $^1$H-NMR, $^2$H-NMR, infrared spectra, mass spectra (where possible due to the limited volatility), single crystal x-ray analysis (for IrClH$_2$Cytpp and IrH$_3$-(Cytpp)-(EtOH)), and elemental analysis.

The cis-dihydride, IrClH$_2$(Cytpp), prepared from an ethanolic mixture of [IrCl(COD)]$_2$ and Cytpp ligand, is air and light stable in the solid state. The presence of cis-dihydrides is identified by $^1$H-NMR and infrared spectra. The Ir-H stretching vibrations are shown at 2245 cm$^{-1}$ and 1995 cm$^{-1}$ (Fig. 3); the two peaks are assigned as hydrides trans to Cl and phosphorus, respectively. The $^1$H-NMR spectrum shows two hydride resonances at different positions; the hydride trans to the central phosphorus appears at -9.13 ppm (d of t) and the hydride trans to Cl is at -22.3 ppm (d of t of d). The phosphorus-hydrogen and hydrogen-hydrogen coupling constants were confirmed by the selective irradiation technique on the Bruker WM-300 NMR spectrometer (Table 4, Fig. 4); thus, structure A-1 is proposed from the spectroscopic data.
Figure 2. Phosphorus-31 NMR spectrum of cis,syn-IrClH$_2$(Cyttpp) (121.470 MHz).
Figure 3. Infrared spectrum of \textit{cis,syn}-IrClH\textsubscript{2}(Cyttpp) (Nujol mull).
Figure 4. Proton-NMR spectrum of cis,syn-IrClH₂(Cyttpp) and selective decoupling of phosphorus for highfield hydride region (300 MHz).
Dahlenberg and coworkers have prepared an analogous complex, IrCl(H)_2(ttp), by direct hydrogenation of IrCl(ttp). The \(^{31}\text{P}\{^{1}\text{H}\})\) and \(^{1}\text{H}-\text{NMR}\) data of both cis-dihydride complexes are compared in Table 5. The significant difference in \(^{31}\text{P}\) chemical shifts of ttp phosphorus in IrCl(H)_2(ttp) from those of Cyttpp analog is not understood at this point. The \(^{31}\text{P}-\text{NMR}\) spectra for iridium complexes, so far, can only be used as an identification tool; in contrast to rhodium, iridium does not provide \(J_{\text{M-P}}\) values, which could qualitatively represent the nature of M-P bonding. Compared to those of Rh-complexes, the \(2J_{\text{P1P2}}\) values in these iridium complexes have not yet been systematically investigated; thus, no empirical correlations have been established between iridium metal oxidation states and \(2J_{\text{PP}}\) values as far as the author is aware. The upfield chemical shifts of phosphorus coordinated to Ir-metal suggests increased shielding; \([\text{PtCl(ttp)\text{]}^+}\), OsCl_2(PPh_3)_3, and IrCl(ttp) show higher chemical shift than the corresponding 4-d analogs (Table 25). In addition, the iridium complexes of Cyttpp or ttp usually exhibit an AB_2 pattern with the A portion (triplet) higher than that of B (doublet), regardless of the ligand trans to P_1; this pattern is true for Rh and Ru analogs only when a strong trans-influencing ligand is trans to the
TABLE 5

Phosphorus-31 And $^1$H-NMR Parameters Of Ir-Hydride Complexes Of Cytpp and ttp

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_{P1}$</th>
<th>$\delta_{P2}$</th>
<th>$J_{P1P2}$</th>
<th>$\delta_{H1}$</th>
<th>$\delta_{H2}$</th>
<th>$\delta_{H3}$</th>
<th>$J_{P1H1}$</th>
<th>$J_{P1H2}$</th>
<th>$J_{P1H3}$</th>
<th>$J_{P2H1}$</th>
<th>$J_{P2H2}$</th>
<th>$J_{P2H3}$</th>
<th>$J_{H1H2}$</th>
<th>$J_{H1H3}$</th>
<th>$J_{H2H3}$</th>
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<tbody>
<tr>
<td>IrCl$_2$H(cytpp)</td>
<td>-33.8</td>
<td>-14.8</td>
<td>23.5</td>
<td>-19.57</td>
<td></td>
<td></td>
<td>133.9</td>
<td>18.6</td>
<td>15.6</td>
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<td></td>
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<tr>
<td>IrCl$_2$(cytpp)</td>
<td>-44.2</td>
<td>-10.0</td>
<td>25.0</td>
<td>8.76</td>
<td>-21.06</td>
<td></td>
<td>133.9</td>
<td>10.6</td>
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<td>5.2</td>
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<tr>
<td>IrCl$_2$(Cytpp)</td>
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<td></td>
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<tr>
<td>IrH$_2$(Cytpp)</td>
<td>-34.8</td>
<td>-8.44</td>
<td>25.6</td>
<td>-10.28</td>
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<td></td>
<td>124.0</td>
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<td>16.6</td>
<td>6.5</td>
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</tr>
<tr>
<td>IrH$_3$(Cytpp)</td>
<td>-23.0</td>
<td>8.57</td>
<td>26.4</td>
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<td>-12.94</td>
<td>-12.66</td>
<td>112.0</td>
<td>15.8</td>
<td>20.0</td>
<td>12.0</td>
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<tr>
<td>mer-IrH$_3$(PPh$_2$)</td>
<td>-13.53</td>
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<td>-11.80</td>
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$^a$The numbering of atoms are consistent with the configuration below.

$^b$Reference, 29

$^c$Reference, 25

$^d$The line broadening of the calculated $^1$H-NMR spectrum was 7 Hz due to the quadrupole moment of iridium.

$^e$Chemical shifts are relative to 85% H$_3$PO$_4$.
central phosphine, P₁. The $^{31}$P-NMR spectra of Ir(I)-triporphosphate complexes will be discussed in detail in section B.

The reaction of [IrCl(COD)]$_2$ and Cytpp in EtOH or MeOH was followed by variable temperature NMR ($^{31}$P and $^1$H) spectra. The deep red reaction mixture at 200 K gives the free COD resonances at 5.906 ppm in $^1$H-NMR spectrum, implying that COD was already dissociated from the coordination sphere. At 230 K, the major species in the $^{31}$P($^1$H)-NMR spectrum has one phosphino group uncoordinated at -8.75 ppm (-8.67 ppm in MeOH) and a broad doublet of doublet at -37.74 ppm (-38.42 ppm in MeOH); the $^1$H-NMR spectrum at 230 K shows two ethanol-OH peaks at 5.498 ppm (free EtOH) and 4.650 ppm (bound EtOH). At 250 K this major part of the $^{31}$P($^1$H) spectrum is the same as the spectrum at 230 K but it becomes more well-defined (Fig. 5). The $^1$H-NMR spectrum also shows coordinated EtOH; when EtOH is coordinated to iridium, the chemical shifts of CH$_3$-, -CH$_2$- are reported to be 1.0 and 2.4 ppm.

<table>
<thead>
<tr>
<th>resonance group</th>
<th>bound EtOH</th>
<th>free EtOH</th>
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<tr>
<td>-OH</td>
<td>4.63 ppm</td>
<td>5.488 ppm</td>
</tr>
<tr>
<td>-CH$_2$-</td>
<td>2.54 ppm</td>
<td>3.540 ppm</td>
</tr>
<tr>
<td>CH$_3$-</td>
<td>0.98 ppm</td>
<td>1.113 ppm</td>
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</table>
Figure 5. Reaction follow-up of [IrCl(COD)]$_2$, CyttP, and EtOH by VT (a) $^{31}$P($^1$H) - (36.43 MHz) and (b) $^1$H-NMR spectra (500 MHz).
From the $^{31}P\{^1H\}$ and $^1H$-NMR data, the intermediate at 230-250 K may be proposed as A-2.

When the temperature warms to 270 K the IrCl(Cytpt)•EtOH complex becomes the predominant species in the $^{31}P\{^1H\}$-NMR spectrum ($\delta P_1 = -16.5$ ppm; $\delta P_2 = 2.01$ ppm; $^{2}J_{P_1P_2} = -31.9$ Hz). At room temperature a mixture of IrCl(Cytpt)•EtOH and IrCl$_2$(Cytpt) is observed in the $^{31}P\{^1H\}$-NMR spectrum; after setting at room temperature for a few hours, the IrCl$_2$-(Cytpt) complex becomes the major species in the $^{31}P\{^1H\}$-NMR spectrum. Some unknown Ir-H species at $\sim$-12.0 ppm in $^1H$-NMR appears in this reaction mixture. When the mixture is refluxed this unknown hydride disappeared from the $^1H$ and $^{31}P\{^1H\}$-NMR spectra.

The deuteride analog was prepared by using either $d_1$-EtOD or $d_6$-EtOD. When $d_1$-CH$_3$CH$_2$OD was used as solvent the Ir-H band at 2245 cm$^{-1}$ in the infrared spectrum almost vanished and a new peak appeared at 1605 cm$^{-1}$ ($\nu_{Ir-H/Ir-D} = 1.40$); the other hydride band at 1995 cm$^{-1}$ remains. The mass spectra with 817 indicates that the mono-deuteride is the major species of the sample. From this $d_1$-EtOD experiment, the hydride trans Cl appears to be from ethanolic
Figure 6. Infrared spectra of deuteride analogs of cis,syn-IrClH2(Cyttp): (a) IrClD$_2$(Cyttp); (b) IrClDH(Cyttp) (KBr).
RO-H. The product from $d_6$-EtOD reaction mixture shows no trace of $v_{\text{Ir-H}}$ at either 2245 or 1995 cm$^{-1}$; those peaks are replaced by weak and broad bands at 1610 cm$^{-1}$ ($\text{Ir-H}/\text{Ir-D} = 1.39$) and 1408 cm$^{-1}$ ($\text{Ir-H}/\text{Ir-D} = 1.42$), respectively. It is concluded from the deuterization experiments that the ethanol molecule oxidatively adds to an iridium-triphosphine complex to give $\text{IrClD(CD}_3\text{CD}_2\text{O}^-)(\text{Cyttp})$, which subsequently undergoes a $\beta$-hydride elimination of $\text{Ir-OCD}_2\text{CD}_3$ to produce $\text{IrCl(D)}_2(\text{Cyttp})$.

The structure of $\text{cis,syn-IrClH}_2(\text{Cyttp})$ was confirmed by an X-ray crystal structure determination; the structure, determined at 159 K, is consistent with the structural assignment (A-1) from the spectroscopic data. The X-ray ORTEP views along the three principal axes of the octahedron are shown in Fig. 7. The following features are observed from the structural analysis: (i) the phenyl ring on the central $P_1$ is syn to $H_2$ and slightly bent out of the plane that contains $P_1$-$\text{Ir-H}_1$; (ii) both 6-membered rings formed by methylene chains are in chair forms; (iii) the four cyclohexyl rings on the terminal phosphorus atoms are also in chair forms; however they are oriented in such a manner that the molecule is chiral; (iv) the iridium atom lies below the basal plane (by 0.168(1) Å) that is defined by $P_1$, $P_2$ and $P_3$. The $\text{Ir-H}_2$ bond length is not known precisely; the $\text{Ir-H}_1$ bond trans to $P_1$ has refined roughly to 1.703(49) Å, which is consistent with other terminal M-H bond lengths.24,27 The
TABLE 6

X-Ray Crystal Data For IrClH$_2$(Cyttp) And IrH$_3$(Cyttp)·EtOH

<table>
<thead>
<tr>
<th>Formula</th>
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<th>IrH$_3$(Cyttp)·EtOH</th>
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<tr>
<td>F.W. (au)</td>
<td>816.48</td>
<td>828.10</td>
</tr>
<tr>
<td>space group</td>
<td>-P$_1$</td>
<td>-P$_2_1$/M</td>
</tr>
<tr>
<td>unit cell</td>
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<td>monoclinic</td>
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<td>12.636(2)</td>
<td>10.737(1)</td>
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<tr>
<td>b, Å</td>
<td>13.110(2)</td>
<td>18.484(3)</td>
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<tr>
<td>c, Å</td>
<td>11.120(1)</td>
<td>11.155(1)</td>
</tr>
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<td>α deg</td>
<td>97.65(1)</td>
<td>90</td>
</tr>
<tr>
<td>β deg</td>
<td>92.02(1)</td>
<td>120.297(9)</td>
</tr>
<tr>
<td>γ deg</td>
<td>78.58(1)</td>
<td>90</td>
</tr>
<tr>
<td>V Å$^3$</td>
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<td>1911.6</td>
</tr>
<tr>
<td>z</td>
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<td>2</td>
</tr>
<tr>
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<td>1.44</td>
</tr>
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<td>150K</td>
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<td>R(F)</td>
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<tr>
<td>$R_w$(F)</td>
<td>0.032</td>
<td>0.041</td>
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Figure 7. ORTEP views of IrCl$_2$(Cyttpp) along the principal axes of an octahedron: (a) z-axis; (b) x-axis; (c) y-axis.
TABLE 7

Selected Bond Lengths And Angles For cis,syn-IrClH$_2$(Cyttpp) $^a$

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<thead>
<tr>
<th>atoms</th>
<th>Distance (Å)</th>
<th>atoms</th>
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<td>Ir-P(1)</td>
<td>2.309(1)</td>
<td>P(1)-C(11)</td>
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<td>Ir-P(2)</td>
<td>2.305(1)</td>
<td>P(2)-C(211)</td>
</tr>
<tr>
<td>Ir-P(3)</td>
<td>2.298(1)</td>
<td>P(3)-C(311)</td>
</tr>
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<td>Ir-Cl</td>
<td>2.528(1)</td>
<td>P(2)-C(221)</td>
</tr>
<tr>
<td>Ir-H(1)</td>
<td>1.703(49)</td>
<td>P(3)-C(321)</td>
</tr>
<tr>
<td>Ir-H(2)</td>
<td>1.629$^b$</td>
<td></td>
</tr>
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</table>

<table>
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<th>Angles (°)</th>
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<tbody>
<tr>
<td>P(1)-Ir-H(1)</td>
</tr>
<tr>
<td>P(2)-Ir-H(1)</td>
</tr>
<tr>
<td>P(3)-Ir-H(1)</td>
</tr>
<tr>
<td>P(1)-Ir-H(2)</td>
</tr>
<tr>
<td>P(2)-Ir-H(2)</td>
</tr>
<tr>
<td>P(3)-Ir-H(2)</td>
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<tr>
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</tr>
<tr>
<td>Cl-Ir-H(2)</td>
</tr>
<tr>
<td>H(1)-Ir-H(2)</td>
</tr>
<tr>
<td>H(1)-Ir-Cl</td>
</tr>
</tbody>
</table>

$^a$Data provided by Dennis Kountz at The Ohio State University.

$^b$The bond distance Ir-H$_2$ is not refined.
Iridium-phosphorus bond lengths are also within the literature range: $d(\text{Ir}-P_1) = 2.309\text{Å}; d(\text{Ir}-P_2) = 2.298\text{Å}; d(\text{Ir}-P_3) = 2.305\text{Å}$ (Table 5). If the hydride ligand exerts a stronger trans-influence than phosphorus, lengthening of the $\text{Ir}-P_1$ bond would be expected. The $d(\text{Ir}-P_1)$ is a little longer than the others; however, this small difference may be due to crystal packing forces rather than to the trans-influence of H. From the observed bond lengths of $\text{Ir}-P_1$ and $\text{Ir}-H_1$ (longer than $\text{Ir}-H_2$ from the Fourier map), the phosphorus seems to exert comparatively strong trans-influence on the hydrogen. The $\text{Ir}-\text{Cl}$ bond distance is one of the longest non-bridging $\text{Ir}-\text{Cl}$ bonds reported ($d(\text{Ir}-\text{Cl}) = 2.528\text{Å}$); other values found for such $\text{Ir}-\text{Cl}$ bonds in octahedral $\text{Ir(III)}$ complexes are 2.34–2.45Å. Such a long $\text{Ir}-\text{Cl}$ bond length nearly approaches values for bridging $\text{Ir}-\text{Cl}-\text{Ir}$ bonds. Clark et al. reported a crystal structure of $\text{IrCl(H)}_2(\text{BDPH})$ (BDPH = $\text{Ph}_2\text{P(CH}_2)_2\text{CH=CH(CH}_2)_2\text{PPh}_2$) and also observed extremely long $\text{Ir}-\text{Cl}$ bond trans to hydride ($2.510\text{Å}$). This remarkable lengthening of $\text{Ir}-\text{Cl}$ bond trans

![Diagram](image-url)
to hydride is presumably ascribed to the strong trans-influence of the hydride. The compound \( \text{IrClH(CO)(PPh}_3)_2^- \cdot (\text{FBF}_3) \) (eq. 11) also gives longer Ir-F (trans to H) bond length (2.272(3) Å) compared to the other Ir-F bonds (d(Ir-F) = 2.08-2.21 Å).  

The iodide analog of \( \text{cis,syn-IrClH}_2\text{(Cyttp)} \) was also prepared from an alcoholic mixture of [IrI(COD)]\(_2\) and the Cyttp ligand. If the reaction mechanism dictates the stereochemistry, the \( \text{IrH}_2\text{I(Cyttp)} \) will also be isolated as the cis-syn isomer. The \( ^{31}\text{P}\{^1\text{H}\}-\text{NMR} \) spectrum shows only one \( \text{AB}_2 \) pattern; the chemical shifts of both \( \text{P}_1 \) and \( \text{P}_2 \) are shifted by 8 ppm upfield compared to the resonances of the Cl-analog (Fig. 8). The \( ^1\text{H}-\text{NMR} \) spectrum gives two hydride resonances at -20.14 ppm (\( \delta\text{Ir-H}_{\text{trans I}} \)) and at -10.28 ppm (\( \delta\text{Ir-H}_{\text{trans P}} \)). The \( ^1\text{H} \) resonance of hydride (\( \text{H}_2 \)) trans to iodide shifts downfield by ~2 ppm (but, still in the range of hydride trans to a halide); the hydride (\( \text{H}_1 \)) trans to phosphorus shifts upfield by ~1 ppm. Thus, the hydride (\( \text{H}_2 \)) trans to iodide is affected more than the one cis to I. The Ir-hydride stretching vibrations of \( \text{IrH}_2\text{I(Cyttp)} \) appear at 2198 cm\(^{-1}\) (\( \nu_{\text{Ir-H}_2} \)) and 1990 cm\(^{-1}\) (\( \nu_{\text{Ir-H}_1} \)). The \( \nu_{\text{Ir-H}_2} \) is moved to a lower frequency than in the case of chloride analog, implying that the iridium-hydride (\( \text{H}_2 \)) bond strength may be weakened when the trans ligand has stronger trans-influence than Cl. Thus, from all the spectroscopic evidence and the elemental analysis, a pure \( \text{cis-IrH}_2\text{I(Cyttp)} \)
Figure 8. Phosphorus-31 NMR spectrum of IrH₂I(Cytt) (36.43 MHz).
Figure 9. Proton-NMR spectrum of \( \text{IrH}_2\text{I(Cyttp)} \) (200 MHz).
Figure 10. Infrared spectrum of IrH₂I(Cyttp) (Nujol mull).
complex is obtained; however, whether this cis-dihydride complex is cis-syn or cis-anti cannot be determined unequivocally without an X-ray structure analysis.

The iridium trihydride complex of Cyttp was prepared cleanly from the reaction of \([\text{IrCl(COD)}]_2\), EtOH/KOH, and Cyttp ligand at room temperature. In contrast, reduction of Ir-Cl bond of IrClH\(_2\)(Cyttp) by LiBEt\(_3\)H, LiAlH\(_4\), and NaBH\(_4\) failed to produce clean syntheses of IrH\(_3\)(Cyttp). Chatt and coworkers also used KOH to transform Ir-Cl bonds to Ir-H as shown in eq. 9.\(^{37}\) In our synthesis of IrH\(_3\)(Cyttp), formation of IrClH\(_2\)(Cyttp) may precede replacement of Cl by ethoxide ion, which would then undergo \(\beta\)-hydride elimination of CH\(_3\)CH\(_2\)O\(^{-}\) to form the trihydride complex.

\[
\begin{array}{c}
\text{OCH}_2\text{CH}_3 \\
\text{Cl}
\end{array} \quad \xrightarrow{\text{KCl}} \quad \left[ \begin{array}{c}
\text{OCH}_2\text{CH}_3 \\
\text{H}
\end{array} \right] \quad \text{KOH} \quad \left[ \begin{array}{c}
\text{H} \\
\text{CH}_3
\end{array} \right] \quad \xrightarrow{\text{CH}_2\text{CHO}} \quad \left[ \begin{array}{c}
\text{H} \\
\text{CH}_3
\end{array} \right]
\]

\[(28)\]

The \(^{31}\text{P}\{^1\text{H}\}-\text{NMR}\) spectrum shows only one \(\text{AB}_2\) pattern; \(\delta P_1(\text{central}) = -23.0\ \text{ppm}; \delta P_2(\text{terminal}) = 8.57\ \text{ppm}; \) \(J_{P_1P_2} = -26.4\ \text{ppm}\) (Fig. 11). The trihydrides, IrH\(_3\)(Cyttp), react with CHCl\(_3\) to give IrClH\(_2\)(Cyttp) and CH\(_2\)Cl\(_2\); whereas dihydrides, IrH\(_2\)X(Cyttp) (X = Cl, I, SnCl\(_3\)) do not react with CHCl\(_3\). The \(^1\text{H}-\text{NMR}\) spectrum shows three separate resonances
Figure 11. Phosphorus-31 NMR spectrum of IrH$_3$(Cyttpp)•EtOH (121.470 MHz).
Figure 12. Proton-NMR spectrum of IrH₃(Cytt)p·EtOH and selective decoupling of phosphorus for highfield hydride region (300 MHz).
Figure 13. Proton-NMR spectrum of IrH$_3$(Cytp)•EtOH:
(b) on Nicolet 500; (a) computer simulation.
Figure 14. Infrared spectrum of $\text{IrH}_3\text{(Cytpp)} \cdot \text{EtOH}$ (Nujol mull).
for the three hydrides at -12.66, -12.88 (δH₁), and -12.94 ppm. The hydride (H₂) syn to the phenyl ring should give a different chemical shift from the hydride (H₃) anti to the phenyl ring; hence the two hydrides H₂ and H₃ have different resonances separated by 0.28 ppm. The more upfield chemical shift is assigned to H₂ (δH₂ = -12.94 ppm) rather than H₃ (δH₃ = -12.66 ppm), because in comparison with the analogous complex, mer-IrH₃(P(C₆H₅)(C₂H₅)₂), the hydride trans to the central phosphine has a chemical shift at -13.53 ppm and the other hydrides trans to each other have a shift at -11.80 ppm (Table 5). Figure 12 shows the hydride region with selective decoupling of the phosphorus nuclei on the Bruker WM-300 spectrometer. The ¹H-NMR parameters are confirmed by the 500 MHz instrument (Nicolet 500) and also by computer simulation, using the PANIC program (Fig. 13). The values of proton couplings, ²J₁H₁H₂, ²J₁H₁H₃, and ²J₁H₂H₃ are not precise because of the broad line width (LB = 7 Hz) due to the quadrupole moment of the iridium (¹⁹³Ir has 1.4 and ¹⁹¹Ir has 1.5 × 10⁻²⁸ m²). The stretching frequencies of three hydrides of the IrH₃(Cyttp) are located at 1998 and 1720 cm⁻¹. The two hydrides trans to each other (H₂ and H₃) appear at extremely low frequency, presumably, due to the strong trans influence on each other.

The structure of IrH₃(Cyttp)•EtOH was determined at 150 K by single crystal X-ray diffraction; it strongly supports the presence of three hydrogens in mer-configuration.
Figure 15. ORTEP views of IrH$_3$(Cyttp).EtOH along the principal axes of an octahedron:
(a) z-axis; (b) y-axis; (c) x-axis.
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<tbody>
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<td>Ir-P(2)</td>
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<td>Ir-H(32)</td>
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<tr>
<td>Ir-H(3)</td>
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<td>Ir-P(3)-C(32)</td>
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<td>Ir-P(2)-C(22)</td>
<td>103.4(4)</td>
<td>P(1)-Ir-H(3)</td>
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<td>Ir-P(3)-C(31)</td>
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<td>P(3)-Ir-H(3)</td>
<td>83.5</td>
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<tr>
<td>Ir-P(2)-C(21)</td>
<td>97.8(3)</td>
<td>H(1)-Ir-H(3)</td>
<td>180</td>
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</table>
A disordered ethanol molecule was found in the crystal lattice. The Ir-P bond lengths are again within the known limit: \( d(\text{Ir}-\text{P}_1) = 2.2763(9) \text{ Å}; d(\text{Ir}-\text{P}_2) = 2.2774(9) \text{ Å}; d(\text{Ir}-\text{P}_3) = 2.2774(9) \text{ Å}. \) The hydrogens were located but not refined to give accurate bond lengths. The ORTEP views are shown in Figure 14: (i) the phenyl ring is coplanar with the mirror plane that contains \( \text{P}_1-\text{Ir}-\text{H}_2 \); (ii) the molecule has a small disorder such that one of the trimethylene rings has a chair orientation, whereas the other ring has a twisted boat orientation; (iii) the cyclohexyl rings have chair configurations; (iv) the Ir atom is above the basal plane (by 0.246(3) Å) toward \( \text{H}_2 \).

Fourier transform ion cyclotron resonance mass spectra were obtained for the complexes of the type \( \text{IrH}_2^X\text{Cyttp} \) (\( X = \text{Cl}, \text{I}, \text{H} \)). The parent peak is not observed under the ICR condition (~1.0 \times 10^{-8} \text{ torr}, 171 - 239 °C); however, the M-2 peak (due to the loss of \( \text{H}_2 \)) is detected for all three compounds. The fragmentation pattern (Figures 15, 16) observed from the complexes \( \text{IrH}_2^X\text{Cyttp} \) (\( X = \text{Cl}, \text{I} \)) is quite surprising, as the major fragmentation involves four consecutive losses of cyclohexyl substituents of phosphine ligands as cyclohexene molecules before breaking the \( \text{Ir}-X \) (\( X = \text{Cl}, \text{I} \)) bond. This fragmentation sequence contradicts the fact that \( \text{Ir}-\text{Cl} \) bond is extraordinarily long; thus, a structural change may be envisioned when \( \text{H}_2 \) is reductively eliminated. The minor fragmentation pattern in Figures 16
Figure 16. FT-ion cyclotron mass spectrum of IrH₂Cl(Cytp).
Figure 17. FT-ion cyclotron mass spectrum of Ir$\text{I}_2$I(Cytp).
Figure 18. FT-ion cyclotron mass spectrum of IrH$_3$(Cyttp).
(a) Fragmentation of IrH₂X(Cyttp) (X=Cl, I)

(b) Fragmentation of IrH₂(Cyttp)

Figure 19. FT-ICR fragmentation sequence of IrH₂X(Cyttp) (X=Cl, I, X).
and 17 involves the cleavage of Ir-X (X = Cl, I) followed by subsequent loss of phenyl ring. The complex IrH₃(Cytpp) loses two molecules of H₂ from the M-2 peak; a possible fragmentation sequence is shown in Fig. 19. Both IrH₂X(Cytpp) (X = Cl,I) (as a major fragmentation process) and IrH₃(Cytpp) cleave the cyclohexyl substituents of the terminal phosphines (P₂) prior to the phenyl group of the central phosphine (P₁).

Iridium-chloride Bond Reactivity

The cis-dihydride complex, IrClH₂(Cytpp) is a non-electrolyte in CH₂Cl₂; metathesis of Ir-Cl bond by TlAsF₆ in THF or in EtOH does not work either. When the reaction mixture of [Ir(COD)(EtOH)₂]AsF₆/NaCl which was generated in situ by NaAsF₆, was treated with the ligand, the product isolated was IrClH₂(Cytpp), not the expected [IrH₂(Cytpp)]AsF₆. Cleavage of the Ir-Cl bond was also attempted, in order to generate [IrH₂(Cytpp)]⁺, by using a Ag⁺ salt. Silver salts are known to be reduced to Ag⁰ by tertiary triphosphine rhodium complexes; the complex IrClH₂(Cytpp) also reduced Ag⁺ so that Ag⁰ is precipitated from the reaction within a few minutes at room temperature. The reaction of AgPF₆ with IrClH₂(Cytpp) was monitored by a ³¹P-NMR spectrum at 200 K; the ³¹P{¹H}-NMR spectrum is consistent with the presence of IrCl(H)₂(Cytpp)(PF₆) which would result from cation-anion association after
Figure 20. Phosphorus-31 NMR spectrum of IrH$_2$(Cytpp)(PF$_6$) at 200 K:
(a) PF$_6$ region; (b) Cytpp region (36.43 MHz).
precipitation of AgCl: $\delta P_1 = -5.81$ ppm; $\delta P_2 = 3.01$ ppm;  
$\wp_{PF_6} = -144.7$ ppm; $J_{P_1-P_2} = 24.41$ Hz; $J_{P_1-P} = 86.7$ Hz;  
$J_{P_2-P} = 135.5$ Hz (Fig. 20). W. Beck et al. also reported that Vaska's compound IrCl(CO)(PPh$_3$)$_2$ reacts with HBF$_4$ and forms a 6-coordinate Ir(III) species, IrCl(H)(PPh$_3$)$_2$(CO)(F-BF$_3$) rather than Ir(III) 5-coordinate species (eq. 11).$^{45,92}$ These observations suggest that 5-coordinate Ir(III) complexes are not stable; thus, weak or non-coordinating anions (e.g., BF$_4^-$, PF$_6^-$, CF$_3$SO$_3^-$) apparently function as anionic ligands to satisfy a 6-coordinate Ir(III) structure. Therefore, a series of reactions which involve Ir-Cl cleavage were designed and achieved as shown in scheme I.

Iridium chloride complexes are known to form Ir-SnCl$_3$ groups on treatment with anhydrous SnCl$_2$. For example, SnCl$_2$ reacts with IrClH$_2$(PPh$_3$)$_3$ or with Na$_2$IrCl$_6$ and PPh$_3$ in alcohol to give IrH$_2$(SnCl$_3$)(PPh$_3$)$_3$ (A-4). The SnCl$_3^-$ anion is known to have a strong trans-influence;$^{94}$ the proton NMR resonance of the hydride trans to SnCl$_3$ shifts downfield from -20.2 to -14.7 ppm when the chloride is transformed to the SnCl$_3$ complex.$^{95}$

\[
\begin{align*}
\text{A-4} & \quad X = \text{Cl or SnCl}_3 \\
\text{H} & \\
\text{P} & \\
\text{Ir} & \\
\text{P} & \\
\text{H} & \\
\text{X} & 
\end{align*}
\]
The infrared stretching frequencies of the hydrides in IrH₂(SnCl₃)(PPh₃)₃, however, shifted to higher wave numbers, 2262 and 2205 cm⁻¹ from 2193 and 2105 cm⁻¹, respectively; the higher νIr-H value in the infrared spectrum is not consistent with the previously seen strong trans influence of SnCl₃⁻ ligand.

In the case of IrH₂(SnCl₃)(CO)(PPh₃)₂ (A-5), where the two hydrides are trans to SnCl₃ and CO, respectively, the νIr-H(trans SnCl₃) decreases to 2112 cm⁻¹ from the νIr-H(trans Cl) at 2222 cm⁻¹.95

\[
\begin{array}{c}
\text{P} \\
\text{Ir} \\
\text{P} \\
\text{H} \\
\text{X} \\
\text{CO}
\end{array}
\]

X = Cl or SnCl₃

The δIr-H(trans SnCl₃) also shifts downfield from -18.4 ppm of IrClH₂(CO)(PPh₃)₂ to -12.5 ppm of IrH₂(SnCl₃)(CO)(PPh₃)₂; this shift is consistent with the effect on the infrared spectrum, in terms of trans influence.

When the complex cis,syn-IrClH₂(CyttP) is treated with anhydrous SnCl₂ in CH₂Cl₂, two isomers were observed in the ¹H- and the ³¹P-NMR spectra (Table 9,10). This mixture was separated by recrystallization from acetone and dichloromethane.
Figure 21. Phosphorus-31 NMR spectrum of IrH₂(SnCl₃)(Cyttpp): (a) mixture; (b) acetone-soluble isomer; (c) acetone-insoluble isomer (36.43 MHz).
Figure 22  Proton-NMR spectrum of IrH₂(SnCl₃)(CyttP): (a) acetone insoluble isomer; (b) mixture (200 MHz).
Figure 23. Infrared spectrum of $\text{IrH}_2(\text{SnCl}_3)(\text{Cyttr})$ (Nujol mull).
acetone soluble: $\delta_{P_1} = -34.7$ ppm, $\delta_{P_2} = -8.40$ ppm.

isomer (60%) $\delta_{H_1} = -12.64$ ppm, $\delta_{H_2} = -17.53$ ppm.

acetone insoluble: $\delta_{P_1} = -33.5$ ppm, $\delta_{P_2} = 0.19$ ppm.

isomer (40%) $\delta_{H_1} = -11.31$ ppm, $\delta_{H_2} = -15.08$ ppm.

The infrared spectrum of the mixture of IrH$_2$(SnCl$_3$)(Cyttp) shows two strong bands at 2058, 2110 and a broad band at 2195 cm$^{-1}$. The 2058 cm$^{-1}$ absorption is assigned to the central phosphine ($P_1$), and the one at 2110 cm$^{-1}$ is attributed to the Ir-H trans to SnCl$_3$. The isomer that is not soluble in acetone may be of neutral molecular form and the spectroscopic data agrees with the configuration of IrH$_2$(SnCl$_3$)(Cyttp) (A-4). The $\nu_{Ir-H}$ at 2195 cm$^{-1}$ and $\delta_{Ir-H}$ at -17.53 ppm are not quite in the range for known iridium hydrides trans to SnCl$_3$. Since elemental analysis supports the composition of C$_{36}$H$_{63}$Cl$_3$IrP$_3$Sn (IrH$_2$(SnCl$_3$)(Cyttp)), the acetone soluble isomer may have SnCl$_3$ group in the molecule, but as in a different configuration. If the iridium to SnCl$_3$ bond is postulated as Ir-CI-SnCl$_2$, then the hydride trans to this bond may give higher $\nu_{Ir-H}$ and more upfield shift of $\delta_{Ir-H}$ than those of the hydride trans to Ir-SnCl$_3$. The Ir-CI bond reacts with SnCl$_2$; however, due to the bulkiness of the SnCl$_3^-$ ligand, as well as the Ir-CI bond character discussed before, formation of the IrH$_2$(Cl-SnCl$_2$)(Cyttp) (60%) may be
preferred to the complex $\text{IrH}_2(\text{SnCl}_3)(\text{Cytpp})$ (40%), which involves the breaking of the Ir-Cl bond.

Although the metathesis of Ir-Cl bond by $\text{Tl}^+$ salts alone is not successful, substitution of Ir-Cl by strong ligands is achieved in the presence of $\text{TlBF}_4$.

$$
\begin{align*}
\text{IrH}_2(\text{Cytpp}) + L + \text{Tl}^+ & \rightarrow \text{IrH}_2(L^+L^-) + \text{TICl} \\
L & = \text{CO, PMe}_2\text{Ph}
\end{align*}
$$  \hspace{1cm} (29)

The reaction represented by eq. (29) may involve either a $\text{S}_\text{N}1$ or $\text{S}_\text{N}2$ mechanism, with formation of $\text{IrH}_2(\text{Cytpp})^+$ (via dissociative mechanism) or $\text{IrClH}_2(\text{Cytpp})L$ (via associative mechanism), respectively. The $\text{S}_\text{N}1$-limit mechanism maintains the stereochemistry, whereas the $\text{S}_\text{N}2$ type reactions cause inversion as in Scheme II.

[Scheme II diagram]
The reaction of IrClH₂(Cyttp) with AgPF₆, which was discussed before, can be a good example of SN₁ mechanism; Ag⁺ is known to catalyze SN₁ mechanism in substitution of alkylhalides. When the IrClH₂(Cyttp) complex is treated with Tl⁺ salts, the reaction does not undergo by typical SN₁ anymore; because no bond breaking of the Ir-Cl was achieved when IrClH₂(Cyttp) complex is treated with Tl⁺. In order to have SN₂ reactions for the reaction in eq. (29), the entering ligand L in Scheme II should be sufficiently small so that the intermediate, IrClH₂(Cyttp)L, can be formed. The ligand L attacks from the opposite side of the Ir-Cl bond (trans attack), where Cl⁻ is a leaving group, in SN₂ reaction. The X-ray structure of IrClH₂(Cyttp) shows that the chloride is in the opposite side (anti) to phenyl ring and this side is very crowded due to the CH₂ chains of cyclohexyl rings (Fig. 7). Hence the ligand L attacks from the adjacent side (syn) to the phenyl ring.

The bulkiness of the entering ligand L in Scheme II decides the reactivity for SN₂ reactions. If the ligand is small, attack of L from the side syn to phenyl ring in spite of the phenyl ring orientation can occur readily; a complete inversion of stereochemistry is expected. If the ligand is bulky, attack of L from the side syn to phenyl ring is no longer easy; the reactivity of the bulky ligands for SN₂ reactions decreases. The substitution reaction undergoes
Figure 24. Phosphorus-31 NMR spectrum of [IrH₂(PMe₂Ph)(CyttP)]BF₄ (36.43 MHz).
Figure 25. Proton-NMR spectrum of $[\text{IrH}_2(\text{PMe}_2\text{Ph})(\text{Cytt})]\text{BF}_4$ (200 MHz).
Figure 26. Infrared spectrum of $[\text{IrH}_2(\text{PMe}_2\text{Ph})(\text{Cytpp})]\text{BF}_4$ (Nujol mull).
TABLE 9

Phosphorus-31 NMR Data Of $\text{IrH}_2X(\text{Cytpp})^{n+}$  

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<thead>
<tr>
<th>$\delta$</th>
<th>$\delta$</th>
<th>$\delta$</th>
<th>$J_{P_1P_2}$</th>
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<td>(-50%)</td>
<td>-55.2</td>
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<td>IrH$_2$(Cytpp)(PMe$_2$Ph)$^+$ (-50%)</td>
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<td>-1.67</td>
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<td></td>
<td></td>
<td></td>
<td>(-50%)</td>
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<td>IrH$_3$(Cytpp)</td>
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$^a$Above complexes have the same configuration shown below.

\[ \text{X=Cl,I,H, SnCl}_3 \ (n=0); \ CO, \ PMe}_2\text{Ph} \ (n=1) \]
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<th>Compound</th>
<th>$\delta H_1$</th>
<th>$\delta H_2$</th>
<th>$\delta H_3$</th>
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<th>$J_{P_2H_1}$</th>
<th>$J_{P_1H_2}$</th>
<th>$J_{P_2H_2}$</th>
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<td>-15.1</td>
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<td>1720</td>
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$^a$The numbering of atoms are consistent with the configuration below.

\[
\begin{array}{c}
\text{Ir} \\
\text{P}_1 \\
\text{P}_2 \\
\text{P}_2 \\
\text{H}_1 \\
\text{H}_2 \\
\end{array}
\]

$X=\text{Cl}, \text{I}, \text{H}, \text{SnCl}_3$ ($n=0$); $\text{CO}, \text{PMe}_2\text{Ph}$ ($n=1$)
with both $S_N1$ and $S_N2$ character, and the stereochemistry can be a mixture of inversion and retention.

The complex $[\text{IrH}_2(\text{Cyttpp})(\text{PMe}_2\text{Ph})]\text{BF}_4$ was isolated from the reaction mixture in eq. (29) in THF. Slight excess amount of PMe$_2$Ph was required to complete this reaction; when exactly one equivalent of PMe$_2$Ph was added, the parent compound, IrClH$_2$(Cyttpp), was still observed (in small quantity) in the $^{31}$P-$^1$H$-$ and $^1$H-NMR spectra. The infrared spectrum of $[\text{IrH}_2(\text{Cyttpp})(\text{PMe}_2\text{Ph})]\text{BF}_4$ shows two iridium-hydride stretching frequencies at 2031 and 2065 cm$^{-1}$. The $^1$H-NMR spectrum, however, shows that the two hydrides in IrH$_2$(Cyttpp)(PMe$_2$Ph) have approximately same chemical shifts, because the Me-$\text{P}$-Me and $\text{Ph}$-$\text{P}$-Ph (in Cyttpp) are very similar ligands.

The $^{31}$P-$^1$H$-$ and $^1$H-NMR spectra of IrH$_2$(Cyttpp)(PMe$_2$Ph) show two isomers, which may be mixtures of cis,syn- and cis,anti-IrH$_2$(Cyttpp)(PMe$_2$Ph) (Fig. 24, 25; Table 9, 10). No predominant species are observed, since PMe$_2$Ph is a bulky ligand; this implies that the reaction has both $S_N2$ and $S_N1$ character.

When the IrClH$_2$(Cytpp) complex is treated with CO(g) and TBF$_4$ in THF, the cationic complex $[\text{IrH}_2(\text{CO})(\text{Cyttpp})]\text{BF}_4$ is isolated. The $^{31}$P-$^1$H$-$NMR spectrum on the Bruker HX-90 spectrometer shows only one AB$_2$ pattern due to one diastereomer form of the complex ($\delta P_1 = -38.8$ ppm; $\delta P_2 = -1.67$ ppm; $J_{P_1P_2} = 22.3$ Hz). However, a spectrum taken on the Bruker
Figure 27. Phosphorus-31 NMR spectrum of $[\text{IrH}_2(\text{CO})(\text{Cyttp})]\text{BF}_4$ (121.470 MHz).
Figure 28. Proton-NMR spectrum of [IrH₂(CO)(Cytpp)]BF₄: selective decoupling of phosphorus for highfield hydride region (300 MHz).
Figure 29. Infrared spectrum of [IrH₂(CO)(Cytpp)]BF₄ (Nujol mull).
WM-300 spectrometer shows less than 5% of the other isomer ($\delta P_1 = -39.8$ ppm; $\delta P_2 = -7.70$ ppm; $J_{P_1P_2} = -2.4$ Hz). The major diastereomer (> 95%) can be the product of $S_N2$ reaction, since the CO ligand is small enough to have a great reactivity for $S_N2$ reactions. Thus, substitution of chloride by CO has more $S_N2$ character than $S_N1$.

The $^1H$-NMR spectrum of [IrH$_2$(CO)(Cytpp)]$BF_4$ obtained on the Bruker WM-300 spectrometer only gives Ir-hydride resonances due to one diastereomer. The hydride trans to CO appears at -11.8 ppm as a quartet and the hydride trans to the central phosphine ($P_1$) appears at -12.1 ppm as a doublet of triplets. Both PR$_3$ and CO ligands have comparable trans-influences on heavy metals (e.g., Pt(II)), the two hydrides occur in the same region. Selective decoupling of one phosphorus nucleus at a time proves that the $^1H$-NMR assignments are as shown in Table 10 (Fig. 27).

The infrared spectrum of [IrH$_2$(CO)(Cytpp)]$BF_4$ shows strong Ir-H bands at 2103 cm$^{-1}$ and ca 2000 cm$^{-1}$ which is screened by a very strong CO stretching frequency at 1980 cm$^{-1}$. Again, hydrides trans to phosphine or CO ligands give both $v_{Ir-H}$ absorptions at similar wave number region. Vibrational couplings between Ir-CO and Ir-H (trans to each other) can be separated by using deuterated analog, IrDH(CO)(Cytpp)$^+$ or IrD$_2$(CO)(Cytpp)$^+$. The analogous complex [IrH$_2$(CO)(PPh$_3$)$_3$]CIO$_4$ shows two $v_{Ir-H}$'s at 2155 and 2118 cm$^{-1}$, and the $v_{CO}$ at 2011 cm$^{-1}$.
A reaction as illustrated in eq. (29) was attempted for a mixture of IrClH₂(Cyttp), SO₂(g) and T&B₄ in THF. No replacement of Ir-Cl bond by SO₂ was observed; this reaction will be discussed in detail later in connection with hydride reactivity.

In conclusion, the Ir-Cl bond in IrClH₂(Cyttp) is not easily broken either in solution or in the gaseous state which can be observed from the FT-ICR mass spectra. Metathesis of Ir-Cl bond can only be achieved by Ag⁺ salt. The chemistry does not seem to agree with the long bond length obtained from the X-ray diffraction study which was discussed earlier; however, the bond length does not necessarily relate directly to the bond reactivity. The cis,syn-IrClH₂(Cyttp) complex undergoes substitution reactions in the presence of strong ligands and Ti⁺ salts. A mixture of two diastereomers (cis,syn and cis,anti) usually results. However, for small ligands, cis,anti-isomer should be predominant from mostly S₉² reaction; for bulky ligands, both cis,syn- and cis,anti-isomers are observed due to the less reactivity of bulky ligand toward S₉² reactions. Thus, the size of the entering ligand determines the stereochemistry.

The νIr-H and δIr-H values correlate with the trans-influence character of the ligands trans to the hydrides. However, it should be recalled here that the origin of chemical shifts of metal hydrides is complicated and
Figure 30. Linear correlation plot of $\nu_{\text{Ir-H}}$ vs $\delta_{\text{Ir-H}}$ in complexes $\text{IrH}_2X(\text{Cytpp})^{n+}$. 
involves more than the trans influence;\textsuperscript{46,47} whereas the $\nu_{\text{Ir-H}}$ is more directly related to the bond strengths, which can be another aspect of the trans influence.\textsuperscript{53} Figure 30 shows a rough linear correlation between $\nu_{\text{Ir-H}}$ and $\delta_{\text{Ir-H}}$ for complexes of the type IrH$_2$X(Cyttp)$^{n+}$ ($X = \text{Cl, I, SnCl}_3, \text{H}$ ($n=0$); $\text{PMe}_2\text{Ph}, \text{CO}$ ($n=1$)). Iridium hydrides, e.g., IrH$_3$(CO)(PPh$_3$)$_2$X are known to correlate $\nu_{\text{Ir-H}}$ and $\delta_{\text{Ir-H}}$ (Fig. 1), and the chemical shifts of iridium hydrides are reported to be independent of the charge of molecules.\textsuperscript{53} However, the hydride trans to hydride, in IrH$_3$(Cyttp) or in mer-IrH$_3$(PPh$_3$)$_3$ (Table 2, Fig. 30), seems to deviate markedly from the correlation plot; it may be due to the strong trans influence of mutually trans hydrides.

The $^{31}$P-NMR parameters of Ir(III) 6-coordinate complexes have been studied extensively; for example, model systems such as IrX$_3$(PR$_3$)$_3$ ($X = \text{Cl, Br, I}$),\textsuperscript{99} IrCl$_2$X(PR$_3$)$_3$,\textsuperscript{99} or IrCl$_2$X(diphos)(PMe$_2$Ph)$^{100}$ are compared in Table 11. Chemical shifts of coordinated monodentate ligands in these iridium(III) complexes are usually shielded more than those of free ligands, whereas the rhodium analogs are all deshielded.\textsuperscript{99} The chelate ring affects the $^{31}$P chemical shifts in such a manner that less shieldings are observed than the analogous Ir(III) complexes with monodentate ligands.

The complexes of the type IrH$_2$X(Cyttp)$^{n+}$ ($X = \text{Cl, I, H, SnCl}_3, n=0$; $\text{CO, PMe}_2\text{Ph}$, $n=1$) and IrClHX(Cyttp)$^{n+}$ ($X = \text{I,}$
### TABLE 11

Phosphorus-31 NMR Data Of IrX₃(PR₃)₃, IrCl₂X(PR₃)₃, And IrCl₂X(PMe₂Ph) (diphos)

| compound type (Ref) | L | X   | 6P₁ | 6P₂ | 6P₃ | 6free | δ₁ | δ₂ | δ₃
|---------------------|---|-----|-----|-----|-----|-------|----|----|----
| Pη₃                 | Cl| 19.5| -47.0| -42.4| -62.0| -15.0| -19.6|
| Pη₃Ph               | Cl| 17.1| -50.1| -40.1| -48.5| 1.5  | -0.4 |
| Pη₃Ph               | br| 16.5| -54.6| -52.3| *    | 6.1  | 4.0 |
| Pη₃Ph               | I | 16.3| -64.7| -72.4| *    | 16.2 | 23.9|
| Pη₃Br               | Cl| 15.7| -60.3| -37.7| -33.7| 7.6  | 5.0 |
| Pη₃Br               | br| 15.0| -42.6| -47.8| *    | 9.9  | 15.1|
| Pη₃I                | I | 15.5| -69.1| -63.3| *    | 16.4 | 30.6|
| Pη₃Me               | Cl| 17.7| -40.3| -37.7| -33.7| 7.6  | 5.0 |
| Pη₃Me               | I | 17.1| -43.0| -54.2| *    | 6.1  | 3.2 |
| Pη₃Ph₂              | Cl| 18.7| -63.6| -56.1| *    | 35.9 | 26.4|
| Pη₃Ph₂              | br| 15.4| -56.1| -47.3| -27.7| 29.2 | 19.7|
| Pη₃Cl               | Cl| 15.7| -38.9| -23.4| *    | 21.3 | 5.0 |
| Pη₃NO₂              | Cl| 432 | 17.3| -29.9| -18.6|       |
| Pη₃NO₂              | I | 445 | 8.3 | -34.5| -14.0|       |
| Pη₃NO₂              | NCS| 441 | 10.9| -36.5| -12.0|       |
| Pη₃NO₂              | Cl| 450 | 5.2 | -39.6| -8.9 |
| Pη₃NO₂              | br| 447 | 4.4 | -43.3| -5.2 |
| Pη₃NO₂              | I | 438 | 1.3 | -50.0| 1.5  |
| Pη₃NO₂              | Py| 398 | 10.7| -34.6| -13.9|
| Pη₃NO₂              | Cu| 320 | 19.2| -41.0| -7.5 |

* δ₁ = δfree - δP₁
SO₂H, n=0; CH₃CN, n=1) show upfield ³¹P chemical shifts compared to Rh-analogs, e.g., RhCl₂H(Cyttp)¹³⁵ or RhHX(ttp)⁺¹⁰¹ (Table 12).

The cis-²J₁P₂ values for Ir(III) complexes with monodentate ligands range from 14.7 to 19.5 ppm in Table 11. The two bond cis-J₁P₂ values for complexes of the types IrH₂X(Cyttp)n⁺ and IrClHX(Cyttp)n⁺ are approximately 20-27 Hz, except for the [IrH₂(Cyttp)(PMe₂Ph)]BF₄ case.

When the infrared spectra of IrH₂X(Cyttp) (X = Cl, I) are compared to those of IrH₂X(Cyttp)n⁺ (X = SnCl₃, H, n=0; PMe₂Ph, CO, n=1), the intensity ratio of the two hydride absorptions, H₁ (trans to central phosphine P₁) and H₂ (trans to ligand X), vary noticeably (Fig. 3, 10, 14, 23, 26, 29). When the ligands X (trans to hydride H₂) are halides, which have weak trans-influences, intensities of the Ir-H₂ bands are smaller than Ir-H₁ bands (Iᵣᵣ-H₁/Iᵣᵣ-H₂ = 1). The band intensities in the infrared spectrum are proportional to the squares of the dipole vectors,¹⁰² which in turn reflect the bond distance and polarization. The differences in band intensities of Ir-H₂ in the above series of complexes, IrH₂X(Cyttp)n⁺, may imply that the dipole vectors of Ir-H₂ may be affected by the nature of ligand X trans to H₂. Thus, by varying the ligand trans to hydride, one may be able to change the bond length and charge separation of Ir-H bonds.
TABLE 12

Phosphorus-31 NMR Data Of IrH₂X(Cyttpp)ⁿ⁺,
IrClHX(Cyttpp)ⁿ⁺, And RhClHX(ttp)⁺ a

<table>
<thead>
<tr>
<th>Compound</th>
<th>¹P₁ (Δ₁)b</th>
<th>¹P₂ (Δ₂)b</th>
<th>¹P₃ (Δ₃)b</th>
<th>Jᵖ₁p₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrH₂Cl(Cyttpp)</td>
<td>-25.6(- 2.5)</td>
<td>-0.68(- 7.3)</td>
<td>26.9</td>
<td></td>
</tr>
<tr>
<td>IrH₂I(Cyttpp)</td>
<td>-34.8( 6.7)</td>
<td>8.48( 0.5)</td>
<td>25.6</td>
<td></td>
</tr>
<tr>
<td>IrH₂(SnCl₃) (Cyttpp)</td>
<td>-33.5( 5.4)</td>
<td>-0.19(- 8.2)</td>
<td>26.8</td>
<td></td>
</tr>
<tr>
<td>IrH₂(OC) (Cyttpp)⁺</td>
<td>-38.8(10.7)</td>
<td>-1.67(- 6.3)</td>
<td>22.3</td>
<td></td>
</tr>
<tr>
<td>IrH₂(Cyttpp) (PMe₂Ph)⁺</td>
<td>-48.8(20.7)</td>
<td>-21.6(13.6)</td>
<td>-66.7(18.2)</td>
<td>32.9</td>
</tr>
<tr>
<td>IrH₃(Cyttpp)</td>
<td>-23.0(- 5.1)</td>
<td>-8.57(-16.6)</td>
<td>26.4</td>
<td></td>
</tr>
<tr>
<td>IrClH(CH₃CN) (Cyttpp)⁺</td>
<td>-21.3(- 6.8)</td>
<td>-19.5(11.5)</td>
<td>26.3</td>
<td></td>
</tr>
<tr>
<td>IrClH(O) (Cyttpp)</td>
<td>-19.1(- 9.0)</td>
<td>-21.5(13.5)</td>
<td>22.8</td>
<td></td>
</tr>
<tr>
<td>IrClHI(Cyttpp)</td>
<td>-25.0(- 3.1)</td>
<td>-37.5(29.5)</td>
<td>24.0</td>
<td></td>
</tr>
<tr>
<td>IrCl₂H₂(Cyttpp)</td>
<td>-32.4(-60.5)</td>
<td>8.3(-16.1)</td>
<td>34.2</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>¹P₁ (Δ₁)c</th>
<th>¹P₂ (Δ₂)</th>
<th>¹P₃ (Δ₃)</th>
<th>Jᵖ₁p₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>RhClH(CH₃CN)(tpp)⁺</td>
<td>24.1(-52.3)</td>
<td>10.0(-17.8)</td>
<td>36.8</td>
<td></td>
</tr>
<tr>
<td>RhClH(O)(tpp)⁺</td>
<td>1.1(-29.3)</td>
<td>4.9(-12.7)</td>
<td>37.8</td>
<td></td>
</tr>
<tr>
<td>RhCl₂H(tpp)-indent</td>
<td>32.4(-60.5)</td>
<td>8.3(-16.1)</td>
<td>34.2</td>
<td></td>
</tr>
</tbody>
</table>

a P₁ = central phosphorus; P₂ = terminal phosphorus; P₃ = phosphorus trans to H₂.

b Δ_i = Δ_free - Δ_coordinated i

Iridium-hydride Reactivity Difference

Distinct spectroscopic properties of the two hydride ligands in IrH$_2$X(CyttP)$^{n+}$ complexes have been discussed so far; these observations lead us to examine the chemical reactivity differences in two hydrogens of IrH$_2$Cl(CyttP). As pointed out before, significant variation in band intensities between the two Ir-H vibrational bands in the infrared spectrum implies that these two Ir-hydride bonds may have different bond distances and/or charge polarizations. Therefore, two major factors for different chemical reactivity of hydrides can be bond-lengthening by the trans-influence, and charge polarization of the Ir-H bonds, which affects the basicity of a metal-hydride. The trans influence exerts in such a way that the hydride trans to the central phosphine (P$_1$) group is labilized while the hydride trans to Cl is still intact. However, it is difficult to believe that there is any sufficient difference in polarization of Ir-H$_1$ (trans to P$_1$) and Ir-H$_2$ (trans to Cl) so that their different hydridic characters of two hydride ligands determine the reactivity.

Shaw and his coworkers found that for complexes of the type IrHX$_2$L$_3$ (L = AsR$_3$ or PR$_3$ trans to hydride) or RuClH(CO)L$_3$, the ligand L trans to hydride exchanges rapidly with other ligands present in solution, whereas exchange of the other ligands occur slowly or not at all (eq. 30).
The reactions illustrated by Eq. (31) involve reactions of hydrides with electrophiles; the surprising feature is that reaction of only one hydride, i.e., the one trans to the central phosphine (P₁), occurs.

\[
\begin{align*}
\text{H} & \quad \text{P} \quad \text{Ir} \quad \text{P} \\
\text{Cl} & \quad \text{Cl} \quad \text{AsR₃} + L \rightarrow \text{H} \quad \text{P} \quad \text{Ir} \quad \text{P} \\
& \quad \text{Cl} \quad \text{Cl} \quad L \\
\end{align*}
\]

\[\text{L} = \text{AsEt₂Ph} < \text{PBu²NPh} \approx \text{PET₂Ph} < \text{PET₃} < \text{P(OEt)₃} \approx \text{PMe₂Ph} < \text{P(OMe)₂Ph}\]

The reaction between IrClH₂(Cyttp) and I₂ produces a compound that gives one ν_{Ir-H} at 2258 cm⁻¹ with a small shoulder at 2240 cm⁻¹ in the infrared spectrum. The spectrum is consistent with a hydride trans to a chloride. The \(^1\text{H}-\text{NMR}\) spectrum of IrClHI(Cyttp) shows hydride resonances only at 20.8 ppm (~80%) and 20.1 ppm (~20%), which occur...
in the chemical shift region appropriate for an Ir(III)-hydride trans to a halide. The $^{31}$P($^1$H)-NMR spectrum shows two sets of AB$_2$ patterns (74%:21%) with $J_{P_1P_2} = 24.0$ Hz; the pattern has the A portion (triplet) downfield from the B portion (doublet) of the spectrum. Since the elemental analysis agrees with the composition IrClHI(Cyttp) and $^1$H-NMR spectrum shows one kind of hydride resonances (trans to Cl), two diastereomers can be considered from reaction Scheme III.

![Scheme III](image)
Figure 31. Infrared spectrum of IrClHI(Cyttp) (Nujol mull).
Figure 32. Proton-NMR spectrum of IrClHI(Cyttp) (200 MHz).
Figure 33. Phosphorus-31 NMR spectrum of IrClHI(Cyttpp) (36.43 MHz).
Thus, the reaction of I₂ with IrClH₂(Cyttp) involves only the hydride trans to the central phosphine (P₁); the product is a mixture of diastereomers of IrClHI(Cyttp) with the proposed structure A-6 and A-7 (Scheme III).

Abstraction of hydride from a transition metal hydride complex by the electrophilic reagents, such as C₇H₇⁺BF₄⁻ or CPh₃⁺BF₄⁻ is synthetically important, which was discovered by Beck and Scholter,¹⁰⁴ utilized by Graham et al.,¹⁰⁵ and also by Legzdins and coworkers.¹⁰⁶

The IrClH₂(Cyttp) complex has bulky substituents on the phosphorus atoms; thus, C₇H₇⁺ does not coordinate but abstracts H⁻ to form C₇H₈, and the solvent molecule fills the vacant site. The infrared spectrum of [IrClH(CH₃CN)(Cyttp)]BF₄ gives only one Ir-H band at 2250 cm⁻¹, which is indicative of hydride trans to Cl. The ¹H-NMR spectrum shows a quartet at -20.3 ppm (~ 75%) and another quartet at -20.35 ppm (~ 25%); this region is diagnostic of a hydride trans to Cl. The ³¹P{¹H}-NMR spectrum collected on the Bruker WM-300 spectrometer shows two AB₂ patterns in ~ 75:25 ratio with similar J₃P₁P₂ values (Fig. 36, Table 13).

Elemental analysis supports the composition [IrClH(CH₃CN)(Cyttp)]BF₄; the compound is a 1:1 electrolyte (118 ohm⁻¹ mol⁻¹ cm⁻²) in acetone, which also indicates only one molecule of CH₃CN is involved in formula. The presence of CH₃CN in [IrClH(CH₃CN)(Cyttp)]⁺ is also confirmed by the
Figure 34. Infrared spectrum of [IrClH(CH$_3$CN)(Cyttpp)]BF$_4$ (Nujol mull).
Figure 35. Proton-NMR spectrum of [IrCl(HCH-CN)(Cytpp)]BF₄ (200 MHz).
Figure 36. Phosphorus-31 NMR spectrum of [IrCl(\text{CH}_3\text{CN})(\text{Cytpp})]BF_4 (121.470 MHz).
TABLE 13
Phosphorus-31 And $^1$H-NMR, And Infrared Data Of IrClH$_X$(Cytttp)$^{n+}$ $^a$

<table>
<thead>
<tr>
<th></th>
<th>$\delta P_1$</th>
<th>$\delta P_2$</th>
<th>$J_{P_1P_2}$</th>
<th>$\delta H_1$</th>
<th>$\delta H_2$</th>
<th>$J_{P_1H_1}$</th>
<th>$J_{P_2H_1}$</th>
<th>$J_{P_1H_2}$</th>
<th>$J_{P_2H_2}$</th>
<th>$\nu_{Ir-H_1}$</th>
<th>$\nu_{Ir-H_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrClHI(Cytttp)</td>
<td>(-80%) -25.0</td>
<td>-37.5 -24.0</td>
<td>NO</td>
<td>-28.8</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>11.9</td>
<td>NO</td>
<td>2250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-20%) -19.5</td>
<td>-26.9 -24.0</td>
<td>NO</td>
<td>-28.1</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>11.9</td>
<td>NO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IrClH(CH$_3$CN)(Cytttp)$^b$</td>
<td>(-75%) -21.34</td>
<td>-19.53 -26.30</td>
<td>NO</td>
<td>-20.3</td>
<td>NO</td>
<td>NO</td>
<td>12.0</td>
<td>NO</td>
<td>2258</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-25%) -19.07</td>
<td>-27.51 -22.80</td>
<td>NO</td>
<td>-20.4</td>
<td>NO</td>
<td>NO</td>
<td>12.0</td>
<td>NO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir(Cl$\cdot$SO$_2$)H(SO$_2$H)(Cytttp)</td>
<td>-44.2</td>
<td>-32.3 -27.5</td>
<td>NO</td>
<td>-21.2</td>
<td>NO</td>
<td>NO</td>
<td>11.9</td>
<td>NO</td>
<td>2260</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$The numbering of atoms are consistent with the configuration below.

\[
\begin{array}{c}
\text{H}_2 \\
\text{P}_1 \\
\text{P}_2 \\
\text{Ir} \\
\text{X} \\
\text{Cl}
\end{array}
\]

X=I,SO$_2$H (n=0); CH$_3$CN (n=1)

$^b$The $^{31}$P-NMR was obtained on WM-300 due to the second order effect on HX-90.
The band at 2290 cm$^{-1}$ with a shoulder at 2305 cm$^{-1}$ is appropriate for the C\=N stretch of coordinated CH$_3$CN. Storhoff and Lewis discussed the reasons for two bands being seen frequently in the $v_{\text{C=\!N}}$ region of acetonitrile complexes.\textsuperscript{107} One is the $v_{\text{C=\!N}}$ band and the other is a combination band resulting from the symmetrical $-\text{CH}_3$ deformation and the C-C stretching vibration which borrows the intensity from the $v_{\text{C=\!N}}$ band. Thus, the product of the hydride abstraction from IrClH$_2$(Cytt) by C$_7$H$_7$BF$_4$ in CH$_3$CN is [IrClH(CH$_3$CN)(Cytt)]BF$_4$; and the structures may also be assigned as A-6 (phenyl ring syn to hydride) and A-7 (phenyl ring anti to hydride) in Scheme III.

The reaction of transition metal hydrides with SO$_2$ under ambient conditions is reported in a few cases, e.g., Ru(PPh$_3$)$_4$(SO$_2$H)$_2$\textsuperscript{108} or IrH(CO)(SO$_2$)(PPh$_3$)$_2$.\textsuperscript{109} In the case of IrH(CO)(SO$_2$)(PPh$_3$)$_2$, which was prepared from the reaction of IrH(CO)(PPh$_3$)$_3$ with SO$_2$, the tautomeric process, $\text{H}-\text{IrSO}_2H \leftrightarrow \text{Ir}-\text{SO}_2$ is still being debated and yet unresolved. Bell and Mingos reported $^1$H-NMR data on IrH(CO)(SO$_2$)(PPh$_3$)$_2$:\textsuperscript{110} $\delta_{\text{Ir-H}} = -2.8$ ppm. The chemical shift of an Ir-H trans to CO in a similar 5-coordinate geometry, IrH(CO)(PPh$_3$)$_3$, appears at -10.9 ppm;\textsuperscript{111} hence, the resonance at -2.8 ppm reported by Bell and Mingos may not be due to the hydride trans to CO. In addition, the $^{31}$P-NMR spectrum at -50$^\circ$ shows an $A_2M$ spin pattern ($\delta_A = 4.0$ ppm; $\delta_M = -2.0$ ppm; $^2J_{\text{AM}} = 13.2$ Hz); this spectrum was
attributed to IrH(CO)(SO$_2$)(PPh$_3$)$_3$ with an Ir-H dative bond. However, no $^1$H-NMR data at -50°C was provided to prove that the species had an Ir-H bond at that temperature.

The reaction of IrClH$_2$(Ctttp) with excess SO$_2$ resulted in the losses of $\nu_{\text{Ir-H}}$ at 1995 cm$^{-1}$ and $\delta_{\text{Ir-H}}$ at -9.13 ppm, which are due to a hydride trans to the central phosphine, P$_1$. The remaining hydride, which is trans to Cl, shows $\nu_{\text{Ir-H}}$ at 2260 cm$^{-1}$ and $\delta_{\text{Ir-H}}$ at -21.2 ppm; thus, it is concluded that only one hydride, i.e., the one trans to P$_1$, reacts with excess SO$_2$ at ambient conditions. An interesting question is what happens to the reacted hydride and SO$_2$. The chelating triphosphine ligand does not usually dissociate from the coordination sphere; hence, a tautomerization of the type Ir-SO$_2$H$\rightleftharpoons$Ir-SO$_2$ probably does not occur in this case.

Jacobson and Wojcicki$^{112,113}$ proposed a bimolecular electrophilic process for the SO$_2$ insertion into M-CR$_3$ bond; the mechanism involves electrophilic attack on carbon, formation of a tight ion-pair, and conversion to S-sulfinate, which in some cases occurred via the O-sulfinate isomer (Scheme IV)

\[
\text{M-CR}_3 + \text{SO}_2 \rightarrow \left[ \begin{array}{c} \text{R} \\
\text{R} \\
\text{S} \\
\text{O} \\
\end{array} \right] \xrightarrow{\Delta} \text{MO}_2\text{SCR}_3 \rightarrow \text{M-S-CR}_3 \\
\text{M-O-S-CR}_3 \\
\]

\text{SCHEME IV}
If the M-H bond is treated with SO$_2$ in a similar manner as M-CR$_3$, insertion of SO$_2$ into the M-H bond is expected. Four possible bonding modes of M-SO$_2$H can be postulated as follows:

Dr. G. Kubas (at the Los Alamos Scientific Lab) provided us unpublished X-ray structure data and the infrared spectrum of ($\eta^5$-Me$_5$C$_5$)Mo(CO)$_3$(SO$_2$H)$_3$. The two S-O bonds in Mo-S inequivalent at 1.52 and 1.64Å, and the $\nu_{S-O}$ vibrations appear at 1003 cm$^{-1}$ and 753 cm$^{-1}$, which are assumed to be as A-11 bonding mode. However, a weak absorption at 2540 cm$^{-1}$ was also observed for ($\eta^5$-Me$_5$C$_5$)Mo(CO)$_3$(SO$_2$H)$_3$; it may be assigned to the $\nu_{S-H}$ as in A-8 or A-9, since the band does not shift with S$^{18}$O$\_2$ labeling.

In the infrared spectrum of IrClH(SO$_2$H)(Cyttp), an S-H stretching frequency is assigned to the weak, broad band at 2500 cm$^{-1}$. The asymmetrical and symmetrical stretching frequencies of the Ir-S$\_8$ group appear at 1141 and 1070 cm$^{-1}$, respectively. Thus, the bonding mode of Ir-SO$_2$H may be proposed as S-sulfinato, Ir-S-H. However, additional bands at 1269 and 1143 cm$^{-1}$ exist; they are another set of asym-
metric and symmetric $v_{SO}$ stretching vibrations. Elemental analysis also suggests two molecules of SO$_2$ per formula; either IrCl(SO$_2$H)$_2$(Cyttp) or IrH(SO$_2$H)(Cl•SO$_2$)(Cyttp) may be considered. The $^{31}P(^1H)$-NMR spectrum shows that most of the sample (over 95%) gives one AB$_2$ pattern ($\delta_{p_1} = -43.70$ and $\delta_{p_2} = -32.06$ ppm). Also, small peaks occur at -16.7 ppm and -21.2 ppm; these resonances grow larger if the sample remains in solution overnight (Fig. 39). The compound is extremely air and moisture sensitive; in fact, it shows a H$_2$O molecule (878 + H$_2$O) in the mass spectrum (FAB). The mass spectrum shows the most intense peak at 878 due to IrCl(SO$_2$)(Cyttp); then it loses SO$_2$ to give 814 (IrCl(Cyttp)). The labile SO$_2$ molecule was already lost under the low operating pressure of the mass spectrometer. If the product was IrCl(SO$_2$H)$_2$(Cyttp), then only one set of $v_{SO}$ bands (or, at least in the same range) are expected in the infrared spectrum. In addition, proton resonances due to $\delta_{Ir-H}$ or vibrational band due to $v_{Ir-H}$ should not have appeared. Thus, the possibility of IrCl(SO$_2$H)$_2$(Cyttp) is unlikely; SO$_2$ only reacts with one of the hydride ligands which is trans to central phosphine and the one trans to Cl is still intact.

When IrClH$_2$(Cyttp) was treated with SO$_2$ in the presence of TlAsF$_6$, the desired product was IrH$_2$(SO$_2$)(Cyttp)$^+$. However, the infrared, $^{31}P(^1H)$- and $^1H$-NMR spectra are identical to the product obtained form the reaction of
Figure 37. Infrared spectrum of $\text{IrH} (\text{SO}_2 \text{H}) (\text{Cl} \cdot \text{SO}_2) (\text{Cytpp})$ (Nujol mull).
Figure 38. Proton-NMR spectrum of $\text{IrH(SO}_2\text{H)}(\text{Cl-SO}_2\text{})(\text{Cytpp})$ (200 MHz).
Figure 39. (a) Phosphorus-31 NMR spectrum of IrH(SO₂H)(Cl·SO₂)(Cytpp); (b) overnight sample (36.43 MHz).
IrClH₂(Cytttp) with SO₂ without the Tl⁺ salt. Again, SO₂ is not a strong enough ligand to undergo a substitution reaction in eq. (29); instead it might have formed a weak bond with chloride which is at an extremely long distance from iridium (d_{Ir-Cl} = 2.528Å).

The complex [PtCl(ttp)]Cl·SO₂ was shown by X-ray study to have a weakly bonded SO₂ to the ionic Cl⁻. In this case, the νSO absorptions appear at 1269 and 1120 cm⁻¹, which are very similar to one set of νSO values (1269 and 1143 cm⁻¹) observed in the infrared spectrum of the product obtained from the reaction of IrClH₂(Cytttp) and SO₂.

Similar association of SO₂ with Ir-halide bond was also observed in the case of Ir(I·SO₂)(CO)(PPh₃)₂(SO₂) (ν₁·SO₂ = 1323, 1140 cm⁻¹). Although, an X-ray crystal structure analysis is advised to elucidate the SO₂ bonding modes, the product can be tentatively assigned as IrH(SO₂H)(Cl·SO₂)⁻(Cytttp) on the basis of spectroscopic and analysis data.

In conclusion, electrophilic attack of I₂ and C₇H₇BF₄ at the hydride trans to central phosphine, P₁, produced two diastereomers as predicted in Scheme III. In both cases, apparently only one hydride (i.e. trans to P₁) reacts with electrophiles, whereas hydride trans to chloride stays intact during the reactions with electrophilic reagents. The hydride trans to hydride in IrH₃(Cytttp) is most reactive; it reacts with CHCl₃ to give IrClH₂(Cytttp) and CH₂Cl₂. The product resulting from the reaction of
IrClH₂(Cyttp) and SO₂ needs further characterization; for example, IrD(SO₂D)(Cl·SO₂)(Cyttp) can be prepared and δ₈-S-D may be obtained from the ²H-NMR spectrum. Nevertheless, even in the presence of excess SO₂, only the hydride trans to the central phosphine (P₁) reacts with SO₂ to give the unusual Ir-SO₂H group. Therefore, the hydride trans to the phosphine group is more reactive toward electrophiles than the hydride trans to Cl; the chemical reactivity appears to be remarkably different.

Photolysis of Iridium-hydride Complexes

G. Geoffroy et al.⁶⁸ reported the photolysis experiments on IrClH₂(PPh₃)₃ and IrH₃(PPh₃)₃. Irradiation of IrClH₂(PPh₃)₃ eliminates reductively the hydrogen molecule in concerted manner and results in the formation of IrCl(PPh₃)₃ within 30 min. The primary photoproduction IrCl(PPh₃)₃ forms a orthometallated IrClH(PhPPh₂) complex on prolonged irradiation; it was formulated on the basis of a νIr-H peak at 2050 cm⁻¹. The Ir(I)-triphenylphosphine complexes, e.g., IrCl(PPh₃)₃, are also known to undergo thermal intramolecular C-H bond activation.³³

The IrH₃(PPh₃)₃ complex also loses H₂ upon irradiation; however, it generates a very reactive species, IrH(PPh₃)₃, which undergoes cyclometallation after losing another molecule of H₂. M.F. Lappert and coworkers claimed that they prepared IrH(PPh₃)₃ by treating IrClH₂(PPh₃)₃ with dimethylaminotrimethylstannane (Me₃Sn-Me₂); however, they
did not provide detailed data of isolated species. Thus, photolysis is a convenient way to produce a reactive Ir(I)-intermediate from Ir-polyhydrides or carbonyl complexes.

The complex IrClH₂(Cyttp) was thought at first to be an analog of IrClH₂(PPh₃)₃; thus, a reductive elimination of H₂ on irradiation was expected. The photolysis of IrClH₂(Cyttp) was carried out under an inert atmosphere (Ar or N₂) irradiating with λ = 350 nm in Rayonet photochemical reactor; the reaction was monitored by infrared (vide supra) and ³¹P-NMR spectra (Fig. 40, 41).

The infrared spectra were obtained for the solution of IrClH₂(Cyttp) and subsequently for the sample during irradiation in benzene or THF (Fig. 40). The IrClH₂(Cyttp) complex shows νIr-H bands at 2200 cm⁻¹ and 1990 cm⁻¹ in THF (2205 cm⁻¹ and 2008 cm⁻¹ in benzene). After 150 min. of irradiation in THF, the νIr-H peak at 2200 cm⁻¹ disappeared but the νIr-H peak at 1990 cm⁻¹ shifted to 1960 cm⁻¹; also a new band at 1720 cm⁻¹ was observed. The iridium hydride stretching frequency at ~1720 cm⁻¹ is appropriate for a hydride trans to a hydride ligand; bridging iridium hydrides appear at 1000-1200 cm⁻¹. Similar infrared spectra were obtained also from benzene solutions of IrClH₂(Cyttp) during irradiation. These infrared spectra suggest that a possible hydride rearrangement from cis to trans occurs; a cis = trans interconversion may occur during the photolysis via reversible H₂ addition.
The photoproduction was obtained after about 4 hours of irradiation; the clear colorless sample of \text{IrClH}_2(Cyttp) turned yellow during the photolysis. The infrared spectrum of the photoproduction shows the \( \nu_{\text{Ir-H}} \) bands at 2200 cm\(^{-1}\), 1960 cm\(^{-1}\) and 1720 cm\(^{-1}\); also a weak band at 2305 cm\(^{-1}\) is observed, whose origin is not clear at this point. The \( ^{31}\text{P-} \)NMR spectrum indicates a mixture of \text{IrCl(Cyttp)} (~ 50%) and \text{IrClH}_2(Cyttp) (~ 50%).

Irradiation of \text{IrClH}_2(Cyttp) in benzene for 2 hrs did not produce an appreciable amount of \text{IrCl(Cyttp)}. A trace of a possible orthometallated complex was observed at -24.98 ppm (doublet), which is a B portion of an AB\(_2\) pattern; this species can be compared with Geoffroy's orthometallated complex after prolonged photolysis of \text{IrClH}_2(\text{PPh}_3)_3. Thus, the \text{IrClH}_2(Cyttp) complex behaves differently from \text{IrClH}_2(\text{PPh}_3)_3 on photolysis. The \text{IrClH}_2(Cyttp) complex yields only ~ 50% of \text{IrCl(Cyttp)} in THF, and does not reductively eliminate much \text{H}_2\) in benzene.

The cyclic voltammogram of \text{IrClH}_2(Cyttp) in \text{CH}_2\text{Cl}_2 does not show any peaks in negative potential range; however, two oxidation (anodic) peaks are observed with \( E_p \) at +0.69V and +1.33V in \text{CH}_2\text{Cl}_2 against Ag/AgCl (Fig. 42). Adding electrons to \text{d}^6-Ir(III) octahedral complexes is not easy because extra electrons have to fill the antibonding \text{e}_g\) orbitals. Hence, an electrochemical process is not a facile route to reduce Ir(III) to Ir(I). The reductive elimination
Figure 40. Infrared spectra of IrClH$_2$(Cyttp) in THF solution during photolysis: (a) starting compound; (b) 150 min; (c) 4 hrs (vide supra).
Figure 41. Phosphorus-31 NMR spectra of the photoproducts from (a) benzene (b) THF (36.43 MHz).
Figure 42. Cyclic voltammogram of $\text{IrCl}_2(\text{Cyttp})$. 
of octahedral complexes to Ir(I) square planar complexes involves a change in spin state, from triplet to singlet; this type of slow process can occur in photolytic conditions. Therefore, the IrClH₂(Cyttp) complex does not seem to have a net reductive elimination even under irradiation condition; a nonproductive photolytic process, which does not involve net loss of H₂ molecule, is suggested.

The deuterium analogs of cis-dihydrides (i.e., IrClDH(Cyttp) or IrClD₂(Cyttp)) were prepared to investigate details of the photolysis process. Deuterium-NMR spectra were used to understand the system; for example, ²H-NMR spectra give resonances only due to deuterium incorporation so that ²H-NMR spectra provide evidence about the fate of the Ir-deuterides.

A sample of IrClDH(Cyttp) in proton solvents such as C₆H₆, CH₂Cl₂ or THF gives δIr-D signals at -8.9 ppm (Jp-D = 18.9 Hz) and -22.04 ppm in ²H-NMR at room temperature. However, predominant resonances appear at 7.5 ppm in the case of benzene, at 5.7 ppm in the case of dichloromethane, and at 4.07 and 1.64 ppm in the case of tetrahydrofuran. These deuterated solvent resonances appear after only one scan is taken (Fig. 43, 44); however, no external deuterated solvents were added to these samples. Thus, the deuterium in the IrClDH(Cyttp) complex is being incorporated to the CR₃-H bonds of the solvents. No significant incorporation
of deuterium into the ortho protons of the phenyl ring or into the cyclohexyl ring protons are observed when a pure IrClH(D(Cyttp)) is used. The same sample in C₆H₆ sat for several days and a ²H-NMR spectrum was obtained again. The figure (45) shows more deuterium incorporation into benzene; indeed, the deuterium content in the sample appeared to be distributed approximately 50:25:25 (d-benzene; Ir-D₁; Ir-D₂), implying that incorporation of deuterium reached equilibrium.

The above ²H-NMR sample in C₆H₆ was recovered after the second ²H-NMR spectrum was taken, and an infrared spectrum of this solid was obtained. An increase in the intensity and broadening of the νIr-H (trans Cl) at 2246 cm⁻¹ was observed, implying that more protons are incorporated in the Ir-D bonds in IrClDH(Cyttp) (Fig. 46) by contacting with protonated solvent. The ¹H-NMR spectrum of IrClDH(Cyttp) in C₆D₆ shows the hydride trans to Cl (H₂) is less abundant than the hydride trans to the phosphine group (H₁) (Fig. 47). The integration ratio of the two hydrides was approximately 2.000:1.672 (Ir-H₁:Ir-H₂); Ir-H₂ should have been significantly smaller than Ir-H₁ according to the mass spectrum and infrared spectrum discussed earlier. The hydrogen on Ir-H₁ may have been deuterated in C₆D₆ solution to some extent, which is a reverse process of deuterium incorporation into the C₆H₆.
Figure 43. Deuterium-NMR spectrum of IrC1DH(Cytp) in CH$_2$Cl$_2$ (46.07 MHz).

Figure 44. Deuterium-NMR spectrum of the filtrate sample from the reaction mixture of [IrC1(COD)]$_2$, Cytp and d$_6$-EtOD (in THF) (76.76 MHz).
Figure 45. (a) Deuterium-NMR spectrum of IrClD(Cyttp) in benzene; (b) spectrum after treatment with C₆H₆ (46.07 MHz).
Figure 46. Infrared spectrum of (a) IrClDH(Cyttp) and (b) spectrum of the sample treated with C₆H₆ for 3 weeks (Nujol mull).
Figure 47. Proton-NMR spectrum of IrClDH(Cytpp) after treatment with C₆H₆(500 MHz).
Figure 48. Deuterium-NMR spectrum of IrClD₂(Cyttp) in THF (76.76 MHz).
Figure 49. Infrared spectrum of yellow solid from the reaction of IrClH$_2$(Cyttp) and CO (Nujol mull).
The dideuteride \( \text{IrClD}_2(\text{Cyttp}) \) in THF also gives deuterated THF as shown by the \(^2\text{H-}^\text{NMR} \) spectra; both methylene positions of \( \text{C}_4\text{H}_8\text{O} \) are deuterated. No iridium hydride vibrations are observed in the infrared spectrum of \( \text{IrClD}_2(\text{Cyttp}) \) (Fig. 48); the reaction mixture of \([\text{IrCl(COD)}]_2\), Cyttp (neat), and \( \text{d}_6\)-EtOH does not give Ir-H resonances either in the \(^1\text{H-}^\text{NMR} \).

In summary, the iridium hydrides of the compound \( \text{IrClH}_2(\text{Cyttp}) \) exchange hydrides with the solvent protons, \( \text{C}_6\text{H}_6 \), \( \text{C}_4\text{H}_8\text{O} \), and \( \text{CH}_2\text{Cl}_2 \) at ambient conditions; this H/D exchange process was studied with using Ir-Deuteride analog of \( \text{IrClH}_2(\text{Cyttp}) \) and protonated solvents by \(^2\text{H-}, \text{ }^1\text{H-}^\text{NMR} \), infrared spectra, and mass spectra.

A benzene solution of \( \text{IrClH}_2(\text{Cyttp}) \) is treated with gaseous CO at ambient conditions; a strong carbonyl stretching frequency at 1730 cm\(^{-1}\) and very weak, broad bands at 1600 cm\(^{-1}\) were observed in the infrared spectrum of an isolated yellow solid (Fig. 49). The origin of this \( \nu_{\text{CO}} \) band at 1730 cm\(^{-1}\) is not clear at this point; it is not due to Ir-\( \text{CH} \) since the complex \([\text{IrH(CH)(PMMe}_3\text{)}_4]\text{PF}_6 \) gives \( \nu_{\text{C=O}} \) at 1600 cm\(^{-1}\). Benzaldehyde in the crystal lattice may be speculated as in R. Eisenberg's example; \( \text{IrH}_3(\text{CO})(\text{dppe}) \) produced a small amount of benzaldehyde upon irradiation under CO. 81

The possible mechanism of deuterium incorporation from dideuteride analogs of \( \text{IrClH}_2(\text{Cyttp}) \) to solvents can be
considered as C-H bond activation of the solvents on the iridium and then reductive elimination of deuterated solvents. Whenever there is a better ligand than solvent such as CO, the IrClH₂(Cyttp) complex may react with CO in benzene and form presumably IrClH(CH)(Cyttp) as in the case of Ir(Cl·SO₂)H(SO₂H)(Cyttp), which may be followed by reaction of Ir-CH with benzene to give benzaldehyde and the parent compound, IrClH₂(Cyttp).

Summary and Conclusion

A series of iridium-hydride complexes of the type IrH₂X(Cyttp)⁺⁺⁺ (X = Cl, I, H, SnCl₃, n=0; X = CO, PMe₂Ph, n=1) is prepared. The Ir-Cl and Ir-H bond reactivities of these octahedral complexes are investigated.

The Ir-Cl bond can be substituted by neutral ligands (e.g., CO, PMe₂Ph) generating 6-coordinated dihydrido
cations. The Ir-Cl bond also reacts with SnCl₂ to produce the Ir-SnCl₃ bond. Metatheses of the Ir-Cl bond can be achieved only by Ag⁺ salts, not by Ti⁺ or Na⁺ salts. In gaseous ion state, the Ir-Cl bond was not cleaved until all the cyclohexyl substituents of the ligand are lost as cyclohexene.

The hydride reactivities of IrClH₂(Cyttp) and IrH₃(Cyttp) are examined. The hydride trans to hydride in IrH₃(Cyttp) is very reactive; it reacts with CHCl₃ to give IrClH₂(Cyttp) and CH₂Cl₂. The hydrides trans to phosphorus in IrClH₂(Cyttp) is reactive toward the electrophiles C₇H₇BF₄, I₂ and SO₂, whereas the hydride trans to halide remains intact. A series of complexes of the type IrClH(X)(Cyttp)ⁿ⁺ (X = I, SO₂H, n=0; X = CH₃CN, n=1) is obtained from the reaction of IrClH₂(Cyttp) and the electrophiles. The non-dissociating nature of the triphosphine ligands results in the formation of the unusual complex, Ir(Cl·SO₂)(H)(SO₂H)(Cyttp) upon treating IrClH₂(Cyttp) with SO₂.

Irradiation of IrClH₂(Cyttp) with UV light does not result in a net reductive elimination of H₂; instead a reversible H₂ addition does occur. The study of reactivity differences of hydride ligands and the non-productive photolysis led the author to discover the H/D exchange via the complexes IrClD₂(Cyttp) or IrClDH(Cyttp), producing
deuterated solvents, d-benzene, d-THF, and d-dichloromethane at ambient conditions.

B. Iridium(I) Complexes of Cyttb

Stability and Reactivity of Iridium(I) Complexes of Cyttb

Most of the studies reported on Ir(I) complexes involve IrCl(CO)(PPh3)2, IrCl(PPh3)3, and IrH(CO)(PPh3)2, and their addition or oxidative addition reactions with O2, SO2, CO or H2, Cl2, HCl, NOBF4, respectively.28,122-124 Compared to the vast investigations on Ir(III) complexes with more than two phosphine ligands, planar d8-Ir(I) complexes with such ligands are not very well documented except the above addition reactions.125 Chemical reactivity of Ir(I) planar complexes can be one of the major reasons, since IrCl(PPh3)3 cannot be treated as an analog of RhCl(PPh3)3.

On heating IrCl(PPh3)3 in a number of solvents (benzene, acetone, chloroform, and cyclohexane) for several hours, it undergoes ortho-metallation and is converted into 6-coordinate IrClH(C6H4PPh2)(PPh3)2.33 The reaction products of iridium-polytertiaryphosphine complexes depend not only on the nature of the solvent but also on the temperature.

For example, the reaction of [IrCl(COD)]2 and PPN(Ph2P(CH2)3P(Ph)(CH2)3N(CH3)2) in benzene at room temperature forms the IrCl(COD)(PPN) complex; coordination of
PPN to iridium occurs only through the two phosphorus atoms to form the complex B-1. 126

The complex [Ir(COD)(ppol)]Cl•2C₂H₅OH (B-2) was obtained from the reaction mixture of [IrCl(COD)]₂ and ppol(Ph₂P-(CH₂)₃P(Ph)(CH₂)₂CH=CH₂) in EtOH; the reaction product in benzene was found to be [IrCl(COD)(ppol)]•C₆H₆ (B-3). 127

The complex IrCl(COD)(Cytpp) was isolated in this research from the reaction of [IrCl(COD)]₂ and Cytpp in benzene or toluene at room temperature. The ³¹P{¹H}-NMR spectrum shows that Cytpp is bonded to the metal via two phosphorus atoms; consequently, one of the terminal phosphine groups is unbonded or "dangling" as shown by B-4. The coordinated COD ligand was confirmed by olefinic protons at
3.93 ppm (4H) in the $^1$H-NMR spectrum, and also by a peak for a metal bound C=C bond at 63.3 ppm in the $^{13}$C-NMR spectrum (Fig. 51).

The comparisons of IrX(COD)LL can be considered for LL = PPN, ppol, and Cytpp. The ligand PPN and Cytpp results in iridium hydrides complexes in alcohol at room temperature; whereas, the Ir-ppol mixture needed to be refluxed to find such impurities.\textsuperscript{127} As the ligand becomes more basic and a better $\sigma$ donor in the order ppol < PPN < Cytpp, bidentate coordination of the potentially tridentate ligands on Ir(I) seems to be preferred, rather than as completely chelated tridentates. It is surprising that the Ir-diolefin bonds of COD are not replaced by the chelating phosphine ligands. The $^{31}$P{$^1$H}-NMR parameters of IrCl(COD)(PPN), IrCl(COD)(ppol)$\cdot$C$_6$H$_6$, [Ir(COD)(ppol)]Cl$\cdot$2EtOH, and IrCl(COD)(Cytpp) are compared in Table 14.
Figure 50. (a) Phosphorus-31 NMR spectrum of IrCl(COD)(Cytpp) (121.470 MHz);
(b) $^1$H-NMR spectrum of IrCl(COD)(Cytpp) (300 MHz).
Figure 51. $^{13}$C-NMR spectrum of IrCl(COD)(Cytpp) (22.62 MHz).
### Table 14

Phosphorus-31 NMR Data of IrX(COD)(\(\text{LL}\)) \(^{a,b}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta_{P_1}^{d}(\Delta_1)^C)</th>
<th>(\delta_{P_2}^{d}(\Delta_2)^C)</th>
<th>(\delta_{P_3}^{d}(\Delta_3)^C)</th>
<th>(J_{P_1P_2}^{C})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrCl(COD)(PPN)</td>
<td>-26.8 (-0.4)</td>
<td>-11.6 (-6.6)</td>
<td>-7.8 (0.0)</td>
<td>44.1</td>
<td>126</td>
</tr>
<tr>
<td>IrCl(COD)(Cyttp)</td>
<td>-27.5 (-0.5)</td>
<td>-23.1 (-15.3)</td>
<td>-7.8 (0.0)</td>
<td>42.4</td>
<td>this work</td>
</tr>
<tr>
<td>IrI(COD)(Cyttp)</td>
<td>-37.0 (9.0)</td>
<td>-32.7 (25.1)</td>
<td>-7.6 (0.0)</td>
<td>42.0</td>
<td>this work</td>
</tr>
<tr>
<td>IrCl(COD)(ppol)•C_6_H_6</td>
<td>-27.2 (0.1)</td>
<td>-11.9 (-6.3)</td>
<td>-27.2 (0.1)</td>
<td>44.5</td>
<td>127</td>
</tr>
<tr>
<td>IrCl(COD)(ppol)•2EtOH</td>
<td>-30.0 (2.9)</td>
<td>3.5 (-21.7)</td>
<td>-28.0 (0.9)</td>
<td>44.5</td>
<td>127</td>
</tr>
</tbody>
</table>

\(^a\) = central phosphorus; \(P_2\) = bound terminal phosphorus; \(P_3\) = dangling phosphorus atom.

\(^b\) = PPN, ppol, or Cyttp.

\(^c\) = \(\Delta_i = \delta_{\text{free}} - \delta_{i}\)

\(^d\) Chemical shifts are relative to 85% \(\text{H}_3\text{PO}_4\).
The Ir(I)-Cyttpp complexes which were prepared by the author to study the stabilization of Ir(I)-polytertiary-phosphine complexes are summarized in Scheme V.

The iodide analog of IrCl(COD)(Cyttpp) was isolated from the reaction of [IrI(COD)]$_2$ and Cyttpp in benzene. The $^{31}$P($^1$H)-NMR spectrum of IrI(COD)(Cyttpp) in THF shows two doublets at -37.0 ($\delta_{P_1}$) and -32.7 ($\delta_{P_2}$) ppm, and a singlet at -7.6 ppm due to free $\text{PCy}_2$ group (Fig. 52). The resonance positions of both $\delta_{P_1}$ (central phosphorus) and $\delta_{P_2}$ (terminal phosphorus) moved about 10 ppm upfield due to
iodide compared to the chloride analog. Since iodide is a large anionic ligand, a cationic species $[\text{Ir(COD)(Cytpp)}]I$ might be envisioned; conductivity measurement gives $A_M = 10 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mol}^{-1}$ in $\text{CH}_2\text{Cl}_2$, suggesting a possible partial electrolyte. However, the $^{31}\text{P}^{(1\text{H})}$-NMR spectrum of the sample in $\text{CH}_2\text{Cl}_2$ shows that the compound is $\text{IrI(Cytpp)}$ in $\text{CH}_2\text{Cl}_2$; no dangling free $-\text{PCy}_2$ resonance was observed ($\delta P_1^t = -19.15 \text{ ppm}; \delta P_2^d = -1.61 \text{ ppm}; J_{P_1 P_2} = 32.2 \text{ Hz}$). The pure $\text{IrI(Cytpp)}$ complex was not isolated as a solid, presumably due to oxidative addition of $\text{CH}_2\text{Cl}_2$ to the $\text{Ir(I)}$-complex; the $^{31}\text{P}^{(1\text{H})}$-NMR spectrum of the isolated solid becomes very complicated. When $\text{IrCl(COD)(Cytpp)}$ dissolved in $\text{CH}_2\text{Cl}_2$, the $^{31}\text{P}$-NMR sample gives the same spectrum as $\text{IrCl(Cytpp)}$.

Attempts to isolate a cationic $[\text{Ir(COD)(Cytpp)}]^+$ complex were not successful. When the Cytpp ligand was added to $[\text{Ir(COD)(acetone)}_2]^+$ that was generated in situ, the tridentate ligand displaces the COD and forms a red complex which is proposed to be $[\text{Ir(Cytpp)}(\text{CH}_3\text{C}^\|\text{CH}_3)]^+$. The $^{31}\text{P}^{(1\text{H})}$-NMR spectrum of $[\text{Ir(Cytpp)}(\text{CH}_3\text{C}^\|\text{CH}_3)]\text{AsF}_6$ shows $\delta P_2$ at 0.6 ppm (doublet) and $\delta P_1$ at -17.13 ppm (triplet). Acetone peaks are observed in the infrared spectrum of the isolated solids at 1730 cm$^{-1}$.

When the $\text{IrCl(COD)(Cytpp)}$ complex is treated with $\text{NaBPh}_4$ or $\text{TlBF}_4$ in $\text{CH}_2\text{Cl}_2$ or in acetone, a bright magenta solution is obtained. This reaction mixture is extremely air-sensitive so that the $^{31}\text{P}$-NMR sample lost its magenta
Figure 52. $^{31}P^{1H}$-NMR spectrum of IrI(COD)(Cytpp) (36.43 MHz).
Figure 53. $^{31}\text{P}^{1\text{H}}$-NMR spectrum of IrI(Cyttpp) in CH$_2$Cl$_2$ (in situ)(36.43 MHz).
Figure 54. \( ^{31}P\text{(}^1\text{H)}\)-NMR spectrum of \([\text{Ir(Cyttp)(CH}_3\text{CCH}_3)]\text{AsF}_6\) in acetone (in situ) (36.43 MHz).
color within a few minutes. The $^{31}$P($^1$H)-NMR spectrum of this species is complicated and is not solved at this point; however, it is definitely not of a simple cation, Ir(COD)(Cyttp)$^+$ or Ir(Cyttp)(solvent)$^+$. As soon as the reaction mixture of IrCl(COD)(Cyttp) and TlBF$_4$ is treated with CO, the yellow dicarbonyl complex, [Ir(CO)$_2$(Cyttp)]$^+$ is produced; its infrared spectrum shows two carbonyl stretching frequencies at 1991 cm$^{-1}$ and 1930 cm$^{-1}$ in solid state; the bands are shifted to 1990 and 1942 cm$^{-1}$ in CH$_2$Cl$_2$, and to 1985 cm$^{-1}$ and 1940 cm$^{-1}$ in CH$_3$CN. The intensity ratio of the asymmetric and symmetric carbonyl stretching frequencies are different in the solid and solution infrared spectra (Fig. 56). The ratio of the intensities of the symmetric and antisymmetric bands is given by eq. (32),$^{102}$ where $\theta$ is the angle between the two carbonyl groups.

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

(32)

In both CH$_3$CN and CH$_2$Cl$_2$ solution, the symmetric band is weaker; $\theta \approx 98^\circ$ for CH$_2$Cl$_2$ and CH$_3$CN is calculated. Thus, cis-configuration of the dicarbonyl can be proposed.

The $^{31}$P($^1$H)-NMR spectrum of the [Ir(CO)$_2$(Cyttp)]BF$_4$ complex has $\delta P_1$ at -42.42 ppm (triplet) and $\delta P_2$ at -11.95 ppm (doublet). Since CO is trans to the central phosphorus
Figure 55. $^31P(1H)$-NMR spectrum of [Ir(CO)$_2$(CyTtp)]BF$_4$ (36.43 MHz).
Figure 56. (a) Infrared spectra of [Ir(CO)$_2$(Cyp)]BF$_4$ (Nujol mull).
(b) the carbonyl region in CH$_3$CN.
$\delta P_1$, $\delta P_2$ seems to be shielded more than $\delta P_2$ as in the case of RhL(CO)$^+$ ($L = ttp$ or Cyttp).$^3$

The complex IrCl(ttp) also forms $[\text{Ir}(\text{CO})_2(ttp)]\text{Cl}$, on treating with CO in toluene for 20 min.$^{29}$ A trigonal-bipyramidal structure was proposed for $[\text{Ir}(\text{CO})_2(ttp)]\text{Cl}$ by Dahlenberg on the basis of the intensity ratio of the two peaks in the infrared spectrum. The $^{31}\text{P}$-NMR parameters and $\nu_{\text{CO}}$ of the Ir(I)-carbonyl complexes with Cyttp or ttp ligand as compared in Table 15.

The reaction of IrCl(COD)(Cyttp) with CO in $C_6H_6$ shows that COD is replaced by CO molecules. Two species are present in the $^{31}\text{P}^{(1)}\text{H}$-NMR spectrum of the isolated solid from the above reaction. A broad $AB_2$ pattern occurs at -5.4 ppm ($\delta P_2$)$^d$ and at -32.0 ppm ($\delta P_1$)$^t$ with $^2J_{P_1P_2} = 22.2$ Hz; and another sharp $AB_2$ pattern occurs at -26.6 ppm ($\delta P_2$)$^d$ and at -39.6 ppm ($\delta P_1$)$^t$ with $^2J_{P_1P_2} = 37.2$ Hz. When the $^{31}\text{P}$-NMR sample of the above mixture is heated in the NMR probe to 78°C, the broad peaks disappear and only the sharp doublet at -26.6 ppm and the triplet at -39.6 ppm remain. The infrared spectrum of the solid which was isolated from the reaction of IrCl(COD)(Cyttp) with CO shows a sharp $\nu_{\text{CO}}$ band at 1980 cm$^{-1}$ with a shoulder at 1970 cm$^{-1}$ and a broad absorption at 1925 cm$^{-1}$. The mixture in the $^{31}\text{P}^{(1)}\text{H}$-NMR spectrum may be ascribed to monocarbonyl and dicarbonyl Ir(I)-complexes, IrCl(CO)(Cyttp) (sharp peaks) and IrCl(CO)$_2$(Cyttp) (broad resonances). On heating, one of the
Figure 57. (a) $^{31}$P($^1$H)-NMR spectrum of a mixture of IrCl(CO)$_2$(Cytpp) and IrCl(CO)(Cytpp) at RT; (b) IrCl(CO)(Cytpp) at 78°C (36.43 MHz).
**TABLE 15**

Phosphorus-31 NMR And Infrared Data Of Iridium(I)-Carbonyl Complexes Of Cyttp And ttp<sup>a</sup>

<table>
<thead>
<tr>
<th></th>
<th>δP&lt;sub&gt;1&lt;/sub&gt;</th>
<th>δP&lt;sub&gt;2&lt;/sub&gt;</th>
<th>J&lt;sub&gt;P&lt;sub&gt;1&lt;/sub&gt;P&lt;sub&gt;2&lt;/sub&gt;&lt;/sub&gt;</th>
<th>ν&lt;sub&gt;CO&lt;/sub&gt; (nujol mull)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(CO)&lt;sub&gt;2&lt;/sub&gt;(Cyttp)]&lt;sub&gt;HF&lt;/sub&gt;₄</td>
<td>-42.4</td>
<td>-11.9</td>
<td>34.8</td>
<td>1942, 1990</td>
</tr>
<tr>
<td>IrCl(CO)(Cyttp)</td>
<td>-39.6</td>
<td>-26.6</td>
<td>37.2</td>
<td>1925, 1980</td>
</tr>
<tr>
<td>IrCl(CO)(ttp)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-35.1</td>
<td>-11.8</td>
<td>42.7</td>
<td>1889, 1918</td>
</tr>
<tr>
<td>[Ir(CO)&lt;sub&gt;2&lt;/sub&gt;(ttp)]Cl&lt;sub&gt;b&lt;/sub&gt;</td>
<td>-45.4</td>
<td>-23.0</td>
<td>35.4</td>
<td>1959, 2009</td>
</tr>
</tbody>
</table>

<sup>a</sup> P<sub>1</sub> = central phosphorus; P<sub>2</sub> = terminal phosphorus.

<sup>b</sup> Reference, 29


TABLE 16

Phosphorus-31 NMR Parameters Of Planar Ir(I)-Complexes

<table>
<thead>
<tr>
<th></th>
<th>$\delta P_1$ ($\Delta_1$)</th>
<th>$\delta P_2$ ($\Delta_2$)</th>
<th>$J_{P_1P_2}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrCl(Cytttp)</td>
<td>-16.8 (-11.3)</td>
<td>+1.98 (-9.78)</td>
<td>30.5</td>
<td>this work</td>
</tr>
<tr>
<td>Ir(I)(cyttpp)$^b$</td>
<td>-19.2 (-8.9)</td>
<td>-1.61 (-6.19)</td>
<td>32.2</td>
<td>this work</td>
</tr>
<tr>
<td>Ir(Cytttp)(CH$_3$CCH$_3$)$^b$</td>
<td>-17.3 (-11.1)</td>
<td>0.60 (-8.40)</td>
<td>33.0</td>
<td>this work</td>
</tr>
<tr>
<td>IrCl(ttp)</td>
<td>-19.9 (-8.3)</td>
<td>2.7 (-10.5)</td>
<td>32.8</td>
<td>29</td>
</tr>
<tr>
<td>Ir(ttp)(CH$_2$-CMe$_3$)</td>
<td>-22.5 (-5.7)</td>
<td>6.7 (-14.5)</td>
<td>29.7</td>
<td>125</td>
</tr>
<tr>
<td>Ir(ttp)(CH$_2$SiMe$_3$)</td>
<td>-23.7 (-4.5)</td>
<td>7.2 (-15.0)</td>
<td>31.6</td>
<td>125</td>
</tr>
<tr>
<td>Ir(ttp)(2-MeC$_6$H$_4$)</td>
<td>-20.6 (-7.6)</td>
<td>0.2 (-8.0)</td>
<td>30.5</td>
<td>125</td>
</tr>
<tr>
<td>Ir(ttp)(4-MeC$_6$H$_4$)</td>
<td>-20.7 (-7.5)</td>
<td>4.8 (-12.6)</td>
<td>29.5</td>
<td>125</td>
</tr>
<tr>
<td>Ir(ttp)(2,4,6-Me$_3$C$_6$H$_2$)</td>
<td>-22.2 (-6.0)</td>
<td>1.2 (-9.0)</td>
<td>31.0</td>
<td>125</td>
</tr>
</tbody>
</table>

$^a$ $P_1$ = central phosphorus = $P_2$ = terminal phosphorus

$^b$ Spectrum observed in-situ

$^c$ $\Delta_i = \delta_{\text{free}} - \delta P_i$
carbonyl ligands of the IrCl(CO)$_2$(Cytpp) might have been lost to give IrCl(CO)(Cytpp) (Fig. 57).

Dahlenberg and Arpac also prepared the complex IrCl(ttp), which is analogous to IrCl(Cytpp), from [IrCl(COE)$_2$]$_2$ and ttp in toluene at room temperature. In this study, isolation of pure IrCl(Cytpp) was not always reproducible from the reaction mixture of [IrCl(COD)]$_2$ and Cytpp in toluene or benzene; the product depends on the concentration, temperature, and solvents. Although the in-situ $^{31}$P{$^1$H}-NMR spectrum of the above reaction shows one AB$_2$ pattern presumably due to IrCl(Cytpp) (δ$P_2$ = 1.98 ppm; δ$P_1$ = -16.8 ppm; $^2$J$P_1P_2$ = 30.5 Hz), the isolated solid after evaporation of the solvent usually contains another compound at -25.6 ppm (δ$P_2$)$_d$ and -37.6 ppm (δ$P_1$)$_t$. When a dilute reaction mixture of [IrCl(COD)]$_2$ and Cytpp is stirred at room temperature for 72 hrs or heated to 70°C in toluene for 1 hr, and the solvent is not evaporated completely to dryness, then by adding hexane to this very concentrated solution (~ 1 mL) a pure IrCl(Cytpp) is usually obtained. The reaction of [IrCl(COD)]$_2$ and Cytpp or IrCl(COD)(Cytpp) in benzene or toluene will be discussed in detail later.

The $^{31}$P-NMR parameters of planar Ir(I)-complexes with Cytpp or ttp ligands (IrLX) are compared in Table 16. The chemical shifts are not very sensitive to the ligand X, although for planar Ir(I) complexes both $P_1$ and $P_2$ are deshielded compared to the free ligands. In addition, the
spectra of the Ir(I) complexes exhibit the A portion of the AB₂ pattern higher than the B part, which is the same trend observed for Pt(II)-tridentate complexes (Table 25).¹²⁸

The two-bond cis-J_p₁p₂ values for 4-coordinate planar Ir(I)-tridentate (tridentate = Cyttp, ttp) complexes are approximately 29-33 Hz, whereas IrCl(PPh₃)₃ has ²J_p₁p₂ = 22.3 Hz.²⁹ The cis-²J_p₁p₂ values for 5-coordinate Ir(I) complexes with the tridentate ligands (PPN, µpol, Cyttp, ttp) exhibit a range of 36-45 Hz. In general, the two bond cis-J_p̅p values decreases as one descends the Co or Ni triad;¹²⁹ this trend is also observed in this work from Rh, Ir, and Pt complexes with Cyttp (Table 17).

Miscellaneous Observations Related to Intramolecular Reactions of IrCl(Cyttp)

Intramolecular C-H activation in Ir(I) complexes with one of its own tertiaryphosphine ligands can be separated into two categories: (i) orthometallation of C-H bonds in one of the substituents of a phosphine ligand (e.g., Bennet,³³, Shaw,³⁴ or Dahlenberg’s¹²⁵ work), and (ii) dehydrogenation of cycloalkane, which is rather a recent observation.

Dehydrogenation of cycloalkanes by use of iridium(I) cationic species has been developed recently by Crabtree (eq. 23, 24).⁷⁸,⁷⁹ Vrieze and coworkers¹³³ discovered in 1978 that one of the cyclohexyl substituents on a
Figure 58. $^{31}\text{P}(^1\text{H})$-NMR spectrum of the solid isolated from the reaction of IrCl(COD)(Cytpp) in benzene (or toluene) after refluxing 0.5 hr (121.470 MHz).
coordinated PCy\textsubscript{3} ligand was dehydrogenated in the reaction of [IrCl(COT)\textsubscript{2}]\textsubscript{2} with PCy\textsubscript{3} in refluxing benzene. This reaction was confirmed by Robinson et al.\textsuperscript{134} treatment of [IrCl(COT)\textsubscript{2}]\textsubscript{2} with PCy\textsubscript{3} in toluene at 20°C yields \[\text{IrClH}_{2}(\text{P(C}_6\text{H}_9)\text{Cy}_2)(\text{PCy}_3)\].

When a mixture of complexes of structure B-5a and B-5b is refluxed, loss of H\textsubscript{2} is observed and \[\text{IrCl(P(C}_6\text{H}_9)\text{Cy}_2)(\text{PCy}_3)\] is isolated as a mixture of isomers with 4,5- and 5,5-membered rings (B-6).

The \textsuperscript{31}P{\textsuperscript{1}H}-NMR data are compared in Table 17. The complex of structure B-5 can be obtained by hydrogenation of B-6 with H\textsubscript{2}(g); no hydrogenation of the double bond in complex B-6 is observed.
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta P_A$</th>
<th>$\delta P_B$</th>
<th>$J_{P_A P_B}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrCl(CO)(PCy$_3$)$_2$</td>
<td>-30.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IrCl(CO)(P(C$_6$H$_9$)Cy$_2$)(PCy$_3$)</td>
<td>-30.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IrCl(P(C$_6$H$_9$)Cy$_2$)(PCy$_3$) (B-6a)</td>
<td>+3.1</td>
<td>+20.8</td>
<td>427</td>
</tr>
<tr>
<td>IrCl(P(C$_6$H$_9$)Cy$_2$)(PCy$_3$) (B-6b)</td>
<td>-12.9</td>
<td>-35.6</td>
<td>356</td>
</tr>
<tr>
<td>IrClH$_2$(P(C$_6$H$_9$)Cy$_2$)(PCy$_3$) (B-5a)</td>
<td>-13.6</td>
<td>-33.3</td>
<td>419</td>
</tr>
<tr>
<td>IrClH$_2$(P(C$_6$H$_9$)Cy$_2$)(PCy$_3$) (B-5b)</td>
<td>-14.3</td>
<td>-30.6</td>
<td>337</td>
</tr>
<tr>
<td>IrClH$_2$(P(C$_6$H$_9$)Cy$_2$)(PCy$_3$)$_b$</td>
<td>+2.6</td>
<td>+20.9</td>
<td>335</td>
</tr>
</tbody>
</table>

aReferences 133, 134

bA 4.5-membered ring is also obtained from hydrogenation of B-6.
In this present study, treatment of \([\text{IrCl(COD)}]_2\) with a solution of Cytpp in refluxing benzene usually produced a cream solid which gives a mixture of two AB$_2$ NMR patterns: B-7 ($\delta P_1 = -16.79$ ppm; $\delta P_2 = 2.02$ ppm; $^2J_{P_1P_2} = 32.31$ Hz) and B-8 ($\delta P_1 = -34.09$ ppm; $\delta P_2 = -22.87$ ppm; $^2J_{P_1P_2} = 25.5$ Hz) (Fig. 58). However, the $^{31}P^{[1H]}$-NMR spectrum obtained in situ from the reaction mixture of IrCl(COD)(Cytpp) heated to 70°C in benzene or toluene shows only one AB$_2$ NMR pattern, which is assigned to B-7. The in situ $^{31}P^{[1H]}$-NMR spectrum from the reaction mixture of \([\text{IrCl(COD)}]_2\) and Cytpp in benzene at room temperature for 72 hrs also gives the spectrum of pure IrCl(Cytpp). If the IrCl(COD)(Cytpp) complex is refluxed more than 4 hrs in benzene or toluene followed by complete evaporation of the solvents, then the isolated solid gives only one AB$_2$ NMR pattern, which is assigned to B-8, in $^{31}P^{[1H]}$-NMR spectrum.

The reaction of IrCl(COD)(Cytpp) in refluxing benzene (or toluene) was followed by $^{31}P^{[1H]}$-NMR spectroscopy on the Bruker HX 90 spectrometer over a period of 12 hrs (Fig. 59). The spectrum of IrCl(COD)(Cytpp) is replaced by the spectrum of IrCl(Cytpp) (B-7) at a probe temperature of 70°C. If the reaction mixture is then cooled to 50°C in the probe, the same spectrum (B-7) is still the only species observed. If the probe is then cooled to room temperature, the $^{31}P^{[1H]}$-NMR spectrum shows the only presence of B-8. When the temperature was cooled to room temperature from 70°C directly,
Figure 59. The Reaction of IrCl(COD)(Cytpp) in benzene (or toluene) monitored by $^{31}$P($^1$H)-NMR spectra (36.43 MHz).
Figure 60. The Reaction of IrCl(COD)(Cyttp) in benzene (or toluene) monitored by $^1$H-NMR spectra (90 MHz).
the $^{31}\text{P}^{(1\text{H})}$-NMR spectrum still shows B-7 as the only species. The solvent of this $^{31}\text{P}^{(1\text{H})}$-NMR sample was evaporated and a new batch of benzene was added to the residue; then, the $^{31}\text{P}^{(1\text{H})}$-NMR spectrum shows complete conversion to B-8 from B-7. The same reaction was followed by $^{1}\text{H}$-NMR spectra on the Bruker HX-90 spectrometer. The IrCl(COD)(Cytpp) shows coordinated olefinic resonances at 3.93 ppm attributed to COD at room temperature. At 70°C, the COD resonances shifted to 5.5 ppm indicating that B-7 does not have olefinic bonds coordinated to the metal. When the sample was cooled to room temperature, the $^{1}\text{H}$-NMR spectrum shows free COD at 5.5 ppm; however, there are other olefinic protons at 5.76 ppm (Fig. 60). These free olefinic proton resonances disappeared when the spectrum was obtained again a few hours later. The resonances at 5.76 ppm may be ascribed to the cyclohexane protons according to Vrieze's group; IrCl(CO)(PCy$_3$)(P(C$_6$H$_9$)Cy$_2$) shows non-coordinated cyclohexene protons at 5.7 ppm. However, there are no free olefinic protons in the $^{1}\text{H}$-NMR spectrum of the isolated B-8. The above observations obtained from $^{31}\text{P}^{(1\text{H})}$- and $^{1}\text{H}$-NMR spectra are summarized in Scheme VII.
Dehydrogenation of cyclohexyl protons on one of the terminal phosphorus atoms in the Cyttp ligand, followed by coordination of the resulting cyclohexene ring to iridium, which was also observed in the gaseous ionic state by FT-ICR mass spectra, may be involved in this reaction as in the case of Vrieze's reactions to produce $\text{IrCl(PC}_6\text{H}_9\text{Cy}_2)(\text{PCy}_3)$. The species that is observed from prolonged heating and/or evaporation of the solution of IrCl(Cyttp) to dryness, or from prolonged photolysis of IrClH$_2$(Cyttp) may be suggested as $\text{IrCl(Cy}_2\text{P(CH}_2)_3\text{P(Ph)(CH}_2)_3\text{P(C}_6\text{H}_9\text{)Cy)} (B-8)$. 
The speculated compound with dehydrogenated cyclohexane was generated in situ from the reaction mixture of IrCl(COD)-(Cytpp) in THF at 70°C, and concentrated HCl was added. A white solid was isolated, whose $^{31}$P-$^1$H-NMR spectrum shows two doublets at -16.45 ppm and -17.40 ppm, and a triplet at -24.56 ppm (B-9). The integration ratio of the two doublets and the triplet is approximately 1:1:1, indicating that the two terminal phosphorus atoms are non-equivalent (Fig. 61). The $^1$H-NMR spectrum of B-9 gives an Ir-hydride resonance at -16.3 ppm (Fig. 62); $\nu_{\text{Ir-H}}$ occurs at 2210 cm$^{-1}$ (broad) in the infrared spectrum. Elemental analysis of this compound shows that there are three chlorides; in the $^1$H-NMR spectrum, some resonances at 4.8 ppm appear presumably due to $^{1}H_{\text{Ir}-\text{Cl}}$ group. Thus B-9 is speculated as IrCl$_2$H(Cytpp-Cl).

The compound B-9 is extremely moisture sensitive; the mass spectrum of the moisture exposed sample shows peak envelopes at 865, which may be calculated as IrCl$_2$H(Cytpp-OH).
Figure 61. $^{31}P(1\text{H})$-NMR spectrum of IrCl$_2$(Cytpp-C1) (36.43 MHz).
Figure 62. $^1$H-NMR spectrum of IrCl$_2$H(Cyttbp-Cl) (300 MHz).
The complex B-8, IrCl(Cy₂P(CH₂)₃P(Ph)(CH₂)₃P(C₆H₉)Cy), was isolated from benzene and ether; its \(^1H\)-NMR spectrum shows free ether peaks at 3.3 ppm and 1.0 ppm. Recrystallization from THF-hexane (non-distilled hexane) caused the appearance of a new \(\nu_{OH}\) band at 3300 cm\(^{-1}\) in the infrared spectrum. Elemental analysis of this complex is consistent with the presence of an OH group; IrCl(Cytpp-OH) may be postulated. The reaction in eq. (33) may be tentatively attributed between a coordinated olefin and HCl or H₂O:
Dehydrogenation of a cyclohexyl group to give an \( \eta^2 \)-olefin bond and their reaction with HCl or H\(_2\)O is suggested for further study in the chemistry of [IrCl(COD)]\(_2\) and Cyttp ligand (Table 18).

Treatment of [IrCl(COD)]\(_2\) with ttp in benzene at room temperature (for 2 hrs) in this study, did not produce the expected IrCl(ttp); whereas [IrCl(COE)]\(_2\) and ttp does react to give IrCl(ttp).\(^{29}\) The isolated solid from the reaction of [IrCl(COD)]\(_2\) and ttp gave a mixture of two species; B-10 (\( \delta P_{\text{PPh}_2} = -15.23 \) ppm; \( \delta P_1^d = -28.36 \) ppm; \( \delta P_2^d = -22.48 \) ppm; \( J_{P_1P_2} = 25.65 \) Hz) and B-11 (\( \delta P_1^t = -41.36 \) ppm; \( \delta P_2^d = -29.54 \) ppm; \( J_{P_1P_2} = 25.6 \) Hz) (Fig. 63). They may be speculated as \( \eta^2 \)-phenyl complexes as follows:

![Chemical structures](image)

The [IrCl(COE)]\(_2\) certainly should be a better starting material to prepare Ir(I)-polyphosphine complexes, since the weakly coordinated mono-olefin COE can dissociate more easily than the chelated diolefin COD at ambient temperature.
Figure 63. $^{31}\text{P}^{1\text{H}}$-NMR spectrum of the solid isolated from the reaction of [IrCl(COD)]$_2$ and ttp in benzene after refluxing (36.43 MHz).
Table 18

Phosphorus-31 NMR Parameters Of Iridium-Cyttp
And ttp Complexes With $\eta^2$-Olefin Bond.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta P_1$</th>
<th>$\delta P_2$</th>
<th>$\delta P_3$</th>
<th>$J_{P_1P_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrCl(Cyttp) (B-7)</td>
<td>-16.9</td>
<td>2.0</td>
<td></td>
<td>31.2</td>
</tr>
<tr>
<td>IrCl(ttp)</td>
<td>-19.9</td>
<td>2.7</td>
<td></td>
<td>32.8</td>
</tr>
<tr>
<td>IrCl(Cyttp) (B-8)</td>
<td>-37.6</td>
<td>-25.6</td>
<td></td>
<td>25.0</td>
</tr>
<tr>
<td>IrCl(ttp) (COD) (B-10)</td>
<td>-28.4</td>
<td>-22.5</td>
<td>-15.2</td>
<td>25.6</td>
</tr>
<tr>
<td>IrCl(ttp) (B-11)</td>
<td>-41.4</td>
<td>-29.5</td>
<td></td>
<td>24.4</td>
</tr>
<tr>
<td>IrCl$_2$H(Cyttp-Cl) (B-9)</td>
<td>-24.6</td>
<td>-16.4</td>
<td>-17.4</td>
<td>22.5</td>
</tr>
</tbody>
</table>

$^aP_1$=central phosphorus; $P_2$=terminal phosphorus; $P_3$=terminal phosphorus with $\eta^2$-olefin bond or with Cl.
Summary and Conclusion

The mixed olefin-phosphine complexes IrX(COD)(Cyttp), where the Cyttp ligand acts as a bidentate, are isolated from the reaction mixture of [IrCl(COD)]_2 and Cyttp at room temperature. Planar Ir(I)-Cyttp complex, IrCl(Cyttp), can be obtained when the reaction mixture is heated. When this mixture is subject to prolonged heating and reduced pressure, dehydrogenation of a cyclohexyl ring on the terminal phosphine occurs, followed by coordination to the iridium center.

Replacement of COD by CO is achieved and produces a mixture of IrCl(CO)(Cyttp) and IrCl(CO)_2(Cyttp) at room temperature. Attempts to isolate Ir(COD)(Cyttp)^+ by metatheses with NaBPh_4 or TiBF_4 failed. However, a pure Ir(CO)_2(Cyttp)^+ complex can be isolated upon treating the above reaction mixture for metathesis reaction with CO(g). The reaction mixture of Ir(COD)(acetone)_2^+ and Cyttp results in Ir(Cyttp)(acetone)^+, where Cyttp acts as a tridentate ligand and the solvent molecule replaces the COD.

C. Rhodium Complexes of Cyttp and ttp:

A Comparative Study of Cyttp and ttp Complexes

Various Cyttp and ttp complexes of rhodium and platinum are prepared and compared to the corresponding ttp analogs. Planar Rh(I)-Cyttp complexes with ligands (e.g., NO_2, NO, CO), which can interact with incoming small gaseous
molecules, are also investigated. Gas molecules such as SO₂, CO or O₂ can bind to the rhodium site directly. However, when a ligand that is coordinated to the metal has a reactive center, the incoming gas molecule can functionalize the ligand. The reactions which include the oxygen transfer in this study are summarized in Scheme VI.

The reaction of RhCl(Cytt) and NaN₃ in EtOH results in the formation of the Rh(NO₂)(Cytt) complex. The ³¹P{¹H}-NMR data indicate a Rh(I) complex: J_p₁-p₂ = -51.0 Hz; J_Rh-p₁ = 142 Hz; J_Rh-p₂ = 137.9 Hz (Table 19). The range of ³¹P-NMR coupling constants for rhodium compounds of triphosphine ligands is outlined in Table 20. The infrared
spectrum of the complex shows a strong band at 1320 cm$^{-1}$ due to the symmetric stretching frequency of NO$_2$; the asymmetric stretching frequency is hidden under the Nujol peaks at 1450 cm$^{-1}$ (Fig. 65). The NO$_2$ stretching frequencies in cobalt-nitro and cobalt-nitrito complexes display markedly different infrared bands. The nitro complex [Co(NH$_3$)$_5$(NO$_2$)]Cl$_2$ gives asymmetric stretching vibration at 1428 cm$^{-1}$ and symmetric stretching frequency at 1310 cm$^{-1}$, whereas the nitrito complex [Co(NH$_3$)$_5$(ONO)]Cl$_2$ exhibits the asymmetric stretching band at 1468 cm$^{-1}$ and symmetric stretching frequency at 1065 cm$^{-1}$. On the basis of comparison with infrared data of the Co(NH$_3$)$_5$(NO$_2$)$_2^+$ the bonding of NO$_2$ to rhodium in this case is assigned as N-bonded Rh-NO$_2$.

An interesting by-product, RhCl(Cytpp)·O$_2$, is also isolated from the above Rh-NO$_2$ synthesis as a precipitate, while the NO$_2$ complex remains in the solution. The $^{31}$P{$^1$H}-NMR and infrared data for the O$_2$-adduct are identical to those of an authentic sample of RhCl(Cytpp)·O$_2$, which can be prepared by bubbling O$_2$ through a solution of RhCl(Cytpp) (Table 21). Also when the RhCl(ttp) complex is reacted with NaNO$_2$ in THF instead of alcohol, the only product isolated is RhCl(ttp)·O$_2$; this formula has been proved by elemental analysis, the $^{31}$P{$^1$H}-NMR and infrared spectra ($\delta$P$_1$ = 15.6 ppm; $\delta$P$_2$ = 7.59 ppm; $J_{P_1-P_2}$ = -47.6 Hz; $J_{Rh-P_1}$ = 129.4 Hz; $J_{Rh-P_2}$ = 103.8 Hz; $\nu_{O_2}$ = 854 cm$^{-1}$).
Figure 64. $^{31}\text{P}({}^1\text{H})$-NMR spectrum of Rh(NO$_2$)(Cytpp) (36.43 MHz).
Figure 65. Infrared spectrum of Rh(NO$_2$)(CyttP): 1400-400 cm$^{-1}$ (Nujol mull).
### TABLE 19

**Phosphorus-31 NMR And Infrared Data Of Selected RhX(Cyttp) Complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta P_1$</th>
<th>$\delta P_2$</th>
<th>$^{1}J_{P_1P_2}$</th>
<th>$^{2}J_{Rh,P_1}$</th>
<th>$^{1}J_{Rh,P_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RhCl(Cyttp)</td>
<td>20.9</td>
<td>9.10</td>
<td>-49.0</td>
<td>174.0</td>
<td>126.0</td>
</tr>
<tr>
<td>RhI(Cyttp)</td>
<td>18.1</td>
<td>-3.32</td>
<td>-32.3</td>
<td>140.4</td>
<td>89.1</td>
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<tr>
<td>Rh(NCS)(Cyttp)</td>
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<td>9.99</td>
<td>-50.9</td>
<td>156.9</td>
<td>124.5</td>
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<tr>
<td>RhN$_3$(Cyttp)</td>
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<td>90.3</td>
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<tr>
<td>RhCN(Cyttp)</td>
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<td>-34.2</td>
<td>120.2</td>
<td>85.8</td>
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<tr>
<td>Rh(NO$_2$)(Cyttp)</td>
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<td>7.72</td>
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<td>137.9</td>
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<td>Rh(SnCl$_3$)(Cyttp)</td>
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<td>6.90</td>
<td>-34.2</td>
<td>126.7</td>
<td>89.4</td>
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<tr>
<td></td>
<td>23.0</td>
<td>6.20</td>
<td>-28.3</td>
<td>111.9</td>
<td>82.4</td>
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<td></td>
<td>15.1</td>
<td>-4.24</td>
<td>-25.0</td>
<td>91.5</td>
<td>80.4</td>
</tr>
</tbody>
</table>

*$_{1}P_1$ = central phosphorus; $P_2$ = terminal phosphorus.*

*Chemical shifts are relative to 85% H$_3$PO$_4$.**
TABLE 20

Range Of $^{31}$P-NMR Coupling Constants For Rhodium Compounds
Of Triphosphine Ligands$^a$

<table>
<thead>
<tr>
<th></th>
<th>$^{2}J_{PP}$ (Hz)</th>
<th>$^{1}J_{Rh,P}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cis</td>
<td>trans</td>
</tr>
<tr>
<td>planar Rh(I)</td>
<td>-31 ~ -58</td>
<td>260 ~ 460</td>
</tr>
<tr>
<td>square pyramidal Rh(III)</td>
<td>-13 ~ -48</td>
<td>209 ~ 355</td>
</tr>
</tbody>
</table>

$^a$Results compiled from References 3, 135, 8.

$^b$Strong ligands are CO, PR$_3$, PF$_2$(OR)$_3$, P(OR)$_3$, alkyl, CN$^-$, SPh$^-$.  

$^c$Weak ligands are Cl$^-$, Br$^-$, OH$^-$, N$_3^-$, NO$_2^-$, SCN$^-$, I$^-$, NCCH$_3$. 
oxygen adduct is the predominant product as less polar solvents are used. The polarity of the solvent affects the metathesis of RhCl(Cyttp) with Na⁺ salts; it occurs more readily in alcohol than in THF. When NaN₂O₂ reacts with residual H₂O in the solvent before it substitutes Rh-Cl bond, then the following reactions may be considered:

\[
\begin{align*}
\text{NaN}_2\text{O}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{HNO}_2 + \text{NaOH} \\
2 \text{HNO}_2 & \longrightarrow \text{N}_2\text{O}_3 + \text{H}_2\text{O} \\
\text{N}_2\text{O}_3 & \longrightarrow \text{N}_2\text{O} + \text{O}_2 \\
\text{Rh} + \text{O}_2 & \longrightarrow \text{RhO}_2
\end{align*}
\]

The first step is favored in THF more than in alcohol because NaOH is not very soluble in THF. If the first step in reaction (34) proceeds according to the reaction condition, then the next steps are likely to occur and produce an oxygen adduct. However, other possible sources of the dioxygen should not be excluded such as oxygen impurity in the N₂ gas cylinder or the oxidation of RhCl(Cyttp) by Rh(NO₂)(Cyttp) as an oxidizing agent. The production of the RhCl(Cyttp)·O₂ adduct from the above reaction mixture, even with the use of an oxygen scavenger column to purify the N₂ gas, eliminates the question of contaminated N₂. If the pure Rh(NO₂)(Cyttp) reacts with RhCl(Cyttp) and gives rise to a formation of the Rh-O₂ adduct, then the oxidation of RhCl(Cyttp) by nitro complex would be confirmed. A
Figure 66. $^{31}p$(H)-NMR spectrum of RhCl(ttp)·O$_2$ (36.43 MHz).
Figure 67. $^{31}P\left(^1H\right)$-NMR spectrum of RhI(ttp)$_2$O$_2$ (36.43 MHz).
Figure 68. (a) $^{31}$P($^1$H)-NMR spectrum of pure RhCl(Cyttp) at RT.
(b) spectrum of mixture, RhCl(Cyttp)/RhCl(Cyttp)•O$_2$ at RT.
(c) spectrum of the mixture at 80°C in situ (36.43 MHz).
<table>
<thead>
<tr>
<th></th>
<th>$\delta P_1$</th>
<th>$\delta P_2$</th>
<th>$J_{P_1P_2}$</th>
<th>$J_{Rh,P_1}$</th>
<th>$J_{Rh,P_2}$</th>
<th>$\nu_{O-O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RhCl(Cyttp)·O₂</td>
<td>21.9</td>
<td>2.30</td>
<td>-33.0</td>
<td>139.2</td>
<td>87.9</td>
<td>850</td>
</tr>
<tr>
<td>RhI(Cyttp)·O₂</td>
<td>16.8</td>
<td>-4.33</td>
<td>-31.8</td>
<td>109.9</td>
<td>90.3</td>
<td>855</td>
</tr>
<tr>
<td>RhCl(ttp)·O₂</td>
<td>15.6</td>
<td>7.59</td>
<td>-47.6</td>
<td>134.3</td>
<td>92.1</td>
<td>854</td>
</tr>
<tr>
<td>RhI(ttp)·O₂</td>
<td>14.5</td>
<td>-3.25</td>
<td>-36.6</td>
<td>117.0</td>
<td>109.4</td>
<td>858</td>
</tr>
</tbody>
</table>

$^aP_1$ = central phosphorus; $P_2$ = terminal phosphorus atoms.
comprehensive understanding of the mechanism from the available data is limited at this point.

The RhI(Cyttp) was synthesized by the author from the reaction mixture of [RhI(COD)]₂ and Cyttp ligand. The compound is air-sensitive, but it is stable enough to isolate and handle for spectroscopic characterization. However, RhI(ttp) was very air-sensitive and the RhI(ttp)•O₂ was isolated, whereas RhCl(ttp) is quite stable in the solid state for a long period of time. The infrared spectra of RhCl(ttp)•O₂ and RhI(ttp)•O₂ give O₂ stretching frequencies at ~ 854 - 858 cm⁻¹. The ³¹P{¹H}-NMR spectrum of RhI(ttp)•O₂ has parameters characteristic of a Rh(III) species (Fig. 67); the spectral data of the Rh•O₂ adducts with both Cyttp or ttp ligands are compared in Table 21.

Transfer of oxygen atoms from the RhX(Cyttp)•O₂ (X = I,Cl) to the phosphine ligands occurs when the solution of these adducts are heated. This reaction was followed by ³¹P{¹H}-NMR (Fig. 68); the AB₂X pattern of RhCl(Cyttp)•O₂ at room temperature is replaced by the spectrum of RhCl(Cyttp) and some phosphine oxides at 80°C in toluene. In order to transfer oxygen atoms from the metal coordination sphere to the ligand, momentary dissociation of one of the phosphino groups are implied at the elevated temperature, followed by the insertion of O₂ between the Rh-P bond.

Insertion of SnCl₂ into a metal halide bond, which produces M-SnCl₂X complexes (where M = Pd,Pt,Rh,Ir, and
where \( X = \text{Cl,Br}, \) has been reported\(^{90,137,138}\) The author has found that the analogous reaction of anhydrous \( \text{SnCl}_2 \) and \( \text{RhCl(CyttP)} \) is extremely moisture and air-sensitive. When wet \( \text{CH}_2\text{Cl}_2 \) was used, a lime green solid was isolated; the solid gives a Rh-H absorption at 2100 cm\(^{-1}\) in the infrared spectrum. When dried \( \text{CH}_2\text{Cl}_2 \) was used, a dark emerald-green complex was isolated; this solid was barely soluble in \( \text{CH}_2\text{Cl}_2 \). The room temperature \(^{31}\text{P}(^1\text{H})\)-NMR spectrum shows three sets of \( \text{AB}_2\text{X} \) patterns (Table 19, Fig. 69). One of the three isomers could be a Rh(I) planar complex with \( \text{SnCl}_3^- \) as ligand (i.e., C-1); the other two isomers could be Rh(I) square pyramidal with \( \text{SnCl}_2 \) being syn-or anti-to the orientation of the central phenyl group (i.e., C-2 and C-3, respectively).

![Chemical Structures](image)

The elemental analysis confirms a composition consistent with \( \text{Rh(SnCl}_3)(\text{CyttP}) \); hence the above three possibilities are envisioned. The \(^{31}\text{P}-^{119}\text{Sn} \) couplings were not observed in the \(^{31}\text{P}(^1\text{H})\)-NMR at room temperature, not only because of the low solubility of the complex, but also due to the presence of isomers shown above. In the case of solid
Rh(SnCl$_3$)(NBD)(PETPh$_2$)$_2$\textsuperscript{137} the coordinated SnCl$_3$ was indicated by two absorptions in the infrared spectrum at 300 and 350 cm$^{-1}$, which was attributed to the Sn-Cl stretching modes. The infrared spectrum of Rh(SnCl$_3$)(Cytpp), however, had a very broad and strong band centered at 250 cm$^{-1}$ due to the KBr plate, hence the Sn-Cl stretching frequency was not recorded (Fig. 70). The $^{31}$P($^1$H)-NMR spectrum of Rh(SnCl$_3$)(NBD)(PETPh$_2$)$_2$ was recorded at -20°C in CH$_2$Cl$_2$; the two bond cis-coupling between $^{119}$Sn and $^{31}$P was 149 Hz and the $^{103}$Rh-$^{31}$P coupling was 131 Hz. The Rh(SnBr$_2$Cl)(NBD)(PETPh$_2$)$_2$ complex exhibited the presence of isomers in the $^{31}$P-NMR spectrum; a halogen scrambling mechanism was speculated as follows:

\[
\begin{align*}
\text{Rh-Cl} + \text{SnBr}_2 & \rightleftharpoons \text{Rh-SnClBr}_2 = \text{Rh-Br} + \text{SnClBr} \\
\text{Rh-Br} + \text{SnBr}_2 & \rightleftharpoons \text{Rh-SnBr}_3 \\
\text{Rh-Cl} + \text{SnClBr}_2 & \rightleftharpoons \text{Rh-SnCl}_2\text{Br} = \text{Rh-Br} + \text{SnCl}_2 \\
\text{Rh Cl} + \text{SnCl}_2 & \rightleftharpoons \text{Rh SnCl}_3
\end{align*}
\]

Pregosin and Sze\textsuperscript{138} observed a mixture of cis and trans isomers for PtCl(SnCl$_3$)(PPh$_3$)$_2$ in CH$_2$Cl$_2$ solution at -50°C by $^{31}$P-NMR spectra; whereas the isolated solid contained only the trans isomer. They also found that both cis- and trans-PtCl$_2$(PR$_3$)$_2$ complexes reacted with SnCl$_2$ to give only
Figure 69. $^{31}\text{P}^{({}^1\text{H})}$-NMR spectrum of Rh(SnCl$_3$)(Cyttpp) (121.470 MHz).
Figure 70. Infrared spectrum of Rh(SnCl₃)(Cytpp): 1400-400 cm⁻¹ (Nujol mull).
the trans-PtCl(SnCl₃)(PR₃)$_2$ complex in the solid state. They suggested that rapid isomerization from a cis to a trans structure might occur; however, a 5-coordinate intermediate cis-PtCl₂(SnCl₂)(PR₃)$_2$ was not excluded.

From the above data of Garralda\textsuperscript{137} and Pregosin,\textsuperscript{138} the M-SnCl$_3$ bond exhibited a dynamic behavior in solution; even at low temperature the SnCl$_2$ group may dissociate and break the M-Sn bond resulting in a structural rearrangement or a halogen exchange. Thus, the presence of structural isomers of Rh(SnCl$_3$)(Cyttp) in solution at room temperature can be explained by a possible dissociation of SnCl$_2$ and formation of a 5-coordinate species:

$$\text{Rh(SnCl}_3\text{)(Cyttp)} \rightleftharpoons \text{RhCl(Cyttp)(SnCl}_2\text{)}$$  \hspace{1cm} (36)

However, whether the isolated solid is one pure isomer or not cannot be concluded without an X-ray structure.

The cationic species, RhCyttp(Y)$^+$, are prepared by using Tl$^+$ or Na$^+$ salts for metathesis and addition of a fourth neutral ligand:

$$\text{RhCl(Cyttp)} + Y + \text{Tl}(\text{Na}^+) \longrightarrow \text{Rh(Cyttp)Y}^+ + \text{TlCl}$$  \hspace{1cm} (37)

$Y =$ CO, P(OMe)$_3$, PF$_3$, PPh$_2$H

Although TlCl precipitation would drive the reaction in a polar solvent, it is not clear at this time whether the
proposed intermediate Rh(Cyttp)(Solv)$^+$ really exists. The $^{31}$P$^1$H-NMR spectrum was employed to follow the generation of Rh(Cyttp)(Solv)$^+$ in THF; no change in $^{31}$P$^1$H-NMR spectra was observed except that resonances of phosphine oxides appeared. However, as soon as the fourth ligand is added to the mixture of RhCl(Cyttp) and Ti$^+$ (Na$^+$), a heavy white precipitate, i.e., TiCl (or NaCl), precipitated.

The complexes [Rh(CO)(Cytttp)]AsF$_6$ and [Rh(CO)\textsubscript{2}(Cytttp)]BF$_4$ are prepared by treating RhCl(CO)(Cytttp), which can be generated in situ, with the respective Na salts. Both compounds have the same CO stretching frequencies and the $^{31}$P$^1$H-NMR data: $\nu_{CO} = 1990$ cm$^{-1}$; $\delta P_1 = -6.88$ ppm; $\delta P_2 = 15.4$ ppm; $J_{P_1-P_2} = -47.6$ Hz; $J_{Rh-P_1} = 118$ Hz; $J_{Rh-P_2} = 109.9$ Hz. A strong infrared band at 700 cm$^{-1}$ corresponds to uncoordinated AsF$_6$; similarly, strong and broad absorptions centered at 1070 cm$^{-1}$ are due to anion BF$_4$. The bending mode ionic BF$_4$ occurs at 550 cm$^{-1}$. The mass spectra of the cation Rh(CO)(Cytttp)$^+$ were obtained by the FAB technique. The cation parent peak appears at 717 and the next ion shows up at 680, which is due to the loss of CO.

The orange crystals of [Rh(Cyttp)(P(OMe)$_3$)]AsF$_6$ were prepared according to reaction (37) with NaAsF$_6$ in MeOH; to avoid a detrimental transesterification reaction, methanol was used as solvent. J. Letts also isolated the BF$_4^-$ analog of this salt. The $^{31}$P$^1$H-NMR data are identical for both salts; it gives a first order AB$_2$MX pattern with 30 lines.
The chemical shift of coordinated P(OMe)₃ is downfield at 126 ppm and does not complicate the triphosphine resonances (Fig. 71). All of the relevant phosphorus chemical shifts and coupling constants are listed in Table 21. The infrared spectrum of [Rh(Cyttp)(P(OMe)₃)AsF₆] shows a strong and broad P-O bond stretch at ca. 1050 cm⁻¹, the symmetric P-O-C stretch at 800 cm⁻¹, and a strong vibration at 700 cm⁻¹ for non-coordinated AsF₆.

The reaction of PF₃ with RhCl(Cyttp) was attempted in order to synthesize Rh(Cyttp)(PF₃)⁺. However, PF₃ in acetone, MeOH and THF reacted with the solvents in the presence of the metal complex. J. Letts also attempted this reaction in EtOH and concluded that a nucleophilic substitution of one of the fluorine atoms in PF₃ by ethoxide occurred. In fact, PX₃ (X=I, Br) is used for halogenating primary alcohols to alkyl halides.¹⁴⁰ The PF₃ also can react with trace amounts of H₂O in the solvent to give HF. The solid which was isolated from the reaction mixture in THF showed an infrared absorption at 2110 cm⁻¹; this peak is assigned to a Rh-H stretching frequency. The source of this hydride may be ascribed to HF, which was generated from hydrolysis of PF₃ by H₂O; HF then oxidatively added to the metal. Other precedents for substitution of PF₃ by alcohol are:¹⁴¹,¹⁴²

\[
\text{Co(NO)(PF₃)₃ + MeOH} \rightarrow \text{Co(NO)(PF₃)₂(MeOPF₂)} \quad (38)
\]
The $^{31}$P-$^1$H-NMR spectrum of the [Rh(Cyttp)(MeOPF$_2$)]AsF$_6$ has a similar pattern to that of [Rh(Cyttp)(EtOPF$_2$)]BF$_4$, except the chemical shift of the central phosphine is shifted to higher field by 6.6 ppm (Fig. 72); the shift may be due to the fact that PF$_2$OR is trans to the central phosphine. In general, $P_1$ (central) is more sensitive to the trans ligand (the fourth ligand) than $P_2$ (terminal) because of the strong trans influence of phosphorus ligands. The infrared spectrum of the compound shows the usual strong band for ionic AsF$_6^-$ at 700 cm$^{-1}$ and three new strong bands at 761, 780 and 812 cm$^{-1}$; two of which belong to the symmetric and asymmetric P-F stretching frequency and one to the P-O-C symmetric stretch. P. Blum assigned frequencies for the similar complex, [Rh(PF$_2$(t-Bu))(ttp)]AsF$_6$, which agreed with the literature value range; they were 823 cm$^{-1}$ and 793 cm$^{-1}$. Thus, the two bands at 812 and 780 cm$^{-1}$ may indicate the P-F asymmetric and symmetric stretching vibrations, respectively. The P-O vibration is located at ca. 1050 cm$^{-1}$ and the P-O-C symmetric stretching frequencies is observed at 761 cm$^{-1}$.

The diphenylphosphino complex, [Rh(Cyttp)(PPh$_2$H)]AsF$_6$ is isolated when HAsF$_6$ is added to the reaction mixture of RhCl(Cyttp), TlAsF$_6$ and PPh$_2$H in THF. The infrared P-H stretching frequency of PPh$_2$H appears at 2320 cm$^{-1}$. Free
Figure 71. $^{31}$P($^1$H)-NMR spectrum of $\text{[Rh(Cytpp)(P(OMe)_3)]AsF}_6$ (36.43 MHz).
Figure 72. $^{31}$P($^1$H)-NMR spectrum of [Rh(Cyttp)(MeOPF$_2$)]AsF$_6$ (36.43 MHz).
Figure 73. $^{31}P\{^1H\}$-NMR spectrum of [Rh(Cyttp)(PPh$_2$H)]AsF$_6$ (121.470 MHz): computer simulated transitions are listed in the Appendix.
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta P_1$</th>
<th>$\delta P_2$</th>
<th>$\delta P_3$</th>
<th>$2J_{P_1P_2}$</th>
<th>$2J_{P_2P_3}$</th>
<th>$2J_{P_1P_3}$</th>
<th>$1J_{Rh,P_1}$</th>
<th>$1J_{Rh,P_2}$</th>
<th>$1J_{Rh,P_3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(CO)(ttp)$^b$</td>
<td>-12.0</td>
<td>6.5</td>
<td>-52.2</td>
<td></td>
<td></td>
<td></td>
<td>113.3</td>
<td>114.3</td>
<td></td>
</tr>
<tr>
<td>Rh(CO)(Cyttp)$^b$</td>
<td>-6.88</td>
<td>15.4</td>
<td>-47.6</td>
<td></td>
<td></td>
<td></td>
<td>118.4</td>
<td>109.0</td>
<td></td>
</tr>
<tr>
<td>Rh(Cyttp)(PPh$_2$H)$^c$</td>
<td>1.37</td>
<td>9.12</td>
<td>-1.95</td>
<td>-48.95</td>
<td>-43.68</td>
<td>256.3</td>
<td>133.9</td>
<td>116.2</td>
<td>131.3</td>
</tr>
<tr>
<td>Rh(Cyttp)(P(OMe)$_3$)$^+$</td>
<td>-6.11</td>
<td>15.3</td>
<td>126.0</td>
<td>-51.3</td>
<td>-50.0</td>
<td>422.4</td>
<td>123.3</td>
<td>119.6</td>
<td>234.4</td>
</tr>
<tr>
<td>Rh(Cyttp)(MeOPF$_2$)$^d$</td>
<td>-15.3</td>
<td>16.1</td>
<td>129.3</td>
<td>-48.8</td>
<td>-51.3</td>
<td>448.8</td>
<td>129.4</td>
<td>109.9</td>
<td>277.5</td>
</tr>
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</table>

$^a$ $P_1$ = central phosphorus; $P_2$ = terminal phosphorus; $P_3$ = monodentate

$^b$ References 3, 101

$^c$ Parameters are confirmed by computer simulation (appendix)

$^d$ $J_{P_1P_2}$, $F$ = 40.3; $J_{P_2P_3}$, $F$ = 6.0; $J_{P_3P_3}$, $F$ = 1264 Hz.
PPh₂H has a resonance at -45 ppm in the ³¹P{¹H}-NMR spectrum; however, when coordinated to the metal, a significant downfield shift is observed due to the deshielding effect of the positive metal center. A first order ³¹P{¹H}-NMR spectrum with an AB₂CX pattern is obtained on the Bruker 300 MHz instrument (Fig. 73); however, on the Bruker 90 MHz instrument the spectrum is second order. The phosphorus parameters, which have been checked by computer simulation, are listed in Table 22.

In order to extend the chemistry discussed above to platinum, the platinum-Cyttp complexes were prepared. T.J. Mazanec had previously studied the ³¹P{¹H}-NMR spectrum of Pt(Me)₂(Cyttp)¹³⁵ as a test molecule for dissociation of the chelating ligand and fluxional behavior of the resulting complex, as in the case of Pt(Me)₂(ttp).¹⁵⁶ In the complex Pt(Me)₂(Cyttp) coordination of Cyttp to Pt metal involved only two phosphorus atoms (i.e., the central phosphorus and one of the terminal phosphorus groups of Cyttp) at all temperatures from 230 K to 360 K.

The complexes [PtCl(Cyttp)]Cl and [PtCl(Cyttp)]NO₃ contain a completely chelated Cyttp ligand, which gives 4-coordinated planar Pt(II) complexes (Fig. 74). The ³¹P{¹H}-NMR parameters of ttp- and Cyttp-Pt(II) complexes are compared in Table 23. Infrared bands which can be assigned to an ionic NO₃⁻ are observed at 1260, 1050, and 800 cm⁻¹ for the complex [PtCl(Cyttp)]NO₃.
Figure 74. $^{31}p(\text{H})$-NMR spectrum of [PtCl(Cyttp)]Cl (36.43 MHz).
### TABLE 23

Phosphorus-31 NMR Parameters Of Pt(II)-ttp And Cytotp Complexes $^a$

<table>
<thead>
<tr>
<th></th>
<th>$P_1$</th>
<th>$P_2$</th>
<th>$J_{P_1P_2}$</th>
<th>$J_{Pt,P_1}$</th>
<th>$J_{Pt,P_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PtCl(Cytotp)]Cl</td>
<td>-14.5</td>
<td>1.80</td>
<td>24.4</td>
<td>3234</td>
<td>2106</td>
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<tr>
<td>[PtCl(ttp)]Cl</td>
<td>-20.7</td>
<td>-3.9</td>
<td>27.0</td>
<td>3134</td>
<td>2229</td>
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</tbody>
</table>

$^aP_1$ = central phosphorus; $P_2$ = terminal phosphorus.
The four-coordinate rhodium complexes are employed to study the interaction with small gaseous molecules such as SO\textsubscript{2} or CO. An oxygen transfer reaction is expected from the reaction of a NO\textsubscript{2}\textsuperscript{−} complex with CO to give either an isocyanate or a nitroso/CO\textsubscript{2} metal complex as follows:\textsuperscript{143,144}

\[
\text{Ar-NO}_2 + \text{CO} \rightarrow \text{Ar-NCO} + \text{CO}_2 \quad (40)
\]

\[
\text{Ni(NO}_2)_2(\text{PET}_3)_2 + \text{CO} \rightarrow \text{Ni(NO}_2)(\text{NO})(\text{PET}_3)_2 + \text{CO}_2 \quad (41)
\]

The Rh(NO\textsubscript{2})(Cyttp) complex reacts with CO and yields two different AB\textsubscript{2}X patterns in the \textsuperscript{31}P{\textsuperscript{1}H}-NMR spectrum (Fig. 76). The infrared spectrum shows characteristic bands for NO\textsuperscript{+}, CO, CO\textsubscript{3}\textsuperscript{2−}, and ONO\textsuperscript{−} (Fig. 75); the CO stretching frequency appears at 1980 cm\textsuperscript{−1}, the NO\textsuperscript{+} at 1873 cm\textsuperscript{−1}, the carbonato at 1660, 1640 (shoulder at 1585), 1040, 735 and 620 cm\textsuperscript{−1}, and ONO at 1440 and 1040 cm\textsuperscript{−1}. The CO\textsubscript{3}\textsuperscript{2−} and ONO\textsuperscript{−} absorptions may be explained by the following mechanism. The Rh(NO\textsubscript{2})(Cyttp) reacts with CO to give an intermediate [Rh(NO\textsubscript{2})(CO)(Cyttp)], which then either transfers an oxygen to give [Rh(Cyttp)(NO)(CO\textsubscript{2})] or isomerizes to Rh(ONO)(Cyttp)(CO). The [Rh(Cyttp)(NO)(CO\textsubscript{2})] undergoes a disproportionation instead of losing CO\textsubscript{2} and results in a mixture of Rh(CO\textsubscript{3})(Cyttp)(NO) (90\%) and Rh(NO\textsubscript{2})(CO)(Cyttp) (10\%).
Figure 75. Infrared spectrum of the solid isolated from the reaction of Rh(NO$_2$)(Cytp) and CO (Nujol mull).
Figure 76. $^{31}\text{P}^1\text{H}$-NMR spectrum of the solid isolated from the reaction of Rh(NO$_2$)(Cytpp) and CO (36.43 MHz).
Since the $\text{NO}^+$ ligand is comparatively a strong trans influence group, the $^{31}\text{P}^{1\text{H}}$-NMR spectrum gives a reversed $\text{AB}_2\text{X}$ pattern with the A portion of the spectrum higher field than the B portion (Table 24). The carbonato bonding mode of $\text{Rh(CO)}_3(\text{Cyttp})(\text{NO})$ can be bidentate as in the case of $\text{Ru(CO)}_3(\text{CO})(\text{Cyttp})$, where the $\text{CO}_3^{2-}$ peaks appear at 1665 and 1620 cm$^{-1}$ in the infrared spectrum.$^8$ a The Os($\text{CO}_3$)Cl(NO)(PPh$_3$)$_2$ complex is known to have a bidentate carbonato structure with infrared absorptions at 1720, 1030, 760, and 662 cm$^{-1}$. Therefore structure C-4 is assigned for the major product of this reaction:

The other minor product has a regular $\text{AB}_2\text{X}$ pattern with $\text{Rh(I)}$ parameters similar to the complex $\text{Rh(NO}_2)(\text{Cyttp})$ with
only a slight change in $J_{\text{Rh-P$_1$}}$ and $\delta_{P_1}$. The $J_{\text{P$_1$-P$_2$}}$ and $\delta_{P_2}$ values are reproducible within the limit of the $^{31}P\{^1H\}$-NMR. The CO stretch of the minor product is at 1980 cm$^{-1}$ and symmetric ONO band is located at 1040 cm$^{-1}$. This compound, Rh(ONO)(Cytpp)(CO), may actually be an intermediate to the formation of the major product. Very recently, a NO$_2$-ONO isomerization in the reaction of the Ni(NO$_2$)$_2$L$_2$ ($L = \text{PMe}_3$, PET$_3$, PCy$_3$, $\frac{1}{2}$ dppe, $\frac{1}{2}$ dppp, etc.) with CO was reported by R. Feltham and coworkers; the Ni$_2$(NO$_2$)(ONO)(CO) was proposed as an active intermediate.

The simple adducts of SO$_2$ on the rhodium metal in square planar RhX(Cytpp) complexes ($X = \text{NCS, I, Cl}$) were quite straightforward$^6$ compared to those of [Rh(Cytpp)Y]AsF$_6$ where Y is a strong π-bonding ligand or a neutral ligand ($Y = \text{CO, P(OMe)$_3$, PF}_2(\text{OME}), \text{PPh}_2\text{H}$). For example, [Rh(CO)(Cytpp)]AsF$_6$ reacts with SO$_2$ and yields orange crystals of [Rh(CO)(Cytpp)(SO$_2$)]AsF$_6$. However, when the volume of the mother liquor was reduced under reduced pressure (~0.2 torr) in an attempt to increase the yield, the solution turned yellow and only the parent compound was observed in the $^{31}P\{^1H\}$-NMR; these observations imply the loss of SO$_2$ at reduced pressure. An excess of SO$_2$ was bubbled again into this yellow solution, and an orange-yellow solid was isolated from the resulting reaction mixture. The infrared and $^{31}P\{^1H\}$-NMR spectra of the solid are indicative of a mixture of Rh(CO)(Cytpp)(SO$_2$)$^+$ and Rh(CO)(Cytpp)$^+$; such a
<table>
<thead>
<tr>
<th>RHX(L) (Z)</th>
<th>ΔP₁</th>
<th>ΔP₂</th>
<th>2J₁P₁P₂</th>
<th>1J₁Rh,P₁</th>
<th>1J₁Rh,P₂</th>
<th>νCD</th>
<th>νSO₂</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>RhCl(Cyttp) (SO₂)</td>
<td>18.8</td>
<td>3.2</td>
<td>-36.0</td>
<td>156.0</td>
<td>107.0</td>
<td>1168, 1030</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>RhI(Cyttp) (SO₂)</td>
<td>11.6</td>
<td>-0.37</td>
<td>-36.1</td>
<td>157.5</td>
<td>107.4</td>
<td>1160, 1025</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Rh(NCS)(Cyttp) (SO₂)</td>
<td>17.2</td>
<td>6.5</td>
<td>-39.1</td>
<td>141.6</td>
<td>109.9</td>
<td>1170, 1030</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>RhI(Cyttp) (CO)</td>
<td>-7.6</td>
<td>15.3</td>
<td>-47.7</td>
<td>118.4</td>
<td>107.6</td>
<td>1940</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>RhCl(Cyttp) (CO)</td>
<td>-14.5</td>
<td>23.3</td>
<td>-50.8</td>
<td>119.0</td>
<td>100.1</td>
<td>1910</td>
<td>6</td>
<td></td>
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<tr>
<td>RhCl(ttp) (CO)</td>
<td>-14.3</td>
<td>13.6</td>
<td>-52.2</td>
<td>110.5</td>
<td>112.3</td>
<td>.</td>
<td>3</td>
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<tr>
<td>Rh(CO₃)(NO)(Cyttp)</td>
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<td>15.8</td>
<td>-47.1</td>
<td>117.0</td>
<td>109.4</td>
<td>ν(CO₃) 1660, 1640 this work v(NO) 1873</td>
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<tr>
<td>Rh(NO₂)(CO)(Cyttp)</td>
<td>20.9</td>
<td>7.44</td>
<td>-49.9</td>
<td>145.3</td>
<td>136.6</td>
<td>1980 v(NO) 1040 this work</td>
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<table>
<thead>
<tr>
<th>RH(L)(Y)(Z)</th>
<th>ΔP₁</th>
<th>ΔP₂</th>
<th>2J₁P₁P₂</th>
<th>1J₁Rh,P₁</th>
<th>1J₁Rh,P₂</th>
<th>νCD</th>
<th>νSO₂</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(CO)(Cyttp) (SO₂)⁺</td>
<td>-1.63</td>
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<td>-40.3</td>
<td>119.0</td>
<td>101.3</td>
<td>2050</td>
<td>1215, 1056 this work</td>
<td></td>
</tr>
<tr>
<td>Rh(CO)(ttp)(SO₂)⁺</td>
<td>-11.3</td>
<td>3.8</td>
<td>-47.2</td>
<td>113.6</td>
<td>113.6</td>
<td>2088</td>
<td>1229, 1220 3</td>
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</tr>
</tbody>
</table>

aP₁ = central phosphorus; P₂ = terminal phosphorus

bX= anion ligand; Y= neutral ligand; Z= gaseous molecule; L= Cyttp or ttp.
mixture suggests the reversibility of the metal-SO$_2$ bonding. The $^{31}$P$\{^1$H$\}$-NMR spectrum (Fig. 78) of the orange crystals, [Rh(CO)(Cytp)(SO$_2$)]AsF$_6$, has a smaller $J_{P_1-P_2}$ and $J_{Rh-P_2}$ values than those of the parent compound, but it gives a similar Rh-P$^1$ coupling. The $^{31}$P$\{^1$H$\}$-NMR parameters and infrared absorptions of this complex compare favorably with [Rh(CO)(SO$_2$)(tt)p]AsF$_6$ in Table 24. Addition of SO$_2$ to the metal does not seem to alter dramatically the bond properties of the Rh-P's as reflected by the $^{31}$P-NMR. The carbonyl stretching frequency in infrared spectrum (Fig. 77) is at 2050 cm$^{-1}$ which is 60 cm$^{-1}$ higher in energy than that of the starting compound; it can be caused by the addition of SO$_2$, which withdraws electron density from the rhodium atom so that the degree of π-bonding between rhodium and carbonyl is decreased in the SO$_2$-adduct. The molecular structure determination of [Rh(CO)(SO$_2$)(tt)p]AsF$_6$ indicates the compound to be square pyramidal with a bent sulfur dioxide in the apical position.$^{147}$ In general, if the metal (e.g., d$^8$, Ir$^I$, Rh$^I$, Pt$^0$)-SO$_2$ adduct exhibits the bent geometry, the S=O infrared stretching frequencies occur near 1200 and 1050 cm$^{-1}$, the SO$_2$ is labile and complexes containing sulfate are formed upon exposure to O$_2$. On the other hand, if the metal (e.g., d$^6$, Mn$^I$, Ru$^{II}$)-SO$_2$ group is coplanar, the S=O stretching frequencies appear near 1300 and 1100 cm$^{-1}$, the SO$_2$ group is not labile and sulfates are not formed upon air-oxidation.$^{149}$ The S=O stretching
Figure 77. Infrared spectrum of [Rh(CO)(CyttP)(SO$_2$)]AsF$_6$ (Nujol mull).
Figure 78. $^{31}\text{P}^{1\text{H}}$-NMR spectrum of [Rh(CO)(Cyttpp)(SO$_2$)]AsF$_6$ (36.43 MHz).
frequencies (particularly the asymmetric stretch) of [Rh(CO)(Cyttpp)(SO\(_2\))]\(^{+}\) appear at higher energies in this complex than in the general case of a square pyramidal SO\(_2\)-adduct (Table 24); this can be due to the decreased basicity of [Rh(CO)(Cyttpp)]\(^{+}\) as compared to the other square-planar complexes. Thus, the sulfur dioxide and carbonyl ligands are competing with each other for electron density from the metal \(d_{z^2}\)-orbital. A very weak bond between metal to SO\(_2\) was demonstrated in the cases of RhCl(PPh\(_3\))\(_2\)(CO)(SO\(_2\))\(^{150}\) and IrCl(PPh\(_3\))\(_2\)(CO)(SO\(_2\)){151}\) The Ir-SO\(_2\) adduct dissociates SO\(_2\) in solution in the absence of excess SO\(_2\) and when heated above 100\(^\circ\)C in the solid state.\(^{150}\) The crystal structures of these compounds showed that they are tetragonal pyramid with bent M-SO\(_2\) groups. The iridium metal is only 0.21 Å above the plane toward the SO\(_2\) and Ir-S bond length is very long, 2.49Å; the rhodium is only 0.24Å above the plane and Rh-S bond is also very large, 2.450Å. The range of Rh-pyramidal SO\(_2\) distances is 2.368(5)-2.450(2)Å in previously reported structures,\(^{147,151,152}\) and the distance of the metal above the approximate plane formed by the four basal ligands in a tetragonal pyramid generally is 0.4-0.5Å.\(^3\) Similar features were observed from the X-ray structure of the [Rh(CO)(SO\(_2\))(ttp)]AsF\(_6\). The Rh-S distance is 2.433(6)Å and the rhodium in only 0.26Å above the plane.\(^{147}\) In fact, the metal atom in [Rh(CO)(SO\(_2\))(ttp)]\(^{+}\) lies much closer to the plane of the four basal ligands than in
RhCl(SO$_2$)(ttp)$^{147}$, RhCl(NO)(ttp)$^+,153$ or even RhCl(ttp)$^{153}$ This planarity of the carbonyl complex may be a consequence of the Π-acceptor CO, which prefers the metal in the basal plane so as to maximize Π*-dΠ back-bonding. In addition, if the basal coordination becomes more planar, the d-orbitals are perturbed in such a way as to destabilize bonding to the axial ligand SO$_2$, and consequently the M-SO$_2$ bond should be weakened. The [Rh(CO)(SO$_2$)(ttp)]$^+$ has CO stretching frequency at 2088 cm$^{-1}$, which is 72 cm$^{-1}$ higher than the [Rh(CO)(ttp)]$^+$; whereas, the [Rh(CO)(cyttpp)(SO$_2$)]$^+$ shows CO band at 2050 cm$^{-1}$, which is only 60 cm$^{-1}$ higher than the [Rh(CO)(Cyttp)]$^+$. This difference may indicate that the [Rh(CO)(Cyttp)(SO$_2$)]$^+$ has better Π*-dΠ back-bonding than the corresponding ttp analog, which eventually would give a shorter Rh to the basal plane distance if P.G. Eller and R.R. Ryan's argument is still valid. An X-ray structure determination of this orange crystal [Rh(CO)(Cyttp)(SO$_2$)AsF$_6$] will be interesting and valuable to support the observation of reversible Rh-SO$_2$ bonds in [Rh(CO)(Cyttp)(SO$_2$)]$^+$.

**Conclusion**

The complexes Rh(NO$_2$)(Cyttp) and Rh(SnCl$_3$)(Cyttp) are prepared in this study to complete the series of RhX(Cyttp) complexes (X = Cl, I, NCS, N$_3$, CN, NO$_2$, SnCl$_3$). The $^{1}J_{Rh,P_1}$ values decrease in a series Cl>NCS>I>NO$_2$>N$_3$>SnCl$_3$>CN, which
is approximately same order of degree in trans influence of the anionic ligands. The coupling constants, $2J_{P_1P_2}$, $1J_{Rh,P_1}$ and $1J_{Rh,P_2}$ are in general smaller for Cytttp complexes than those of ttp analogs.

A series of planar ionic Rh(I) compounds of the type $[\text{Rh(Cytttp)}Y]\text{AsF}_6$ ($Y = \text{CO}, \text{P(OMe}_3\), \text{PF}_2(\text{OMe}), \text{PPh}_2\text{H}$) are isolated. The ligands Y have strong trans influence and AB$_2$X NMR patterns with A portion being higher than B are observed. Trans phosphorus coupling ranges from 250 to 450 Hz; trans phosphine-phosphite couplings are greater than the trans phosphine-phosphine couplings. Similar results have been reported by P. Blum for the complexes $\text{Rh(ttp)}Y^+$ ($Y = \text{CO}, \text{PF}_2\text{tBu}, \text{PET}_3, \text{P(OMe)}_3$).

The Cytttp complexes of Rh(I), Ir(I), Pt(II), Ru(II) are compared in Table 25. The chemical shifts of central phosphorus, $P_1$ are more upfield than those of terminal phosphorus, $P_2$, except in the case of $\text{RhCl(Cytttp)}$. The $2J_{P_1P_2}$ values decrease in the order of $\text{Rh(I)}>\text{Ru(II)}>\text{Ir(I)}>\text{Pt(II)}$.

The oxygen adducts of $\text{RhX(Cytttp)•O}_2$ or $\text{RhX(ttp)•O}_2$ ($X = \text{Cl, I}$) results in similar $^{31}$P-NMR parameters ($1J_{Rh,P_1}$, $1J_{Rh,P_2}$) and infrared data ($\nu_{O_2}$). These O$_2$-adducts can be converted to their original compounds $\text{RhX(Cytttp)}$ or $\text{RhX(ttp)}$ and phosphine oxides at elevated temperatures. An oxygen transfer is demonstrated for the complex, $\text{Rh(NO}_2)(\text{Cytttp})$ by
### TABLE 25

Comparisons Of Phosphorus-31 NMR Parameters Of
Rh(I), Ir(I), Pt(II), Ru(II) Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \delta P_1 )</th>
<th>( \delta P_2 )</th>
<th>( ^2J_{P_1P_2} )</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuCl(_2)(Cyttwp)</td>
<td>-5.6</td>
<td>15.4</td>
<td>38</td>
<td>135</td>
</tr>
<tr>
<td>RhCl(Cyttwp)</td>
<td>20.9</td>
<td>9.1</td>
<td>49.0</td>
<td>this work</td>
</tr>
<tr>
<td>IrCl(Cyttwp)</td>
<td>-16.8</td>
<td>1.98</td>
<td>30.5</td>
<td>this work</td>
</tr>
<tr>
<td>[PtCl(Cyttwp)]Cl</td>
<td>-14.5</td>
<td>1.80</td>
<td>24.4</td>
<td>this work</td>
</tr>
<tr>
<td>RuCl(_2)(PPh(_3))(_3)</td>
<td>75.7</td>
<td>24.1</td>
<td>30.5</td>
<td>157</td>
</tr>
<tr>
<td>RhCl(PPh(_3))(_3)</td>
<td>48.9</td>
<td>32.2</td>
<td>37.5</td>
<td>158</td>
</tr>
<tr>
<td>IrCl(PPh(_3))(_3)</td>
<td>15.3</td>
<td>22.7</td>
<td>22.3</td>
<td>29</td>
</tr>
<tr>
<td>PtCl(PPh(_3))(_3)(^+)</td>
<td>12.5</td>
<td>23.2</td>
<td>19.0</td>
<td>159</td>
</tr>
</tbody>
</table>

\(^a\) \( P_1 \) = central phosphorus; \( P_2 \) = terminal phosphorus
treat it with CO. A major product, Rh(CO$_3$)(NO)(Cytpp) from the above reaction is observed by spectroscopy.

A simple SO$_2$ adduct is produced from the reaction of [Rh(CO)(Cytpp)]AsF$_6$ and SO$_2$ as in the ttp case. No interaction between the incoming SO$_2$ and the CO is observed. In the case of RhX(CO)(Cytpp) (X = Cl, I), SO$_2$ replaces CO and forms RhX(Cytpp)(SO$_2$). The complex [Rh(CO)(Cytpp)(SO$_2$)]AsF$_6$ loses SO$_2$ under reduced pressure and generates the starting compound, which then can be recovered to the SO$_2$-adduct by treating it with additional SO$_2$. The reversibility of SO$_2$ in the complex Rh(CO)(Cytpp)(SO$_2$)$^+$ can imply that the difference in electronic and steric environment of the two ligands affects the bonding nature of SO$_2$ to rhodium. A stable [Rh(ttp)(P(OMe)$_3$)(SO$_2$)]AsF$_6$ have been isolated. However, the Cytpp analog is not isolated at room temperature, unlike from the other SO$_2$-adducts, RhX(Cytpp)•(SO$_2$) (X = Cl, I, NCS). The $\nu_{SO_2}$ stretching frequencies fall in the range of bent SO$_2$ groups for both series of SO$_2$-adducts.

The carbonyl complex, RhCl(CO)(ttp), has been isolated as pure isomer form. The RhCl(CO)(Cytpp), however, exists as two isomers, which subsequently are metamorphosed by NaBF$_4$ and result in a pure [Rh(CO)(Cytpp)]BF$_4$. The Cytpp analog, RhCl(CO)(Cytpp) is isolated as diastereomers, where CO can be either syn or anti to the central phenyl ring. The difference in steric requirement of Cytpp and ttp ligand can
decide the configuration of molecules and possibly the presence of diastereomers.

D. Rh(I) Complexes with Secondary Phosphine Ligands

The complexes \([\text{Rh(Cyttp)}\text{PPh}_2\text{H}]\text{AsF}_6\), \([\text{Rh(PPH}_2\text{H})_4]\text{AsF}_6\), and \([\text{Rh(dppp)}\text{PPh}_2\text{H}]\text{AsF}_6\) were prepared for the purpose of utilizing the compound to generate a phosphido bridge. These secondary phosphino complexes can be used to link different metal complexes; in principle, heteronuclear phosphido-bridged complexes can be synthesized by treating these complexes with appropriate bases to generate coordinated phosphide anions, which then may react with other metal complexes of the type, e.g., \([\text{M(solv)L}_1\text{L}_n]^+\) \((m = 2, 3; n = 1, 2)\).

The complex \(\text{RhCl(Cyttp)}\) was treated at room temperature with \(\text{LiPPh}_2\), which was generated in situ. The possible product could either be a phosphido-bridged dimer, \([\text{Rh(Cyttp)}\text{PPh}_2)]_2\), or a metal substituted phosphe complex, \(\text{Li[Rh(Cyttp)(PPh}_2\text{H}]_2}\). The PPh_2 resonances appear upfield as two sets of doublets of doublets of doublets at \(-30.35\) ppm and \(-33.79\) ppm in the \(^{31}\text{P}\{^1\text{H}\}-\text{NMR spectrum (Fig. 79). However, no triplet due to a symmetric Rh-P-Rh bridge is observed; hence, the product is not } [\text{Rh(Cyttp)}\text{PPh}_2)]_2\). Small cis-phosphorus couplings between chelate phosphorus \((P_1)\) and phosphido-phosphorus \((P_M)\) are observed: \(J_{P_1-P_M} = \)
9.77 Hz; $J_{P^-P^-} = 7.35$ Hz; $J_{Rh-P} = 69.58$ Hz; $J_{P_1-P_1} = 11.0$ Hz; $J_{Rh-P} = 70.2$ Hz. From the $^{31}P{^1H}$-NMR data, the two $PPh_2$-groups are non-equivalent and they are only coupled to one of the phosphorus atoms in the chelate ring. The structure D-1 is proposed on the basis of $^{31}P{^1H}$-NMR parameters.

P. Kreter also postulated a terminal phosphide in cis-Rh(dppe)(CO)$_2$(PPh$_2$); in fact similar $^{31}P$-parameters were observed: $^1J_{Rh-PPh_2} = 40.3$ Hz, cis $^2J_{P-PPh_2} = 11.0$ Hz. The cis-coupling between bridging phosphide and phosphine ligands is usually around 20 Hz. When a phosphide becomes terminal, i.e., $PPh_2$− the s-character will be decreased for Rh-PPh$_2$ bond that the $J_{Rh-PPh_2}$ and $J_{P-PPh_2}$ are smaller than the usual values.

The complex $[Rh(PPh_2H)_4]AsF_6$ has four P-H sites for reactions and this complex may be used to form a heterometal cluster. From this $^{31}P$-NMR spectral data, this complex seems to have square planar geometry: $J_{Rh-P} = 129$ Hz; $δP = 6.69$ ppm (Fig. 80).

The mixed-phosphine compound $[Rh(dppe)(PPh_2H)_2]AsF_6$ was isolated from a 1:1 mixture of $Rh(PPh_2H)_4^+$ and dppe; it was
Figure 79. (a) $^{31}$P($^1$H)-NMR spectrum of phosphido region of Li[Rh(Cytpp)(PPh$_2$)$_2$]
(b) Cytpp region (36.43 MHz).
Figure 80. $^{31}P\{^1H\}$-NMR spectrum of $[\text{Rh}(\text{PPh}_2\text{H})_4]\text{AsF}_6$ (36.43 MHz).
Figure 81. (a) $^{31}P\{^1H\}$-NMR spectrum of $[\text{Rh}(\text{dppp})(\text{PPh}_2\text{H})_2]\text{AsF}_6$ (121.470 MHz); (b) computer simulated spectrum: transitions are listed in the Appendix.
### TABLE 26

Phosphorus-31 NMR Parameters Of Rh(I) Complexes With Secondary Phosphine Ligands

<table>
<thead>
<tr>
<th></th>
<th>$\delta P_1$</th>
<th>$\delta P_2$</th>
<th>$\delta P_3$</th>
<th>$\delta P_4$</th>
<th>$J_{P_1P_2}$</th>
<th>$J_{P_1P_3}$</th>
<th>$J_{P_1P_4}$</th>
<th>$J_{P_2P_3}$</th>
<th>$J_{P_3P_4}$</th>
<th>$J_{Rh,P_1}$</th>
<th>$J_{Rh,P_2}$</th>
<th>$J_{Rh,P_3}$</th>
<th>$J_{Rh,P_4}$</th>
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</thead>
<tbody>
<tr>
<td>Rh(PPh$_2$H)$_4^+$</td>
<td>7.42</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Rh(dpdp)(PPh$_2$H)$_4^+$</td>
<td>13.63</td>
<td>13.61</td>
<td>5.49</td>
<td>5.45</td>
<td>-48.55</td>
<td>257.6</td>
<td>-44.01</td>
<td>-44.01</td>
<td>-56.94</td>
<td>127.4</td>
<td>127.2</td>
<td>128.8</td>
<td>128.6</td>
</tr>
<tr>
<td>Rh(dppe)(PPh$_2$H)$_4^+$</td>
<td>63.5</td>
<td>4.2</td>
<td></td>
<td></td>
<td>223</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh(Cyttp)(PPh$_2$H)$_4^+$</td>
<td>1.37</td>
<td>9.12</td>
<td>-4.95</td>
<td></td>
<td>-48.95</td>
<td>256.3</td>
<td>-43.68</td>
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</tr>
</tbody>
</table>

*a* Numbering of atoms:

![Diagram of atom numbering]

*Parameters are determined by computer simulation (see appendix): $J_{P_2P_4} = 259.0$ Hz.*

*Data provided by L. Chen at the Ohio State University.*
characterized by $^{31}\text{P}\{^1\text{H}\}$-NMR and elemental analysis. The $^{31}\text{P}\{^1\text{H}\}$-NMR gives a second order AA'BB'X pattern on Bruker WM-300 (Fig. 81). The computer simulated parameters are listed in Table 26; these data are also compared with those of $[\text{Rh(dppe)}(\text{PPh}_2\text{H})_2]\text{AsF}_6$. The complex can be treated with a base, e.g., MeLi, to form an anion, $[\text{L}_2\text{Rh(PPh}_2\text{)}_2]^{-}$ as in the case of $\text{Rh(Cyttp)(PPh}_2\text{)}^{-}$. 
APPENDIX

Calculated and Observed $^{31}\text{P}^{(1}\text{H})\text{NMR Transitions.}$
Transitions (calculated) from the $^{31}$P($^1$H)-NMR spectrum of
[Rh(dppp)(PPh$_2$H)]AsF$_6$. 

<table>
<thead>
<tr>
<th>$F_1$</th>
<th>$F_2$</th>
<th>Transition</th>
<th>Intensity</th>
<th>Error</th>
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<tr>
<td>4</td>
<td>9</td>
<td>423.211</td>
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<td>423.104</td>
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<tr>
<td>10</td>
<td>17</td>
<td>431.596</td>
<td>0.686</td>
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