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Design and synthesis of chelating triphosphine ligands and their use in the activation of metal complexes

Zeiher, E. H. Kelle, Ph.D.
The Ohio State University, 1989
DESIGN AND SYNTHESIS OF CHELATING TRIPHOSPHINE LIGANDS
AND THEIR USE IN THE ACTIVATION OF METAL COMPLEXES

DISSERTATION

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

By
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1989
To My Family
ACKNOWLEDGMENTS

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Bis(3-diphenylphosphinopropyl)cyclohexylphosphate and Its Complexes", 21st
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FIELDS OF STUDY

MAJOR FIELD: Inorganic Chemistry
Studes in Coordination Chemistry,
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CHAPTER I

INTRODUCTION

A. General

Transition metal complexes, especially those containing tertiary phosphine ligands, have been widely studied because of their usefulness in catalytic systems.14 Since the 1955 discovery by Wilkinson5 of the first stable transition metal hydride, ReH(η3-Cp)2, a great deal of interest has been focused on transition metal hydride and polyhydride complexes. Pioneering work was done on transition metal polyhydrides by Chatt, Coffey and Shaw,6 Wilkinson,7 Bennett,8 and Tolman9 in the 1960's and early 1970's. Transition metal hydrides have been the subject of numerous reviews10-17 and books.18-20 They are active in catalyzing H/D exchange,21-23 hydroformylation,24 olefin hydrogenation and isomerization,25,26 and hydrosilation.28

Green and Jones11 have proposed several general categories for the synthesis of hydride complexes. These include: direct hydrogenation, reduction of metal halides, hydride transfer from solvent, reverse carbonylation, hydrolysis of alkali metal salts of complex carbonyls, and protonation.

Addition of H2 to coordinatively unsaturated metal centers often yields metal hydride complexes. These oxidative addition reactions
increase the oxidation state of the metal by two units. Examples of oxidative addition of H₂ are shown in equations 1 and 2.²⁹,³⁰

\[
\text{trans-}[\text{IrCl(CO)(PPh}_3)_2] + H_2 \rightarrow \text{IrH}_2\text{Cl(CO)(PPh}_3)_2
\]

(1)

\[
\text{IrCl(ttp)} + H_2 \rightarrow \text{IrH}_2\text{Cl(ttp)}
\]

(2)

Oxidative addition also occurs when C-H adds to a metal to form stable aryl or alkyl metal hydrides.²¹b,c,⁶,¹⁰⁸ An example is shown below which consists of addition of benzene to a photochemically generated 16 e⁻ species.¹⁰⁹

\[
hv \quad [\text{IrH(CO)}(\text{dppe})] + \text{Ph-H} \rightarrow [\text{IrH}_2(\text{Ph})(\text{CO})(\text{dppe})]
\]

(3)

dppe = 1,2-bis(diphenylphosphino)ethane

The internal oxidative addition process is cyclometallation, in which a C-H bond located on a ligand adds to the metal center. Two examples are shown below.³¹,³²

\[
[\text{Ir(COE)}_2\text{Cl}]_2 + (t\text{-Bu})_2\text{P(CH}_2)_3\text{P}(t\text{-Bu})_2 \rightarrow \text{Ir}
\]

(4a)
The reduction of metal halides using reducing agents such as NaBH₄, LiAlH₄, and LiBH₄ is another common method of preparing transition metal hydrides. Two examples are shown below.

\[
\text{LiAlH}_4 \\
\text{IrCl}_2\text{H}(\text{PPh}_3)_3 \rightarrow \text{mer-IrH}_3(\text{PPh}_3)_3
\]  

(5)

\[
\text{LiBH}_4 \\
\text{IrCl}_3(\text{PET}_3)_3 \rightarrow \text{IrH}_5(\text{PET}_3)_2
\]  

(6)

In the absence of an external source of hydrogen, hydrogen abstraction from the solvent often occurs. The following reaction is known to occur in refluxing ethanol.

\[
\text{IrCl}(_2\text{H}(\text{PPh}_3)_3 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{IrH}_2\text{Cl}(\text{PPh}_3)_3 + \text{CH}_3\text{CHO}
\]  

(7)

Hydrolysis of metal carbonyl cations is also known to produce metal hydrides as shown below.

\[
\text{IrCl}_2(\text{CO})_2(\text{PPh}_3)_2 + \text{H}_2\text{O} \rightarrow \text{IrCl}_2(\text{CO})(\text{PPh}_3)_2(\text{CO}_2\text{H})
\]  

(8)

160°C-180°C

\[
\text{IrCl}_2(\text{CO})(\text{PPh}_3)_2(\text{COH}) \rightarrow \text{IrHCl}_2(\text{CO})(\text{PPh}_3)_2 + \text{CO}
\]  

(9)
Finally, protonation of a coordinatively unsaturated metal complex also yields a metal hydride. \(^{37}\) (This reaction can also be classified as an oxidative addition reaction.)

\[
\text{IrCl(CO)(PPh}_3)_2 + \text{HBF}_4 \rightarrow \text{IrCl(Ph}_3)_3 \text{H}
\]

Because of their widespread applications and their relative ease of formation, transition metal polyhydride complexes continue to provide fertile ground for study by organometallic chemists.

B. Effects of Ligands

Tertiary phosphine ligands are frequently used to stabilize transition metal complexes in a variety of metal oxidation states. Following the pioneering work by F. C. Mann\(^ {38}\) on the synthesis of trivalent phosphorus derivatives, a variety of phosphines became available for use in the study of metal complexes. Because of the central role of phosphorus(III) compounds in organometallic chemistry, considerable interest has been focused on the steric and electronic factors which influence metal-phosphorus bonding. Phosphorus(III) behaves as a \(\sigma\) donor (through a filled \(sp^3\) hybrid orbital), and it can behave as a \(\pi\) acceptor (\(\pi\) acid) by accepting electron density into the empty \(d\) orbitals as illustrated below.
Steric effects are traditionally measured in terms of the cone angle, \( \theta \), first proposed and defined by Tolman.\(^{39,40}\) Tolman also proposed \( \chi_1 \) values for phosphine donors which are a measure of the net electron donating ability of the ligand, and include both \( \sigma \) and \( \pi \) effects.\(^{41}\) Numerous additional works have been dedicated to the study of the steric and electronic factors affecting metal phosphorus bonding.\(^{42-46}\) Work within this group has focused on the use of chelating polyphosphine ligands. While the chemistry of polyphosphines is not as extensive or as well developed as the chemistry of monodentate phosphines, it encompasses a considerable body of literature nonetheless. Polydentate
phosphines are highly useful because they provide (1) more control than monodentate phosphines of the coordination number, stoichiometry, and stereochemistry of the resulting metal complexes, (2) a method for tailoring the basicity at the metal center, (3) the ability to tailor the steric demands of the ligand, (4) slower intra- and inter-molecular exchange processes owing to the chelate effect, and (5) detailed structural and bonding information in the form of metal-phosphorus and phosphorus-phosphorus coupling constants. The disadvantage of polyphosphines is, of course, that they are difficult and often expensive to synthesize. In spite of this difficulty, over the past 15 years, a variety of synthetic routes to chelating polyphosphine systems have begun to emerge.\textsuperscript{67-60}

Chelates of the type shown in 1 below consist of phosphines connected to a capping unit by flexible hydrocarbon (generally two or three carbons long).\textsuperscript{61-66} The capping unit (A) can be another 2-electron donor such as phosphorus or nitrogen, or it can be a non-donating CH or CR group. The resultant ligand is either tri- or tetradeicate, and, owing to its unique structure, is ideal for coordinating in a facial manner. Figure 1 shows several other examples of chelating polyphosphines.
In the design of a chelating polyphosphine, there are several ways
to modify the ligands, thus tailoring them for a specific function.
First, the number of donor sets can be modified. Figure 1 shows examples
of bidentate, tridentate, tetradeutantate and pentadentate phosphines (2-5,
respectively). Second, the chain length can be modified. The most common
chain lengths are two and three carbons long. Third, the electron
donating ability of the chelate can be altered by changing the identity
of the substituent groups (R and R') of the phosphorus atoms.

Research within the Meek group has focused almost entirely on
tridentate systems which contain a propylene linkage in the backbone.
The two ligands used within the group (designated ctp, and Cyttp) are
shown below.

Chelates containing a propylene linkage tend to coordinate in a
meridional fashion and do not bridge metal centers. Figure 2 shows the
preferred geometries of ttp and Cyttp.

One of the goals of this research was to develop and investigate a
new ligand system with properties similar to those of ttp and Cyttp but
which extended our knowledge of tridentate chelate systems. Several
Figure 1: Examples of Chelating Polyphosphine Ligands
systems were considered, including a cyclic ligand, \((\text{PhP})_3(\text{CH}_2)_9\), similar to those synthesized by Diel,\textsuperscript{59} Kyba,\textsuperscript{67-70} and others.\textsuperscript{71-75}

The ligand which proved most accessible and most interesting, however, was bis(3-diphenylphosphinopropyl)cyclohexylphosphine, ttp*, shown below.

\[
\text{Ph}_2\text{P} \quad \text{Cy} \quad \text{Ph}_2\text{P}
\]

\(\text{ttp}^*\)

The specific alteration in ttp* (substituting cyclohexyl for phenyl on the central phosphorus atom of ttp) is of interest for several reasons. First it is both sterically more demanding than ttp and more basic than ttp. On the other hand, it is sterically less demanding and less basic than Cyttp. Thus, a comparison of its complexes to those of ttp and Cyttp should yield a more complete picture of the metal-phosphorus bonding in tridentate systems. Second, it imparts increased electron density at a new site. When chelated to a metal, this site of increased basicity should strongly influence the activity of the ligand trans to it. To date, only one similar ligand, with t-butyl on the central phosphorus, has been synthesized.\textsuperscript{76}

In order to study this new chelate system, \(^{31}\text{P}\) NMR will be extremely useful. Since the chelate prevents rapid intra- and intermolecular exchange of phosphine ligands, information can be gleaned from the chemical shifts and the values of the phosphorus-phosphorus coupling.
Figure 2: Observed Geometries of Chelated Metal Complexes
constants in the systems. In the case of a spin active metal such as Rh or Pt, metal-phosphorus coupling constants provide additional information.

C. Activated Metal Phosphine Systems

Since much of the transition metal hydride chemistry finds its roots in catalytically active systems, catalyst precursors and potentially reactive intermediates are of special interest. Most catalytic mechanisms involve unsaturated metal centers which are generated through loss of a ligand, often a phosphine. The best known system, of course, is the Wilkinson catalyst,\(^7\) \(\text{Rh(PPh}_3\text{)}_3\text{Cl}\). In this case, the catalytically active species is generally believed to be \(\text{Rh(PPh}_3\text{)}_2\text{Cl(Sol)}\), which results from the loss of one phosphine ligand.\(^7,24b,27\) The open coordination site can then be occupied by a variety of molecules such as \(\text{CO}, \text{C}_2\text{H}_4\), or olefins. If, on the other hand, \(\text{H}_2\) oxidatively adds to the Rh center, the series of reactions outlined in Figure 3 can occur. In Figure 3 is the proposed mechanism for the hydrogenation of olefins with the Wilkinson Catalyst.

More recently, a great deal of interest has been focused on the actual oxidative addition of \(\text{H}_2\) to a metal center. In 1984, Kubas observed the first example of a side-on coordinated molecular hydrogen ligand (\(\eta^2\) \(\text{H}_2\)) on a metal fragment.\(^77-79\) The complex, \(\text{mer-trans W(CO)}_3(\text{PiPr}_3)_2(\text{H}_2)\), was studied by low temperature X-ray and neutron diffraction techniques, which established the locations of the hydrogen atoms. Later, Crabtree\(^80-81\) proposed that NMR relaxation measurements (\(T_1\)) could be used to distinguish coordinated molecular hydrogen from classical dihydrides. The side-on bound nature of the coordinated molecular hydrogen, as well as its observed equilibria with classical dihydrides,\(^77-84,66c\) make it an ideal
Figure 3: Proposed Mechanism for the Hydrogenation of Olefins with Wilkinson Catalyst
model for an intermediate in the oxidative addition process. Molecular hydrogen complexes can be viewed as "cautomers of hydrides", or as "arrested intermediates in hydride formation."

\[ H_2 \quad M \quad H \quad M \]

The following model for molecular hydrogen bonding has been described by Crabtree.

In a manner similar to that employed by the \( \pi \) acid CO, the \( \sigma \) orbital of \( H_2 \) donates electron density into the empty metal \( d_\sigma \) orbital. In turn, the filled metal \( d_\pi \) orbital back donates electron density into the \( \sigma^* \) orbital of the \( H_2 \) ligand. It is the extent of this back donation that determines whether the H-H bond breaks, resulting in a dihydride, or whether the bond remains intact, resulting in a "nonclassical hydride" (molecular hydrogen species). Thus, \( H_2 \) may be viewed as a \( \pi \) acid. It is
important to note that as an increase in the dπ to σ* donation occurs, the H-H bond is lengthened until it finally breaks.

The previously mentioned NMR relaxation time measurements (T₁'s) have proven to be very useful in distinguishing between classical and nonclassical hydride ligands. The T₁ of a molecule can be measured by the inversion recovery method. This employs the pulse sequence 180°-t-90°, and measures how rapidly the inverted spins recover their equilibrium magnetization along the direction of the applied magnetic field. By varying t, one can pinpoint the actual relaxation time of the molecular hydrogen or hydride ligand. Figure 4 shows an example of the inversion recovery spectra for [IrH(H₂)(bq)(PPh₃)₂]SbF₆ (bq = ⁷,₈-benzoquinolinate, shown below). The H₂ ligands clearly relax faster than the hydride ligand of the same complex. T₁ is a measure of the dipole-dipole relaxation of protons located less than 2Å apart. The rate of dipole-dipole relaxation is given in Equation 11. The characteristic relaxation time of a species, T₁(DD), is the inverse of R(DD) for that species.
Since the $R(DD)$ is proportional to $r^{-6}$, Equation 11 shows that the smaller the internuclear distance between two hydrogen atoms, $r$, the faster the rate of relaxation (and the shorter $T_1$). Crabtree further notes that the inversion recovery method relies on $T_c$, the rotational correlation time of the molecule. Since $T_c$ depends on the moment of inertia of a molecule and on the solvent viscosity, these two factors must remain comparable in all systems studied if we are going to be able to make direct comparisons of $T_1$ values. In order to make $T_1$ values more generally applicable, it is necessary to study their temperature dependence. Equation 11 predicts that $T_1$ will go through a minimum when the Brownian motion (measured by $T_c$) is best matched with the Larmor frequency, $\omega$. This should occur when:

$$T_c = \frac{0.63}{2\pi\nu}$$  \hspace{1cm} (12)

Figure 5 shows the typical variation of $T_1$ with temperature.\textsuperscript{81}

Two more points need to be made about the $T_1$ technique. First, when a complex to be studied is a polyhydride, both classical (hydridic), and nonclassical (molecular hydrogen) ligands may exist within one molecule.
Figure 4: The Inversion Recovery Spectra of [IrH2(bq)(PPh3)2]·SbF6− at -85°C and 500 MHz
Figure 5: Variation of $T_1$ with Temperature
Fluxionality within the molecule can then cause an averaging of the $T_1$ values for all of the atoms involved. This averaging will be governed by Equation 13 below.

$$\left( N_c + N_n \right) \left( T_{1(\text{obs,min})} \right)^{-1} = N_c \left( T_{1(c,\text{min})} \right)^{-1} + N_n \left( T_{1(n,\text{min})} \right)^{-1}$$

$N_c$ - number of classical hydrides in the molecule  \hspace{1cm} (13)

$N_n$ - number of nonclassical hydrides in the molecule.

Second, in the practical application of $T_1$ values, observations to date have shown that nonclassical species generally have $T_1(\text{min})$ values of $< 80$ ms. Classical species, on the other hand, have $T_1(\text{min})$ values of $> 150$ ms. Tables 1 and 2 summarize the initial results of Crabtree's $T_1$ experiments.
### Table 1

#### The T<sub>1</sub> Values for Some Hydrides

<table>
<thead>
<tr>
<th>Complex</th>
<th>T&lt;sub&gt;1&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>T&lt;sub&gt;1&lt;/sub&gt;(n)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
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<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1600</td>
<td>-</td>
<td>d&lt;sub&gt;4&lt;/sub&gt;-toluene, 203K</td>
</tr>
<tr>
<td>IrH&lt;sub&gt;2&lt;/sub&gt;(PCy&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>820</td>
<td>-</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;, 193K</td>
</tr>
<tr>
<td>[IrH&lt;sub&gt;2&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;)(PCy&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]&lt;sup&gt;+&lt;/sup&gt;</td>
<td>48&lt;sup&gt;c&lt;/sup&gt;,73&lt;sup&gt;d&lt;/sup&gt;</td>
<td>37</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;, 193K</td>
</tr>
<tr>
<td>IrH&lt;sub&gt;2&lt;/sub&gt;(bq)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>30&lt;sup&gt;c&lt;/sup&gt;,390&lt;sup&gt;d&lt;/sup&gt;</td>
<td>30</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;, 193K</td>
</tr>
<tr>
<td>Fe(H&lt;sub&gt;2&lt;/sub&gt;)H&lt;sub&gt;2&lt;/sub&gt;(PEtPh&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>24</td>
<td>12</td>
<td>d&lt;sub&gt;4&lt;/sub&gt;-toluene, 203K</td>
</tr>
<tr>
<td>Ru(H&lt;sub&gt;2&lt;/sub&gt;)H&lt;sub&gt;2&lt;/sub&gt;(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>38</td>
<td>20</td>
<td>d&lt;sub&gt;4&lt;/sub&gt;-toluene, 203K</td>
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<td>OsH&lt;sub&gt;4&lt;/sub&gt;(P&lt;sub&gt;2&lt;/sub&gt;-tolyl)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>620</td>
<td>-</td>
<td>d&lt;sub&gt;4&lt;/sub&gt;-toluene, 203K</td>
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<td>ReH&lt;sub&gt;5&lt;/sub&gt;(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>78&lt;sup&gt;e&lt;/sup&gt;</td>
<td>25</td>
<td>d&lt;sub&gt;4&lt;/sub&gt;-toluene, 203K</td>
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<tr>
<td>ReH&lt;sub&gt;5&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;)(dpe)</td>
<td>79&lt;sup&gt;e&lt;/sup&gt;</td>
<td>25</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;, 203K</td>
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<td>ReH&lt;sub&gt;5&lt;/sub&gt;(H&lt;sub&gt;2&lt;/sub&gt;)(dpe)</td>
<td>110</td>
<td>33</td>
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<td>ReH&lt;sub&gt;5&lt;/sub&gt;(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>-</td>
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<td>290 (ax)</td>
<td>-</td>
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<tr>
<td></td>
<td>618 (eq)</td>
<td>-</td>
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<tr>
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<td>-</td>
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</tr>
<tr>
<td>[W&lt;sub&gt;10&lt;/sub&gt;3(PMePh&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;]&lt;sup&gt;+&lt;/sup&gt;</td>
<td>205&lt;sup&gt;f&lt;/sup&gt;</td>
<td>-</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;, 203K</td>
</tr>
<tr>
<td>W&lt;sub&gt;6&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;Ph)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>166&lt;sup&gt;f&lt;/sup&gt;</td>
<td>-</td>
<td>d&lt;sub&gt;4&lt;/sub&gt;-toluene, 203K</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;Fe(CO)&lt;sub&gt;4&lt;/sub&gt;</td>
<td>3000</td>
<td>-</td>
<td>d&lt;sub&gt;4&lt;/sub&gt;-toluene, 203K</td>
</tr>
<tr>
<td>ReH&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>2500</td>
<td>-</td>
<td>d&lt;sub&gt;4&lt;/sub&gt;-methanol, 205K</td>
</tr>
</tbody>
</table>

<sup>a</sup> bq = 7,8-benzoquinolinate  
<sup>d</sup> dpe = Ph<Psub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> Cy = C<sub>6</sub>H<sub>11</sub>. For references, see experimental.  
<sup>b</sup> by inversion/recovery ±10% in ms.  
<sup>c</sup> calculated as shown in the text (eq.13) based on the formulation shown.  
<sup>d</sup> for the nonclassical hydrides.  
<sup>e</sup> for the classical hydrides.  
<sup>f</sup> unpublished neutron diffraction data<sup>31</sup> are interpreted in terms of a disordered but classical structure for the PPh<sub>2</sub> complex. Since the least soluble tautomer will crystallize, this result does not tell us what structure is adopted in solution.  
<sup>i</sup> intermediate values not interpretable in terms of a structure.
### Table 2

**Variable Temperature T₁ Data**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp[°C]</th>
<th>T₁[min]</th>
<th>δ(λ)</th>
<th>δ(μ)</th>
<th>structure</th>
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<tbody>
<tr>
<td>CpRu(PPPh)₃H</td>
<td>238</td>
<td>300</td>
<td>1.68</td>
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<tr>
<td>[M₆(CO)₆(PPPh)₂]⁺</td>
<td>210</td>
<td>245</td>
<td>1.63</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>H₃(PCy)₃</td>
<td>&lt;193</td>
<td>&lt;820</td>
<td>&gt;2</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>ReH₃(H₂)(PPPh)₂</td>
<td>200</td>
<td>1100</td>
<td>1.07</td>
<td>nc</td>
<td></td>
</tr>
<tr>
<td>ReH₃(H₂)(dppe)²⁻</td>
<td>222</td>
<td>67</td>
<td>1.11</td>
<td>nc</td>
<td></td>
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<tr>
<td>ReH₃(H₂)(P(η-C₆H₄F)₃)₂</td>
<td>200</td>
<td>55</td>
<td>1.07</td>
<td>nc</td>
<td></td>
</tr>
<tr>
<td>ReH₃(H₂)(PCy)₃</td>
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<td>&lt;650</td>
<td>&lt;1.1</td>
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</tr>
<tr>
<td>[ReH₆(PPPh)₃]⁺</td>
<td>200</td>
<td>245</td>
<td>1.63</td>
<td>c</td>
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</tr>
<tr>
<td>Ru(H₂)H₂(PPPh)₃</td>
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<td>30</td>
<td>1.04</td>
<td>nc</td>
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</tr>
<tr>
<td>[Os(H₂)H₃(PPPh)₃]⁺</td>
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<td>25</td>
<td>1.03</td>
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<td>MoH₄(PMePh₂)₄</td>
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<td>165</td>
<td>1.53</td>
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<td>235</td>
<td>181</td>
<td>1.55</td>
<td>c</td>
<td></td>
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<tr>
<td>W₆F₆(PMe₂Ph)₄⁺</td>
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<td>179</td>
<td>1.57</td>
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<tr>
<td>W₆F₆(CO)₃(Pt-PPh)₂</td>
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<td>5¹</td>
<td>0.85</td>
<td>0.8</td>
<td>d</td>
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<tr>
<td>[FeH₆(H₂)(dppe)²]⁺</td>
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<td>0.5¹ ²</td>
<td>0.56</td>
<td>0.8⁶</td>
<td>c</td>
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<tr>
<td>[H₄(H₂)₂(ox)(PPPh)₃]⁺</td>
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<td>0¹</td>
<td>0.31</td>
<td>0.92</td>
<td>nc</td>
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</table>

---

**Abbreviations**: as in Table 1. *solvents* as in Table 1 and at 250 MHz, unless stated, b of the turning point, c at the turning point, d <0.02Å, calculated as described in the text (a = 3.1), e classical, c; non-classical, nc. f at 500 MHz, g by eq.1, this value is equivalent to a T₁(min) of SSms at 250 MHz. At the lowest temperature, the observed T₁ at 250 MHz, was indeed SSms, and so we were very close to the minimum, h in d₅-hexanol. i from ref. 1; original measurement at 200 MHz, but T₁ value shown here calculated for 250 MHz. j by neutron diffraction. k from ref. 2; original measurement at 200 MHz, but T₁ value shown here calculated for 250 MHz. l of the dihydrogen resonance. m by X-ray diffraction. n by solid state NMR. o 150

*original paper references
In conclusion, transition metal polyhydrides remain an area of extremely active research interest. The discovery of molecular hydrogen-containing species challenges much of our previous knowledge about hydrogen-containing transition metal complexes. In the coming years, polyphosphine complexes are expected to assume an even more important role in organometallic chemistry. Their unique advantages can help us greatly in our efforts to gain new insights into organometallic reaction mechanisms, since they can provide highly tailored, specific environments for the active species.
CHAPTER II
EXPERIMENTAL

A. Reagents and Chemicals

Cyclohexylphosphine, dicyclohexylphosphine, phenylphosphine, and diphenylphosphine were purchased from Pressure Chemical Co., Pittsburgh, PA, and were used without further purification. Rhodium trichloride trihydrate (RhCl$_3$·3H$_2$O), iridium trichloride trihydrate (IrCl$_3$·3H$_2$O) and ammonium hexachloroiridate(IV) ((NH$_4$)$_2$IrCl$_6$) were purchased from Engelhard Industries, Newark, NJ, or were obtained on loan from the Johnson Matthey Co., Malvern, PA. Reagent-grade chemicals were purchased from Aldrich Chemical Co., Milwaukee, WI, Strem Chemical Co., Newburyport, MA, or Alpha Products, Danvers, MA, and were used without further purification, unless otherwise stated.

B. Physical Methods and Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 283B grating spectrophotometer from 400 to 200 cm$^{-1}$ as pressed potassium bromide pellets, Nujol mulls (with potassium bromide or cesium iodide windows) or in solution. Spectra were calibrated against the sharp 1601 cm$^{-1}$ peak of polystyrene film. A Bruker AM-250 spectrometer or a Bruker 500 MHz spectrometer was used to obtain proton (250.13 MHz), phosphorus-31 (101.25 MHz), and carbon-13 (62.9 MHz) spectra in 5 mm tubes. Residual solvent
proton or carbon-13 resonances were used as internal standards for the $^1H$ and $^{13}C$ NMR spectra. Phosphorus chemical shifts were determined relative to 85% $H_3PO_4$ as an external standard. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona.

C. General Experimental Procedures

All reactions were performed in a well-ventilated fume hood. High purity nitrogen or argon was used to provide an inert atmosphere. The nitrogen and argon were purified by passing the gas through a deoxygenating column (Ridox, purchased from Fischer Scientific Company, Fairlawn, NJ), and a column containing anhydrous calcium sulfate to remove water vapor. Solvents were distilled under argon from the appropriate drying agents$^{106}$ immediately prior to use. Additional inert atmosphere was provided by a Vacuum Atmospheres H#43 inert atmosphere box equipped with a Mo-40 catalyst system. All manipulations were performed using standard Schlenk techniques.$^{107}$

D. Ligand Preparation

1. Ph$_2$P(CH$_2$)$_3$Cl

All glassware was flame-dried immediately prior to use. The 1-bromo-3-chloropropane was degassed using a freeze-pump-thaw cycle for three repetitions. All other solvents were degassed immediately prior to use by passing a stream of dry $N_2$ through them for 30 minutes. Freshly distilled, degassed THF (350 mL) was placed in a 2 L 3-neck flask equipped with a mechanical stirring motor and a pressure equalizing dropping funnel. The THF was cooled to -78°C in a Dry Ice/isopropyl alcohol slush
bath. Using a syringe, 22.5 mL (0.134 mol; 25 g) of Ph₂PH and 13.2 mL (0.134 mol; 21 g) of 1-bromo-3-chloropropane were syringed into the cold THF. Under an inert atmosphere, 14.4 g (0.134 mol) of LiN(i-propyl)₂ was weighed out, dissolved in 150 mL of THF, and placed in the pressure equalizing dropping funnel. The LDA solution was added dropwise to the stirred Ph₂PH solution over a period of 2 h. Each addition of LDA solution caused a transient yellow color to appear which immediately faded. When the addition was complete, the mixture was stirred at -78°C for 2 h. After this time a $^{31}$P($^1$H) NMR spectrum of the solution showed the reaction to be complete. The reaction was quenched with 200 mL of degassed, distilled H₂O and allowed to warm (with stirring) to room temperature. Following the addition of 200 mL of diethylether, the organic layer was removed by using a double-ended needle and dried by stirring over Na₂SO₄ overnight. (The aqueous layer was washed with 4 x 125 mL of diethylether and the washings combined with the organic layer.) The diethylether solution was transferred to a 250 mL flask using a double-ended needle fitted with a glass plug which was covered with a piece of filter paper. The Na₂SO₄ residue was broken up and washed several times with ether (total volume of ether used was 200 mL). The solvent was removed under vacuum and the resulting yellow oil heated, in vacuo at 60°C for 3 hr. Yield: 32.7 g (93%).

2. Li₂PhP

Freshly distilled, degassed hexane (200 mL) was placed in a 3-neck, 1 L flask equipped with a reflux condenser and a pressure equalizing dropping funnel. Using a syringe, 6.8 mL (0.062 mol, 6.8 g) of PhPH₂ was transferred into the hexane. The dropping funnel was then filled with
54.1 mL (0.135 mol, 8.6 g) of n-butyllithium (as a 1.6M hexane solution) using a transfer needle. The n-BuLi was slowly added to the reaction mixture over a 30 min period. Once the addition was complete, the reaction mixture was allowed to reflux for 1h and then was cooled to room temperature. A bright yellow precipitate results. The hexane was removed and the precipitate was washed in hexane (3 x 50 mL) and diethylether (3 x 50 mL). Finally, the precipitate was slurried in 150 mL of degassed ether.

4. Ph₂P(CH₂)₃(Ph)(CH₂)₃PPh₂ (tcp)

The Ph₂P(CH₂)₃Cl was dissolved in 400 mL of diethylether and placed in a 1L Schlenk flask. The yellow Li₂PPh slurry was transferred to the flask under an N₂ atmosphere. As the Li₂PPh was added the solution first turned dark orange and then faded upon stirring. The mixture was stirred for 18 h under an N₂ atmosphere. A ³¹P(¹H) NMR spectrum of a sample of the reaction mixture (which was hydrolyzed with a drop of H₂O) showed an essentially complete reaction. A small amount of PhPH₂ impurity was visible at δ -125 ppm. The reaction mixture was hydrolyzed with 60 mL of degassed ethanol and 200 mL of degassed H₂O. The organic layer was transferred to a flask containing Na₂SO₄. The water layer was washed with benzene (6 x 100 mL) and the washings were added to the organic layer. These layers were dried over Na₂SO₄ for 48 h. After drying the organic layer was removed from the Na₂SO₄ using a double-ended needle fitted with a glass plug which was covered with filter paper. The Na₂SO₄ residue was broken up and washed with dry, degassed benzene (3 x 150 mL). The washings were combined with the previously removed organic layer. The solvent was removed in vacuo at 40°C leaving a viscous yellow oil. Yield:
33.7g (45%). A 0.14M solution was prepared by dissolving 20.35g of the ligand in 250 mL of benzene.

5. CyP((CH$_2$)$_3$OH)$_2$

This material was prepared by C. Supplee as described in reference 91.

6. CyP(O)((CH$_2$)$_3$OH)$_2$

The colorless CyP((CH$_2$)$_3$OH)$_2$ oil (20.8g; 0.09 mol) was dissolved in 100 mL of freshly distilled acetone and placed in a 500 mL flask equipped with a pressure equalizing dropping funnel. A 30% aqueous solution of H$_2$O$_2$ (13 mL) was combined with 50 mL of acetone and degassed for 45 min using an argon stream. The H$_2$O$_2$ solution was placed in the dropping funnel and was added dropwise to the CyP((CH$_2$)$_3$OH)$_2$ solution which was maintained at 0°C. After the addition was complete (~1h) the mixture was stirred for 12h at 0°C. The acetone was removed in vacuo and the residue treated with 100 mL of benzene to form a benzene/H$_2$O azeotrope. The remaining solvent was removed in vacuo. The resulting pale yellow oil was distilled under vacuum at 110°C for 18h. Yield: 22.0g (98%).

7. P(O)((CH$_2$)$_3$Cl)$_2$

The phosphine oxide was dissolved in 100 mL of CH$_2$Cl$_2$ and added dropwise from a dropping funnel to a refluxing solution of PCl$_3$ (45.7g; 0.22 mol) in CH$_2$Cl$_2$. The mixture was allowed to reflux for 8h. During this time, the solution was constantly swept with an argon stream to remove the HCl by-product. This stream was vented to the atmosphere by a bubbler filled with aqueous NaOH. After cooling to room temperature, the solvent was removed in vacuo to give a deep-orange oil. This oil was hydrolyzed with 300 mL of a saturated NaHCO$_3$ solution. The solution was
dried over MgSO₄ for 12h and filtered using a double-ended needle fitted with a glass plug covered with filter paper. The solvent was removed in vacuo at room temperature to give an orange oil. Yield: 19.5g (77%).

8. LiPPh₂

Using a syringe, 31 mL (0.18 mol; 33g) of Ph₂PH was added to 100 mL of a hexane/THF solution (50:50 mixture) in a 500 mL flask. A pressure equalizing dropping funnel was filled with 111 mL (0.178 mol) of n-butyllithium (as a 1.6M hexane solution) and this solution was allowed to drop slowly over a 1h period into the Ph₂PH solution which was maintained at 0°C. After the addition of several mL of n-BuLi a deep-orange color resulted. When the addition was complete, the solution was stirred for 1h at 0°C and then for 2h at room temperature. A thick yellow precipitate formed. Excess THF (approximately 100 mL) was added to dissolve this precipitate.

9. CyP(O)((CH₂)₂PPh₂)

The CyP(O)((CH₂)₂Cl)₂ was dissolved in 200 mL of THF and placed in a 500 mL flask fitted with a pressure equalizing dropping funnel. The dropping funnel was filled with the LiPPh₂/THF solution and the LiPPh₂ was added slowly to the ligand oxide solution which was maintained at 0°C. The initial dropping rate was 1 drop/s, but the rate slowed considerably and the addition took 12h. After the LiPPh₂ addition was complete the reaction mixture was stirred for 1h at 0°C and then for 18h at room temperature. This was followed by 1h of refluxing. During this time the color changed from a dark red-orange to a lighter orange. The solution was cooled and hydrolyzed with 75 mL of absolute ethanol. The solvent was removed in vacuo and the resulting light brown oil was heated to 130°C in
vacuo for 6h to remove excess PPh$_2$H. The final product was a light brown, waxy residue. Yield: Due to the presence of LiCl at this point the yield could not be determined.

10. CyP((CH$_2$)$_3$PPh$_2$)$_3$

The CyP(O)((CH$_2$)$_3$PPh$_2$)$_2$ (55g, approximately 0.089 mol) was dissolved in benzene and the reaction mixture was cooled to 0°C. A slight excess of Si$_2$Cl$_4$ (7.9 mL, 0.046 mol) was cooled, placed in a dropping funnel, and added dropwise to the ligand oxide solution at 0°C. The solution was then warmed to room temperature and allowed to stir for 12h, followed by refluxing for 2h. After cooling, the solution was carefully hydrolyzed with 30% aqueous NaOH while being maintained at 0°C. A copious white precipitate formed. (NaOH solution was added until precipitation was complete.) The precipitate must be thoroughly broken up to insure a good yield of the product. The slurry was stirred overnight and then extracted with several portions of benzene. (The total volume of the extracts was 500 mL). The combined extracts were filtered through a glass frit and dried over MgSO$_4$ for 12h. The brownish color lightens considerably during this step. The MgSO$_4$ was filtered off and the resulting solution was pumped down to an oil. The oil was subjected to a Krugelrohl distillation at 102°C for 6h to remove PPh$_2$H impurities. Finally the oil was dissolved in benzene and passed through a two-inch tall neutral alumina column to remove oxide and salt impurities. The resulting solution was stripped of solvent, in vacuo, and yielded a viscous white oil.

Final yield: 27g (53% based on P((CH$_2$)$_3$OH)$_2$
11. Attempted Synthesis of (Ph)P(CH₂)₃P(Ph)(CH₂)₃P(Ph)(CH₂)₃

A. Reaction of [Ir(COE)₂Cl₂] and PhHP(CH₂)₃PPh. A sample containing 0.28 g (0.3 mmol) of [Ir(COE)₂Cl₂] was dissolved in 50 mL of toluene and 0.10 mL (0.17 g; 0.65 mmol) of PhHP(CH₂)₃PPh was added via syringe. A yellow precipitate formed and was immediately filtered. Poor solubility prevented obtaining acceptable spectroscopic data.

B. Reaction of [Ir(COE)₂Cl₂] and PhHP(CH₂)₃PPh in Acidic Media. A solution of 0.3 g (0.4 mmol) of [Ir(COE)₂Cl₂] and 50 mL of toluene was acidified with a drop of aqueous HCl to cut down on possible polymerization. Using a syringe 0.10 mL (0.17 g; 0.65 mmol) of PhHP(CH₂)₃PPh was added. The resulting yellow precipitate was filtered off and dried in vacuo.

E. Iridium Complexes

1. [Ir(COD)Cl]₂

The Ir(IV) salt (NH₄)₂IrCl₄ (5.45 g; 12.4 mmol) was stirred in 28 mL of distilled water and 10 mL of isopropyl alcohol in a 250 mL flask. Using a pipet, 5.0 mL of cyclooctadiene (COD) was added. The mixture was allowed to reflux for 18 h; during this time a red oil appears. The solution was allowed to cool to room temperature over a 2-3 h period, which resulted in the formation of large red crystals. These were filtered off and dried in vacuo. Yield: 3.8 g (92%).

2. [Ir(COE)₂Cl₂]

A sample of (NH₄)₂IrCl₄ (6.0 g; 14 mmol) was dissolved in a mixture of 90 mL of distilled water and 30 mL of isopropyl alcohol. Using a pipet, 10.0 mL of cyclooctene (COE) was added, and the resulting mixture
was allowed to reflux for 4h; during this time an orange oil formed. The mother liquor was removed with a double-ended needle, and cold ethanol was added to the oil. The oil was placed in the freezer overnight and an orange powder formed. The powder was filtered off, washed with 5 mL of cold ethanol, and dried in vacuo.

Yield: 5.0 g (82%).

3. Ir(Cyttp)H₂Cl (anti isomer)

Method A. A portion (0.86g; 13 mmol) of [Ir(COD)Cl]₂ was slurred in 100 mL of absolute ethanol and 10.3 mL of a Cyttp/benzene solution (0.4 mL/mmol:4.1 mmol) was added. The resulting solution was allowed to reflux for 1.5h and then cooled to room temperature. The solution was concentrated in vacuo until a white precipitate appeared. The precipitate was filtered off and recrystallized from a minimum of CH₂Cl₂ and ethanol. The final product was filtered off and dried in vacuo.

Yield: 2.1g (25%).

Method B. The viscous Cyttp oil (3.8g; 6.4 mmol) was transferred to a 250 mL flask and was dissolved in 100 mL of degassed ethanol. (When cooled slightly the oil is viscous enough to transfer by dipping a stirring rod into it and transferring the portion which clings to the rod. Heating with a heat gun will cause the oil to flow off of the rod.) A carefully measured amount (2.2g, 3.2 mmol) of [Ir(COD)Cl]₂ was added. The resulting solution was refluxed for 2h. After cooling in an ice bath both the pale yellow Ir(Cyttp)H₂Cl precipitated from solution. The precipitate was filtered off, washed with ethanol (2 x 4 mL), and dried in vacuo.

Yield: 3.4g (66%).
4. **Ir(ttp*)H₂Cl (anti isomer)**

   **Method A.** A sample of Cyttp oil (1.8 g; 3.2 mmol) was dissolved in 200 mL of ethanol and 0.85g (1.3 mmol) of [Ir(COD)Cl]₂ was added. The mixture was refluxed overnight. Cooling produced a pale yellow precipitate which was filtered off, washed with 10 mL of ethanol and dried in vacuo.

   Yield: 1.6g (79%).

   **Method B.** The same procedure was used as above, except the solution was stirred at room temperature overnight.

   Yield: 1.7g (83%).

   **Elemental Analysis:** Calculated (found) -- C 52.95 (53.98); H 5.57 (5.80); P 11.38 (10.78); Cl 4.34 (4.59).

5. **Ir(ttp)H₂Cl**

   A sample of ttp oil (0.95g; 1.7 mmol) was dissolved in 100 mL of absolute ethanol and 0.67g (1.0 mmol) of [Ir(COD)Cl]₂ was added. After refluxing for 2h and cooling, a white precipitate appeared. This was filtered off, washed with ethanol (2 x 2 mL), and dried in vacuo. No yield was calculated.

6. **Ir(ttp)H₃**

   **Method A.** The Ir(ttp)H₂Cl powder (0.2g; .3 mmol) was dissolved in 50 mL of ethanol to which an excess of KOH (0.2g; 3.6 mmol) was added. The solution was heated to reflux for 1h or stirred at room temperature overnight. The resulting white precipitate was filtered off, washed once in ethanol, and dried in vacuo.

   **Method B.** The base 1,8-diazobicyclo[5,4,0]-7-undecene (DBU) was used in place of KOH.
Both methods A and B give a clean product whose $^3$P and $^1$H NMR spectra correspond to those reported for Ir(ttp)H$_2$.

7. Ir(Cyctp)H$_2$

A sample (0.83g; 1.0 mmol) of Ir(Cyctp)H$_2$Cl was dissolved in 100 mL of absolute ethanol and 0.18g (3.2 mmol) of KOH was added. After 3h of refluxing the solution was cooled to room temperature and the volume reduced in vacuo until a fine white powder appeared. This was filtered off, washed with ethanol (2 x 2 mL), and dried in vacuo.

Yield: 0.83g (100%).

8. Ir(ttp*)H$_2$

A sample (1.0g; 1.3 mmol) of Ir(ttp*)H$_2$Cl was dissolved in 70 mL of absolute ethanol and an excess (0.13g, 2.3 mmol) of KOH was added. The mixture was stirred overnight at room temperature. The resulting white precipitate was filtered off, washed in ethanol (2 x 3 mL), and dried in vacuo.

Yield: 0.74g (74%).

Elemental Analysis: Calculated (found) -- C 56.61 (56.87); H 6.07 (5.92); P 12.16 (12.43).

9. Attempted Synthesis of Ir(ttp*)Cl

The ttp* oil (0.77g; 1.4 mmol) was dissolved in a minimum amount of toluene (~ 50 mL) and 0.61g (0.68 mmol) of [Ir(COE)Cl]$_2$ was added. The mixture was stirred for 10 min, and then the volume was reduced until yellow powder began to appear. Cold hexane (10 mL) was added to cause precipitation. After collecting by filtration and washing with hexane (2 x 2 mL), the brown precipitate was dried in vacuo. The precipitate has low solubility in hydrocarbon and chlorinated solvents.
10. Ir(Cyttp)Cl

Method A. The Cyttp oil (2.0g; 3.4 mmol) was dissolved in 100 mL of freshly distilled toluene, and 1.5g (1.7 mmol) of [Ir(COE)₂Cl]₂ was added. The mixture was stirred at room temperature for 10 min and then concentrated in vacuo to yield a yellow precipitate. Cold hexane (20 mL) was added to complete the precipitation. The solid was filtered off, washed with hexane (2 x 2 mL), and dried in vacuo.

Yield: 0.97g (35% based on the formula Ir(Cyttp)Cl)

³¹P NMR: three sets of AX₂ patterns were observed:

Species A  Pₐ - -17.2 ppm (t), Pₚ - 1.6 ppm (d), Jₚₚ - 31 Hz;
Species B  Pₐ - -37.2 ppm (t), Pₚ - -25.3 ppm (d), Jₚₚ - 25 Hz;
Species C  Pₐ - -18.1 ppm (t), Pₚ - -28.3 ppm (d), Jₚₚ - 22 Hz.

Method B. The Cyttp oil (0.28g; 0.48 mmol) was dissolved in 15 mL of absolute ethanol and 0.17g (0.25 mmol) of [Ir(COD)Cl]₂ was added. When yellow precipitate first appeared, it was filtered off, washed with ethanol (2 x 1 mL), and dried in vacuo. Only species B was visible in the ³¹P NMR.

Elemental analysis: Calculated (found)

C 53.05 (52.00); H 7.54 (7.58); P 11.40 (11.16)

11. Addition of H₂ to Ir(Cyttp)Cl.

Condition 1. A sample of Ir(Cyttp)Cl was dissolved in d₆-toluene and cooled in a Dry Ice/methanol bath. A stream of H₂(g) was bubbled through the cold solution for 5 min. A portion of the solution was placed in a pressure NMR tube and the tube was pressurized with 12 psi of H₂ gas. Variable temperature NMR spectra (³¹P and ¹H) were taken at temperatures between -80°C and +30°C. No evidence of a hydricidic species was seen.
Condition 2. A sample of Ir(Cyttpp)Cl was dissolved in toluene and was placed in a flask under an H₂ atmosphere. The H₂ atmosphere was maintained during the entire time, and the system was vented to a Hg bubbler. The solution was refluxed for 2h and then cooled to room temperature. The solvent was removed by evaporation under an H₂ stream, and the sample was redissolved in d₄-toluene. Both syn and anti isomers of Ir(Cyttpp)H₂Cl are observed in the NMR spectra.

Condition 4. A solid sample of Ir(Cyttpp)Cl was placed in a flask under an H₂ atmosphere and rapidly stirred using a stirring bar, in the solid state overnight. A ³¹P{¹H} NMR spectrum shows both the syn and anti isomers of Ir(Cyttpp)H₂Cl and Ir(Cyttpp)Cl to be present.

12. Attempts to Convert syn/anti Mixtures of Ir(Cyttpp)H₂Cl into the Pure anti Isomer.

Condition 1. A mixture of syn/anti isomers of Ir(Cyttpp)H₂Cl was dissolved in d₄-toluene. The mixture was placed in an NMR tube and H₂ gas was added. The sample was frozen and the tube sealed. After heating at 80°C for 1h the sample converted to the pure anti isomer.

Condition 2. A sample was treated as in condition 1 above, except D₂ was used in place of H₂. Both syn and anti isomers were observed; however, the ratio of isomers after the reaction was 3:1 (anti:syn) whereas before the reaction the ratio was 1:1.

Condition 3. A solution of syn and anti isomers was heated in toluene under an H₂ atmosphere which was vented to a Hg bubbler. No conversion to the pure anti isomer occurred.
Condition 4. A sample of syn and anti isomers of Ir(Cyttp)H$_2$Cl was heated in d$_4$-toluene in a sealed NMR tube at 80°C for 1h in the absence of added H$_2$. No conversion to the anti isomer occurred.

Condition 5. A sample of syn and anti isomers of Ir(Cyttp)H$_2$Cl was dissolved in d$_4$-toluene (~1.5 mL) and placed in an NMR tube. No H$_2$ gas was added. One drop of absolute ethanol was added to increase the polarity of the solvent, and the tube was sealed. After heating for 1h at 80°C conversion to the pure anti isomer was observed.

13. Reaction of anti-Ir(Cyttp)H$_2$Cl with BCl$_3$ and Added Ligand

The anti isomer of Ir(Cyttp)H$_2$Cl (0.17g; 0.21 mmol) was dissolved in benzene, and 30 l (0.21 mmol) of PMe$_2$Ph was added to the stirred solution. A stream of BCl$_3$ gas was bubbled through the solution which turned yellow immediately. Within 30 min, a yellow precipitate fell out. The precipitate was filtered off, washed in benzene (2 x 2 mL), and dried in vacuo.

14. Reaction of anti-Ir(Cyttp)H$_2$Cl with BCl$_3$

Ir(Cyttp)H$_2$Cl was dissolved in benzene and BCl$_3$ was bubbled through the solution. After 30s the color of the solution turned yellow. Bubbling was continued and a yellow precipitate formed. The precipitate was filtered off, washed in benzene (2 x 2 mL), and dried in vacuo.

15. Reaction of PPhMe$_2$ and BCl$_3$

A stream of BCl$_3$ gas was bubbled through a dichloromethane solution of PPhMe$_2$ for 1 min.

16. Synthesis of [Ir(ttp)H$_4$]*BF$_4$

A solution of Ir(ttp)H$_3$ (~ 50mg) in CD$_2$Cl$_2$ was placed in an NMR tube and cooled in a Dry Ice/isopropyl alcohol bath. A drop of cold HBF$_4$Et$_2$O
was added and the solution was agitated. The solubility increased upon addition of the acid. The $^3P(^1H)$ and $^1H$ NMR spectra were recorded at 303K and 193K before acid addition and at 193, 223, 253, 283, and 303K after the acid addition.

17. Synthesis of $[\text{Ir}(\text{Cyttpp})H_4]^+ \text{BF}_4^-$

The procedure described in synthesis 16 above, was used.

18. Synthesis of $[\text{Ir}(\text{ttp}^*)H_4]^+ \text{BF}_4^-$

Method A. The general procedure described in synthesis 16 was used.

Method B. The above procedure was used, except all manipulations were done under an $H_2$ atmosphere. The solvent had $H_2$ gas bubbled through it for 5 min. The sample was loaded into a pressure resistant NMR tube and a pressure of 10 psi of $H_2$ gas was placed over the solution.

19. Protonation of $\text{Ir}(\text{ttp})H_2\text{Cl}$

A sample of $\text{Ir}(\text{ttp})H_2\text{Cl}$ was dissolved in CD$_2$Cl$_2$ and placed in an NMR tube. The sample was cooled in Dry Ice/isopropyl alcohol and a drop of cold HBF$_4$Et$_2$O was added. NMR spectra were recorded at the temperatures listed in synthesis 17.

20. Synthesis of $[\text{Ir}(\text{Cyttpp})H_2\text{P(OMe)}_3]^+ \text{BF}_4^-$

Method A. A sample of $\text{Ir}(\text{Cyttpp})H_3$ was dissolved in CH$_2$Cl$_2$, and the solution was frozen in $N_2$. When the solution thawed, while it was still cold, HBF$_4$Et$_2$O (1 drop) was added. A few drops of P(OMe)$_3$ were added and the mixture was stirred for 5 min. A white precipitate (~10mg) formed. The solvent was decanted off and the precipitate dried in vacuo.

Method B. The same procedure was used as in method A, but stoichiometric amounts of acid and phosphite were added using a microliter syringe.
21. Synthesis of $[\text{Ir(Cyttp)H}_2(\text{CO})]^{\text{BF}_4}$

A sample of Ir(Cyttp)H$_2$ was dissolved in CH$_2$Cl$_2$, the solution was frozen and then thawed. To the cold solution, one drop of HBF$_4$Et$_2$O was added. A stream of CO gas was bubbled through the solution for 2 min until a white precipitate (~10mg) formed. The solution was decanted and the precipitate dried in vacuo.

22. Reaction of $[\text{Ir(Cyttp)H}_2]^{\text{BF}_4}$ with N$_2$

The procedure used for synthesis 21 was followed, except N$_2$ was used instead of CO. No precipitate formed, but removal of solvent gave a yellow oil.

23. Synthesis of $[\text{Ir(ttp)H}_2(\text{PPh}_3)]^{\text{SbF}_6}$

Method A. A sample of Ir(ttp)H$_3$ (approx 100 mg) and excess PPh$_3$ (approx 100 mg) were dissolved in 10 mL of CH$_2$Cl$_2$. The temperature was lowered to 147K in a Dry Ice/isopropyl alcohol bath. A drop of HSbF$_6$ was added and the solution was allowed to warm slowly to room temperature. The solvent was removed in vacuo and the sample redissolved in CD$_2$Cl$_2$.

Method B. A sample of Ir(ttp)H$_3$ (approx 100 mg) was dissolved in 10 mL of CH$_2$Cl$_2$ and cooled to 147K. A drop of HSbF$_6$ was added and then PPh$_3$ (approx 100 mg) was added. The solution was warmed slowly to room temperature. The solvent was removed in vacuo, and the sample redissolved in CD$_2$Cl$_2$.

24. Synthesis of $[\text{Ir(Cyttp)H}_2(\text{PPh}_3)]^{\text{SbF}_6}$

The same procedures described in methods A and B of synthesis 23 were used.
25. Synthesis of \( \text{Ir(tcp*)H}_2\text{(PPh}_3\text{)}\)'SbF\(_6\)'

The same procedures described in methods A and B of synthesis 23 were used.

26. \(\text{Ir(Cyttp)H}_2\text{(p-tolyl-N-CH-N-p-tolyl)}\)

A sample of \(\text{Ir(Cyttp)H}_2\) (0.59g; 0.75 mmol) was dissolved in 30 mL of \(\text{CH}_2\text{Cl}_2\), and 0.7g (3.1 mmol) of 1,3-di-p-tolylcarbodiimide was added. The solution was stirred for 48h. The volume was reduced in vacuo to 5 mL and 5 mL of hexane was added to precipitate the product. The white precipitate was filtered off, washed with hexane (1 x 1 mL) and dried in vacuo.

Yield: 0.20g (26%).

27. \(\text{Ir(ttp*)H}_2\text{(p-tolyl-N-CH-N-p-tolyl)}\)

A sample of \(\text{Ir(ttp*)H}_2\) (0.39g; 0.51 mmol) was dissolved in 20 mL of \(\text{CH}_2\text{Cl}_2\), and 0.51g (2.3 mmol) of 1,3-di-p-tolylcarbodiimide was added. After stirring for 10 min a white precipitate formed. The precipitate was filtered off, washed in hexane (1 x 1 mL) and dried in vacuo.

28. \(\text{Ir(ttp)H}_2\text{(p-tolyl-N-CH-N-p-tolyl)}\)

A sample of \(\text{Ir(ttp)H}_2\) (0.35g; 0.46 mmol) was dissolved in 30 mL of \(\text{CH}_2\text{Cl}_2\), and 0.50g (2.2 mmol) of 1,3-di-p-tolylcarbodiimide was added. The solution was stirred for 10 min; the volume was then reduced to 5 mL and 5 mL of hexane was added to precipitate the product. The white precipitate was filtered off, washed in hexane (1 x 1 mL) and dried in vacuo.

Yield: 0.35g (97%).
29. \( \text{Ir(Cyttp)H(p-tolyl-N-CH=N-p-tolyl)} \)

A sample, consisting of 0.1 g (0.1 mmol) of \( \text{Ir(Cyttp)H}_2 \text{Cl} \) was combined with 0.30 g (0.75 mmol) of \( \text{TlBF}_4 \) and 0.20 g (0.90 mmol) of 1,3-di-p-tolylcarbodiimide in 2 mL of \( \text{CD}_2 \text{Cl}_2 \). The solution turned to an orange slurry within 5 min, and after 10 min turned to a yellow slurry. The slurry was transferred to an NMR tube and heated with a heat gun for 1 min increments. The total heating time was 2 min. The sample was periodically examined by \( ^{31}\text{P}(^1\text{H}) \) and \( ^1\text{H} \) NMR spectroscopy to determine when the reaction was complete.

30. \( \text{Ir(ttp*)H(p-tolyl-N-CH=N-p-tolyl)} \)

A sample, consisting of 0.1 g (0.1 mmol) of \( \text{Ir(ttp*)H}_2 \text{Cl} \) was combined with 0.20 g (0.50 mmol) of \( \text{TlBF}_4 \) and 0.20 g (0.90 mmol) of 1,3-di-p-tolylcarbodiimide in 2 mL of \( \text{CD}_2 \text{Cl}_2 \). The mixture turned green, and was allowed to reflux for 15 min. Periodically, the reaction was monitored using \( ^{31}\text{P}(^1\text{H}) \) and \( ^1\text{H} \) NMR spectroscopy.

31. \( \text{Ir(ctp)H(p-tolyl-N-CH=N-p-tolyl)} \)

A sample, consisting of 0.39 g (0.49 mmol) of \( \text{Ir(ctp)H}_2 \text{Cl} \) was combined with 0.20 g (0.50 mmol) of \( \text{TlBF}_4 \) and 0.22 g (0.99 mmol) of 1,3-di-p-tolylcarbodiimide in 5 mL of \( \text{CH}_2 \text{Cl}_2 \). The solution was stirred for 1 h, and then the grayish precipitate of \( \text{TlBF}_2 \) was filtered off. The solvent was removed from the remaining brown filtrate in vacuo.

32. \( \text{Ir(Cyttp)H}_2(p-coiyl-N-CH=N-p-tolyL) \)

Using a Dry Ice/isopropyl alcohol bath, a sample of 0.34 g (0.43 mmol) of \( \text{Ir(Cyttp)H}_2 \) in 5 mL of \( \text{CH}_2 \text{Cl}_2 \) was cooled to 147 K. One drop of aqueous \( \text{H}_2\text{SbF}_6 \) was added, followed by 0.48 g (2.2 mmol) of 1,3-di-p-tolylcarbodiimide. The solution was allowed to slowly warm to room temperature.
while stirring (12h). The addition of 5 mL of hexane caused an oil to form. The entire solution was brought to dryness in vacuo.

33. Ir(ttp*)H\textsubscript{2}(p-tolyl-N-CH-N-p-tolyl)\textsubscript{2}

The procedure described in 32 was carried out using 0.24g (0.31 mmol) of Ir(ttp*)H\textsubscript{2} and 0.33g (1.5 mmol) of 1,3-di-p-tolylcarbodiimide.

34. Ir(ttp)H\textsubscript{2}(p-tolyl-N-CH-N-p-tolyl)\textsubscript{2}

The procedure described in 32 was carried out using 0.02g (0.03 mmol) of Ir(ttp)H\textsubscript{2} and 0.06g (0.27 mmol) of 1,3-di-p-tolylcarbodiimide.

F. Rhodium Complexes

1. Synthesis of [Rh(COD)Cl\textsubscript{2}]

Some RhCl\textsubscript{3} (4.0g; 15 mmol) was dissolved in 40 mL of a degassed ethanol/water solution (5 parts ethanol to 1 part water), and 5.3g (6 mL; 49 mmol) of 1,5-cyclooctadiene was added. The mixture was allowed to reflux for 18h; during this time the solution turned from purple to orange-yellow. Cooling to room temperature produced an orange precipitate which was filtered off, washed in pentane (3 x 5 mL) and the ethanol-water mixture (5 mL portions, approx 50 mL total) until no Cl\textsuperscript{-} appears in the washings. (The washings were tested with an AgBF\textsubscript{4} solution.)

Yield: 13.4g (88%)

2. Synthesis of Rh(ttp)Cl

The ttp oil (0.97g; 1.7 mmol) was dissolved in 30 mL of absolute ethanol and heated to reflux. An ethanol solution of 0.44g (0.89 mmol) of [Rh(COD)Cl\textsubscript{2}] was added. The color of the solution turned orange and yellow precipitate began to form immediately. Refluxing was continued for
10 min. The solution was cooled, filtered off, and the precipitate washed with ethanol (2 x 2 mL).

Yield: 0.85g (68%)

3. Synthesis of Rh(Cyttp)Cl

A sample of Rh(COD)Cl₂ (0.31g; 1.3 mmol) was dissolved in THF, and 5.0 mL (1.3 mmol) of Cyttp in benzene solution (4 mL/mmol) was added. The solution was stirred for 1h at room temperature, the solvent was removed, and the product was recrystallized from hot ethanol. The final product was a yellow powder.

Yield: 0.37g (42%)

4. Synthesis of Rh(ttp*)Cl

The ttp* oil (0.69g; 1.2 mmol) was dissolved in ethanol and 0.34g (0.69 mmol) of [Rh(COD)Cl]₂ was added. The mixture was stirred at room temperature overnight. After 18h a heavy yellow precipitate was observed. This was filtered off, washed with ethanol (2 x 2 mL), and dried in vacuo.

Yield: 0.24g (28%)

5. Synthesis of Rh(ttp*)Cl₃

Method A. The ttp* oil (0.90g; 1.6 mmol) was dissolved in 50 mL of CH₂Cl₂ and 0.49g (0.95 mmol) of [Rh(COD)Cl]₂ was added. The mixture was stirred at room temperature overnight. Addition of ethanol caused a yellow solid to precipitate. The solid was filtered off, washed with ethanol (1 x 2 mL), and recrystallized from CH₂Cl₂/ethanol.

Yield: 0.20g (16%)

Method B. A sample of Rh(ttp*)Cl (100 mg; 0.14 mmol) was stirred in CH₂Cl₂. Mild heating (50°C) for 30 min caused conversion to
Rh(ttp*)Cl. The \(^{31}\)P NMR spectra were identical to the compound isolated in method A.

6. Synthesis of [Rh(COD)(sol)]'PF\(_6\)'

A sample (0.15g; 0.3 mmol) of [Rh(COD)Cl]\(_2\) and 0.20g (0.79 mmol) of AgPF\(_4\) were dissolved in 30 mL of acetone and stirred for 30 min. The AgCl was removed by filtration. The filtrate was used the next step.

7. Synthesis of [Rh(Cyttp)(sol)]'PF\(_6\)'

The filtrate was collected from synthesis 6, and 2.5 mL (0.63 mmol) of Cyttp solution in benzene (stock solution) was added. The color changed from yellow to orange immediately. Attempting to remove the solvent in vacuo yielded an orange oil.

8. Reactions of [Rh(Cyttp)(sol)]'PF\(_6\)'

The [Rh(Cyttp)(sol)]'PF\(_6\) oil was dissolved in acetone and 160 psi of hydrogen was added in a Parr bomb. The mixture was stirred for 3h. Only starting material was visible in the \(^{31}\)P and \(^1\)H NMR spectra.

9. Attempts to Synthesize Rh(Cyttp)H\(_2\)Cl

Method A. A sample of Rh(Cyttp)Cl was dissolved in benzene, placed in a Parr bomb and pressurized to 160 psi with H\(_2\) gas. The solution was stirred at room temperature for 18h. The bomb was opened in an inert atmosphere box and the solvent was removed from the product in vacuo.

Method B. A sample of Rh(Cyttp)Cl was dissolved in benzene and treated with an excess of NaBH\(_4\). A stream of H\(_2\) gas was bubbled through the solution for 10 min and the solution was stirred for 1h. No hydride-containing products were detected by high-field \(^1\)H NMR techniques.

Method C. By analogy with work done by Nappier and Meek,\(^5\) the complex [Rh(Cyttp)HCl]'BF\(_4\) was formed by adding Rh(Cyttp)Cl in ethanol/
CH₂Cl₂ to a solution of HBF₄ in ethanol. After stirring for 1h a yellow powder was seen. This was filtered off, washed in ethanol (2 x 2 mL), and dried in vacuo. A sample of this salt was dissolved in ethanol and treated with excess NaBH₄. The resulting gold powder was filtered off and dried in vacuo. No hydrides were detected using high-field §H NMR.

Method D: ligand replacement. A sample of Wilkinson's Catalyst, Rh(PPh₃)₃Cl was slurried in degassed benzene and placed in a Parr bomb which was pressurized to 80 psi with H₂. After 2h of stirring the purple slurry had turned to an orange solution (Rh(PPh₃)₂H₂Cl(sol)). Storage under an N₂ atmosphere caused the solution to darken, but an H₂ sweep regenerated the original color. A Cytpp solution was added and the color immediately turned from orange to yellow. The solution was removed by passing an H₂ stream over it.

10. Synthesis of Rh(Cytpp)Cl-H₂

A sample of Rh(Cytpp)Cl was dissolved in CD₂Cl₂ and placed in a pressure NMR tube. (Some oxide impurities are present.) The solution was cooled to 147K and H₂ was bubbled through it for 20 min. The tube was then pressurized to 12 psi with H₂. Variable temperature NMR spectra were obtained from 193K to 303K. At 223K the tube was opened (while in a Dry Ice/isopropyl alcohol bath and under a stream of Ar) and more CD₂Cl₂ was added. A stream of H₂(g) was bubbled through the solvent for an additional 5 min, the tube was repressurized, and data collection continued.
G. Platinum Complexes

1. Synthesis of [Pt(ttp*)Cl]Cl

The ttp* oil (0.31g; 0.55 mmol) was dissolved in 50 mL of benzene and 0.20g (0.54 mmol) of Pt(COD)Cl₂ was added. The mixture was refluxed for 3h. After cooling, the resulting white precipitate was filtered off, washed in hexane (2 x 2 mL), and dried in vacuo.

Yield: 0.34g (75%)

Elemental Analysis: Calculated (found) -- C 51.80 (50.27); H 5.20 (5.40); P 11.13 (11.68); Cl 8.49 (8.25).

2. Synthesis of [Pt(ttp*)I]I

The ttp* oil (0.21g; 0.37 mmol) of ttp* oil was dissolved in 10 mL of benzene and 0.21g (0.38 mmol) of Pt(COD)I₂ was added. The resulting solution was refluxed for 2h; as the solution cooled to room temperature, an orange precipitate formed. This was filtered off, washed with hexane (2 x 1 mL), and dried in vacuo.

Elemental Analysis: Calculated (found) -- C 42.49 (39.82); H 4.27 (4.15); P 9.13 (8.28); I 24.94 (26.54).
A. Ligand Chemistry

1. Modified Preparation of Ph₂P(CH₂)₃P(Ph)(CH₂)₃PPh₂(ttp)

The standard method of preparation of the chelating ligand Ph₂P(CH₂)₃P(Ph)(CH₂)₃PPh₂ (ttp) has been described in detail in the literature. This general method is outlined in reactions 14 through 17 below.

\[
\begin{align*}
\text{Ph₂PH} + n\text{BuLi} & \rightarrow \text{Ph₂PLi} + \text{Butane} \quad (14) \\
\text{Ph₂PLi} + \text{Cl(CH₂)₃Cl} & \rightarrow \text{Ph₂P(CH₂)₃Cl} + \text{LiCl} \quad (15) \\
\text{PhPH₂} + n\text{BuLi} & \rightarrow \text{PhPLi₂} + 2 \text{Butane} \quad (16) \\
\text{PhPLi₂} + 2\text{Ph₂P(CH₂)₃Cl} & \rightarrow \text{Ph₂P(CH₂)₃P(Ph)(CH₂)₃PPh₂} \\
& \quad + 2\text{LiCl} \quad (17)
\end{align*}
\]

The ttp used in this work, however, was prepared using modifications based on the work of Kyba and coworkers. The first modification was the use of 1-bromo-3-chloropropane instead of 1,3-dichloropropane. When 1,3-dichloropropane is used, a large (10-fold) excess is required. The purpose of this excess is to prevent diphenylphospide from displacing both chlorine atoms to form the bidentate phosphine Ph₂P(CH₂)₃PPh₂. When
1-bromo-3-chloropropane is used, the bromine end of the molecule undergoes nucleophilic substitution reactions faster than the chlorine end. This favors formation of \( \text{Ph}_2\text{P(CH}_2\text{)}_3\text{Cl} \) over formation of the bidentate product. Thus the reaction can be run using a one to one ratio of \( \text{Ph}_2\text{PH} \) to \( \text{Br(CH}_2\text{)}_3\text{Cl} \) rather than an excess of the dihalopropane. The second modification of the standard procedure is the use of lithium diisopropylamide (LDA) rather than n-butyllithium to generate the phosphide salt \( \text{LiPPh}_2 \). Since LDA is a weaker base than n-butyllithium, it can be used to generate the phosphide salt in situ, thereby eliminating the need to isolate the salt. Thus reactions 14 and 15 were combined to form a one-step synthesis of \( \text{Ph}_2\text{P(CH}_2\text{)}_3\text{Cl} \). The remainder of the synthesis is the same as that outlined in reactions 16 through 17.

The use of 1-bromo-3-chloropropane and LDA in ligand syntheses was further explored by Meek and Green.\(^8\) They used these modifications to produce ttp, Cyttp and \( \text{(p-CF}_3\text{C}_6\text{H}_4\text{)}_2\text{P(CH}_2\text{)}_3\text{P(Ph)(CH}_2\text{)}_3\text{P(p-CF}_3\text{C}_6\text{H}_4\text{)}_2 \) (CF\(_3\) ttp). In a further modification they proposed the initial generation of \( \text{PhP(}\text{CH}_2\text{)}_3\text{Cl}_2 \) followed by reaction with two equivalents of \( \text{LiPR}_2 \). Reactions 18 through 20 outline their modified ligand preparation.

\[
\begin{align*}
\text{PhPH}_2 + \text{Br(CH}_2\text{)}_3\text{Cl} + \text{LDA} & \rightarrow \text{Cl(CH}_2\text{)}_3\text{P(Ph)(CH}_2\text{)}_3\text{Cl} \quad (18) \\
\text{HPR}_2 + \text{nBuLi} & \rightarrow \text{LiPR}_2 + \text{Butane} \quad (19) \\
\text{Cl(CH}_2\text{)}_3\text{P(Ph)(CH}_2\text{)}_3\text{Cl} + \text{LiPR}_2 & \rightarrow \text{R}_2\text{P(CH}_2\text{)}_3\text{P(Ph)(CH}_2\text{)}_3\text{PR}_2 \quad (20)
\end{align*}
\]

Their method has an advantage over the one used in this work since it generates the lithium diphenylphosphide in situ. In this work the insoluble, pyrophoric \( \text{LiPPh}_2 \) had to be carefully transferred as a THF slurry in steps 16 and 17 of Scheme 1.
2. Preparation of \( \text{Ph}_2 \text{P} \left( \text{CH}_2 \right)_2 \text{P} \left( \text{Cy} \right) \left( \text{CH}_2 \right)_2 \text{P} \text{Ph} \) (\( \text{ttp}^* \))

One of the goals of this research was to study the influence that changes in the chelating ligands exert on metal complexes. Previous work within the Meek group focused on comparisons of metal complexes of \( \text{ttp} \) versus those of \( \text{Cyttp} \).\(^{89}\) Other recent work explored new ligands such as \( p-\text{CF}_3 \text{ctp} \), and the unsymmetric \( \text{Ph}_2 \text{P} \left( \text{CH}_2 \right)_2 \text{P} \left( \text{Ph} \right) \left( \text{CH}_2 \right)_2 \text{PCy}_2 \).\(^{89a,90}\) In order to complement the work done on \( \text{ttp} \) and \( \text{Cyttp} \) complexes, a new ligand, with intermediate steric and electronic properties, was proposed. In this new chelate, bis(3-diphenylphosphinopropyl)cyclohexylphosphine, \( \text{ttp}^* \), the phenyl group on the central phosphorus atom of \( \text{ttp} \) is replaced with a cyclohexyl group. (See species 12 through 14.) Dahlénburg has successfully synthesized similar ligands in which the central phosphorus atom has \( R = t-\text{Bu}, \text{Me} \).\(^{76}\)

While both \( \text{ttp} \) and \( \text{Cyttp} \) possess a high degree of symmetry, they differ in their steric and electronic properties. \( \text{Cyttp} \) is both more sterically demanding (by an estimated 30°),\(^{89b}\) and more basic than \( \text{ttp} \). In addition, \( \text{Cyttp} \) complexes are more soluble in hydrocarbon solvents than the corresponding \( \text{ttp} \) complexes. In contrast to \( \text{Cyttp} \), the steric requirements for \( \text{ttp}^* \) are estimated to be only 8° greater than for \( \text{ttp} \) (22° less than for \( \text{Cyttp} \)). Similarly, \( \text{ttp}^* \) is expected to be more basic than \( \text{ttp} \) and somewhat less basic than \( \text{Cyttp} \). In addition, it was hoped that the solubility of the metal \( \text{ttp}^* \) complexes in hydrocarbons would be greater than \( \text{ttp} \) and somewhat less than \( \text{Cyttp} \). Finally, the site of increased basicity in \( \text{ttp}^* \) (compared to \( \text{ttp} \)) is at the central phosphorus atom, whereas the sites of increased basicity in \( \text{Cyttp} \) are located on the wing phosphorus atoms. This should result in interesting reactivity in
the metal complexes of ttp* since the available electron density will be trans to an active ligand, rather than trans to another member of the chelate itself.

The synthesis of ttp* was carried out using known methods, and is outlined in Scheme 2. The final yield of ttp* is 52%, based on CyP((CH₂)₃OH)₂, which was previously prepared by Supplee.
CyP((CH₂)₃OH)₂ is a colorless oil with a single ³¹P(¹H) NMR resonance at δ -19.2 ppm. Low temperature (0°C) oxidation of CyP((CH₂)₃OH)₂ with a hydrogen peroxide solution yields a yellow oil, CyP(O)((CH₂)₃OH)₂ with a ³¹P(¹H) NMR resonance at δ +53.7 ppm. Note that a characteristic downfield shift of the phosphorus atom is observed upon oxidation (Δδ = 70 ppm). This reflects the decreased electron density around the phosphorus atom as a result of the electron withdrawing effect of oxygen. The purpose of this oxidation is to protect the phosphorus atom during the subsequent steps. Treatment of the phosphine oxide with refluxing PCl₅ followed by hydrolysis of the excess PCl₅ and drying yields the bis(3-propylchloro)-cyclohexylphosphine oxide, CyP(O)((CH₂)₃Cl)₂. Its ³¹P(¹H) NMR spectrum shows a singlet at δ 43.2 ppm. The attachment of the wing phosphorus atoms is achieved by slowly adding LiPPh₂ to a cold, stirred solution of CyP(O)((CH₂)₃Cl)₂ over a period of 12h. After hydrolysis and removal of solvent, CyP(O)((CH₂)₃PPh₂)₂ is isolated as a brown, waxy solid. Its ³¹P(¹H) NMR spectrum shows a singlet at δ 48.4 ppm (CyP(O)-) and a singlet at δ -18.5 ppm (-PPh₂). No phosphorus-phosphorus coupling occurs through the propylene backbone. The final step in the synthesis consists of the reduction of the phosphine oxide to phosphine using Si₂Cl₆. The product, CyP((CH₂)₃PPh₂)₂, shows two singlets in the ³¹P(¹H) NMR spectrum, at δ -23.6 ppm (-PCy-) and at δ -18.6 ppm (-PPh₂). The ligand is purified by a kugelrohl distillation at 102°C to remove any PPh₂H impurities, followed by passing a benzene solution of the ligand through a neutral alumina column to remove any oxide impurities. After removing the solvent,
Synthesis of \( \text{ftp}^* \)

\[
\text{CyPH}_2 + \text{CH}_2\text{OH} \xrightarrow{\text{AIBN, h v}} \text{CyPH}_2\left(\text{CH}_2\text{OH}\right)_2 \quad \text{(21)}
\]

\( \text{clear oil} \)

\[
\text{CyPH}_2\left(\text{CH}_2\text{OH}\right)_2 + \text{H}_2\text{O}_2 \xrightarrow{\text{acetone}} \text{CyPH}_2\left(\text{CH}_2\text{OH}\right)_2 \quad \text{(22)}
\]

\( \text{yellow oil} \)

\[
\text{CyPH}_2\left(\text{CH}_2\text{OH}\right)_2 + 2 \text{PCl}_5 \xrightarrow{\text{CH}_2\text{Cl}_2} \text{CyPH}_2\left(\text{CH}_2\text{Cl}\right)_2 \quad \text{(23)}
\]

\( \text{orange oil} \)

\[
\text{PPh}_2\text{H} + \text{BuLi} \xrightarrow{\text{hexane/THF}} \text{LiPPh}_2 \quad \text{(24)}
\]

\( \text{yellow slurry} \)

\[
\text{CyPH}_2\left(\text{CH}_2\text{Cl}\right)_2 + \text{PPh}_2\text{H} \xrightarrow{\text{THF}} \text{CyPH}_2\left(\text{CH}_2\text{PPh}_2\right)_2 \quad \text{(25)}
\]

\( \text{brown, waxy} \)

\[
\text{CyPH}_2\left(\text{CH}_2\text{PPh}_2\right)_2 + \text{Si}_2\text{Cl}_6 \xrightarrow{\text{C}_6\text{H}_6} \text{CyPH}_2\left(\text{CH}_2\text{PPh}_2\right)_2 \quad \text{(25)}
\]

\( \text{white oil} \)

Scheme 2
CyP((CH₂)₃PPh₂)₂ was isolated as a viscous white oil. The chemical shifts of the intermediates are summarized in Table 3.

A comparison of the ³¹P NMR parameters for various tridentate chelates is given in Table 4. (The common abbreviations used for ligand nomenclature are listed in Table 5). From Table 4, it is clear that substitution of a cyclohexyl group for a phenyl group causes a downfield shift in the ³¹P NMR. When cyclohexyl is substituted on the central phosphorus atom (as in the case of ttp*) the resonance shifts 4.3 ppm downfield relative to ttp, and when cyclohexyl groups are substituted on the wing phosphorus atoms (as in the case of Cyttp) the resonance shifts 10.3 ppm downfield relative to ttp. One should notice that there are two opposing trends at work in the chelating systems. First, increased electron density at an atom causes an upfield shift in the ³¹P NMR, as can be seen from the following series.

\[
(F_3C\overbrace{\bigg|}^{\text{C}})_2PH < Ph_2PH < Cy_2PH
\]

\[\begin{align*}
-42.2 \text{ ppm} & \quad -42.4 \text{ ppm} & \quad -58.8 \text{ ppm}
\end{align*}\]

Based on electronic effects alone, we would expect the substitution of a cyclohexyl group for a phenyl group to result in an upfield shift. The second trend, however, is that increased steric crowding causes a downfield shift in the NMR. Comparison of the chemical shifts of P(t-Bu)₃ and P(i-Bu)₃ illustrate this point.

\[
P(t\text{-Bu})_3 > P(i\text{-Bu})_3
\]

\[\begin{align*}
61.9 \text{ ppm} & \quad -40.0 \text{ ppm}
\end{align*}\]
### Table 3

**$^{31}$P Shifts for Intermediates in ttp* Synthesis$^a,b$**

<table>
<thead>
<tr>
<th>Intermediate</th>
<th>P1 $\delta$</th>
<th>P2 $\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CyP(CH$_2$CH$_2$CH$_2$OH)$_2$</td>
<td>-19.2</td>
<td></td>
</tr>
<tr>
<td>CyP(CH$_2$CH$_2$CH$_2$OH)$_2$</td>
<td>53.7</td>
<td></td>
</tr>
<tr>
<td>CyP(CH$_2$CH$_2$CH$_2$Cl)$_2$</td>
<td>43.2</td>
<td></td>
</tr>
<tr>
<td>CyP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$</td>
<td>48.4</td>
<td>-18.5</td>
</tr>
<tr>
<td>CyP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$</td>
<td>-23.6</td>
<td>-18.6</td>
</tr>
</tbody>
</table>

---

$a$ The central phosphorus atom is designated P$_1$, and the wing phosphorus atoms are designated P$_2$

$b$ in CD$_2$Cl$_2$
Table 4

$^{31}$P NMR Shifts for Various Tridentate Ligands $^{a,b}$

<table>
<thead>
<tr>
<th>L</th>
<th>P1</th>
<th>P2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$ttp</td>
<td>-28.0</td>
<td>-16.9</td>
</tr>
<tr>
<td>ttp</td>
<td>-28.2</td>
<td>-18.1</td>
</tr>
<tr>
<td>ttp$^*$</td>
<td>-23.9</td>
<td>-18.8</td>
</tr>
<tr>
<td>Cyttlp</td>
<td>-28.2</td>
<td>-7.8</td>
</tr>
</tbody>
</table>

$^{a}$ The central phosphorus atom is designated $P_1$, and the wing phosphorus atoms are designated $P_2$

$^{b}$ in CD$_2$Cl$_2$
Table 5

Nomenclature for Tridentate Chelates

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>L</th>
<th>R</th>
<th>R'</th>
</tr>
</thead>
<tbody>
<tr>
<td>ttp</td>
<td>Ph</td>
<td>Ph</td>
</tr>
<tr>
<td>Cytp</td>
<td>Cy</td>
<td>Ph</td>
</tr>
<tr>
<td>CF₃ttp</td>
<td>F₃C−〇</td>
<td>Ph</td>
</tr>
<tr>
<td>ttp⁺</td>
<td>Ph</td>
<td>Cy</td>
</tr>
</tbody>
</table>

*a The central phosphorus atom is designated P₁, and the wing phosphorus atoms are designated P₂.*
The results in Table 4, therefore, suggest that steric factors predominate over electronic factors in both Cyttp and ttp*. Comparisons of the metal complexes of ttp, Cyttp, and ttp* will be discussed later in this chapter.

3. Attempted Synthesis of the Cyclic Ligand PhP(CH₂)₅P(Ph)(CH₂)₅P(Ph)CH₂P

Several attempts were made to synthesize a cyclic tridentate phosphine ligand of the type shown below.

![Cyclic Ligand Diagram](image)

1,5,9 triphosphacyclododecane (R = Ph)

This ligand could be considered analogous to the cyclopentadienyl anion, since both are six-electron donors, and both should occupy a facial site on a metal ion. The cyclopentadienyl anion has been used extensively in metal systems by Bergman and others. In addition, similar ligands containing four phosphorus donor atoms should be studied for their similarities to the porphyrins. A simple synthetic route to cyclic phosphorus donor ligands could stimulate research in these areas.

Pioneering work on cyclic phosphorus ligands has been done by Kyba, Rosen, Heck, and Diel. Many of their complexes contain mixed phosphorus and heteroatom cycles. Of those containing only
phosphorus donors, several are tetrade andate.\textsuperscript{70,72} Kyba's\textsuperscript{67,68} ligands all contain eleven-membered ring systems of the general form shown below.

\[ \text{mesitylene} \cdot \text{Mo}(\text{CO})_3 \rightarrow \text{mesitylene} \cdot \text{Mo}(\text{CO})_3 \]

In order to achieve synthesis of the macrocycle 16, Kyba employed high dilution techniques.

There is only one example of a phosphorus-containing twelve-membered ring macrocycle, and it was prepared using the metal template synthesis outlined in steps 26 and 27 below.

\[ \text{mesitylene} \cdot \text{Mo}(\text{CO})_3 \rightarrow \text{mesitylene} \cdot \text{Mo}(\text{CO})_3 \]

Since there was no readily available source of allylphenylphosphine for the present work, the following synthesis was devised.
The reaction between \([\text{Ir(COE)}_2\text{Cl}]_2\) and \(\text{HPhP(CH}_2\text{)}_3\text{PPhH}\) did not proceed cleanly. Several attempts produced a largely insoluble, dark yellow powder, or a species with a multitude of signals in the \(^{31}\text{P}^{'\text{H}}\) NMR spectrum. One possible explanation of the results is that the bidentate phosphine acted as a bridging ligand between two metal centers to form a polymeric species.

It would, perhaps, be more profitable to use high dilution techniques to design a more general synthesis, similar to those used for ttp, Cyttp, and ttp*. A proposed synthesis is outlined below in Scheme 4.

\[
\begin{align*}
\text{HPhP(CH}_2\text{)}_3\text{PPhH} + \text{nBuLi} &\rightarrow \text{LiPhP(CH}_2\text{)}_3\text{PPhLi} \quad (31) \\
\text{PhP((CH}_2\text{)}_3\text{Cl)}_2 + \text{LiPhP(CH}_2\text{)}_3\text{PPhLi} &\rightarrow (\text{PhP(CH}_2\text{)}_3)_3, \quad (32)
\end{align*}
\]

\text{Scheme 4}

The use of high dilution techniques is necessary to prevent the formation of polymeric species like 17.
Because of the problems described, this work was discontinued.

4. Metal Complexes of tcp*: Comparisons with ttp and Cyttp Complexes

In order to compare tcp* to Cyttp and ttp, a series of metal complexes of tcp* was synthesized. The metals chosen were Rh, Pt, and Ir, since a large number of Cyttp and ttp complexes of those metals were available for comparison. The Rh and Pt complexes were especially interesting, since metal phosphorus coupling constants can provide insight into the relative metal phosphorus bond strengths and bond distances within a series of chelated metal complexes.

The complex [Rh(COD)Cl]$_2$ reacts cleanly with two equivalents of tcp* in refluxing ethanol to give the yellow Rh(tcp*)Cl. If the reaction is carried out in dichloromethane, a different product, Rh(tcp*)Cl$_3$, results. The assignment of the two products as the Rh(I) and the Rh(III) chlorides is based on the magnitude of their Rh-P coupling constants. The species assigned as Rh(tcp*)Cl exhibits an AX$_2$M pattern in the $^{31}$P($^1$H) NMR spectrum with the "A" portion at 16.4 ppm and the "X" portion at 9.1 ppm ($^2$J$_{PP}$ = 50.6 Hz; $^1$J$_{PCRh}$ = 156 Hz; $^1$J$_{PPRh}$ = 134 Hz). The species assigned as Rh(tcp*)Cl$_3$ also exhibits an AX$_2$M pattern in its $^{31}$P($^1$H) NMR spectrum. The "A" portion is centered at 14.4 ppm, and the "X" portion at -1.9 ppm ($^2$J$_{PP}$ = 32.6 Hz; $^1$J$_{PCRh}$ = 121 Hz; $^1$J$_{PPRh}$ = 94 Hz). According to Blum and Mazanec, the values for one bond Rh-P coupling constants for Rh(I) complexes fall in the range of 140 to 180 Hz for $P_c$ (trans to Cl') and 110
to 145 Hz for $P_w$ (trans to P). The values of one bond Rh-P coupling constants for Rh(III) fall in the range of 120 to 156 Hz for $P_c$ and 79 to 120 Hz for $P_w$. The experimental findings in this work are consistent with these compiled data. The Rh(I) species can be oxidized to the Rh(III) species by stirring in dichloromethane. Presumably this reaction is the result of oxidation by trace impurities of HCl found in chlorinated solvents. The $^{31}P\{^1H\}$ NMR spectra for Rh(ttp*)Cl and Rh(ttp*)Cl$_2$ are shown in Figure 6. Table 6 summarizes the spectral parameters for some selected

\[
\begin{align*}
[\text{Rh(COD)Cl}]_2 + 2 \text{ttp}^* & \xrightarrow{\text{EtOH}} \text{Rh(ttp*)Cl} \\
\Delta;1h & \xrightarrow{\text{CH}_2\text{Cl}_2} \\
[\text{Rh(COD)Cl}]_2 + 2 \text{ttp}^* & \xrightarrow{\text{CH}_2\text{Cl}_2\text{overnight}} \text{Rh(ttp*)Cl}_3
\end{align*}
\]

Scheme 5

Rh complexes. Useful information can be obtained from the values of the metal-phosphorus coupling constants.$^{6}$ A large value for $^{1}J_{\text{PM}}$ indicates a strong metal-phosphorus interaction and is, therefore, indicative of a short metal-phosphorus bond distance. On the other hand, a small value for $^{1}J_{\text{PM}}$ indicates a weak metal-phosphorus interaction and a long bond distance. A comparison of the $^{1}J_{\text{PM}}$ values for the Rh(I) complexes reveals
that the ttp* complex has the smallest J value and, therefore, the longest Pc to Rh bond of the three complexes. As expected, lengthening of the Pc-Rh bond causes the Pw-Rh bonds to shorten. This is reflected in the value of $^1J_{PwRh}$ which is larger for the ttp* case than for the ttp or the Cyttp case. The lengthening of the Pc-Rh bond in the case of ttp* is probably due to the increased steric demands of the cyclohexyl substituent relative to a phenyl substituent. In the Rh(III) cases, it is interesting to note that the ttp* complexes have J values almost identical to the J values for the ttp complexes. Of the three complexes chosen for comparison, the longest metal-phosphorus bonds are those in the Cyttp complex (for both Pc-Rh and Pw-Rh). This indicates that Cyttp is bound more loosely to the metal than ttp or ttp*. Again, this is attributed to the steric constraints imposed by the presence of four bulky cyclohexyl groups on the ligand. A second factor which contributes to this "loose" bonding of Cyttp is the fact that Rh(III) is smaller than Rh(I) and therefore exhibits poorer metal-ligand orbital overlap and longer bonds. (This poorer metal-ligand overlap also explains the observation that $^1J_{PwRh}$ values for Rh(III) complexes are smaller than for Rh(I) complexes.)

A similar series of platinum complexes was explored. The Pt(I) complexes were synthesized from ttp* and the appropriate platinum COD halide as shown in Equations 33 and 34.

$$\text{Pt(COD)Cl}_2 + \text{ttp}^* \rightarrow \text{C}_6\text{H}_{15} \underset{3h; \Delta}{\rightarrow} \left[\text{Pt(ttp*Cl}_2\right] \text{Cl} \quad (33)$$

$$\text{Pt(COD)I}_2 + \text{ttp}^* \rightarrow \text{C}_6\text{H}_{15} \underset{2h; \Delta}{\rightarrow} \left[\text{Pt(ttp*Il}_1\right] \quad (34)$$
Figure 6: $^{31}$P NMR Spectra of Rh Complexes of ttp$^*$ (a) Rh(ttp$^*$)Cl$_3$ (b) Rh(ttp$^*$)Cl$_3$
Table 6

$^{31}$P NMR DATA FOR SELECTED Rh COMPLEXES$^a, b, c$

<table>
<thead>
<tr>
<th></th>
<th>$\delta P^1$</th>
<th>$\delta P^2$</th>
<th>$^2J_{P}P$</th>
<th>$^1J_{P1M}$</th>
<th>$^1J_{P2M}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(ttp)Cl</td>
<td>15.5</td>
<td>7.6</td>
<td>51.9</td>
<td>162.5</td>
<td>128.7</td>
</tr>
<tr>
<td>Rh(ttp*)Cl</td>
<td>16.4</td>
<td>9.1</td>
<td>50.6</td>
<td>156.0</td>
<td>134.0</td>
</tr>
<tr>
<td>Rh(Cyttp)Cl</td>
<td>20.6</td>
<td>9.2</td>
<td>49.0</td>
<td>174.0</td>
<td>126.0</td>
</tr>
<tr>
<td>Rh(ttp)Cl$_3$</td>
<td>25.4</td>
<td>7.3</td>
<td>36.5</td>
<td>122.0</td>
<td>94.2</td>
</tr>
<tr>
<td>Rh(ttp*)Cl$_3$</td>
<td>14.4</td>
<td>-1.9</td>
<td>32.6</td>
<td>121.0</td>
<td>94.0</td>
</tr>
<tr>
<td>Rh(Cyttp)Cl$_3$</td>
<td>5.3</td>
<td>-2.9</td>
<td>27.5</td>
<td>106.2</td>
<td>78.5</td>
</tr>
</tbody>
</table>

$^a$ Spectra recorded in CD$_2$Cl$_2$. $^b$ Chemical shift values in ppm. $^c$ Coupling constant values in Hz. $^d$ P1 is the central phosphorus atom of the chelate, P2 are the wing phosphorus atoms of the chelate.
The \([\text{Pt(ttp})\text{Cl}]\text{Cl}\) was isolated as a white powder, and the iodide analog as a yellow powder. Both complexes exhibit an AX2M pattern in the \(^{31}\text{P}(^1\text{H})\) and \(^{195}\text{Pt}\) NMR spectra. Sample spectra are shown in Figure 7 for \([\text{Pt(ttp})\text{Cl}]\text{Cl}\). In the \(^{31}\text{P}(^1\text{H})\) NMR spectrum, the "A" portion of the spectrum is located at -21.6 ppm and the "X" portion is observed at -2.5 ppm (\(^{1}J_{\text{PP}} = 26\) Hz; \(^{1}J_{\text{Pm}} = 3062\) Hz; \(^{1}J_{\text{Pn}} = 2324\) Hz). The \(^{195}\text{Pt}\) satellites are clearly visible in the phosphorus spectrum and are the result of phosphorus coupling to the \(^{195}\text{Pt}\) center. (Since \(^{195}\text{Pt}\) has \(I = 1/2\) and a natural abundance of 33\%, the spectrum appears to have a "triplet" structure.) The \(^{195}\text{Pt}\) NMR shift is a doublet of triplets located at -4773.9 ppm. Similar spectra were observed for \([\text{Pt(ttp})\text{I}]\text{I}\). Table 7 lists the spectral parameters for some selected Pt complexes. As in the case of the Rh(I) metal complexes, the \(^{1}J_{\text{Pm}}\) value for \([\text{Pt(ttp})\text{Cl}]\text{Cl}\) is smaller than for either the ttp or the Cyttt analogues, indicating that the \(\text{Pc-Pt}\) bond is longer when \(L = \text{ttp}\). Likewise, the \(^{1}J_{\text{Pn}}\) value for the ttp* complex is larger than for the ttp and Cyttt analogues, which is indicative of a shortened \(\text{P}_{\omega}-\text{Pt}\) bond when \(L = \text{ttp}\). The \([\text{Pt(CF}_{3}\text{ttp})\text{Cl}]\text{Cl}\) complex, it should be noted, has an unusually small value for \(^{1}J_{\text{Pn}}\). Based on this evidence, its \(\text{Pc-Pt}\) bond should be even longer than the one observed for \([\text{Pt(ttp})\text{Cl}]\text{Cl}\). This is unexpected since the electronic and steric parameters of \(\text{CF}_{3}\text{ttp}\) are very similar to those of ttp.\(^{85}\) A final point of interest in the Pt systems is a comparison between \([\text{Pt(ttp})\text{Cl}]\text{Cl}\) and \([\text{Pt(ttp})\text{I}]\text{I}\). Replacement of the chloride ions by iodide causes a significant upfield shift (of 358 ppm) in the \(^{195}\text{Pt}\) NMR spectrum and in the \(^{31}\text{P}\) NMR spectrum for both phosphorus atom resonances. In general, upfield shifts in the NMR are indicative of a more shielded atom.\(^{96}\) These data are
\[ \delta \text{Pt} = -4773.9 \text{ ppm} \]

\[ \delta \text{P}_2 = -2.5 \text{ ppm} \]

\[ \delta \text{P}_1 = -21.6 \text{ ppm} \]

\[ \ddot{J}_{\text{PP}} = 26 \text{ Hz} \]

\[ \ddot{J}_{\text{PIM}} = 3062 \text{ Hz} \]

\[ \ddot{J}_{\text{P2M}} = 2324 \text{ Hz} \]

Figure 7: $^{195}$Pt and $^{31}$P NMR Spectra of [Pt(ttp*)Cl]Cl (a) $^{195}$Pt Spectrum (b) $^{31}$P Spectrum
consistent with the fact that iodide is less electronegative than chloride and thus the iodide complex has more electron density available to the metal center and the attached phosphorus ligands.

Finally, the complexes Ir(ttp*)H₂Cl and Ir(ttp*)H₃ were prepared as shown in Scheme 6 below.

\[
\text{[Ir(COD)Cl]}_2 + 2 \text{ttp}^* \xrightarrow{\text{KOH; EIOH}} \text{Ir(ttp')H₃}
\]

Scheme 6

The iridium dihydridemonochloride Ir(ttp*)H₂Cl was isolated as a yellow powder from the reaction of [Ir(COD)Cl]₂ and ttp* in refluxing ethanol. The \(^1\)H and \(^31\)P(\(^1\)H) spectra of Ir(ttp*)H₂Cl are shown in Figure 8. The complex can be converted to the white Ir(ttp*)H₃ by stirring overnight in ethanolic KOH or by refluxing in ethanolic KOH for one hour. Alternatively, Ir(ttp*)H₃ can be synthesized directly from \([\text{Ir(COD)Cl}]_2, \text{ttp}^*, \text{and KOH}\) in refluxing ethanol. The \(^1\)H and \(^31\)P(\(^1\)H) NMR spectra for Ir(ttp*)H₃ are shown in Figure 9. The spectra in Figures 8 and 9 are
Table 7

NMR DATA FOR SELECTED Pt COMPLEXES

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta P_1$</th>
<th>$\delta P_2$</th>
<th>$^2J_{PP}$</th>
<th>$^1J_{P1M}$</th>
<th>$^1J_{P2M}$</th>
<th>$\delta Pt$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[Pt(CF_3ttt)Cl]Cl$</td>
<td>-20.9</td>
<td>-2.8</td>
<td>27</td>
<td>3025</td>
<td>2264</td>
<td></td>
</tr>
<tr>
<td>$[Pt(ttpp)Cl]Cl$</td>
<td>-20.7</td>
<td>-3.7</td>
<td>27</td>
<td>3134</td>
<td>2229</td>
<td></td>
</tr>
<tr>
<td>$[Pt(ttpp')Cl]Cl$</td>
<td>-21.6</td>
<td>-2.5</td>
<td>26</td>
<td>3062</td>
<td>2324</td>
<td>-4773.9</td>
</tr>
<tr>
<td>$[Pt(Cyttt)Cl]Cl$</td>
<td>-20.4</td>
<td>-4.0</td>
<td>24</td>
<td>3236</td>
<td>2152</td>
<td></td>
</tr>
<tr>
<td>$[Pt(ttpp')I]I$</td>
<td>-32.5</td>
<td>-14.7</td>
<td>26</td>
<td>2972</td>
<td>2308</td>
<td>-5131.8</td>
</tr>
</tbody>
</table>

$^a$ Chemical shifts are given in ppm  $^b$ recorded in CD$_2$Cl$_2$  $^c$ P1 refers to the central phosphorus atom of the chelate, P2 refers to the wing phosphorus atoms of the chelate  $^d$ Hz
typical spectra for IrLH₂Cl and IrLH₃ species, and they exhibit no unusual features. Table 8 summarizes the NMR data for selected Ir complexes. Note that the central phosphorus atom of the ttp* complexes is always more shielded than that of its ttp and Cyttp analogues. This is true for all of the Rh, Pt, and Ir complexes described herein, with the exception of Rh(ttp*)Cl, whose central phosphorus atom has essentially the same chemical shift as the central phosphorus atom of Rh(ttp)Cl.

5. Conclusions

A modified and improved synthesis of ttp was devised which yields clean products under milder conditions than previously used. This method cuts down on the formation of by-products, reduces the need for a large excess of reagents, and eliminates one step from the synthetic route.

Several attempts were made at trying to synthesize a tridentate cyclophosphane ligand which would bind to the face of a metal in a manner formally similar to Cp*. A template synthesis was unsuccessful, and it became clear that high dilution methods would be necessary to synthesize the proposed ligand.

A new linear tridentate phosphine, Ph₂P(CH₂)₃P(Cy)(CH₂)₃PPh₂, (ttp*), was synthesized. This molecule incorporated an electron-releasing group on the central phosphorus atom of the chelate, and its steric and electronic properties were designed to be intermediate between those of ttp and Cyttp. Several metal complexes of ttp* were synthesized and compared with their ttp and Cyttp analogues. Finally, using metal-phosphorus coupling constant values and ³¹P NMR chemical shifts, it was possible to make some general observations about the ttp* ligand.
Figure 8: $^{31}\text{P}$ and $^1\text{H}$ NMR Spectra of Ir(tp$^\text{s}$)H$_2$Cl (a) $^1\text{H}$ Spectrum, Hydride Region (b) $^{31}\text{P}$ Spectrum
Figure 9: $^{31}$P and $^1$H NMR Spectra of Ir(ttp$^*$)H$_3$ (a) $^1$H Spectrum, Hydride Region
(b) $^{31}$P Spectrum
### Table 8

$^{31}P$ and $^1H$ NMR Data for Selected Ir Compounds$^{a,b}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta P_1$</th>
<th>$\delta P_2$</th>
<th>$\delta H_1$</th>
<th>$\delta H_2$</th>
<th>$\delta H_3$</th>
<th>$J_{PHH}$</th>
<th>$J_{P2H}$</th>
<th>$J_{PP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir(ttpp)H$_2$Cl</td>
<td>-28.7 (l)</td>
<td>-12.0 (d)</td>
<td>-8.6 (d of l)</td>
<td>-21.5 (m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir(ttpp*)H$_2$Cl</td>
<td>-31.9 (l)</td>
<td>-11.4 (d)</td>
<td>-8.2 (d of l)</td>
<td>-21.3 (m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir(Cyttp)H$_2$Cl</td>
<td>-25.3 (l)</td>
<td>-0.1 (d)</td>
<td>-10.0 (d of l)</td>
<td>-22.4 (m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir(ttpp)H$_3$</td>
<td>-31.3 (l)</td>
<td>-8.6 (d)</td>
<td>complex multiplet from -10.5 to -12.5 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir(ttpp*)H$_3$</td>
<td>-32.4 (l)</td>
<td>-3.6 (d)</td>
<td>complex multiplet from -10.5 to -11.6 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir(Cyttp)H$_3$</td>
<td>-23.1 (l)</td>
<td>+8.5 (d)</td>
<td>complex multiplet from -12.7 to -13.6 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Recorded in CD$_2$Cl$_2$  
(b) Chemical shift values in ppm  
(c) central phosphorus atom  
(d) wing phosphorus atoms  
(e) trans to central phosphorus atom  
(l) cis to all phosphorus atoms  
(g) coupling constant values in Hz
B. Qualitative Study of Syn and Anti Isomers of Ir(Cyttp)H₂Cl

1. Isolation and Interconversion of Isomers

It is well-known that transition metal phosphine complexes such as Ir(PR₃)₃H₂Cl can exist as several isomers. Most notably, the phosphines can adopt either a meridional or a facial configuration around the metal center. It is also known that in the case of chelating triphosphine ligands such as ttp (which use a propylene linkage) the most common configuration is the meridional configuration.⁸⁹ (A recently discovered exception is the case of Ru(S₂CH₂)(Cyttp)⁸⁹d which contains a facially coordinated chelate.) In the case of IrLH₂Cl (L = ttp, Cyttp, ttp*), another type of isomer is expected. The substituent on the central phosphorus atom of the chelate can be on the same side of the metal phosphorus plane as the chloride or the hydride ligand. If the substituent is on the same side of the plane as the chloride ligand, the isomer obtained is the syn isomer; if it is on the same side of the plane as the hydride ligand the isomer obtained is the anti isomer. The structures of both isomers are shown below.
Yang reports that refluxing \([\text{Ir(COD)Cl}]_2\) with two equivalents of Cyttp in ethanol results in the formation of only one isomer of \(\text{Ir(Cyttp)H}_2\text{Cl}\). She identified the complex as the anti isomer, based on crystallographic data. By making use of the Nuclear Overhauser Effect (NOE), Socol and Meek were able to demonstrate that the anti isomer persisted in solution. In a similar manner, treatment of \([\text{Ir(COD)Cl}]_2\) with two equivalents of ttp in refluxing ethanol produces only one isomer of \(\text{Ir(ttp)H}_2\text{Cl}\). Dahlenburg, however, reports a second isomer of \(\text{Ir(ttp)H}_2\text{Cl}\) which is formed via the direct hydrogenation of the square planar \(\text{Ir(ttp)Cl}\). These two reports presumably represent both the anti and syn isomers of \(\text{Ir(ttp)H}_2\text{Cl}\). In order to further study the isomers of \(\text{Ir(ttp)H}_2\text{Cl}\) and \(\text{Ir(Cyttp)H}_2\text{Cl}\), isolation of \(\text{Ir(Cyttp)Cl}\) was undertaken.

Dahlenburg and Arpec prepared \(\text{Ir(ttp)Cl}\) from the reaction of \([\text{Ir(COE)}_2\text{Cl}]_2\) with ttp in toluene at room temperature. Yang reports that attempts to make \(\text{Ir(Cyttp)Cl}\) from \([\text{Ir(COD)Cl}]_2\) and Cyttp in toluene or benzene do not give reproducible results. Rather, two complexes can be observed, depending on the reaction conditions (\(^{31}\text{P}({}^1\text{H})\) NMR: for complex A: \(P_c - -16.8\) ppm, triplet, \(P_w - 1.98\) ppm, doublet, \(J_{pp} = 30.5\) Hz; for complex B: \(P_c - -37.6\) ppm, triplet, \(P_w - -25.6\) ppm, doublet, \(J_{pp} = \) not given).

When \([\text{Ir(COE)}_2\text{Cl}]_2\) and two equivalents of Cyttp are stirred together in toluene for ten minutes (at room temperature), a yellow powder results. The \(^{31}\text{P}({}^1\text{H})\) NMR spectrum reveals the same two species cited by Yang (species A: \(P_c - -17.2\) ppm, triplet, \(P_w - 1.6\) ppm, doublet, \(J_{pp} = 31\) Hz; and species B: \(P_c - -37.2\), triplet, \(P_w - -25.3\) ppm, doublet, \(J_{pp} = 25\) Hz). In addition, a third species is observed. Species C has the following
$^{31}$P-$^{1}$H NMR parameters: $P_c = -18.1$ ppm, triplet, $P_w = -28.3$ ppm, doublet, $^{2}J_{PP} = 22$ Hz. The $^{31}$P-$^{1}$H NMR spectrum of "Ir(Cyttp)Cl" is shown in Figure 10. Heating the sample in toluene for one hour at 80°C results in the disappearance of species B; species A and C remain, in a 3:1 ratio. Continued heating (12 hr., 80°C) causes the A:C ratio to increase to 4.6:1; however, decomposition begins at this point. (Either species C is converted into species A, or heating causes C to decompose faster than A.) Attempts to separate the three species using a silica column resulted in mixtures of all three components. A look at the $^{1}$H NMR indicates that no hydridic species are present; thus neither species A, B, or C can be explained as the result of internal cyclometallation reactions like the one shown below.

A second attempt at preparing pure Ir(Cyttp)Cl was made using the following method. The Cyttp oil was dissolved in degassed ethanol and a carefully measured amount of [Ir(COD)Cl]$_2$ was added. After 10 minutes of stirring at room temperature, a yellow powder began to appear. The powder was filtered off and dried in vacuo overnight. The $^{31}$P-$^{1}$H NMR spectrum of the powder reveals a clean AX$_2$ pattern with the "A" portion at -25.2 ppm.
Figure 10: $^{31}$P NMR Spectra of Species A, B, and C from the Attempted Synthesis of Ir(Cyttp)Cl (a) Before Heating (b) After 2 h at 80°C
and the "X" portion at -37.0 ppm ($^{1}J_{PP} = 25$ Hz). This species, which corresponds to species B in the above discussion, remains stable in the solid state when stored under an argon atmosphere. (The spectrum of the clean species is shown in Figure 11.) If species B is allowed to remain in ethanol, it eventually produces $\text{anti-Ir(Cyttp)H}_2\text{Cl}$.

In all subsequent reactions with $\text{H}_2$, the "Ir(Cyttp)Cl" produced from the above reactions (either pure B or a mixture of A, B, and C) give identical results. While the identity of compound C (obtained from the first method mentioned above) is not known, species A and B are probably two intermediates which result from the reaction between $[\text{Ir(COD)Cl}]_2$ and Cyttp. One possibility is that B is really a dimeric Cyttp complex with bridging chloride ligands while species A represents the monomeric complex.

This proposal is consistent with the fact that both species A and B react with $\text{H}_2$ to give identical products. Finally, one can further speculate that species C, which is observed only when the biscyclooctene iridium dimer is used (as opposed to the cyclooctadiene dimer), represents either a solvated Ir(I) chloride, or a species which retains coordinated cyclooctene. This is consistent with the evidence presented in Figure 10.
Figure 11: \( ^{31} \text{P} \) NMR Spectrum of "Ir(Cytmp)Cl", Species B
Heating the mixture of A, B, and C results in the disappearance of the dimeric species (B), while the amount of the monomeric species (A) increases. The increase observed for species C (with coordinated COE) is attributed to the large relative concentration of COE available, since the heating was done on a concentrated NMR sample in a sealed NMR tube.

When a sample of "Ir(Cyttp)Cl" in toluene is placed under an H₂ atmosphere and stirred for 2 hours at 110°C, the ³¹P(¹H) NMR shows two AB₂ patterns. The first (Pₑ = -25.5 ppm, P₇ = -0.8 ppm, ²Jₚₓ = 26 Hz) corresponds to the anti isomer of Ir(Cyttp)H₂Cl which has been previously characterized. The second AB₂ pattern (Pₑ = -44.8 ppm, P₇ = +0.8 ppm, ²Jₚₓ = 26 Hz) is assigned to the syn isomer. Likewise, in the ¹H NMR, two doublets of triplets and two multiplets are observed. The resonances at -9.2 ppm (d of t) and -22.5 ppm (m) are assigned to the anti isomer; the resonances at -10.0 ppm (d of t) and -23.5 (q of d) are assigned to the syn isomer. Figures 12 and 13 show the ³¹P and ¹H NMR spectra for the mixture of isomers. The pure syn isomer can be isolated if the reaction between H₂ and Ir(Cyttp)Cl is run at -80°C. It can be seen that there is a remarkable shift difference in the ³¹P NMR spectra of the syn and the anti isomers. The central phosphorus atom of syn-Ir(Cyttp)H₂Cl is nearly 20 ppm upfield from the central phosphorus atom of anti-Ir(Cyttp)H₂Cl. A similar shift difference is observed in the case of syn- and anti-Ir(ttp)H₂Cl. Based on this information, the isomer obtained by Dahlenberg is identified as syn-Ir(ttp)H₂Cl since its central phosphorus atom has a chemical shift 17 ppm upfield from the chemical shift of the central phosphorus atom of the isomer obtained by Meek. (The Meek isomer described at the beginning of this section is anti-Ir(ttp)H₂Cl.) The IR
Figure 12: $^{31}$P NMR Spectrum of a Mixture of Syn and Anti Isomers of Ir(Cyttp)$_2$Cl
Figure 13: $^1$H NMR Spectrum of A Mixture of Syn and Anti Isomers of Ir(Cyttp)H$_2$Cl
spectra of the syn and anti isomers of IrLH2Cl (L - ttp, Cyttpp) are also distinctive. Figure 14 shows the IR spectra of the syn and anti isomers. Table 9 summarizes the relevant data for both the syn and anti isomers of IrLH2Cl (L - ttp, Cyttpp).

A series of reactions was undertaken in order to determine which factors promoted the isomerization of syn Ir(Cyttpp)H2Cl to anti Ir(Cyttpp)H2Cl. A mixture of the two isomers obtained by direct hydrogenation of Ir(Cyttpp)Cl was dissolved in d₄-toluene and, after saturating the toluene with H₂, was placed in an NMR tube and sealed. Heating the sealed tube at 80°C for 1 hour caused conversion to the pure anti isomer (Figure 15). In contrast to this, if the isomeric mixture is heated in H₂ saturated toluene in a vessel vented to a H₂ bubbler, no conversion occurs (Figure 16). Apparently, a high pressure of H₂ gas (such as that generated in the sealed NMR tube) is necessary for the conversion to occur. A similar reaction is observed when a mixture of isomers in d₄-toluene is exposed to D₂ gas and heated in a sealed NMR tube for 1 hour at 80°C. Before the addition of D₂ gas, a 1:1 ratio of isomers is observed. After the reaction with D₂ the ratio of isomers is 3:1 (anti Ir(Cyttpp)H2Cl is the major species). It is not clear, however, from the data whether this change in the isomer ratio is the result of syn to anti conversion or the result of selective incorporation of D₂ into the syn isomer (Figure 17).

Finally, it should be noted that, whereas even prolonged heating in toluene (in the absence of added H₂ gas) does not cause conversion of the syn isomer to anti isomer, the addition of a drop of ethanol to 1.5 ml of toluene followed by heating (80°C, 1 hr) does cause conversion to the pure
Figure 14: Infrared Spectra of (a) syn Ir(CyItp)H₂Cl and (b) anti Ir(CyItp)H₂Cl.
Table 9  
Comparison of Spectral Parameters for Syn and Anti Ir(I)H₂Cl

<table>
<thead>
<tr>
<th></th>
<th>δP₁^c</th>
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<th>δH₁^e</th>
<th>δH₂^f</th>
<th>Jₚₖₐₜ^g</th>
<th>Jₚ₂ₚₙ</th>
<th>Jₚₚ</th>
<th>Vₚₖ</th>
<th>Vₚₚ</th>
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<tr>
<td>Ir(ppy)H₂Cl</td>
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<td></td>
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<td></td>
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<td>2005</td>
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<td>30</td>
<td>1970</td>
<td>2250</td>
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<tr>
<td>Ir(Cyttp)H₂Cl</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>syn</td>
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<td>+0.8 (d)</td>
<td>-10.0 (d of l)</td>
<td>-23.5 (m)</td>
<td>153</td>
<td>14.0</td>
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<td>2000</td>
<td>2240</td>
</tr>
<tr>
<td>anti</td>
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<td>1930</td>
<td>2260</td>
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</table>

(a) NMR spectra recorded in CD₂Cl₂; IR spectra recorded as nujol mulls between CsI plates  
(b) Chemical shift values in ppm; vibrational frequencies in cm⁻¹  
(c) central phosphorus atom  
(d) wing phosphorus atoms  
(e) trans to central phosphorus atom  
(f) cis to all phosphorus atoms  
(g) coupling constant values in Hz
Figure 15: $^1$H NMR Spectra of an Isomeric Mixture of Syn and Anti Ir(Cyttp)H$_2$Cl (a) Before Heating (b) After Heating in a Sealed NMR Tube for 1h, 80°C
Figure 16: $^1$H NMR Spectra of an Isomeric Mixture of Syn and Anti Ir(Cytlp)H$_2$Cl (a) Before Heating (b) After Heating in an Open System for 1h at 80°C
anti isomer. Since conversion occurs in a polar solvent but not in a nonpolar solvent, the following ionic mechanism is proposed.

\[
\text{syn-Ir(CyttpH}_2\text{Cl} \rightleftharpoons [\text{Ir(CyttpH}_2\text{)]}^+ \text{Cl} \rightleftharpoons \text{anti-Ir(CyttpH}_2\text{Cl}}
\]

Scheme 7

2. Reactions with Lewis Acids

In order to test the mechanism proposed in Scheme 7, an independent method of generating \([\text{Ir(CyttpH}_2\text{)]}^+\) was sought. Production of the cation was attempted using Lewis acid rather than metal cations to remove the chloride ligand. The Lewis acid method is superior to the metal cation method for two reasons. First, removal of the chloride by a Lewis acid generates the necessary counter ion in situ. Second, the need to remove an MCl (M = Tl, Ag) byproduct is avoided. The Lewis acids considered for this study were \(\text{AlCl}_3\) and \(\text{BCl}_3\).

A difficulty encountered with both Lewis acids was their tendency to hydrolyze in moist air to form HCl.

\[
\begin{align*}
\text{AlCl}_3 + 3\text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3 + 3\text{HCl} \\
\text{BCl}_3 + 3\text{H}_2\text{O} & \rightarrow \text{B(OH)}_3 + 3\text{HCl}
\end{align*}
\]

Treatment of \(\text{Ir(CyttpH}_2\text{Cl}\) with \(\text{AlCl}_3\) in toluene at room temperature resulted in the formation of a white solid. A characteristic single hydride stretching frequency at 2318 cm\(^{-1}\) in the IR identified the compound as \(\text{Ir(CyttpHCl)}_2\). This species is the result of the reaction between
Figure 17: $^1$H NMR Spectra of an Isomeric Mixture of Syn and Anti Ir(Cyttp)H$_2$Cl (a) Before Heating with D$_2$ (b) After Heating with D$_2$ in a Sealed NMR Tube for 1h, 80°C
Ir(Cyttpp)H₂Cl and HCl. Attempts to purify the AlCl₃ by sublimation gave only low yields of clean AlCl₃.

\[
\text{Ir(Cyttpp)H₂Cl + HCl ----> Ir(Cyttpp)HCl₂ + H₂} \tag{37}
\]

As an alternative, BCl₃ was chosen for the Lewis acid. Gaseous BCl₃ has several advantages over AlCl₃. First, because it is a gas, problems of removing excess reagent from the reaction mixture were minimized; thus, smaller concentrations of HCl impurity were present. The method used to remove residual HCl from the gas is outlined in Figure 18.

First, the -78°C trap was used to remove H₂O from the gas stream. Second, the -120°C trap was used to condense BCl₃ into the reaction flask. Finally, HCl was condensed in the liquid N₂ trap to prevent pump damage. The major drawback of this purification procedure is that it is difficult to observe the progress of the reaction or to know the rate at which BCl₃ is being condensed into the receiving flask. An alternative (which has the disadvantage of yielding a small amount of Ir(Cyttpp)HCl₂ as a byproduct) is to use the BCl₃(g) directly from the cylinder without prepurification.

When BCl₃ is bubbled through a toluene solution of Ir(Cyttpp)H₂Cl, to which one equivalent of PPhMe₂ has been added, the solution turns from colorless to yellow, and a heavy yellow precipitate forms. (The purpose of the added phosphine is to trap the Ir(Cyttpp)H₂⁺ intermediate.)

The infrared spectrum of the product reveals several points. First, the two metal hydride stretching frequencies visible in the starting material at 2020 cm⁻¹ and 2240 cm⁻¹ are replaced by a single weak stretching
To prevent pump damage

To condense H$_2$O

To condense BCl$_3$ into the reaction flask

Figure 18: Purification System for BCl$_3$ Gas.
frequency at 2240 cm⁻¹. Second, a strong vibration between 600 cm⁻¹ and 750 cm⁻¹, characteristic of B-Cl, appears. Last, the metal chloride stretch visible in the starting material at 235 cm⁻¹ has shifted to 305 cm⁻¹. Figure 19 shows the IR spectra of the starting material and the product.

The ³¹P(¹H) NMR spectrum of the product exhibits the following features: a doublet at -21.0 ppm; a 1:1:1:1 quartet at -10.3 ppm; and a broad singlet at 10.0 ppm. In addition, several broad, unresolved resonances are visible in the regions of -17, -21, and -37 ppm (Figure 20). The broad singlet at +10.0 ppm does not correspond to either free PPhMe₂ (-406.0 ppm) or to OPPhMe₂ (31.0 ppm), and it is not observed when BCl₃ and Ir(Cytmp)H₂Cl are combined in the absence of added ligand. It can, therefore, be assigned to HPPhMe₂⁺ which results from the protonation of the added ligand. In the absence of added ligand, the quartet at -10.3 ppm also disappears. An independent synthesis of the PhMe₂P:BCl₃ adduct gives rise to an identical quartet. Interestingly, coupling to both ¹⁰B and ¹¹B is visible in the spectrum of the authentic sample of the adduct (Figure 21). Also, in the absence of added ligand the broad ³¹P(¹H) NMR resonances at -17 and -21 ppm disappear.

In order to further probe the nature of the broad resonances, a series of variable temperature NMR experiments was undertaken. Figures 22 and 23 show the results of these experiments. The yellow precipitate from the reaction of BCl₃ with Ir(Cytmp)H₂Cl and PPhMe₂ was dissolved in CH₂Cl₂ (20% CD₂Cl₂) and its ³¹P(¹H) NMR spectrum was recorded. The spectrum at ambient probe temperature (303K) is shown in part a of Figure 22. If the major product of the reaction is the salt [Ir(Cytmp)H₂(PPhMe₂)]⁺.
Figure 19: Infrared Spectra of Ir(Cytip)H₂Cl (a) Before treatment with BCl₃ and PPhMe₂ (b) After Treatment. Spectra Recorded as Nujol Mulls Between CsI Plates
Figure 20: $^{31}$P NMR Spectrum of the Products from the Reaction of Ir(CyttP)H$_2$Cl with BCl$_3$ and PPhMe$_2$
Figure 21: $^{31}$P NMR Spectrum of PhMe$_2$P:BCl$_3$. See Appendix A for a Discussion of the Observed Couplings.
it is possible that the monodentate phosphine is involved in a fluxional process which could account for the observed broadness in the spectrum. When the temperature is lowered to 185K (spectrum b), however, the broad resonances remain essentially unchanged. The major difference between spectra a and b is that the PhMe2P:BCl3 adduct resonances have broadened due to the increased quadrupolar effects of boron at low temperatures. Since there are only minor differences between spectra a and b, it seems unlikely that the observed broadness is caused by a fluxional process. Since no "low temperature limit" was reached in spectrum b, higher temperatures were explored. For the high temperature experiment, a sample was completely dissolved in toluene (20% d₆-toluene) giving a nearly colorless solution. The ³¹P(¹H) NMR spectrum at 350K is shown in Figure 23, spectrum c. The broad resonance at -15 ppm resolves into a clean triplet (-22.4 ppm; ²JPP = 24 Hz), and the broad resonance formerly visible at -22 ppm separates into a doublet (-26.6 ppm; ²JPP = 24 Hz) and the remaining broad resonance at -26 ppm. The resonance at -42 ppm remains unaffected. Surprisingly, the resonance at +10.0 ppm is absent. When the sample is returned to 303K, all of the broad resonances are absent (spectrum d). The doublet at -26.6 ppm shows a dramatic increase in intensity. Based on spectrum d, this doublet probably represent the "A" portion of two different AX₂ spin systems. The labeling on spectra a-d is based on the final products observed in the high temperature experiments. When the sample was removed from the probe, a copious white precipitate, presumably PhMe2P:BCl3 and [HPPhMe₂]⁺[BCl₄]⁻, was visible.
Figure 22: Variable Temperature $^{31}$P NMR Spectra of the Reaction of Ir(Cyttp)H$_2$Cl with BCl$_3$ and PPh$_3$Mo$_2$ (a) 303K (b) 185K
Figure 23: Variable Temperature $^{31}$P NMR Spectra of the Reaction of Ir(Cytt)(H)$_2$Cl with BCl$_3$ and PPhMe$_2$ (c) 350K (d) 303K
It is interesting to note that the AXᵡ patterns observed in the variable temperature spectra are similar to those reported for the two isomers of Ir(Cyttp)HCl₂. The results of the variable temperature experiments are summarized in Table 10. Based on the information in Table 10 and the spectra in Figures 22 and 23, compound 1 is probably syn-Ir(Cyttp)HCl₂ and compound 2 is anti-Ir(Cyttp)HCl₂. The ¹H NMR spectrum of the mixture in spectra a-d (Figures 22 and 23) shows only one hydride resonance, at -21.2 ppm, which is consistent with the ¹H NMR spectra of both isomers of Ir(Cyttp)HCl₂. The broadness observed in spectra a and b suggests that, at room temperature or below, the reaction does not simply yield two isomers of Ir(Cyttp)HCl₂. A possible intermediate is a species in which Cl⁻ coordinates to the metal center through hydride bridges, rather than acting as a simple anion. This structure is consistent with spectra a and b since the observed broadness would be a result of the quadrupolar effects of the boron atom.

A final important point needs to be made. The starting material for the reaction with BCl₃ consisted of the pure anti isomer of Ir(Cyttp)H₂Cl, yet, at the conclusion of the reaction, both syn- and anti-Ir(Cyttp)HCl₂ are produced. Although it was not possible to isolate an intermediate
### Table 10

Variable Temperature NMR Data from the Reaction of Ir(Cyttp)H₂Cl with BCl₃ and PPhMe₂

<table>
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<th>Complex</th>
<th>δP₁ᶜ</th>
<th>δP₂ᵈ</th>
<th>Jₚᵖᵍ</th>
</tr>
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<tr>
<td>Ir(Cyttp)H₂Clᵇ syn</td>
<td>-15.3</td>
<td>-19.5</td>
<td>24.0</td>
</tr>
<tr>
<td>Ir(Cyttp)H₂Clᵇ anti</td>
<td>-35.0</td>
<td>-20.4</td>
<td>21.0</td>
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<tr>
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<td>——</td>
</tr>
<tr>
<td></td>
<td>-22.4ᶠ</td>
<td>-26.6ᶠ</td>
<td>——</td>
</tr>
<tr>
<td>Complex 2</td>
<td>-36.8ᵇ,e</td>
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<td>——</td>
</tr>
<tr>
<td></td>
<td>-44.0ᶠ</td>
<td>-26.6ᶠ</td>
<td>——</td>
</tr>
</tbody>
</table>

(a) Chemical shift values in ppm  (b) recorded in CD₂Cl₂  (c) central phosphorus atom  (d) wing phosphorus atoms  (e) at 303 and 185 K  (f) in d₈ toluene at 303 and 350 K  (g) coupling constant values in Hz
species, the data are, nevertheless, consistent with a mechanism in which chloride first dissociates to form a five-coordinate species. Attack of

\[
\begin{align*}
\text{PhP} & \quad \text{Ir} \\
\text{H} & \quad \text{H} \\
\text{PR}_2 & \quad \text{PR}_2
\end{align*}
\]

an incoming nucleophile will yield two isomers depending on whether it enters above the plane of the phosphorus atoms or below the plane.

3. Conclusions

Several conclusions can be drawn from this study of the two isomers of Ir(Cyttp)H₂Cl. First, it is possible to isolate either the syn isomer, the anti isomer, or a mixture of both isomers, depending on the reaction conditions used. Second, the syn to anti conversion only occurs (1) in polar media, (2) when a chloride abstractor is present or (3) under pressure of added H₂. Third, although it was not isolated, all data are consistent with the formation of a five-coordinate ionic intermediate, [Ir(Cyttp)H₂]⁺X⁻, which participates in the conversion process and which can yield either the syn or the anti isomer. Finally, when driven to completion with heat, all of the reactions studied in this section yield the anti isomer, indicating that it is probably the "thermodynamic product", whereas the syn isomer is best described as a "kinetic product".
C. Molecular Hydrogen Complexes of Iridium

One useful method of generating molecular hydrogen complexes of transition metals is by the protonation of a metal polyhydride complex. This method has been used successfully by Crabtree\(^9\) and others.\(^{100}\) The complexes chosen for protonation in this study were the series of iridium trihydrides IrLH\(_3\) where L = ttp, Cyttp, ttp*. Figure 24 shows a typical \(^1\)H NMR of the hydride region of IrLH\(_3\). All of the hydride resonances are located between -10 and -13 ppm and are overlapped. These systems are ideal candidates for the attempted generation of molecular hydrogen species since, with the exception of the chelate, all of the ligands are hydrides. Also, based on the "\(\pi\) acid" description of molecular hydrogen bonding, one might expect that changes in the basicity of the metal center could have a dramatic impact on the stability of the molecular hydrogen complexes. Using metal systems involving the three chelating ligands mentioned above should provide some insight into the nature of these changes. Finally, Crabtree\(^8\) hints that steric factors could influence the location of the \(\eta^2\) H\(_2\) fragment, causing it to be more stable at a basic metal site than would be otherwise expected. This effect could be readily observed in chelated systems, since chelates are more rigid than their monodentate analogs. Again, the proposed series of chelated systems have gradual changes in their steric requirements which could shed light on this proposed effect.

The following reactions were carried out at low temperatures (< -80°C) in an NMR tube.
Figure 24: $^1$H and $^{31}$P NMR Spectra of Ir(CyttP)$_3$H$_3$ (a) $^1$H Spectrum, Hydride Region (b) $^{31}$P Spectrum
In all cases the solvent was CD$_2$Cl$_2$. Protonation of the trihydrides resulted in an immediate increase in solubility, consistent with the formation of the corresponding tetrahydride salts. The results of the protonation experiments for each of the three trihydrides are discussed below.

Case 1: Protonation of Ir(ttp)H$_3$

Ir(ttp)H$_3$ is a white solid which is moderately soluble in most hydrocarbon and chlorinated solvents. Its characteristic resonances ($^{31}$P($^1$H) NMR: -8.5 ppm, -31 ppm; $^1$H NMR: overlapping signals from -11 ppm to -13 ppm) are clearly visible in the NMR spectra at 193K. The phosphorus resonances at -8.5 and -31 ppm represent the expected doublet and triplet, respectively, of an AX$_2$ pattern. Small traces of Ir(ttp)HCl$_2$, presumably resulting from the reaction of the dihydride with traces of HCl impurity in the solvent, are also visible in the hydride region of the $^1$H NMR (-9 ppm, d of t and -22 ppm, m). These resonances are only visible at high magnification.

Protonation of the solution with HBF$_4$ etherate causes a new set of resonances to appear. These are assigned to the cationic Ir(ttp)H$_4^+$. Again, the $^{31}$P($^1$H) NMR shows the expected AX$_2$ pattern (-17 ppm, d; -36 ppm, t) of the chelate. The hydride resonances, at -5.5 and -10.0 ppm, are
both broad. The more upfield of the two resonances exhibits some residual coupling to phosphorus which is reminiscent of a triplet structure. The $T_1$ values for the resonances are 12 ms for the resonance at -5.5 ppm and 72 ms for the resonance at -10.0 ppm. According to the Crabtree criterion, hydrides with a $T_1$ value of less than 80 ms are considered nonclassical (molecular H₂) species. Since, however, coupling of heteroatoms to molecular hydrogen fragments is rarely observed, the hydride at -10.0 ppm probably has a significant amount of classical character. As the solution is warmed in the NMR probe, the hydride resonances coalesce into a broad resonance at -7.8 ppm which sharpens as the temperature increases. The $T_1$ values for this signal range from 8 ms to 50 ms, all well within the accepted range for nonclassical structures.

In the $^{31}P(^{1}H)$ NMR they are seen at -2.1 ppm (d) and -22 ppm (t); the corresponding resonance in the $^{1}H$ NMR occurs at -31.0 ppm. It has a $T_1$ value greater than 200 ms, and is clearly a classical hydride. This set of resonances is assigned to Ir(ttp)H₂⁺, the five-coordinate species resulting from the loss of coordinated H₂. Note that at 303 K this is the predominant species. Scheme 8 summarizes the reactions seen upon protonation.
The fully fluxional species, represented by the bis-dihydrogen species, "C", may be represented in another way as well.
If the fluxional process is rapid with respect to the NMR time scale, all of the hydrogen atoms will appear equivalent. This is consistent with the single, sharp resonance for the molecular hydrogen complex seen in the $^1\text{H}$ NMR at 253K and 283K. (The rapid relaxation of the $\text{H}_2$ fragment causes coupling to phosphorus to be lost.) The $^{31}\text{P}(^1\text{H})$ NMR and the $^1\text{H}$ NMR spectra for the protonation reaction are shown in Figures 25 and 26. The $T_1$ values are included beneath each resonance. Table 11 summarizes the information contained in the spectra.

A separate variable temperature experiment was undertaken to determine if the loss of $\text{H}_2$ is a reversible process. Since $\text{Ir(ttp)}\text{H}_2^+$ does not exist in appreciable quantities until $T = 253\text{K}$, the test for temperature-dependent reversibility was done in the 253K to 303K temperature range. The results of this experiment are shown in Figures 27 and 28. Protonation of $\text{Ir(ttp)}\text{H}_3$ at 253K results in conversion to $\text{Ir(ttp)}(\text{H}_2)_2^+$. Warming results in the formation of a second species, previously identified as $\text{Ir(ttp)}\text{H}_2^*$. As before, this is the only species visible in the $^{31}\text{P}(^1\text{H})$ NMR at 303K. (A small amount of $\text{Ir(ttp)}\text{H}_4^+$ is still visible in the $^1\text{H}$ NMR, however.) Recooling results in the reappearance of $\text{Ir(ttp)}(\text{H}_2)_2^+$, as can be seen in both the $^{31}\text{P}$ and the $^1\text{H}$ NMR spectra. The reconversion to $\text{Ir(ttp)}(\text{H}_2)_2^+$ is, however, incomplete; this is probably because the released $\text{H}_2$ dissolves in the solvent. If the concentration of $\text{H}_2$ in the solvent is low, conditions are unfavorable for its recoordination to the metal center. Bubbling additional $\text{H}_2$ through the solvent should increase the amount of $\text{Ir(ttp)}(\text{H}_2)_2^+$ regenerated.

An interesting feature of these spectra is the new species visible when the solution is cooled below 253K ($^{31}\text{P}(^1\text{H})$ NMR: -5.0 ppm, d, -25.0
Figure 25: Variable Temperature $^{31}$P NMR Spectra of [Ir(tpp)$_4$]BF$_4$
Figure 26: Variable Temperature $^1$H NMR Spectra of [Ir(ttp)H$_4$]$^+$ BF$_4^-$. $T_1$ Values are Listed Below Each Peak.
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<th>temp. (K)</th>
<th>$\delta$ P1</th>
<th>$\delta$ P2</th>
<th>$\delta$ H</th>
<th>$T_1$ (ms*)</th>
<th>Remarks</th>
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</thead>
<tbody>
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<td>193</td>
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<td>-11.5 to -12.0 (m)</td>
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<td>Before protonation</td>
</tr>
<tr>
<td>193</td>
<td>-36 (l)</td>
<td>-17 (d)</td>
<td>-5.5 ; -10.0 (broad)</td>
<td>12 ; 72</td>
<td>After protonation</td>
</tr>
<tr>
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<td>-8.1</td>
<td>8</td>
<td></td>
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<tr>
<td>253</td>
<td>-36 (l)</td>
<td>-17 (d)</td>
<td>-7.9 ; -31</td>
<td>24 ;</td>
<td></td>
</tr>
<tr>
<td>283</td>
<td>-22 (l)</td>
<td>-21. (d)</td>
<td>-7.9 ; -31</td>
<td>35 ; &gt;200</td>
<td>minor species</td>
</tr>
<tr>
<td>283</td>
<td>-38 (l)</td>
<td>-17 (d)</td>
<td>-7.9 ; -31</td>
<td>35 ; &gt;200</td>
<td>major species</td>
</tr>
<tr>
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<td>-17 (d)</td>
<td>-7.8 ; -31</td>
<td>50 ; &gt;200</td>
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</tr>
<tr>
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<td>-1.5 (d)</td>
<td>-7.8 ; -31</td>
<td>50 ; &gt;200</td>
<td>major species</td>
</tr>
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</table>

(a) Recorded in CD$_2$Cl$_2$  
(b) Chemical shift values in ppm  
(c) central phosphorus atom  
(d) wing phosphorus atoms  
(e) measured by the Inversion recovery method; where two values are listed, they correspond to the two hydride peaks previously listed
108 ppm, t; \(^1H\) NMR: -25.0 ppm, s). One possible interpretation is that this species arises from traces of \(\text{Ir(ttp)H}_2\text{Cl}\) originally present in the sample. Protonation of this species would result in \(\text{Ir(ttp)H}_3\text{Cl}^+\), which could decompose by either of two routes. Loss of HCl would provide an additional source of \(\text{Ir(ttp)H}_2^+\). Alternatively, loss of H\(_2\) would generate \(\text{Ir(ttp)HCl}^+\). These reaction pathways are shown in Scheme 10.

The low temperature protonation of an authentic sample of \(\text{Ir(ttp)H}_2\text{Cl}\) with traces of \(\text{Ir(ttp)HCl}_2\) (a common byproduct resulting from \(\text{Ir(ttp)H}_2\text{Cl}\) reacting with residual HCl in the solvent) did not proceed cleanly. Before protonation, \(\text{Ir(ttp)H}_2\text{Cl}\) (\(^31\)P\(^{\text{H}}\) NMR: -12.0 ppm, d, -28.7 ppm, t; \(^1H\) NMR: -8.6 ppm, d of t, -21.5 ppm, m) and \(\text{Ir(ttp)HCl}_2\) (\(^31\)P\(^{\text{H}}\) NMR: -20.3 ppm, d, -33.5 ppm, t; \(^1H\) NMR: -19.9 ppm, q) are clearly visible. Protonation with HBF\(_4\) etherate (at 147K) yields a species which can tentatively be assigned to \(\text{Ir(ttp)H}_3\text{Cl}^+\) (\(^31\)P\(^{\text{H}}\) NMR: -12.5 ppm, br, -21.8 ppm, br; \(^1H\) NMR: -20.2 ppm, br) and to \(\text{Ir(ttp)HCl}_2^+\) (\(^31\)P\(^{\text{H}}\) NMR: -16.2 ppm, br, -23.5 ppm, br; \(^1H\) NMR: -18.0 ppm, br). Warming yields other, unidentified species with phosphorus chemical shifts at -9 and -15 ppm. The appearance and persistence of the resonance at -15 ppm, even at T - 283K when the resonance at -9 ppm is almost nonexistent, suggests that it is actually the "A" portion of an AX\(_2\) pattern whose "X" portion is the doublet at -17 ppm. The resonance at -23 ppm, which was originally associated with the -16 ppm resonance, broadens and disappears as the -15 ppm resonance grows in. While this occurs, the resonance at -16.2 ppm resolves and shifts slightly to -17 ppm. (Note that in going from 193K to 253K, the entire spectrum exhibits a slight, temperature-dependent, upfield shift.) At T = 253K, the \(^31\)P\(^{\text{H}}\) NMR spectrum is relatively clean.
Figure 27: $^{31}$P NMR Spectra Showing the Behavior of [Ir(ttp)H₄]$^+$ BF₄$^-$ upon Warming and Recooling
Figure 28: $^1$H NMR Spectra Showing the Behavior of [Ir(tpp)H$_4$]$^+$BF$_4^-$ upon Warming and Recooling
(there are only two major species), which suggests that, below this temperature, the observed resonances may be due to the "frozen out" resonances of a process which is fully fluxional at 253K. Possible processes are the mer \textendash\ fac interconversion of the chelate, on the scrambling of H and Cl within the molecule. Since the hypothetical species resulting from the protonation are both seven-coordinate, and since seven-coordinate species are known to be highly fluxional,\textsuperscript{102} this suggestion seems reasonable. Further broadening of the $^{31}$P($^1$H) NMR spectrum at 283K and above seems to indicate an intermolecular scrambling process whose high temperature limit is not reached until T > 303K. It is abundantly clear, however, that the species generated via the protonation of Ir(ttp)H$_2$Cl and Ir(ttp)HCl$_2$ are not responsible for the unidentified species observed in the protonation of Ir(ttp)H$_3$. Figures 29 and 30 show the results of the protonation of Ir(ttp)H$_2$Cl and Ir(ttp)HCl$_2$. 
An alternative explanation for the spectra in Figures 27 and 28 may be that they represent solvated species of the formula Ir(ttp)H₂(S)⁺.

Case 2: Protonation of Ir(Cyttp)H₂

Like its ttp analog, Ir(Cyttp)H₂ is a white solid, but it is more readily soluble in hydrocarbon and chlorinated solvents than Ir(ttp)H₂. Its characteristic resonances (31P(¹H) NMR: 8.5 ppm, br, -22 ppm, br; ¹H NMR: -12 to -13 ppm, m) are clearly visible, though broadened, in the NMR at 193K. (This broadness can be attributed to the large amount of solid present in the tube before protonation.) Again, as in the ttp case, traces of the dihydride chloride species, Ir(Cyttp)H₂Cl, can be seen in both the 31P(¹H) and ¹H NMR spectra.

Protonation with HBF₄ etherate results in an immediate increase in solubility (in CD₂Cl₂) owing to the formation of the tetrahydride salt, [Ir(Cyttp)H₄]⁺BF₄⁻. This salt has 31P(¹H) NMR resonances at +0.8 ppm (d), and -28 ppm (t). The hydride region of the ¹H NMR reveals two resonances: one broad, at -6 ppm, and one which appears as a pseudo quartet at -13 ppm. Integration shows that they are in a ratio of 1:1. The broad resonance has a T₁ value of 17ms, whereas the "quartet" has a T₁ value of 195ms. Thus, according to the T₁ criterion, the resonance at -6 ppm can be attributed to a molecular hydrogen fragment, while the resonance at -13 ppm must be attributed to a classical hydride. Warming to 223K causes the signal at -13 ppm to broaden, and, at the same time, its T₁ value drops dramatically from 195ms to 31ms. Further warming causes the two hydride signals to coalesce by the time T = 283K. At this point the T₁ value is 11ms. At all temperatures ≥ 223K, the species behaves as a nonclassical,
Figure 29: Variable Temperature $^{31}$P NMR Spectra of the Protonated Ir(ttp)H$_2$Cl
Figure 30: Variable Temperature $^1$H NMR Spectra of the Protonated Ir(ppy)$_2$Cl
molecular hydrogen containing species. The two hydride resonances seen at $T = 223$ and $T = 253$ can be viewed either as a bis($H_2$) complex, or as the result of a slow fluxional process which exchanges classical and non-classical hydrides. This species remains stable even at 303K. It should be noted that, as in the case of $\text{Ir(ttp)H}_4^\ast$, a second hydride species is visible at -33 ppm at higher temperatures. This second species is also visible in the $^{31}P(^1H)$ NMR as an AX$_2$ pattern at 9.9 ppm (d) and -16.4 ppm (t). Again, like the $\text{Ir(ttp)H}_4^\ast$ case, the appearance of this second species is consistent with the loss of $H_2$ and the subsequent formation of the five-coordinate species, $\text{Ir(Cyttp)H}_2^\ast$ as shown in Equation 41. Figures 31 and 32 show the $^{31}P(^1H)$ and $^1H$ NMR spectra for the protonation of

$$\text{Ir(Cyttp)H}_4^\ast \quad \text{Ir(Cyttp)H}_2^\ast$$

Equation 41

$\text{Ir(Cyttp)H}_2$. The $T_1$ values for the hydrides are listed beneath the corresponding resonances in the $^1H$ NMR spectra.
Figure 31: Variable Temperature $^{31}$P NMR Spectra of [Ir(Cyttp)H$_4$]$^+$ BF$_4^-$
Figure 32: Variable Temperature $^1$H NMR Spectra of [Ir(Cyttp)H$_4$]$^+$ BF$_4^-$
In a separate experiment, the cationic tetrahydride generated via protonation of Ir(Cyctp)H₄ was tested for temperature-dependent, reversible behavior of the hydride ligands. A sample of Ir(Cyctp)H₄ in CD₂Cl₂ was protonated with HBF₄Et₂O at 147K, and placed in the cool NMR probe. ³¹P(¹H) and ¹H NMR spectra were recorded at 193K, 223K, 253K, 283K and 303K. The sample was then slowly cooled to 193K. Figure 33 shows the ¹H NMR spectra from the reversibility experiment. These spectra clearly show that the fluxional process described earlier is reversible. Although T₁ measurements were not taken, it can be safely assumed that these are reversible as well. The corresponding ³¹P(¹H) NMR spectra, shown in Figure 34, reveal only a slight broadening of the resonances at low temperature. Recall that, in the case of Ir(ttp)H₄⁺, the loss of H₂ to form Ir(ttp)H₂⁺ was nearly complete, and the temperature-dependent reformation of Ir(ttp)H₄⁺ could easily be detected in both the ³¹P(¹H) and ¹H NMR spectra. In contrast, only a small portion of Ir(Cyctp)H₄⁺ loses H₂ to form Ir(Cyctp)H₂⁺. It is therefore not possible to determine the extent to which lost H₂ recoordinates with Ir(Cyctp)H₂⁺ as the temperature is lowered. Again, the low accessibility of the dissolved H₂ probably accounts for the fact that Ir(Cyctp)H₄⁺ persists after its formation.

Case 3: Protonation of Ir(ttp*)H₄

Like its ttp and Cyttp analogs, Ir(ttp*)H₄ is a white solid soluble in hydrocarbon and chlorinated solvents.
Figure 33: $^1$H NMR Spectra Showing the Temperature Dependant Reversible Behavior of [Ir(Cytip)H$_4$]$^+$BF$_4^-$
Figure 34: $^{31}$P NMR Spectra Showing the Temperature Dependant Reversible Behavior of (Ir(Cytp)H$_4$)$^+$ BF$_4$.$^-$
Several attempts were made to follow the low temperature protonation of Ir(ttp*)H₃ with HBF₄·Et₂O. In the first attempts, the Ir(ttp*)H₃ solution was cooled to 147K and protonated with a drop of cold HBF₄·Et₂O. The protonation was marked by a rapid, vigorous evolution of H₂ gas. Attempts to find any trace of a molecular hydrogen species by NMR spectroscopy were unsuccessful. In the final attempt, the CD₂Cl₂ solvent was first saturated with H₂ by bubbling a dry stream of H₂ through it for 5 minutes. The Ir(ttp*)H₃ was then loaded into a special high-pressure NMR tube and dissolved in the H₂ saturated CD₂Cl₂. The sample was cooled and protonated as before, but this time an additional 10 psi of H₂ gas was added to the tube before it was sealed. Even under these conditions, only trace amounts of the tetrahydride cation were detected. The presence of the tetrahydride can be deduced from the two broad humps centered at -10.2 and -14.5 ppm in the ²H NMR at 193K. A large hydride resonance is visible at -31.5 ppm at all temperatures tested. Based on the behavior of the ttp and Cytttp analogs, this resonance is assigned to the five-coordinate Ir(ttp*)H₂⁺ species, which is consistent with the rapid evolution of gas observed upon protonation. Although the low intensities of the resonances at -10.2 and -14.5 ppm in the ²H NMR prevented T₁ measurements, the resonance at -31.5 ppm was tested, and has a T₁ value of 355ms, well within the accepted range for a classical hydride. Figure 35 shows the ¹H NMR for the protonation of Ir(ttp*)H₃.

4. Comparisons of the tetrahydride cations, IrLH₄⁺

The stabilities and behaviors of the cationic tetrahydrides, Ir(L)H₄⁺, depend strongly on the ligand chosen. Several points can be
Figure 35: $^1$H NMR Spectrum of the Protonation of Ir(ttp')H$_3$ under 12 psi of H$_2$ at 223K
made by comparing the case of L - ttp with the case of L - Cyttp. First, it can be seen in both the $^1$H NMR spectra that the five-coordinate IrLH$_2^*$, resulting from loss of H$_2$ in IrLH$_4^*$, appears at much higher temperatures, and in smaller concentrations, when L - Cyttp than when L - ttp. In the Cyttp case, IrLH$_2^*$ is not observed until T = 283K, whereas it is visible (in small concentrations) even at 193K when L - ttp. A similar increase in stability of molecular hydrogen complexes containing PCy$_3$ over those containing PPh$_3$ has been observed by Crabtree.$^{31}$ A possible explanation for this increase in stability when L - Cyttp can be suggested if we look at the bonding of molecular hydrogen fragments versus the bonding of a classical hydride. As mentioned in the introduction, the preferred bonding model$^{31}$ involves $\sigma$ donation from the molecular hydrogen orbitals into the metal $d_\pi$ orbitals. The filled metal $d_\pi$ orbitals then back donate into the $\sigma^*$ orbitals of the H$_2$ fragment. As with any $\pi$ acid,
complexes should be better at backbonding to the molecular hydrogen fragment than the complexes of ttp. The final result is a stronger metal-dihydrogen σ bond for the Cyttp complexes. A factor which can affect the temperature at which the fluxional process is observed is the increase in the steric requirements of Cyttp versus those of ttp. The added congestion in the Cyttp case may cause a slowing of the process depicted in Schemes 8 and 9.

Based purely on this argument, however, one would expect complexes of ttp*, which has a stronger basicity than ttp and a weaker basicity than Cyttp, to have a stability greater than ttp complexes and lower than Cyttp complexes. Clearly this is not the case. Before discussing the possible explanations for the erratic behavior of Ir(ttp*)H₄⁺, however, a few more points need to be made about the comparisons between complexes where L = ttp and L = Cyttp.

A second point of comparison between the IrLH₄⁺ complexes is that when L = Cyttp, the coalescence point for the two molecular hydrogen resonances is at a much higher temperature (253K vs 223K) than it is in the case where L = ttp. There are two possible explanations for this behavior. First, the Ir(Cyttp)H₄⁺ may actually exist as a bis-dihydrogen complex, Ir(Cyttp)(H₂)₂⁺. The two H₂ fragments would be in slightly different environments due to the orientation of the phenyl group on the central phosphorus atom of the chelate (as shown below). An alternate explanation is that the increase steric bulk of Cyttp versus ttp causes the fluxional process (which equivalences the molecular hydrogen and the hydrides) to be slow, even at 253K.
One final point should be made in the comparison between the L-Cyttp and the L-ttp cases. The enhanced stability (hence the reduced fluxionality) of Cyttp allows us to observe an interesting point. Initial protonation does not result in the formation of a bis molecular hydrogen complex or a fluxional species. At this point, in the 193K $^1$H NMR spectrum, only the more downfield of the two hydride peaks appears as a molecular hydrogen fragment. In addition to its large $T_1$ value, the upfield resonance exhibits residual coupling to phosphorus, a phenomenon which is not generally observed in conjunction with molecular hydrogen fragments. The resonance appears as a pseudo-quartet which can only arise from the hydrogen that is cis to all three phosphorus atoms of the chelate. Thus, it can be concluded that initial protonation occurs at a site trans to the central phosphorus atom of the chelate to form Ir(Cyttp)H$_4$(H$_2$)$^+$. Evidence for this same general pattern can also be seen in the case where L-ttp. Even in this case, the more upfield resonance (in the 193K $^1$H NMR spectrum) exhibits residual coupling to the phosphorus atoms. This effect is less easy to see, however, in the ttp case since Ir(ttp)H$_4^+$ is more highly fluxional than Ir(Cyttp)H$_4^+$, even at low temperatures.
Returning to the case of Ir(ttp*)H₄⁺, recall that, based on a pure ligand basicity argument, one would expect the stability of Ir(ttp*)H₄⁺ to be intermediate between the stabilities of Ir(ttp)H₄⁺ and Ir(Cyttp)H₄⁺, since the basicity of ttp* is greater than that of ttp but less than that of Cyttp. This, however, is not the case: Ir(ttp*)H₄⁺ is much more unstable than either of its analogs. A possible explanation lies in the fact that the site of increased electron density in ttp* is on the central phosphorus atom of the chelate. If, as suggested above, the initial protonation of IrLH₄ occurs trans to the central phosphorus atom of the chelate, we can suggest the following argument. If the trans effect of the basic "PCy" moiety causes a lengthening of the meridional metal hydride bond in Ir(ttp*)H₃, it follows that the M-H₂ bond in Ir(ttp*)H₄⁺ will be longer than in either of the other two cases (L = ttp or Cyttp). This bond lengthening results in a poorer H₂ to H₂ overlap, as well as poorer dₓ to σ* backbonding. It is this poor overlap which encourages the rapid loss of H₂ from the molecule.

As can be seen from these examples, the ease of formation and stability of the molecular hydrogen complexes are heavily dependent on the electronic nature of the chosen chelate.

5. Molecular Hydrogen Trapping Experiments

Since the IrLH₄⁺ species are all labile with respect to the loss of H₂, it should be possible to trap them by the addition of a neutral ligand, L', as shown below in Equation 42. Since most stable molecular hydrogen
complexes were formed when \( L = \text{Cytp} \), the first trapping experiments were done on the complex \( \text{Ir(Cytp)}\text{H}_4^+ \).

A dichloromethane solution of \( \text{Ir(Cytp)}\text{H}_3 \) was protonated with HBF\(_4\)Et\(_2\)O at 147K and divided into three portions which were kept at low temperature. The three portions were treated with P(OMe)\(_3\), CO, and N\(_2\), respectively. Treatment with a drop of P(OMe)\(_3\) results in the formation of an oily white residue whose \(^{31}\text{P}^{1\text{H}}\) NMR spectrum is shown in Figure 36. A pseudo triplet is visible at -4.5 ppm which is attributed to an overlapping doublet of doublets from the wing phosphorus atoms which are coupled to both P(OMe)\(_3\), and the central phosphorus atom of the chelate, P\(_c\). A pseudoquartet is seen at -47.5 ppm which is attributed to an overlapping doublet of triplets arising from P\(_c\) coupled to the two wing phosphorus atoms and to P(OMe)\(_3\). Finally, a pseudoquartet is observed at +93 ppm, which is attributed to an overlapping doublet of triplets arising from P(OMe)\(_3\), coupling to all three phosphorus atoms in the chelate. The \(^1\text{H}\) NMR shows the hydrides as complex multiplets located between -13.2 and -14.4 ppm (Figure 37). The NMR evidence strongly suggests the structure shown below, where P(OMe)\(_3\), is located cis to all three phosphorus atoms of the chelate (trans PP coupling is known to be on the order of 100 Hz, much larger than cis PP coupling\(^{96}\)).

Bubbling CO through a cold solution of \( \text{Ir(Cytp)}\text{H}_4^+ \) proceeds cleanly to produce a new species, presumably \( \text{Ir(Cytp)}\text{H}_2(\text{CO})^+ \). The \(^{31}\text{P}^{1\text{H}}\) NMR

\[
\text{IrL}_4^+ + L' \rightarrow \text{Ir(L)L'H}_2^+ + H_2
\]

\( L = \text{ttp, Cyttp, ttp*} \)

\( L' = \text{P(OR)}_3, \text{PR}_3, \text{CO, N}_2 \)
The spectrum of the white powder shows a doublet at -1.0 ppm (assigned to Pw) and a triplet at -38.2 ppm (assigned to Pc). The hydrides are located at -11.6 ppm (a quartet) and -11.9 ppm (a doublet of triplets). The more upfield of the two resonances represents the hydride trans to Pe, and the downfield resonance represents the hydride cis to all three phosphorus atoms in the chelate. The proposed structure is shown above.

Bubbling N₂ through a cold solution of Ir(Cyttpp)H₄⁺ does not proceed cleanly. The resulting yellow powder shows at least six distinct doublets in the J₃P⁺H NMR, indicative of at least six different compounds.

Since the trapping experiments described above showed promise, a set of experiments involving the tetrahydride salts of all three chelates was designed. In order to maximize the amount of information available from NMR measurements, PPh₃ was chosen as the added ligand. A phosphine, rather than a phosphite, was chosen for the following reasons. First, triphenylphosphine is an air-stable solid, which is easier to work with than the liquid, air-sensitive trimethylphosphite. Second, phosphines are more convenient to observe in the NMR since they generally resonate in the same region as the chelate (+50 ppm to -50 ppm) whereas phosphites are shifted considerably downfield. Third, phosphites tend to produce oils.
Figure 36: $^{31}P$ NMR Spectrum of [Ir(Cytp)H$_2$P(OMe)$_3$] $^*$BF$_4$ $^*$. 
Figure 37: $^1$H NMR Spectrum of [Ir(Cyttp)H$_2$P(OMe)$_3$]$^+ BF_4^-$
while phosphines have the advantage of giving solid products. A second modification of the above trapping experiments involved the use of HSBF₆ instead of HBF₄Et₂O. It was hoped that the larger cation would aid in the crystallization of the products.

Two different reaction schemes were used. The first involved protonation of IrLH₃ followed by addition of L', and the second involved mixing IrLH₃ and L' followed by protonation. The order of addition of the reagents has no effect on the final product.

When a cold dichloromethane solution of Ir(Cyttp)H₃ is treated with HSBF₆ and PPh₃ (in any order) the reaction mixture gives rise to one clean compound. The proposed structure, shown below, is consistent with the following NMR data.

\[
\begin{align*}
    \text{IrLH}_3 + H^+ & \quad \rightarrow \quad \text{IrLH}_4^+ \quad \rightarrow \quad \text{Ir(L)L'H}_2^+ \\
    \text{IrLH}_3 + L' & \quad \rightarrow \quad \text{Ir(L)L'H}_2^+
\end{align*}
\]
In the $^{31}\text{P}('\text{H})$ NMR the quartet at -4.3 ppm is attributed to PPh$_3$ (C). It is an overlapped doublet of triplets arising from coupling to the three phosphorus atoms of the chelate ($^3J_{CA} = 9.8$ Hz, $^3J_{CB} = 16.6$ Hz). The doublet of doublets at -20.6 ppm arises from the wing phosphorus atoms (B) which are coupled to the central phosphorus of the chelate ($^2J_{BA} = 26.3$ Hz) and to PPh$_3$ ($^4J_{BC} = 15.6$ Hz). Finally, the triplet of doublets at -44.0 ppm arises from the central phosphorus atom of the chelate (A) which is coupled to both the wing phosphorus atoms ($^2J_{AB} = 26.2$ Hz) and to PPh$_3$ ($^2J_{AC} = 9.8$ Hz). In the $^1\text{H}$ NMR, both hydrides appear as doublets of quartets, a condition which is only satisfied by a structure in which each hydride is located trans to one phosphorus atom and cis to three phosphorus atoms ($^1\text{H}$ NMR: $E$ = -11.0 ppm, $^2J_{EA} = ^2J_{EB} = 12.6$ Hz, $^2J_{EC} = 103.6$ Hz; $D$ = -13.7 ppm, $^2J_{DB} = ^2J_{DC} = 12.0$ Hz, $^2J_{DA} = 111.1$ Hz). Figures 38 and 39 show the relevant spectra.

In the cases where L = ttp or ttp*, a completely different spectral pattern is observed. Both complexes, when protonated and treated with PPh$_3$ (in any order), yield clean white compounds. In both cases, the $^{31}\text{P}('\text{H})$ NMR spectra show six resonances. If a structure like the one proposed for Ir(Cytcp)H$_2$(PPh$_3$)$^+$ is assumed, then two compounds must be present.

Theoretically, the loss of H$_2$ from Ir(L)H$_4^+$ could occur at either of two possible sites, as shown below.

![Diagram](image-url)
Figure 38: $^{31}$P NMR Spectrum of [Ir(Cyttp)H$_2$(PPh$_3$)]$^+$ SbF$_6^-$
Figure 39: $^1$H NMR Spectrum of $[\text{Ir(CyttlP)}H_2(PPh_3)]^{*} \text{SbF}_6^{-}$
Similarly, the trapped species, Ir(L)H₂(PPh₃)⁺, could contain PPh₃ at either of the same two sites. Thus, two isomers of Ir(L)H₂(PPh₃)⁺ are possible.

An obvious problem with the above proposal is that if indeed, the six resonances in the ³¹P(¹H) NMR represent two isomers, there should be four hydride resonances visible in the ¹H NMR. Only two hydride resonances are visible, however, and each must be trans to one phosphorus atom and cis to three others. These criteria can both be met by only one isomer of IrLL'H⁺ (see 40 above). An attempt to make the hydrogen atoms of any isomer equivalent requires that they be trans to one another. Such a structure is clearly inconsistent with the observed couplings.

A second problem is that the splitting patterns observed in the ³¹P(¹H) NMR are not consistent with a structure like the one proposed for Ir(Cyttp)H₂(PPh₃)⁺. The following structures, and a consistent interpretation of the NMR data are therefore proposed. (The discussion will center on the case where L = ttp*.)

In the ³¹P(¹H) NMR, the resonance centered at 8.8 ppm is due to PPh₃ (D); the small coupling responsible for the triplet structure is the result of nearly equal coupling to Pₐ and Pₐ (overlapped d of d, ²J₁ₓ₁ = ²J₁ₖ = 14.4 Hz). The large doublet structure arises from trans coupling to Pₐ.
The resonance at -14.1 ppm is assigned to Ph₂PR (B) ($^{2}J_{DB} = 281.4$ Hz). The resonance at -14.1 ppm is assigned to Ph₂PR (B) ($^{2}J_{DB} = 281.4$ Hz). Again the large doublet structure is the result of trans coupling to PPh₃ (D) ($^{2}J_{BD} = 281.3$ Hz). The more downfield of these two shifts was assigned to PPh₃ since it is expected to be less shielded than PPh₂R, which was assigned to the more upfield shift. Based on similar reasoning, the resonance at -35.8 ppm (m) was assigned to PPh₂R (C) and the resonance at -49.0 ppm ($^{3}J_{AB} - ^{2}J_{AC} - ^{2}J_{AD} = 18.0$ Hz) to PCy₂ (A). As noted previously, each hydride appears as a doublet of quartets (values for the coupling constants are shown on the spectra). The data for Ir(ttp)H₂(PPh₃)⁺ are analogous to those described for the L - ttp* case. Figures 40, 41, 42, and 43, show the spectra for both cases. The results of this experiment are summarized in Table 12.

Again, as was the case for the variable temperature Tᵢ experiments, it can be seen that changes in the nature of the ligand have a great influence on the nature of the final product. This is demonstrated by the fact that Ir(Cyttp)H₂(PPh₃)⁺ has a different structure than either Ir(ttp)H₂(PPh₃)⁺ or Ir(ttp*)H₂(PPh₃)⁺. The most probable intermediates for
the cases where $L = \text{tcp}$, $\text{ttp}^*$, are five-coordinate trigonal bipyramidal structures with the chelate occupying two meridional sites and one apical site (Structure 43, below). In the case of $L = \text{Cyttp}$, the steric requirements of the cyclohexyl groups force the three phosphorus atoms of the chelate to remain in the same plane (Structure 44) in the intermediate as well as in the final product.

\[
\begin{array}{cc}
\text{43} & \text{44} \\
\end{array}
\]

D. Insertions of Unsaturated Species into the Metal-Hydrogen Bonds

In order to further probe the reactivity of the various iridium hydrides discussed in the previous sections, their reactions with unsaturated species were considered. A great deal of interest has focused on the activation of CO$_2$ by transition metal complexes, since insertions of CO$_2$ into M-H or M-C bonds represent an important step in the production of carbon-containing complexes from CO$_2$. Thus the activation of CO$_2$ and CO$_2$-like molecules is of interest. For this particular set of experiments the CO$_2$ analog chosen was 1,3-di-p-tolyl-carbodiimide, CH$_3$-(C$_6$H$_4$)-N-C=N-(C$_6$H$_4$)-CH$_3$. The reactions which were considered were the reactions of Ir(L)H$_3$, Ir(L)H$_2$Cl, and Ir(L)H$_4^*$ with the diimide. (In all cases $L = \text{tcp}$, $\text{Cyttp}$ or $\text{ttp}^*$).
Figure 40: $^{31}$P NMR Spectrum of [Ir(ttp*)$_2$(PPh$_3$)]$^+$/SbF$_6^-$

- $\delta = 8.8$ ppm, $J_{DA} = J_{DB} = 14.4$ Hz
- $J_{DB} = 281.4$ Hz
- $\delta = -14.1$ ppm, $J_{BC} = 11.6$ Hz
- $J_{BA} = 18.0$ Hz
- $J_{BD} = 281.3$ Hz
- $\delta = -35.8$ ppm
- $J_{AB} = J_{AC} = J_{AD} = 18.0$ Hz
- $\delta = -49.0$ ppm
\[ \delta = -11.0 \text{ ppm} \]
\[ J_{FA} = J_{FB} = J_{FD} = 14.6 \text{ Hz} \]
\[ J_{FC} = 103.7 \text{ Hz} \]

\[ \delta = -13.7 \text{ ppm} \]
\[ J_{EB} = J_{EC} = J_{ED} = 14.6 \text{ Hz} \]
\[ J_{EA} = 123.4 \text{ Hz} \]

Figure 41: \(^1\text{H NMR Spectrum of [Ir(ttp\(^*\)]H}_2\text{(PPh}_3\text{)]}^+\text{SbF}_6^-\)
$\delta = 5.3$ ppm
$J_{DA} = J_{DC} = 12.6$ Hz
$J_{DB} = 280$ Hz

$\delta = -19.7$ ppm
$J_{AC} = 11.8$ Hz
$J_{BA} = 19.5$ Hz
$J_{BD} = 280$ Hz

$\delta = -34.0$ ppm

$\delta = -47.0$ ppm

Figure 42: $^{31}$P NMR Spectrum of [Ir(ttp)H$_2$(PPh$_3$)]$^+$ SbF$_6^-$
Figure 43: $^1$H NMR Spectrum of [Ir(tlp)H$_2$(PPh$_3$)]$^+$ SbF$_6^-$
Table 12

$^{31}\text{P}$ and $^1\text{H}$ NMR Shifts for Trapped Molecular Hydrogen Species $^a, b$

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ Pc</th>
<th>$\delta$ Pw</th>
<th>$\delta$ Pw$^*$</th>
<th>$\delta$ PPh$_3$</th>
<th>$\delta$ H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir(Cytp)H$_3^c$</td>
<td>-23.1</td>
<td>8.5</td>
<td>-</td>
<td>-</td>
<td>-12.7 to -13.6 overlapping multiplets</td>
</tr>
<tr>
<td></td>
<td>-28.2</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>-6, -13; -9 (t &lt; 253K); (t &gt; 253K)</td>
</tr>
<tr>
<td></td>
<td>-16.5</td>
<td>10.0</td>
<td>-</td>
<td>-</td>
<td>-32</td>
</tr>
<tr>
<td>[Ir(Cytp)(PPh$_3$)H$_2^*$]$^c$</td>
<td>-44.0</td>
<td>-20.5</td>
<td>-</td>
<td>-4.3</td>
<td>-13.7; -11.0 (trans to P$_2$; trans to PPh$_3$)</td>
</tr>
<tr>
<td>Ir(Cytp)H$_4^*$</td>
<td>-31.3</td>
<td>-8.6</td>
<td>-</td>
<td>-</td>
<td>-10.5 to -12.5 overlapping multiplets</td>
</tr>
<tr>
<td></td>
<td>-35.6</td>
<td>-17.5</td>
<td>-</td>
<td>-</td>
<td>-5.5; -10; -8 (t = 193 K); (t &gt; 193K)</td>
</tr>
<tr>
<td>Ir(Cytp)H$_2^*$</td>
<td>-22.7</td>
<td>-2.1</td>
<td>-</td>
<td>-</td>
<td>-31</td>
</tr>
<tr>
<td>[Ir(Cytp)(PPh$_3$)H$_2^*$]$^c$</td>
<td>-47.0</td>
<td>-19.7</td>
<td>-34.0</td>
<td>5.3</td>
<td>-11.8; -10.5 (trans to P$_2$; trans to PPh$_3$)</td>
</tr>
<tr>
<td>Ir(ttp)H$_3^c$</td>
<td>-32.4</td>
<td>-3.6</td>
<td>-</td>
<td>-</td>
<td>-10.5 to -11.5 overlapping multiplets</td>
</tr>
<tr>
<td>Ir(ttp')H$_4^*$</td>
<td>-19.7</td>
<td>-1.2</td>
<td>-</td>
<td>-</td>
<td>-31.5</td>
</tr>
<tr>
<td>[Ir(ttp)(PPh$_3$)H$_2^*$]$^d$</td>
<td>-49.0</td>
<td>-14.1</td>
<td>-35.8</td>
<td>8.8</td>
<td>-13.7; -11.0 (trans to P$_2$; trans to PPh$_3$)</td>
</tr>
</tbody>
</table>

(a) recorded in CD$_2$Cl$_2$  (b) chemical shifts in ppm

(c) $X = H, PPh_3$

(d) $[\text{Pc}\begin{array}{c} H \\ Pw \end{array}]_{\text{PPh}_3}$
1. Reactivity of Iridium Trihydrides

The trihydride of Cyttcp, Ir(Cyttcp)H₃, reacts cleanly with di-p-tolyl-carbodiimide either in a 1:1 ratio or with a 5-fold excess of diimide in CH₂Cl₂ to produce the white compound, Ir(Cyttcp)H₂(N(R)CHN(R)). The ³¹P(¹H) NMR spectrum of the compound consists of the AB₂ pattern which is typical of coordinated Cyttcp (Pₑ = -25.8 ppm, P₃ = -1.5 ppm; ²Jₚₚ = 26 Hz) and shows no unusual features. In the ¹H NMR a high field resonance at 7.9 ppm is assignable to the CH group of the coordinated ligand. In the hydride region, the following resonances are visible: a doublet of triplets at -9.5 ppm (²JₚCH = 128 Hz; ²Jₚₚ = 15.7 Hz) and a multiplet at -23.3 ppm.

The ¹H NMR is characteristic of a complex with H trans to Pₑ (the d of t) and H cis to all three phosphorus atoms of the chelate (the m); a structure consistent with the observed spectrum is shown below. Although both

\[
\begin{align*}
\text{Ir} & \quad \text{PhP} \quad \text{PCy₂} \\
\text{Cy₂P} & \quad \text{H} \\
\text{:N--CH--NR} & \quad \text{R} \\
\end{align*}
\]

\[R = \text{p-tolyl}\]
syn or anti isomers are theoretically possible, the preferred structure is probably the anti isomer, for reasons discussed previously.

For the case of Ir(ttp*)H₃, analogous behavior is observed. When treated with a five-fold excess of carbodiimide a new complex, Ir(ttp*)H₂(NRCHNR) forms. The observed spectra consist of an AX₂ pattern in the ³¹P(¹H) NMR (Pₓ = -38.6 ppm; Pᵧ = -7.4 ppm; ²Jₓᵧ = 27.5 Hz) and two hydrides in the ¹H NMR (H trans to Pₓ (d of t): -8.9 ppm; ²JₓPC₃ = 135 Hz; H cis to Pₓ and Pᵧ: -20.7 ppm (m)). A structure exactly analogous to 45 above can be drawn. In contrast to the case of Ir(Cyttp)H₃, however, a 1:1 ratio of Ir to diimide results in an incomplete reaction which consists of at least three different products (by ³¹P(¹H) NMR spectroscopy). Only by using an excess of diimide can a single clean product be observed.

In the case of Ir(ttp)H₃, like the case of Ir(ttp*)H₃, an excess of diimide is required to produce a single clean compound. Again, the results are consistent with the structure shown in 45. As before, the ³¹P(¹H) NMR spectrum consists of an AX₂ pattern (Pₓ = -34.2 ppm; Pᵧ = -10.0 ppm; ²Jₓᵧ = 29.2 Hz) and the ¹H NMR spectrum shows two hydrides (H trans to Pₓ (d of t): -8.6 ppm; ²JₓPC₃ = 122 Hz). Figures 44 and 45 show the characteristic ³¹P and ¹H NMR spectra for the reactions discussed above. (The case where L = Cyttp was chosen for the purpose of illustration.)

2. Reactivity of Iridium Dihydride Chlorides

The reaction between Ir(L)H₂Cl and diimide is likewise subject to a straightforward interpretation. In this case, however, a reactive site must be generated by first removing the chloride ion with a metal salt.
(TfBF₄ or AgBF₄ work well). If Ir(L)H₂Cl is treated with diimide in the absence of a chloride abstractor, no reaction occurs.

When Ir(Cyttp)H₂Cl is combined with excess TfBF₄ and excess p-tolyl-N=C=N-p-tolyl in CD₂Cl₂ an orangish color appears and then fades, leaving a pale yellow slurry. After 2 min of gentle heating (with a heat gun) the reaction is essentially complete. The ³¹P(¹H) NMR spectrum shows one major species: P_C = -35.8 ppm; P_H = -17.7 ppm; ²J_PP = 22 Hz; likewise the major species in the ¹H NMR is a five-line pattern centered at -23.8 ppm (it can be described as an overlapping d of t, ²J_PCH = 24.7 Hz, ²J_PCH = 12.5 Hz). The species is best described by the structure shown below.

The CH proton is visible at very high field (9.7 ppm) in the ¹H NMR. In addition, vibrations characteristic of a bidentate formamidinato group are visible at 1260, 1510 and 1540 cm⁻¹ in the IR spectrum.¹⁰⁵ The relevant NMR spectra are shown in Figures 46 and 47.

The reaction between Ir(ttp*)H₂Cl and excess diimide in the presence of Tf⁺ ion gives a similar product (³¹P(¹H) NMR: P_C = -37.2 ppm; P_H = -9.9
Figure 44: $^{31}P$ NMR Spectrum of Ir(Cyttp)$_2$(RN—CH=NR)
Figure 45: $^1$H NMR Spectrum of Ir(Cytt$\beta$)$_2$(RN–CH=NR)
ppm; $^2J_{PP} = 23\text{ Hz}; ^1H\text{ NMR: } -23.2\text{ ppm (m), } +8.6\text{ ppm (br)}.\) This reaction, however, is much more sluggish than the one where L - Cyttpp. Even after 15 min of refluxing in CD$_2$Cl$_2$, the ratio of product to starting material is only 1:5. Again, the observed product is consistent with the structure shown in 46.

The reaction of Ir(ttp)H$_2$Cl and diimide in the presence of Tt*, like its ttp* analog, does not go to completion even after several hours at room temperature. In this case a large portion of starting material and two separate products are visible. Both products show the expected AB$_2$ pattern in the $^3P(^1H)$ NMR (species A: $P_C = -30.0\text{ ppm, } P_W = -16.5\text{ ppm; } ^2J_{PP} = 27\text{ Hz; species B: } P_C = -40.0\text{ ppm, } P_W = -11.0\text{ ppm, } ^2J_{PP} = 24\text{ Hz}) and a multiplet in the $^1H\text{ NMR (species A -20.5 ppm (pseudoquartet), } ^2J_{PP} = 11.8\text{ Hz; species B: } P_C = -22.5\text{ ppm; } ^2J_{PC} = 24\text{ Hz; } ^2J_{PW} = 12.5\text{ Hz).}$. The two species, A and B, are best described as the anti and syn isomers, respectively, of structure 47.

The failures of Ir(ttp*)H$_2$Cl and Ir(ttp)H$_2$Cl to react as cleanly as Ir(Cyttpp)H$_2$Cl probably reflects the fact that Cyttpp is better able to stabilize the positively charged "Ir(L)H$_2^*"\text{ intermediate than either ttp* or ttp. Its relatively large electron-releasing ability (compared to ttp* and ttp) make it the best chelate for stabilization of positively charged intermediates."

3. Reaction of Iridium Tetrahydride Salts

Finally, the reactivity of Ir(L)H$_4^*\text{ salts was tested with carbodiimide. Since loss of H}_2\text{ in the salts generates "Ir(L)H}_2^*", it was expected that the products obtained would be the same as those observed
Figure 46: $^{31}$P NMR Spectrum of Ir(Cytp)H(RN=CH=NR)
Figure 47: $^1$H NMR Spectrum of $\text{Ir(Cytp)H(RN\text{=}CH\text{=NA})}$
for the case of the activated dihydride species discussed above. This, however, is not the case.

In all cases \((L = \text{Cyttp, ttp*, ttp})\) two products form which appear as \(\text{AB}_2\) patterns in the NMR. In addition, in each case, two hydridic resonances which correspond to apical hydrides (cis to 3 phosphorus atoms) appear. These hydridic resonances are always in the same proportion to one another as the \(\text{AB}_2\) patterns observed in the \(^{31}\text{P}[^1\text{H}]\) NMR are to one another and do not, therefore, belong to two hydrides within the same molecule. The observed chemical shifts, in all three cases, do not correspond to the resonances assigned to the syn and anti forms of the bidentate formamidinato complexes described in the preceding paragraphs.

The following tentative explanation is proposed. Since the cationic \(\text{Ir}(L)\text{H}_2^+\) (from the protonation of \(\text{Ir}(L)\text{H}_3\)) has twice the number of hydrogen atoms available as the cationic \(\text{Ir}(L)\text{H}_2^+\) (from \(\text{Ir}(L)\text{H}_2\text{Cl}\)) it can allow 2 molecules of diimide to insert into the M-H bonds (each in a monodentate fashion), rather than one molecule of diimide to insert (in a bidentate fashion). The proposed structure is shown below.

\[
\begin{align*}
\text{N(R)} & \text{—CH=} \text{NR} \\
\text{R} & \text{= p-tolyl}
\end{align*}
\]
The two observed forms represent the syn and anti isomers of this structure. To date, however, it has not been possible to obtain sufficiently clean samples in quantities large enough to permit elemental analysis. The proposed product remains speculative, pending confirmation by elemental analysis. The results of these experiments are compiled in Table 13.

E. Rhodium Complexes

\([\text{Rh(COD)Cl}]_2\) reacts readily with CyttP in THF or benzene to produce a yellow solution. Bubbling \(\text{H}_2\) through the resulting solution, however, produces no apparent change. Reducing the volume of solvent and adding ethanol causes a bright yellow powder to precipitate. The \(^{31}\text{P}(^1\text{H})\) NMR spectrum of the powder shows a clean AX\(_2\)M pattern; however, no hydrides are visible in the \(^1\text{H}\) NMR spectrum. This powder is therefore not the desired \(\text{Rh(Cyttp)H}_2\text{Cl}\). A solution of \(\text{Rh(Cyttp)Cl}\) in benzene was reacted in a Parr bomb under 160 psi of \(\text{H}_2\) gas at room temperature overnight. The product was isolated by removal of solvent, and its \(^1\text{H}\) NMR spectrum examined. Even at these high pressures, only a small hydride signal at -20 ppm was observed.

Several alternate routes to the desired \(\text{Rh(Cyttp)H}_2\text{Cl}\) were attempted. The reaction of \(\text{Rh(Cyttp)Cl}\) with a hydride source, \(\text{NaBH}_4\), failed to produce any hydridic species, although a vast change in the solubility of the resulting species was observed. (Its solubility in hydrocarbon solvents was decreased, perhaps indicating the formation of a salt.)

Since the reactivity of "\(\text{Rh(Cyttp)H}_2\text{Cl}\)" was the point of interest, and since the formation of a reactive site required removal of chloride,
Table 13

$^{31}$P and $^1$H NMR Data for the Reaction of Ir(III)$_4^+$ with 1,3-Di-p-tolyloborodiimidetrace b

<table>
<thead>
<tr>
<th>Reaction Product</th>
<th>δP$_1^{c}$</th>
<th>δP$_2^{d}$</th>
<th>J$_{PP}^{e}$</th>
<th>δH</th>
<th>J$_{PH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir(Cyttp)$_4^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-26.3</td>
<td>-18.0</td>
<td>24</td>
<td>-22.0</td>
<td>14.0</td>
</tr>
<tr>
<td>2</td>
<td>-16.9</td>
<td>-21.1</td>
<td>25</td>
<td>-21.2</td>
<td>12.0</td>
</tr>
<tr>
<td>Ir(Cyttp)$_4^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-31.5</td>
<td>-15.3</td>
<td>26</td>
<td>-20.5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-31.2</td>
<td>-14.5</td>
<td>27</td>
<td>-19.8</td>
<td></td>
</tr>
<tr>
<td>Ir(Cyttp)$_4^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-22.0</td>
<td>-13.0</td>
<td>26</td>
<td>-18.8</td>
<td>12.5</td>
</tr>
<tr>
<td>2</td>
<td>-21.0</td>
<td>-20.1</td>
<td>25</td>
<td>-20.0</td>
<td>12.4</td>
</tr>
</tbody>
</table>

(a) Recorded in CD$_2$Cl$_2$  (b) Chemical shift values in ppm  (c) central phosphorus atom  (d) wing phosphorus atoms  (e) coupling constant values in Hz
It was decided to try to obtain Rh(Cyccp)H₂(solvent). [Rh(COD)Cl]₂ was first treated with AgPF₄ in acetone to form two molecules of [Rh(COD)- (sol)][PF₄]'. The AgCl was removed by filtration, and then a Cyccp solution was added to the Rh solution. An immediate color change from yellow to orange was observed. Attempts to remove the solvent, however, resulted in the formation of a glassy oil. Because of the problems associated with the oil, the solvate was generated in situ for all subsequent reactions. A stream of H₂ was passed through an acetone/Rh(Cyccp)(acetone)⁺ solution, but the "product" which resulted was an oily residue which showed no signs of hydride ligands when examined by ¹H NMR.

One final attempt was made to isolate a Rh(Cyccp)H₂Cl complex. This reaction involved a ligand displacement reaction between the dihydride of Wilkinson's catalyst and Cyccp. According to Wilkinson,⁷ in an H₂-saturated solvent, Rh(PPh₃)Cl takes up H₂ to form Rh(PPh₃)₂H₂Cl(sol) (48) or a bridged dimeric species (49). Both of these species are shown below.

Both 48 and 49 are subject to the facile loss of H₂. Sweeping a solution of 48 and 49 with H₂ gas causes loss of H₂, and bubbling H₂ through the resulting solution regenerates the hydrides.
A sample of the purple Rh(PPh₃)Cl was slurried in degassed benzene and treated with 160 psi of H₂ gas for 2 hours. When complete, the reaction mixture was a light orange solution. The color of the solution darkens on standing, but it is easily regenerated by bubbling H₂ through the solution. The addition of Cyttpp (as a benzene solution) caused the rhodium solution to turn from orange to yellow within minutes. The ³¹P(¹H) NMR spectrum of this solution showed free PPh₃ and the AB₂M pattern characteristic of coordinated Cyttpp. The remaining solvent was removed under an H₂ stream and the residue redissolved in C₄D₆. The ¹H NMR spectrum, however, showed no evidence of a hydridic species. From the evidence presented by these experiments, if the Rh(Cyttpp)H₂Cl complex does form, it is extremely unstable with respect to loss of H₂.

Since all attempts at isolating Rh(Cyttpp)H₂Cl were unsuccessful, it is possible that the species does not exist as a classical dihydride. It was therefore proposed that the species might exist as a molecular hydrogen complex, Rh(Cyttpp)ClH₂. In order to investigate this possibility, the following experiment was undertaken.

A sample of Rh(Cyttpp)Cl was dissolved in CD₂Cl₂ and its ³¹P(¹H) NMR spectrum was taken. Two species were visible, both exhibiting AX₂M patterns, with overlapping "A" portions. The major species, with Pᵥ = 8.8 ppm corresponds to Rh(Cyttpp)Cl, while the minor species, with Pᵥ = 1.7 ppm is identified as Rh(Cyttpp)ClO₂. Integration reveals that approximately 25% of the complex consists of oxide. (The oxide presumably is present because the sample was old, and over time became exposed to increasing concentrations of O₂, even though it was stored in a Schlenk tube.) Since the oxygen adduct will not be able to react with H₂, a preliminary test
was run on the mixture. Bubbling $H_2$ through the solution at 147K for 20 minutes results in a new species which was assigned to Rh(Cyttp)Cl$H_2$ ($^{31}P(\text{H})$ NMR: $P_e = -6.8$ ppm, $P_w = 15.5$ ppm, $J_{\text{P}Rh} = 118.0$ Hz, $J_{\text{P}Rh} = 109.6$ Hz, $J_{PP} = 47.4$ Hz). At 193K the low solubility of the new species prevented a reasonable $^1H$ NMR from being taken. At $T = 223K$ more solvent was added, and the sample was treated with $H_2$ for an additional 5 minutes. This enabled a reasonable $^1H$ NMR spectrum to be collected. Two resonances are visible in the hydride region of the spectrum. One, at -8.4 ppm, appears as a large doublet; the other at -18.8 ppm is a broad multiplet. Although the poor signal-to-noise ratio prevented collection of $T_1$ data, the general appearance of the spectrum resembles the spectra for the iridium dihydrides more closely than it resembles the spectra for the molecular hydrogen complexes of iridium. The absence of Rh-H coupling is a puzzling feature of this spectrum. This lack of coupling tends to support a molecular hydrogen formulation rather than a classical dihydride formulation. The true nature of the species will remain unclear until sufficient quantities of it are produced and $T_1$ data can be obtained. Figures 48 and 49 show the relevant spectra for the Rh complexes. The NMR data for the complexes are collected in Table 14.

Conclusion

Rhodium hydride complexes of Cyttp are extremely elusive. Although various routes have been explored which have considered the possibility of both classical hydrides and molecular hydrogen species, it has not been possible to isolate a rhodium hydride complex of Cyttp in this study.
Figure 48: $^{31}$P NMR Spectrum of Rh(Cytt)Cl•H$_2$ (Rh(Cytt)Cl and Rh(Cytt)Cl•O$_2$ Present as Impurities)
Figure 49: $^1$H NMR Spectrum of Rh(Cyttp)Cl•H$_2$ (Rh(Cyttp)Cl and Rh(Cyttp)Cl•O$_2$ Present as Impurities)
Table 14

Chemical Shifts of the Proposed O₂ and H₂ Adducts of Rh (Cyttpp)Cl \(^{a,b}\)

<table>
<thead>
<tr>
<th></th>
<th>(\delta P1) (^{c})</th>
<th>(\delta P2) (^{d})</th>
<th>(J_{R-P1}) (^{e})</th>
<th>(J_{R-P2})</th>
<th>(J_{PP})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(Cyttpp)Cl</td>
<td>-23 to -20 (overlapped)</td>
<td>8.8 (d of d)</td>
<td>——</td>
<td>125.3</td>
<td>49</td>
</tr>
<tr>
<td>Rh(Cyttpp)Cl-O₂</td>
<td>-23 to -20 (overlapped)</td>
<td>1.7 (d of d)</td>
<td>——</td>
<td>89.1</td>
<td>33</td>
</tr>
<tr>
<td>Rh(Cyttpp)Cl-H₂</td>
<td>-6.8 (d of t)</td>
<td>15.5 (d of d)</td>
<td>118.0</td>
<td>109.6</td>
<td>47</td>
</tr>
</tbody>
</table>

(a) obtained from variable temperature experiments run in CD₂Cl₂  (b) Chemical shift values in ppm  (c) central phosphorus atom  (d) wing phosphorus atoms  (e) coupling constant values in Hz
Appendix A
The observed splitting in the $^{31}\text{P}^1\text{H}$ NMR spectrum of the $\text{Me}_2\text{PhP:BCl}_3$ adduct can be described as a combination of coupling to both $^{11}\text{B}$ and $^{10}\text{B}$. Coupling of phosphorus to $^{11}\text{B}$ yields a 1:1:1:1 quartet with $J_{\text{P}^{11}\text{B}} = 160$ Hz. Coupling to $^{10}\text{B}$ ($I = 3$) yields a heptet which is partially obscured by the $^{11}\text{B}$ quartet. Using gyromagnetic ratios to calculate the magnitude of the coupling constant we predict $J_{\text{P}^{10}\text{B}} = 53$ Hz. The observed coupling constant to $^{10}\text{B}$ is approximately 80 Hz. The calculation is described below.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Natural Abundance</th>
<th>$I$</th>
<th>Expected Splitting: $2NI + 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{11}\text{B}$</td>
<td>81.2%</td>
<td>3/2</td>
<td>4 lines</td>
</tr>
<tr>
<td>$^{10}\text{B}$</td>
<td>18.8%</td>
<td>3</td>
<td>7 lines</td>
</tr>
</tbody>
</table>

The magnitude of splitting arising from isotopic substitution can be calculated using gyromagnetic ratios ($\gamma$).

$$\gamma = \frac{\mu_N}{\hbar I}$$

$$\gamma_{11\text{B}} = \frac{\mu_{11\text{B}}}{N_{11\text{B}}} \frac{I_{11\text{B}}}{N_{11\text{B}}} = \frac{\mu_{11\text{B}}}{N_{11\text{B}}} I_{11\text{B}} = 2.6880 \quad 3 \quad = 3.$$  

$$\gamma_{10\text{B}} = \frac{\mu_{10\text{B}}}{N_{10\text{B}}} \frac{I_{10\text{B}}}{N_{10\text{B}}} = \frac{\mu_{10\text{B}}}{N_{10\text{B}}} I_{10\text{B}} = 1.8006 \quad 3/2$$

The expected magnitude of coupling to $^{10}\text{B}$ is therefore:

$$J_{\text{P}^{10}\text{B}} = \frac{J_{\text{P}^{11}\text{B}}}{3} = \frac{160}{3} = 53 \text{ Hz}$$
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   (h) See also references 77, 79, 80, 81, 99, 100, and 101.


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(g) See also references 80, 81, and 85.


(c) See also references 85 and 100.


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