INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.

2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in "sectioning" the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.
URIARTE, RICHARD JOSEPH
SYNTHESIS AND CHARACTERIZATION OF
PHOSPHORUS-CONTAINING MIXED-DONOR LIGANDS AND
THEIR COMPLEXES WITH COBALT, IRIDIUM, RHODIUM
AND PLATINUM.

THE OHIO STATE UNIVERSITY, PH.D., 1978
SYNTHESIS AND CHARACTERIZATION OF PHOSPHORUS-CONTAINING
MIXED-DONOR LIGANDS AND THEIR COMPLEXES WITH
COBALT, IRIDIUM, RHODIUM AND PLATINUM

DISSERTATION

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

By

Richard Joseph Uriarte, B.S., M.S.

* * * * *

The Ohio State University

1978

Reading Committee:

Dr. Devon W. Meek
Dr. Andrew Wojcicki
Dr. Eugene P. Schram

Approved By

Dr. Devon W. Meek
Adviser

Department of Chemistry
ACKNOWLEDGEMENTS

I thank Professor Devon W. Meek for his guidance during this investigation and the other members of his research group, especially D. L. Dubois, K. D. Tau, and T. J. Mazenec, for their helpful discussions. I would also like to thank Dr. Meek, T. Mazenec, and P. Kreter for the many hours they spent with the Bruker spectrophotometer.

I appreciate the guidance by H. E. Pence and J. C. Kotz during my undergraduate years.

Finally, I would like to express my sincere gratitude to my parents, family, and especially to Judy for their patience, understanding and support during this investigation.
VITA

March 8, 1950 .......... Born - Brooklyn, New York
1972 ................ B.S. (Chemistry) SUNY at Oneonta, Oneonta, New York
1972-1977 ............ Teaching Associate, The Ohio State University, Columbus, Ohio
1974 ................ M.S. (Inorganic Chemistry), The Ohio State University, Columbus, Ohio
1977-1978 ............ Research Associate, The Ohio State University, Columbus, Ohio

PUBLICATIONS


FIELDS OF STUDY

Major Field: Inorganic Chemistry

Studies in Coordination Chemistry. Dr. Devon W. Meek
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>ii</td>
</tr>
<tr>
<td>VITA</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>Chapter</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td></td>
</tr>
<tr>
<td>A. Ligands</td>
<td>1</td>
</tr>
<tr>
<td>B. Catalysis</td>
<td>15</td>
</tr>
<tr>
<td>II. EXPERIMENTAL</td>
<td>36</td>
</tr>
<tr>
<td>A. Reagents and Chemicals</td>
<td>36</td>
</tr>
<tr>
<td>B. Physical Measurements and Instruments</td>
<td>37</td>
</tr>
<tr>
<td>C. General Experimental Procedure</td>
<td>40</td>
</tr>
<tr>
<td>D. Ligand Preparations</td>
<td>40</td>
</tr>
<tr>
<td>E. Metal Complexes</td>
<td>53</td>
</tr>
<tr>
<td>III. RESULTS AND DISCUSSION</td>
<td>63</td>
</tr>
<tr>
<td>A. Ligands</td>
<td>63</td>
</tr>
<tr>
<td>B. Studies of etp-CN and etp-NH₂ Systems</td>
<td>93</td>
</tr>
<tr>
<td>C. Studies Using PPN</td>
<td>105</td>
</tr>
<tr>
<td>D. Studies of Pt(L)(CH₃)₂ Systems</td>
<td>126</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>143</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Catalytic Processes which Incorporate Transition Metal-Phosphine Complexes</td>
</tr>
<tr>
<td>2</td>
<td>Comparison of $^{31}$P nmr Parameters for the series (W(CO)$_4$L) where L = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1,2,3)</td>
</tr>
<tr>
<td>3</td>
<td>$^{31}$P Coordination Shifts (Δ) and Ring Contributions (ΔR) for a Series of Platinum(II) Diphosphine Complexes</td>
</tr>
<tr>
<td>4</td>
<td>Typical Examples for Preparing Bi- and Tridentate Ligands</td>
</tr>
<tr>
<td>5</td>
<td>Practical Considerations to be Evaluated Before Choosing a Catalytic Process</td>
</tr>
<tr>
<td>6</td>
<td>Potential Disadvantages when Anchoring a Homogeneous Catalyst</td>
</tr>
<tr>
<td>7</td>
<td>Materials Commonly Used to Anchor Metal Complexes for Use in Catalysis</td>
</tr>
<tr>
<td>8</td>
<td>Common Methods Used for Attaching Phosphine Substrates to Polymers</td>
</tr>
<tr>
<td>9</td>
<td>Comparative Rates of Olefin Hydrogenation with Rh(PPh$_3$)$_3$Cl for Various Olefins</td>
</tr>
<tr>
<td>10</td>
<td>Mixed Solvent Hydrogenation of Using Rh(PPh$_3$)$_3$Cl</td>
</tr>
<tr>
<td>11</td>
<td>Asymmetric Hydrogenation Using A (+) diop-Rh Complex</td>
</tr>
<tr>
<td></td>
<td>RCH=C(S)L + H$_2$ $\xrightarrow{\text{catalyst}}$ RCH$_2$CH(S)(L)</td>
</tr>
<tr>
<td>12</td>
<td>Hydrogenation of 1-Octene with Cobalt and Rhodium Complexes Containing Polydentate Phosphine Ligands</td>
</tr>
<tr>
<td>13</td>
<td>Spectral Data on Compounds Prepared via the Coupling Method</td>
</tr>
<tr>
<td>14</td>
<td>Spectral Data on Compounds Prepared via the Free Radical Method</td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>15</td>
<td>Phosphorus-31 Data for Rh(etp)Cl and Rh(etp-CN)Cl</td>
</tr>
<tr>
<td>16</td>
<td>$^{31}P$ and $^1H$ nmr Data for $</td>
</tr>
<tr>
<td>17</td>
<td>Chemical Shift and $J_{pp}$ Data for Various Unsymmetrical Bis-Phosphine Transition Metal Complexes</td>
</tr>
<tr>
<td>18</td>
<td>$^{31}P$ nmr Data for $(CH_3)_2P(CH_2)<em>2PPh, Ph_2P(CH_2)<em>2P(Ph)$ (neo-$C</em>{10}H</em>{19}$) and Their Dimethylplatinum Complexes</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The Hydrogenation of Alkenes Catalyzed by Wilkinson's Compound</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>The Hydrogenation of Alkenes by IrClCO(PPh₃)$_₂$ via the Unsaturated Mechanism</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>The Hydrogenation of Alkenes by Rh(H)(CO)(PPh₃)$_3$</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>Apparatus Used for Supported-Catalyst Hydrogenation Experiments</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>The Proton nmr Spectrum of Ph$_2$P(CH$_2$)$_3$Cl and PPH</td>
<td>66</td>
</tr>
<tr>
<td>6</td>
<td>The $^{31}$P nmr Spectra of PPH</td>
<td>69</td>
</tr>
<tr>
<td>7</td>
<td>Synthetic Uses of PPH</td>
<td>70</td>
</tr>
<tr>
<td>8</td>
<td>Stoichiometric Control via the Free Radical Method</td>
<td>71</td>
</tr>
<tr>
<td>9</td>
<td>The Proton nmr Spectrum of PHN</td>
<td>73</td>
</tr>
<tr>
<td>10</td>
<td>$^{31}$P nmr Spectra for PN$_2$ and PHN</td>
<td>74</td>
</tr>
<tr>
<td>11</td>
<td>The Method for Supporting PPN on a Solid Glass Support</td>
<td>77</td>
</tr>
<tr>
<td>12</td>
<td>The $^{31}$P{¹H} nmr Spectrum of etp-CN</td>
<td>78</td>
</tr>
<tr>
<td>13</td>
<td>The ESCA Spectrum of the Aldehyde Glass</td>
<td>80</td>
</tr>
<tr>
<td>14</td>
<td>The ESCA Spectrum of the Aldehyde Glass Plus PP$_2$N</td>
<td>81</td>
</tr>
<tr>
<td>15</td>
<td>The Proton nmr Spectrum of PPNH$_2$ (Benzene d$_6$)</td>
<td>83</td>
</tr>
<tr>
<td>16</td>
<td>The Proton nmr Spectrum of PPNH$_2$ (Benzene d$_6$ and D$_2$O)</td>
<td>84</td>
</tr>
<tr>
<td>17</td>
<td>The $^{31}$P{¹H} nmr Spectrum of PPNH$_2$</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>The $^{31}$P nmr Spectrum of PPNH$_2$ Supported on a Glass</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>The $^{31}$P nmr Spectrum of Supported PPNH$_2$ After Dissolving the Glass Support with NaOMe</td>
<td></td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>20</td>
<td>The ESCA Spectrum of PPNH&lt;sub&gt;2&lt;/sub&gt; Supported on Glass</td>
<td>88</td>
</tr>
<tr>
<td>21</td>
<td>The Proton nmr Spectrum of PPN</td>
<td>90</td>
</tr>
<tr>
<td>22</td>
<td>The &lt;sup&gt;31&lt;/sup&gt;P nmr Spectrum of Rh(etp-CN)Cl</td>
<td>96</td>
</tr>
<tr>
<td>23</td>
<td>A Comparison of the Infrared Spectra of Co(etp)Cl&lt;sub&gt;2&lt;/sub&gt; and Co(etp-CN)Cl&lt;sub&gt;2&lt;/sub&gt; for the 1500-2000 cm&lt;sup&gt;-1&lt;/sup&gt; Region</td>
<td>98</td>
</tr>
<tr>
<td>24</td>
<td>The &lt;sup&gt;31&lt;/sup&gt;P&lt;sup&gt;1&lt;/sup&gt;H nmr Spectrum of Co(etp-CN)(CO)</td>
<td>99</td>
</tr>
<tr>
<td>25</td>
<td>The 600-700 nm Visible Region of CoCl&lt;sub&gt;2&lt;/sub&gt; (in Ethanol) Used for Comparing the Amount of CoCl&lt;sub&gt;2&lt;/sub&gt; Bonded to Glass</td>
<td>161</td>
</tr>
<tr>
<td>26</td>
<td>The ESCA Spectrum of Glass-Supported P&lt;sub&gt;2&lt;/sub&gt;N + CoCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>102</td>
</tr>
<tr>
<td>27</td>
<td>The Results of the Catalytic Hydrogenation of 1-Octene Using Supported Co(etp-NH&lt;sub&gt;2&lt;/sub&gt;)Cl&lt;sub&gt;2&lt;/sub&gt; + OMH-1</td>
<td>103</td>
</tr>
<tr>
<td>28</td>
<td>The &lt;sup&gt;31&lt;/sup&gt;P&lt;sup&gt;1&lt;/sup&gt;H nmr Spectrum of [M(PPN)Cl]&lt;sub&gt;2&lt;/sub&gt;BPh&lt;sub&gt;4&lt;/sub&gt; (254&lt;sup&gt;o&lt;/sup&gt;K)</td>
<td>108</td>
</tr>
<tr>
<td>29</td>
<td>The &lt;sup&gt;31&lt;/sup&gt;P&lt;sup&gt;1&lt;/sup&gt;H nmr Spectrum of [Pd(PPN)Cl]&lt;sub&gt;2&lt;/sub&gt;BPh&lt;sub&gt;4&lt;/sub&gt; (254&lt;sup&gt;o&lt;/sup&gt;K)</td>
<td>109</td>
</tr>
<tr>
<td>30</td>
<td>The &lt;sup&gt;31&lt;/sup&gt;P&lt;sup&gt;1&lt;/sup&gt;H nmr Spectrum of [Pt(PPN)Cl]&lt;sub&gt;2&lt;/sub&gt;AsF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>110</td>
</tr>
<tr>
<td>31</td>
<td>J&lt;sub&gt;P-M-P&lt;/sub&gt; for Group VIA Complexes (i.e., M(CO)&lt;sub&gt;4&lt;/sub&gt;L Where M = Cr, Mo, W)</td>
<td>113</td>
</tr>
<tr>
<td>32</td>
<td>The &lt;sup&gt;31&lt;/sup&gt;P&lt;sup&gt;1&lt;/sup&gt;H nmr Spectrum of Pt(PPN)Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>115</td>
</tr>
<tr>
<td>33</td>
<td>Theoretical AB Type Spectra for Two Nuclei of Spin 1/2 Having &lt;sup&gt;v&lt;/sup&gt;δ = 10 c.p.s.</td>
<td>116</td>
</tr>
<tr>
<td>34</td>
<td>The &lt;sup&gt;31&lt;/sup&gt;P&lt;sup&gt;1&lt;/sup&gt;H nmr Spectrum of Rh(PPN)Cl</td>
<td>119</td>
</tr>
<tr>
<td>35</td>
<td>The Results of the Catalytic Homogeneous Hydrogenation of 1-Octene Using Rh(PPN)Cl</td>
<td>121</td>
</tr>
<tr>
<td>36</td>
<td>The Results of the Catalytic Homogeneous Hydrogenation of 1-Octene Using Ir(PPN)Cl</td>
<td>124</td>
</tr>
<tr>
<td>37</td>
<td>The &lt;sup&gt;31&lt;/sup&gt;P&lt;sup&gt;1&lt;/sup&gt;H nmr Spectrum of (CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;P(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;PPh&lt;sub&gt;2&lt;/sub&gt;</td>
<td>128</td>
</tr>
<tr>
<td>38</td>
<td>The &lt;sup&gt;31&lt;/sup&gt;P&lt;sup&gt;1&lt;/sup&gt;H nmr Spectrum of Ph&lt;sub&gt;2&lt;/sub&gt;P(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;P(Ph)neo-C&lt;sub&gt;10&lt;/sub&gt;H&lt;sub&gt;19&lt;/sub&gt;</td>
<td>129</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES (continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>The $^{31}$P{$^{1}$H} nmr Spectrum of Pt (Ph)$_2$P(CH$_2$)$_2$P(CH$_3$)$_2$</td>
<td>130</td>
</tr>
<tr>
<td>40</td>
<td>The $^{31}$P{$^{1}$H} nmr Spectrum of Pt (Ph)$_2$P(CH$<em>2$)$<em>2$P(Ph) neo-C$</em>{10}H</em>{19}$ (CH$_3$)$_2$</td>
<td>131</td>
</tr>
<tr>
<td>41</td>
<td>The $^{31}$P{$^{1}$H} nmr Spectrum of Ph$_2$P(CH$_2$)$_2$P(Ph)(CH$_2$)$_3$PPh$_2$</td>
<td>132</td>
</tr>
<tr>
<td>42</td>
<td>The $^{31}$P{$^{1}$H} nmr Spectrum of Recrystallized Pt(eptp)(CH$_3$)$_2$ at 263°K</td>
<td>135</td>
</tr>
<tr>
<td>43</td>
<td>The $^{31}$P{$^{1}$H} nmr Spectrum of Pt(eptp)(CH$_3$)$_2$ at 263°K</td>
<td>136</td>
</tr>
<tr>
<td>44</td>
<td>The $^{31}$P{$^{1}$H} nmr Spectrum of Pt(eptp)(CH$_3$)$_2$ at 283°K</td>
<td>137</td>
</tr>
<tr>
<td>45</td>
<td>The $^{31}$P{$^{1}$H} nmr Spectrum of Pt(eptp)(CH$_3$)$_2$ at 293°K</td>
<td>138</td>
</tr>
<tr>
<td>46</td>
<td>The $^{31}$P{$^{1}$H} nmr Spectrum of Pt(eptp)(CH$_3$)$_2$ at 303°K</td>
<td>139</td>
</tr>
<tr>
<td>47</td>
<td>The $^{31}$P{$^{1}$H} nmr Spectrum of Pt(eptp)(CH$_3$)$_2$ at 373°K</td>
<td>140</td>
</tr>
</tbody>
</table>
A. Ligands

Over the years, transition metal-phosphine complexes have been utilized in a variety of catalytic processes (Table 1). In addition, selected complexes have been used in model systems for nitrogen fixation,\(^1,2\) as proposed intermediates in catalytic processes,\(^3,6\) in chiral synthesis,\(^5,6\) and for the activation and stabilization of small molecules.\(^7-9,15\) Although the transition metal site in these complexes is the center of attention, the phosphine ligands bonded to this metal play a most important role in determining both the reactivity and the stereochemistry in these complexes.\(^10,11\) Subtle changes made in these ligands can lead to drastic changes in resulting complexes. This can be illustrated by reviewing some work originated by Wilkinson.\(^12\) The rate of hydrogenation of cyclohexene with \(\text{RL}_3\text{Cl}\) (\(L = \text{PPh}_3\)), \(^1\), can be altered by substituting in the position para to the phosphorus on the phenyl ring.
TABLE 1

CATALYTIC PROCESSES WHICH INCORPORATE TRANSITION METAL-PHOSPHINE COMPLEXES

<table>
<thead>
<tr>
<th>Process</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homogeneous hydrogenation of olefins</td>
<td>a,b,c</td>
</tr>
<tr>
<td>Isomerization and rearrangement of olefins</td>
<td>b,d</td>
</tr>
<tr>
<td>Oxidations</td>
<td>e,f,g</td>
</tr>
<tr>
<td>Hydrosilations</td>
<td>h</td>
</tr>
<tr>
<td>Hydroformylations</td>
<td>a,h</td>
</tr>
<tr>
<td>Carbonylations</td>
<td>i,j,k</td>
</tr>
<tr>
<td>Olefin metathesis</td>
<td>l,m,n</td>
</tr>
<tr>
<td>Dimerization, oligomerization, cyclooligomerization of olefins</td>
<td>h</td>
</tr>
</tbody>
</table>

References:

k. J. F. Roth, ibid., 19, 12 (1975).
TABLE 1 (continued)

The rates of hydrogenation increased according to scheme 1.

\[ P(p-C_6H_4F)_3 < PPh_3 < P(p-C_6H_4OCH_3)_3 \]  
(Scheme 1)

This suggested that electron donating groups in the para position made the phosphine more basic (thus increasing activity), and electron withdrawing groups made the ligands less basic (therefore decreasing activity). Tolman later added that this activity change probably reflects the different rates of oxidative addition of \( \text{H}_2 \) to these complexes. The conclusion from these results was that more basic phosphine ligands yielded better catalysts. But when Wilkinson replaced the phenyl groups on these phosphines with ethyl groups, the more basic phosphines gave decreased rates of catalysis (Scheme 2).

\[ \text{PPh}_3 > \text{PPh}_2\text{Et} > \text{PPhEt}_2 > \text{PEt}_3 \]  
(Scheme 2)

This result was rationalized on the basis that the oxidative addition of \( \text{H}_2 \) was indeed faster, but that the 18-electron \( \text{H}_2\text{RhL}_3\text{Cl} \) was more stable than previous complexes. The vacant sites for the coordination of olefin were less likely to be created by the more stable complex—thus a decrease in rate.

When Perego et al. attempted to prepare the trisisopropylphosphine derivative of Wilkinson's compound, they did not isolate \( \text{Rh}(\text{PR}_3)_3\text{Cl} \); they obtained instead the compound, \( \text{RhCl}(\text{N}_2)(\text{PPr}^\text{i}_3)_2 \), containing side-on bonded dinitrogen. It was an unexpected result because a small change in the ligand resulted in dramatic changes for the activation of nitrogen and other small molecules (\( \text{O}_2, \text{C}_2\text{H}_4 \)) not
stabilized by \( \text{Rh(PPh}_3)_3 \text{Cl} \).

\[
\text{Cl} \\
\text{R}_3 \text{P} \rightarrow \text{Rh} \rightarrow \text{PR}_3 \\
\text{N=NN}
\]

In addition to altering the reactivity of complexes by modifying their ligands, mechanistic information can also be supported by looking at complexes of similar ligands. Tolman\(^{13}\) suggested that \( P_1 \) in complex 3 dissociated rapidly to form complex 4 in the second step of olefin hydrogenation by Wilkinson's compound.

Although the intermediate could not be isolated or detected spectroscopically, line shape analysis strongly indicated this mechanism. However, incorporating more bulky phosphine ligands (e.g., \( \text{P(t-Bu)}_3 \))\(^{16}\) or \( \text{P(Cy)}_3 \))\(^{17}\), intermediates of type 5 could be isolated.
Both the isolation of these intermediates, and the line shape analysis points to the mechanism suggested.

From the previous examples it can be seen that there are two major factors that should be considered in the design of phosphine ligands to be used in catalytic applications: (i) electronic effects and (ii) steric effects. While Wilkinson was one of the first researchers to show both of these effects and relate them to the rate of olefin hydrogenation, researchers have recently been looking more closely at the steric demands or bulkiness of ligands as shown in recent investigations.

Although a plethora of transition metal phosphine complexes have been reported over the years, there have only recently been advances made in the synthesis and design of polydentate phosphine ligands. The major difference between monodentate and polydentate ligands lies in the alkyl chain that connects phosphorus atoms (6-8).

As a result of this backbone there are several advantages that polydentate ligands can simultaneously incorporate over their monodentate counterparts in transition metal complexes. These include:
(1) Increase basicity at the metal center.²³,²⁴
(2) Control of stoichiometry.²⁵
(3) Control of stereochemistry, magnetic properties, and electronic ground states.²⁶,²⁷
(4) Slow down or stop inter and intra molecular exchange.
(5) Stabilize unusual coordination numbers.²⁸,²⁹

In addition, the importance of multidentate ligands in bioinorganic catalysis has been illustrated.³⁰ It has been shown that metal-phosphorus coupling constants depend on structural constraints in chelate complexes (Table 2). A similar effect can be seen when monitoring the differences in $^{195}$Pt-P coupling constants in complexes ⁹-¹¹.³¹,³²

![Chemical structures and coupling constants](image)

At 298°K, Pt(P\(_3\))₄ dissociates to Pt(P\(_3\))₃ and P\(_3\), while complex ¹¹ does not dissociate even at 333°K. When investigating the chemistry
of transition metal-chelate complexes, one must be very careful in extrapolating to monodentate analogs.

An important factor often overlooked when considering chelating phosphines is the length of the carbon backbone connecting the phosphorus atoms. Over the past several years there have been explicit examples where chain length has directly affected the coordination geometry about the metal ion, and it is generally agreed upon that steric factors are responsible for the stereochemical changes observed. Rigo \cite{33,34} illustrated this point using \( \text{Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2 \) \( (n=1,2,3) \) in complexes such as \( \text{M(Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2\text{)}_2\text{X}_2 \) where \( \text{M} = \text{Ru, Os} \)

\[
\begin{align*}
\text{M(Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2\text{)}_2\text{X}_2 & & \text{where M = Ru, Os} \\
& & n = 1,2,3 \\
& & X = \text{halide}
\end{align*}
\]

When \( n = 1 \) or 2, a six-coordinate molecular species is formed, but upon increasing the backbone to \( n = 3 \), greater crowding results and a halide ion is eliminated from the metal to form a five-coordinate cationic complex. This rationale is in agreement with the different chelate-bite angles \( (\text{P-M-P}) \) found by Palenik \cite{35,36} in three palladium complexes, \( \text{Pd(Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2\text{)}_2\text{Cl} \) \( (n=1,2,3) \)

\[
\begin{align*}
\text{Pd(Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2\text{)}_2\text{Cl} & & \text{Chelate bite angle} \\
& & (\text{P-M-P}) \\
& & n=1 : 73^\circ \\
& & n=2 : 86^\circ \\
& & n=3 : 91^\circ
\end{align*}
\]
Meek et al.\textsuperscript{37,38} had earlier found that with a similar diphosphines, both trigonal bipyramidal and square base pyramidal five coordinate structures could be stabilized by choosing the proper chain length. When $n = 2$, the square pyramid complex 14 was formed, and when $n = 3$, structure 15 was stabilized.

The steric requirements placed on the metal center by different backbone lengths can be used to favor preferential bonding in moieties capable of linkage isomerization. In PdL(NCS)$_2$ (where $L = \text{Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2$) Meek and Palenik\textsuperscript{39,40} correlated the P-M-P angle for $n = 1,2,3$ to the mode of bonding for the thiocyanate. It was found that when $n = 1$, the angle was 73.3° and that both thiocyanates were S bonded. For the two carbon chains, the angle increased to 85.1° and the two thiocyanates were S and N bonded. Upon increasing the chain length to $n = 3$, the angle opened up to 89.3° and both species were N bonded. This trend was correlated to steric effects due to the fact that when S bonded, the thiocyanate sweeps out a larger cone angle around the transition metal (16).
Depending on the size of the transition metal being studied, one must remember that polydentate ligands have the potential for dimerizing or polymerizing metal complexes. When \((\text{Rh(CO)}_2\text{Cl})_2\) was reacted with \(\text{Ph}_2\text{P(CH}_2\text{)_n}\text{PPh}_2\) \((n = 1-4)\), a monomeric complex was formed only when \(n = 2\) \((17)\).

For \(n = 1,3,4\), only dimeric compounds, \(18\), were formed. In a series of platinum methyl compounds, Bennett\(^\text{42}\) found that monomeric structures were formed with \(n = 2\) or \(3\) \((\text{ligand} = \text{Ph}_2\text{P(CH}_2\text{)_n}\text{PPh}_2\) in complex, \(19\)) and that for \(n = 1\), only very small amounts of monomeric compound could be isolated; the majority is the phosphine bridged oligomer \(20\).
Stereochemical control can also be invoked with phosphines of higher "dentate order" than bidentate phosphines. Using etp, 21, and ttp, 22, it was found that for comparable cobalt (I) complexes, etp, which forms five membered metallocyclic rings upon coordination, has a smaller bite angle as compared to ttp, which forms six membered rings on complexation.

The different constraints by these ligands cause trigonal-bipyramidal, 23, and square-pyramidal, 24, structures to be formed in comparable cobalt(I) complexes.

When the chain length is increased to n > 4, it is possible that the ligand would trans-span a metal instead of chelating in the
normal cis fashion. Also, rigid backbones help facilitate trans-spanning and keep intermolecular bridging to a minimum. Examples of ligands used for this purpose are illustrated in 25 - 28.\(^{44-47}\)

\[(Bu^t)_2P(CH_2)_nP(Bu^t)_2\]
\[n=10-13,15\]

\[25\]

\[(Bu^t)_2P(CH_2)_nP(Bu^t)_2\]

\[27\]

Bidentate phosphine ligands containing two-carbon backbones display an unusual effect in the \(^{31}P\) nmr when bonded to diamagnetic transition metals. An anomalously large downfield chemical shift (21 to 52 ppm) relative to free ligand is observed upon formation of a five-membered metallocycle which does not occur with either the 1- or 3-carbon backbone cases (Tables 2 and 3).\(^{48-50,54,55}\) The various ligands investigated in these studies are shown below, 29-31.

\[Ph_2P(CH_2)_nPPh_2\]
\[(n = 2,3,4)\]

\[29\]

\[Ph_2PCH_2OPPh_2\]

\[30\]
### TABLE 2
COMPARISON OF $^{31}\text{P}$ NMR PARAMETERS FOR THE SERIES $(\text{W(CO})_4L)$ WHERE $L = \text{Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2$ ($n = 1,2,3)^{a}$

<table>
<thead>
<tr>
<th></th>
<th>$n = 1$</th>
<th>$n = 2$</th>
<th>$n = 3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>complex (ppm)</td>
<td>-23.6</td>
<td>+40.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Ligand (ppm)</td>
<td>-23.6</td>
<td>-12.5</td>
<td>-17.3</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>0</td>
<td>+52.6</td>
<td>+17.3</td>
</tr>
<tr>
<td>$J_{w-p}$ (Hz)</td>
<td>202</td>
<td>231</td>
<td>222</td>
</tr>
</tbody>
</table>


### TABLE 3
$^{31}\text{P}$ COORDINATION SHIFTS ($\Delta$) AND RING CONTRIBUTIONS ($\Delta_R$) FOR A SERIES OF PLATINUM(II) DIPHOSPHINE COMPLEXES$^{a}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta$</th>
<th>$\Delta_R$</th>
<th>$J_{\text{Pt-P}}$(Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PtCl}_2\text{dppe}$</td>
<td>53.4</td>
<td>42.2</td>
<td>3609</td>
</tr>
<tr>
<td>$\text{PtCl}_2\text{dppp}$</td>
<td>11.4</td>
<td>-4.5</td>
<td>3408</td>
</tr>
<tr>
<td>$\text{cis-PtCl}_2(\text{PMePh}_2)_2$</td>
<td>25.6</td>
<td>- -</td>
<td>3620</td>
</tr>
<tr>
<td>$\text{PtEt}_2\text{dppe}$</td>
<td>57.4</td>
<td>39.2</td>
<td>1602</td>
</tr>
<tr>
<td>$\text{PtEt}_2\text{dppp}$</td>
<td>20.0</td>
<td>-2.9</td>
<td>1592</td>
</tr>
<tr>
<td>$\text{PtEt}_2\text{dpdp}$</td>
<td>34.0</td>
<td>12.6</td>
<td>1677</td>
</tr>
<tr>
<td>$\text{cis-PtEt}_2(\text{PMePh}_2)_2$</td>
<td>32.6</td>
<td>- -</td>
<td>1667</td>
</tr>
</tbody>
</table>

In addition, this deshielding effect seems to be additive: for each five-member metallocyclic ring involving a phosphorus atom, approximately a 50 ppm downfield chemical shift is added. An example is illustrated in 32-34.

\[
\begin{align*}
\text{CO} & \quad \text{CO} \\
\text{CO} & \quad \text{CO} \\
\text{CO} & \quad \text{CO} \\
\end{align*}
\]

\[\Delta \quad -56.1 \text{ ppm} \quad -88.3 \text{ ppm} \quad -150 \text{ ppm} \]

Although Grimm et al.\textsuperscript{48} ruled out ring strain\textsuperscript{52} in the five-membered ring as a contributing factor to this deshielding, Baird\textsuperscript{54} suggests that there is a correlation between ring strain and ring contributions. He suggests, "the more strained the system, the larger the shielding contribution of \( \Delta_R \) to the observed chemical shift."\textsuperscript{54} He also states that there is no apparent relationship between \( J_{\text{Pt-P}} \) and \( \Delta_R \). This effect is still not fully understood.

In the past, polydentate phosphine ligands have been prepared using normal organic preparative methods. These included:
a) Grignard reagents, b) alkali phosphides (nucleophilic attack on organic halides, and c) addition of P-H bond across a vinyl or a selected allyl bond. Recently, the methods of Grimm, King, and Meek have received the most attention for the construction of polydentate ligands. Examples of typical reactions are shown in Table 4. Although each of these synthetic methods can be suited for certain reactions, there are some limitations or disadvantages associated with each. The coupling reaction requires organic halides or polyhalides which are either difficult to obtain or frequently do not react completely. The base-catalyzed method is limited solely to products with \( n = 2 \), whereas the free radical reaction can be utilized to produce \( n = 2 \) and selected \( n = 3 \) products. In order to prepare conveniently a variety of polydentate ligands with specific donors at selected structural sites, a combination of methods previously mentioned would be needed.

B. Catalysis

Many advances have been made in both heterogeneous and homogeneous catalysis since their conception approximately eighty and twenty years ago, respectively. Although heterogeneous applications have been studied much longer than those of homogeneous nature, more detailed information is known about the mechanisms of homogeneous catalysts due to the availability of spectroscopic tools amenable to their study. Before discussing several aspects of homogeneous hydrogenation, it would be appropriate to define first the function of a catalyst. J. Kotz said, "The function of a catalyst, whether homogeneous or heterogeneous, is to increase the rate of a thermodynamically
### TABLE 4

**TYPICAL EXAMPLES FOR PREPARING BI- AND TRIDENTATE LIGANDS**

| A. | Ph₃P + Na $\xrightarrow{\text{NH}_3, -78^\circ C}$ Ph₂P⁻Na⁺ + NaPh  
|    | NaPPh₂ + Cl(CH₂)₃Cl → Ph₂PCH₂CH₂CH₂Cl₂  
|    | Ph₂P(CH₂)₃Cl + NaPPh₂ → Ph₂P(CH₂)₃PPh₂  
| B. | Ph₂PCl + 2Li → Ph₂PLi + LiCl  
|    | Ph₂PLi + CH₂→CH₂ → Ph₂PCH₂CH₂O⁻Li⁺  
|    | Ph₂PCH₂CH₂O⁻Li⁺ + Ph₂PCl → Ph₂PCH₂CH₂OPPh₂ + LiCl  
| C. | Ph₂PC≡C + H₃PPh₂ $\xrightarrow{\text{t-BuOK}}$ Ph₂PCH₂CH₂PPh₂  
| D. | Ph₂PH + C≡CPPh₂ $\xrightarrow{\text{AIBN}}$ Ph₂PCH₂CH₂PPh₂  
| E. | PhPH₂ + 2 H₂C=CH₂NH₂ $\xrightarrow{\text{AIBN}}$ PhP(CH₂CH₂CH₂NH₂)₂  
| F. | (RO)ₙPR' (3-n) $\xrightarrow{\text{vitride}}$ R''O $\xrightarrow{\text{nR''X}}$ (3-n)P'R'  

---


allowed reaction by lowering the activation-energy barrier for the process. In addition, if several reaction paths are possible, a catalyst may increase product specificity by either lowering the barrier for one path or by raising it for another. Two methods of lowering this activation energy can be envisioned: "coordination of an olefin may make it more susceptible to nucleophilic attack (as in PdCl₂-catalyzed oxidation of ethylene to acetaldehyde), or both reactants may be brought into close proximity by being coordinated to adjacent sites on the catalytic metal (as in hydrogenations, polymerizations, cyclo-oligomerizations, and nitrogen fixation)."

Serious study in catalysis has proceeded using three major catalyst types: a) homogeneous, b) heterogeneous and c) polymer-supported (heterogenized-homogeneous) catalysts. The pros and cons of each process have been well documented. Some considerations that should be evaluated before selecting a process are listed in Table 5. Even though homogeneous catalysts are equivalent or have an advantage over heterogeneous catalysts in six of the seven categories listed in Table 5, it is usually still more profitable for industry to use heterogeneous systems. This decision is based on the fact that even though homogeneous systems possess greater selectivity and efficiency (turnover rate and conditions used), separating the catalyst from the products after use represents a major problem. Incorporation of both catalyst types has produced a third kind which retains many of the characteristic advantages of both parents. Two approaches have been investigated: a) polymer-supported catalysts and c) fluid-bed systems.
### TABLE 5

**PRACTICAL CONSIDERATIONS TO BE EVALUATED BEFORE CHOOSING A CATALYTIC PROCESS**

1) separation of catalyst  
2) efficiency  
3) reproductivity  
4) specificity  
5) controllability  
6) thermal stability  
7) solvents


### TABLE 6

**POTENTIAL DISADVANTAGES WHEN ANCHORING A HOMOGENEOUS CATALYST**

1) Possible change of mechanism when attached to the polymer  
2) Greater possibility of contamination  
3) Increased time and cost in preparing the catalyst  
4) Decreased yields or rates due to the introduction of steric hinderance from the polymer

In addition to the advantages that would be expected from polymer supported catalysts, potential disadvantages could be introduced as a result of interactions with the polymer. These disadvantages are listed in Table 6. Most of these problems are a function of the support selected and can be minimized or eliminated by a proper choice of support. The materials commonly used as supports and the common methods of anchoring phosphines to them are displayed in Tables 7 and 8. From these tables, it can be seen that a variety of both supports and phosphines have been explored. Although many metals have been examined in these supported complexes, only one example of a supported polydentate ligand has been reported. In addition to catalysis, it has been shown that supported compounds can also be used with success in organic synthesis (35). Thus, it seems that this "third generation" catalyst will make an important impact in the future of catalysis.
TABLE 7
MATERIALS COMMONLY USED TO ANCHOR METAL COMPLEXES
FOR USE IN CATALYSIS

A. Inorganic: silica, zeolites, glass, clay, metal oxides
B. Organic: polystyrene polyamines, silicates, polyvinyls, polyallyls,
polybutadienes, polyamino acids, urethanes, acrylic polymers, cellulose, cross-linked dextrans, agarose.


Homogeneous hydrogenation catalysts have been the subject of many investigations over the past decade, and several excellent reviews on this topic have recently appeared. Although the reaction of hydrogen with alkenes to form alkanes is thermodynamically allowed, the hydrogen molecule is quite stable and needs a catalyst in order to be "fixed" for use in this catalysis. The most thoroughly-studied catalyst to date has been the rhodium complex Rh(PPh₃)₃Cl, Wilkinson's compound. Two possible mechanistic sequences have been postulated: the hydride route, 36, and the unsaturated route, 37.

\[
\begin{align*}
\text{Hydride Route} \\
\text{L} \text{M} + \text{H}_2 & \rightarrow \text{L} \text{MH}_2 \rightarrow \text{complex} \\
\text{L} \text{M} + \text{alkane} & \rightarrow \text{L} \text{MH}_2 \rightarrow \text{complex} \\
\end{align*}
\]
Table 8. Common Methods Used for Attaching Phosphine Substrates to Polymers
Supporting kinetic data\^76 and nmr line-shape analysis\^10 supported Wilkinson's contention that the correct mechanism was indeed the hydride route. Details concerning this mechanism are shown in Figure 1. Other complexes do, however, follow the unsaturated mechanism. Examples of two variations of this mechanism, IrCl\textsubscript{2}CO(PPh\textsubscript{3})\textsubscript{2} and RhH(CO)(PPh\textsubscript{3})\textsubscript{3}, are shown in Figures 2 and 3. At first glance, it would seem that the metal site in RhH(CO)(PPh\textsubscript{3})\textsubscript{3} could not conveniently accommodate an olefin for catalysis. But \textsuperscript{1}H nmr studies show that although a static five-coordinate structure occurs at -35°C (hydride signal 19.69 T; doublet of quartets \( J_{P-H} = 14\) hz, \( J_{Rh-H} = 1\) hz) at higher temperatures, this signal broadens due to phosphine exchange arising from dissociation (equation 38).

\[
\text{RhH(CO)(PPh\textsubscript{3})\textsubscript{3}} \rightleftharpoons \text{RhH(CO)(PPh\textsubscript{3})\textsubscript{2}} + \text{PPh\textsubscript{3}} \quad 38
\]

Rapid hydrogen-deuterium exchange occurs when Rh(H)CO(PPh\textsubscript{3})\textsubscript{3} is dissolved in benzene with an atmosphere of deuterium (i.e., 39).
Figure 1. The Hydrogenation of Alkenes Catalyzed by Wilkinson's Compound
Figure 2. The Hydrogenation of Alkanes by IrCl(CO)(PPh₃)₂ via the Unsaturated Mechanism

Figure 3. The Hydrogenation of Alkenes by Rh(H)(CO)(PPh₃)₃
From these mechanisms, certain circumstances that must be met for homogeneous olefin hydrogenation catalysis can be seen. The first requirement is the activation of dihydrogen—i.e., the incorporation of dihydrogen into transition metal complexes forming transition metal hydrides. This is accomplished by a basic metal oxidatively adding $H_2$ to form two $M$-H bonds, (40),

$$L_{n}^{m} + H_2 \underset{H}{\overset{n+2}{\leftrightarrow}} L_{n+1}^{m-H}$$

which are usually cis (equation 41).
This process is believed to be the limiting step in many catalytic processes. The ability of transition metal complexes to perform this activation, however, is only the first requirement needed for catalysis. The iridium analogue of Wilkinson's compound, which activates hydrogen at a faster rate than the rhodium complex, is inactive. Even though hydrogen was taken up by the complex, it was concluded that no activity occurred because: a) the iridium-hydrogen bonds are somewhat stronger than rhodium-hydrogen bonds thus making $\text{H}_2$ addition irreversible, and b) the six-coordinate iridium species formed is non-dissociable and remains intact in solution. These conclusions are supported somewhat by the fact that $\text{Ir(PPh}_3)_2\text{Cl}$ generated \textit{in situ} is a very good hydrogenation catalyst for olefins. This leads to the second condition required for olefin hydrogenation. There must be a vacant site on the metal on which the olefin can bond to at the proper time. Figures 1-3 show that somewhere in each catalytic cycle a phosphine dissociates, and an olefin-metal bond forms.
Once an olefin-hydride complex exists, a facile hydrogen transfer can occur to first produce an alkyl metal bond, then through reductive elimination to produce an alkane plus the regenerated catalyst. This reaction occurs so readily that only two cases have been reported in the literature where an hydrido olefinic metal complex has been isolated (i.e., prior to metal hydrido addition across the coordinated alkene), 42 and 43.

\[ L = \text{P} \cdot \text{O}_2 \cdot \text{R}, \text{P} \cdot \text{O}_3 \]

Although these are the only pre-addition intermediates isolated, Halpern, Seyler, and Otsaka have isolated alkyl intermediates with more complicated conjugated olefins in conjunction with HCo(CN)\(_3\) 3–87,88
and \( \text{Cp}_2\text{MoH}_2 \) \(^{89,90}\) respectively, \(44, 45\).

\[
\begin{align*}
\text{(CH)}_2\text{Co-alkyl} & \quad \text{CO}_2\text{Me} \\
\text{where olefins used are:} & \quad \text{(Cp)}_2\text{Mo(H)-C-H} \\
\rangle\text{C}=&\text{C}<^x & \quad \text{CH}_2\text{CO}_2\text{Me} \\
\text{where the olefin =} & \quad \text{where the olefin =} \\
\text{C}_2\text{O}_2, \text{CN, Ph,} & \quad \text{MeO}_2\text{CC(H)}_2 \\
\text{C}_4\text{H}_5\text{N} & \quad \text{C}_4\text{H}_5\text{N}
\end{align*}
\]

There are many factors that can change the rate of olefin hydrogenation by transition metal complexes. Different steric arrangements about the olefin yield quite different hydrogenation rates with \( \text{Rh(PPh}_3\text{)}_3\text{Cl} \) \(^{91}\) (Table 9). Oxygen impurities present during hydrogenation can react with triphenylphosphine and actually enhance the rate of hydrogenation by Wilkinson's compound.\(^{92}\) Addition of various aluminum compounds has increased the rates by forming \( \text{Rh(PPh}_3\text{)}_3\text{Br} \) with \( \text{AlBr}_3 \) and \( \text{Rh(PPh}_3\text{)}_3\text{H} \) with \( \text{Al(Bu}^1\text{)}_3 \).\(^{93}\) Different solvents also affect the rate of catalysis.\(^{91,94,95}\) Either an increase or decrease of rates could be observed depending on which complex in \(~46~\) was stabilized more by the solvent.

\[
\begin{align*}
\text{RhL}_3\text{Cl} + \text{solvent} & \rightleftharpoons \text{RhL}_2\text{Cl(solvent)} + \text{L} \\
\text{Rh(H)}_2\text{Cl(L)}_2(\text{solvent}) + \rangle\text{C}=&\text{C}< & \rightleftharpoons \text{Rh(H)}_2\text{Cl(L)}_2(\text{olefin}) + \text{solvent}
\end{align*}
\]

\(~46~\)
When comparing hydrogenation rates for 1-hexene : 1 octene, a ratio of 1.7 is obtained for benzene, acetone, or THF. When solvents of greater coordinating power (i.e., CH₂CH, CH₃NO₂, DMF or DMSO) are used, a drastic decrease in rate is noticed. However, when chlorobenzene or 2,2,2-trifluoroethanol are used, ratios of 5 and 7 respectively are obtained. Although alcohols have a tendency to increase the rate of hydrogenation, more isomerization products are usually formed. Differences in rates with mixed solvent have also been observed (Table 10). Finally, one must be careful that the solvent of choice does not react with the catalyst or intermediates; for example, chloroform reacts with Wilkinson's compound to give the inactive complex Rh(H)Cl₂(PPh₃)₂. However, non-reactive chlorinated solvents can sometimes give higher rates of catalysis. Crabtree illustrated this point using cationic iridium complexes which Osborn had found to be less active than their rhodium analogues in solvents such as acetone, ethanol, or THF. He assumed that a polar but non-coordinating solvent was needed; thus, dichloromethane was chosen. Rates up to 300 times that of Wilkinson's compound were obtained for the hydrogenation of 1-methyl-cyclohexene using these iridium complexes. Therefore, solvents used in hydrogenations can play a very important role in determining rates and must be carefully selected.

Compounds containing unusual steric effects, as previously mentioned, can change catalyst activity, and catalysts incorporating chiral ligands have been shown to hydrogenate prochiral substrates in large enantiomeric excess. An efficient asymmetric hydrogenation catalyst incorporating the end product of 47 has been used by Knowles
TABLE 9
COMPARATIVE RATES OF OLEFIN HYDROGENATION WITH \( \text{Rh(PPh}_3)_3\text{Cl} \) FOR VARIOUS OLEFINS

<table>
<thead>
<tr>
<th>Group</th>
<th>Comparative Rates of Hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Terminal cis trans</td>
<td></td>
</tr>
<tr>
<td>B. for ( \text{H}_2\text{C=CHR} )</td>
<td>( \text{R} = \text{CN} &gt; \text{CO}_2\text{Me} &gt; \text{Ph} &gt; \text{alkyl} )</td>
</tr>
<tr>
<td>C.</td>
<td>![Chemical Structures]</td>
</tr>
<tr>
<td>17</td>
<td>0.49</td>
</tr>
</tbody>
</table>

TABLE 10
MIXED SOLVENT HYDROGENATION OF \( \text{O} \) USING \( \text{Rh(PPh}_3)_3\text{Cl} \)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( k \times 10^2 \text{M}^{-1}\text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Chemical Structure]</td>
<td>31.6</td>
</tr>
<tr>
<td>![Chemical Structure] + hexane</td>
<td>15.0</td>
</tr>
<tr>
<td>![Chemical Structure] + 2 butanone</td>
<td>29.6</td>
</tr>
</tbody>
</table>
to produce α-amino acids, but the preparation of the ligand is somewhat complicated and tedious. Three examples of bidentate phosphine ligands that incorporate these effects in various metal catalysts are shown in 48-50.

It has been suggested that the resulting chirality of prochiral substances can be predicted successfully by examining CPX models and determining the favored intermediates of the reactions. This is done by using either steric or polar arguments. When the rhodium catalyst system (\(\text{Rh(olefin)}_2\text{Cl}_2 + (+)\text{diop}\)) was used on a variety of prochiral olefins, the stable intermediate, 51, was suggested and the chirality of the vast majority of products was correctly predicted (Table 11).

![Diagram 51]

Hence, in the future we may be able to predict how certain catalysts behave if we can tailor our ligands properly.

Polydentate phosphine, metal hydride complexes containing rhodium and cobalt have been used as catalysts for the homogeneous hydrogenation of olefins. Vast differences in hydrogenation rates were reported when \(\text{ttp, 52, and etp, 53, were used in analogous complexes (Table 12).}

In fact, the effect of rates was reversed compared with Kagan's results
TABLE 11
ASymmetric Hydrogenation using a (+) DIOP-Rh complex $RCH-\text{C(S)L} + H_2 \xrightarrow{\text{catalyst}} RCH\text{CH(S)(L)}$.

<table>
<thead>
<tr>
<th>S</th>
<th>L</th>
<th>R</th>
<th>Configuration</th>
<th>Predicted</th>
<th>Found</th>
<th>% Enantiomeric excess</th>
</tr>
</thead>
<tbody>
<tr>
<td>COO$^-$</td>
<td>Ph</td>
<td>H</td>
<td>R</td>
<td>R</td>
<td></td>
<td>63</td>
</tr>
<tr>
<td>COOme</td>
<td>Ph</td>
<td>H</td>
<td>R</td>
<td>S</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>COO$^-$</td>
<td>NHCOMe</td>
<td>Ph</td>
<td>S</td>
<td>S</td>
<td></td>
<td>70</td>
</tr>
<tr>
<td>COOme</td>
<td>NHCOMe</td>
<td>Ph</td>
<td>S</td>
<td>S</td>
<td></td>
<td>55</td>
</tr>
<tr>
<td>COOH</td>
<td>NHCOMe</td>
<td>H</td>
<td>S</td>
<td>S</td>
<td></td>
<td>72</td>
</tr>
<tr>
<td>COOH</td>
<td>NHCOMe</td>
<td>Ph-p-OH</td>
<td>S</td>
<td>S</td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>NHCOMe</td>
<td>Ph</td>
<td>Me</td>
<td>R</td>
<td>R</td>
<td></td>
<td>78</td>
</tr>
<tr>
<td>Et</td>
<td>Ph</td>
<td>H</td>
<td>S</td>
<td>R</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Ph</td>
<td>OSiMe$_3$</td>
<td>H</td>
<td>S</td>
<td>S</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>OSiMe$_3$</td>
<td>t-Bu</td>
<td>H</td>
<td>R</td>
<td>R</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>COO$^-$</td>
<td>-CH-COMe</td>
<td>H</td>
<td>R</td>
<td>-</td>
<td></td>
<td>88</td>
</tr>
</tbody>
</table>

(i.e., Kagan found the \( n = 3 \) bidentate-phosphine chain length produced a better catalyst than when \( n = 2 \)).

\[
\begin{align*}
\text{PhP(CH}_2\text{CH}_2\text{PPh}_2\text{)}_2 & \quad \text{PhP(CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{)}_2 \\
\text{etp} & \quad \text{ttp} \\
\end{align*}
\]

More importantly, it was stressed that since polydentate ligands are used in these catalysts, no dissociation of phosphines occurs, and a different mechanism must be sought.

**TABLE 12**

**HYDROGENATION OF 1-OCTENE WITH COBALT AND RHODIUM COMPLEXES CONTAINING POLYDENTATE PHOSPHINE LIGANDS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hydrogen uptake</th>
<th>Time (hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HCo(ttp)CO} )</td>
<td>0 ± 10</td>
<td>24</td>
</tr>
<tr>
<td>( \text{HCo(etp)CO} )</td>
<td>0 ± 10</td>
<td>18</td>
</tr>
<tr>
<td>( \text{HCo(tripod)CO} )</td>
<td>0 ± 10</td>
<td>24</td>
</tr>
<tr>
<td>( \text{HCo(ttp)PPhMe}_2 )</td>
<td>0 ± 10</td>
<td>30</td>
</tr>
<tr>
<td>( \text{HCo(ttp)PPh}_3 )</td>
<td>50 ± 5</td>
<td>8.5</td>
</tr>
<tr>
<td>( \text{H}_3\text{Co(ttp)} )</td>
<td>700 ± 50</td>
<td>5</td>
</tr>
<tr>
<td>( \text{H}_3\text{Co(etp)} )</td>
<td>1220 ± 50</td>
<td>3.5</td>
</tr>
<tr>
<td>( \text{HRh(ttp)} )</td>
<td>1010 ± 50</td>
<td>3</td>
</tr>
<tr>
<td>( \text{(BH}_3\text{)Rh(etp)} )</td>
<td>300 ± 40</td>
<td>8</td>
</tr>
</tbody>
</table>


Several researchers, in an attempt to develop enhanced activity in various catalysts, have prepared phosphorus ligands which also
contain other donor atoms. King,\textsuperscript{104} for example, prepared a p-dimethylamino substituted phosphine, \textsuperscript{54}, to study the influence that both the electron donating and the potentially coordinating amino group would have in the corresponding derivative of Wilkinson's complex, \textsuperscript{55}.

\[
\text{(CH}_3\text{)}_2\text{N}P\text{Ph}_2 \quad \text{(CH}_3\text{)}_2\text{N}P\text{Ph}_2 \text{Cl} \quad \text{RhCl}
\]

Roundhill,\textsuperscript{105,106} on the other hand, prepared chelating ligands, (56-58), which would form stable compounds with various low-valent platinum metals and could be considered candidates for hydrogenation catalysts.

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

Although both groups obtained interesting and worthwhile results, complexes with these new ligands did not enhance reactivity as much as was originally expected.
CHAPTER II

EXPERIMENTAL

A. Reagents and Chemicals

Diphenylphosphine \((\text{Ph}_2\text{PH})\), phenylphosphine \((\text{PhPH}_2)\), and 2-cyanoethylphosphine \((\text{N}=\text{CCH}_2\text{CH}_2\text{PH}_2)\) were obtained from either Strem Chemical Company, Danvers, Massachusetts, or Pressure Chemical Company, Pittsburgh, Pennsylvania, and were used as obtained. Phenyldivinylphosphine, \((\text{CH}_2=\text{CHPPh}_2)\), and diphenylvinylphosphine, \((\text{CH}_2=\text{CH})_2\text{PPh}\), from Strem or Pressure Chemical Company were vacuum distilled (<0.1 torr) prior to use. Samples of 2-dimethylphosphinoethylidiphenylphosphine (dmdp) and 2-diphenylphosphinoethylneomenthylphenylphosphine (dppn) were kindly supplied by Professor R. B. King of the University of Georgia. The purity of these reagents was checked by \(^1\text{H}\) and \(^{31}\text{P}\) nmr. All organic starting materials were reagent grade and were distilled under nitrogen prior to use to improve the purity and to remove oxygen. All reagent-grade solvents used were dried and degassed prior to use. The precious metals in these studies were purchased or obtained from either Englehard Industries or Matthey Bishop, Inc. Their solutions were filtered prior to use. GlycoPhase CFG glass for the supported work was purchased from Pierce Chemical Company, Rockford, Illinois.
B. Physical Measurements and Instruments

Solid state infrared spectra were measured on a Perkin Elmer 337 or 457 grating spectrophotometer from 400 to 4000 cm\(^{-1}\) and 250 to 4000 cm\(^{-1}\) respectively as either Nujol mulls or pressed potassium bromide pellets. A polystyrene film was utilized for calibration.

Proton magnetic-resonance spectra were collected on a Varian A60A, EM360, or a Bruker HX90 spectrometer with TMS as an internal standard at ambient temperature (~30°C). The Bruker instrument was run in the Fourier-mode and was standardized by observing the proton resonance occurring from the slight amount of non-deuterated solvent impurity occurring in deuterium solvents.

Fourier mode, proton noise decoupled, phosphorus-31 nuclear magnetic resonance spectra were collected on a Bruker HX90 spectrometer operating at 36.43 MHz. These samples were run using 10 mm nmr tubes. In some cases, deuterated solvents (~20%) provided an internal deuterium lock. These spectra were standardized using an external reference by (a) obtaining the spectrum, (b) inserting a coaxial tube containing 85% phosphoric acid and collecting that spectrum, and (c) adding the two spectra together to obtain a referenced spectrum. In other cases the deuterated solvent and a secondary standard, trimethylphosphite, (\(\delta = 58.09\) Hz relative to \(\text{H}_3\text{PO}_4\)) were contained in a coaxial tube which was placed in the sample tube throughout the collection of data.

A minor disadvantage of this latter method is that spinning sidebands appear if the insert tube is assymetric. The accuracy of the spectrum obtained depends on both the sweep width and data collection.
points but usually lies in the range of \( \pm .5 \) Hz. Changes in solvents and in concentrations can lead to reproducibility errors, but these are minor and are usually kept in the range of \( \pm .2 \) ppm. All spectra are reported with respect to 85% \( \text{H}_3\text{PO}_4 \), and positive chemical shifts are downfield from the standard.

Mass spectra were measured by Mr. C. R. Weisenberger at The Ohio State University on an AEI MS-9 mass spectrometer. Spectra were normally recorded using a 70 e.v. source.

Elemental analyses were performed by either M.H.W. Laboratories, Phoenix, Arizona, or by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Hydrogenation experiments were carried out on an automatic gas-measuring device which was designed and constructed by Mr. Robert Fagan of the Department of Chemistry at The Ohio State University. The standard procedure for sample testing was:

1. Place 0.100 mmol of the sample to be tested in a Schlenk flask containing a magnetic stirring bar and evacuate to remove all traces of air.

2. Under a reverse flow of nitrogen, 50 mmol of olefin was introduced into the flask via a syringe.

3. Enough solvent was then added to bring the total volume of the system to 50 ml.

4. The contents of the flask were then frozen to \(-196^\circ\text{C}\) and the flask was evacuated.
5. Under static vacuum, the solid was allowed to melt and was then refrozen. A dynamic vacuum was then again pulled on the system, and this freeze-thaw cycle was repeated three times.

6. After pulling a dynamic vacuum on the system for the third time, the stopcock was closed, and the flask was connected to the hydrogenation apparatus. The connective tubing was then evacuated and filled with $H_2$ five times to insure purity. After the flask reached room temperature, the stirring bar was activated to cause agitation, the flask was charged with $H_2$, and the experiment proceeded. (Normal charging time was approximately 2 minutes.)

7. The automatic gas-measuring device measured aliquots of hydrogen charged into the system and also plotted aliquots vs. time on a chart recorder.

8. After the experiment was completed, all of the volatile components were removed under static vacuum. These products were analyzed using a Varian aerograph series 1200 gas chromatograph which was equipped with a 12-foot column containing 20% $\beta$, $\beta'$-oxidopropionitrile on chromosorb P, and a flame ionization detector.

The volume of hydrogen gas used during an experiment can be obtained from the equation:

$$V_2 = 1.487 \times 10^{-2} \frac{N(\Delta P)T_2}{P}$$

where: $V_2$ = the volume of $H_2$ added to the flask at $P = P_p$ (cc),

$N$ = number of machine counts,

$\Delta P = \Delta P_{\text{set}} - P_{\text{cycle}}$ (normally machine constant set at 50 for these experiments)
\[ T_2 = \text{temperature of experimental solution (°K)} \]
\[ P_p = \text{manifold pressure of H}_2 \text{ (in torr: normally set at 839 torr).} \]

The number of mmoles of hydrogen used can then be calculated from the volume of hydrogen and the ideal gas law.

All photochemical reactions were carried out in pyrex vessels using a Rayonet RPR-100 photochemical reactor containing 16 x 350 nm bulbs. Prior to photolysis, the Schlenk flasks used for this reaction were evacuated, flushed with nitrogen, and filled under a positive nitrogen pressure to exclude oxygen. All photolysis reactions had nitrogen flowing through the system during the experiment.

C. General Experimental Procedure

Standard techniques for the manipulation of air sensitive compounds were used for the ligands and complexes presented here.109 These included the use of Schlenk vessels, glove bags and making transfers with flushed syringes or stainless steel transfer needles. High-purity nitrogen was used as an inert gas throughout this investigation, and solvents were deoxygenated by either the freeze-thaw method or by bubbling nitrogen through them for 30 minutes.

D. Ligand Preparations

1. Preparation of \( \text{Ph}\stackrel{\text{H}}{\rightarrow}\text{PCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \), PHN

\[ \text{PhPH}_2 + \text{CH}_2=\text{CH}-\text{CH}_2\text{NH}_2 \xrightarrow{h\nu} \text{Ph}\stackrel{\text{H}}{\rightarrow}\text{PCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \]

A pyrex Schlenk flask containing 11.0 g of \( \text{PhPH}_2 \) (0.1 mole), 5.7 g of allylamine (0.1 mole), and 100 mg of AIBN under constant
stirring was irradiated (350 nm) for 12 hours. The crude product was vacuum distilled and the 110°C fraction (1.5 torr) was collected as the product (65% yield).

\[ ^{31}P \text{ nmr (C}_6\text{H}_6) : \delta = -52.4 \text{ ppm (d)} \]
\[ J_{P-H} = 204 \text{ Hz} \]

\[ ^1H \text{ nmr (C}_6\text{D}_6) : \tau = 2.8 \text{ (m, phenyl)}, \tau = 7.5-8.35 \text{ (m, CH}_2\text{),} \]
\[ \tau = 9.05 \text{ (s, NH}_2\text{),} \tau = 4.15 \text{ (t, 1/2 P-H resonance, } J = 1.5 \text{ Hz)}. \]

infrared (neat) : P-H, 2280 cm\(^{-1}\)
NH\(_2\), 3370, 3275 cm\(^{-1}\)

2. Preparation of PhP(CH\(_2\)CH\(_2\)CH\(_2\)NH\(_2\))\(_2\), FN\(_2\)

A pyrex Schlenk flask containing 7.0 g of PhPH\(_2\) and 9.1 g of freshly distilled allylamine (2.5 mole excess) under constant stirring was irradiated (350 nm) for 12 hours. The crude product was then vacuum distilled at 130°C (< .1 torr) to yield 13.5 g of a clear colorless oil (95% yield).

\[ ^{31}P \left[^1H\right] \text{ nmr (C}_6\text{H}_6) : \delta = -24.5 \text{ ppm (s)} \]

3. Preparation of Ph\(_2\)PCH\(_2\)CH\(_2\)Si(OEt)\(_3\)

A Schlenk flask containing 5 g of Ph\(_2\)PH (6.026 mole), 5.1 g of (EtO)\(_3\)SiCH=CH\(_2\), and 100 mg of AIBN under constant stirring was
photolyzed overnight. Vacuum distillation of the resulting solution yielded 7.5 g of \( \text{Ph}_2\text{PCH}_2\text{S}i\text{(OEt)}_3 \) (b.p., 160-165°C, < 1 torr), which corresponds to a 75% yield.

\[
\text{\(^{31}\text{P}\) nmr (C\(_6\text{H}_6\)) : } \delta = -9.9 \text{ ppm (s)}
\]

\[
\text{\(^1\text{H}\) nmr (C\(_6\text{D}_6\)) : } \tau = 2.7 \text{ (m, phenyl)}, \tau = 7.86 \text{ (m, CH}_2\text{)}, \tau = 6.23 \text{ (q, CH}_2\text{ from -OEt)}, \tau = 8.8 \text{ (t, from -OEt), J = 7 Hz (ethyl group)}
\]

4. Preparation of \( \text{N}_2\text{CCH}_2\text{CH}_2\text{P(CH}_2\text{CH}_2\text{PPh}_2\text{)}_2 \), etp-CN

\[
\text{N} = \text{CCH}_2\text{CH}_2\text{P(Ch}_2\text{CH}_2\text{PPh}_2\text{)}_2 + 2 \text{CH}_2\text{=CH}_2\text{PPh}_2 \xrightarrow{\text{hv}} \text{etp-CN}
\]

A pyrex Schlenk flask containing 6 g (0.069 mole) of \( \text{H}_2\text{PCH}_2\text{CH}_2\text{C}=\text{N} \), 30. g of \( \text{Ph}_2\text{PCH}=\text{CH}_2 \) (0.14 mole), and 100 mg of AIBN was irradiated (350 nm) with stirring for 18.5 hours. More diphenylvinylphosphine (1.5 ml) was added and the flask irradiated for an additional 4-hour period. The product was then heated to 90°C in vacuo to remove any remaining volatile materials. Yield : 99% (based on 2-cyanoethylphosphine).

\[
\text{\(^{31}\text{P}\) nmr (C\(_6\text{H}_6\)) : } \delta = -21.0 \text{ ppm (t, PhP)}
\]

\[
\delta = -13.9 \text{ ppm (d, -PPh}_2\text{)}
\]

\[
J_{\text{P-P}} = 24.9 \text{ Hz.}
\]

\[
\text{\(^1\text{H}\) nmr (C\(_6\text{H}_6\)) : } \tau = 2.8 \text{ (m, phenyl), } \tau = 8.25 \text{ (m, CH}_2\text{)}
\]

infrared (neat) : \(-\text{C}=\text{N}, 2260 \text{ cm}^{-1}\)

Mass : the parent ion \( M^+ \) occurs at m/e = 511
5. Preparation of \( \text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{P(CH}_2\text{CH}_2\text{PPh}_2)\text{)_2, PP}_2\text{N} \)

\[ \text{N=CH}_2\text{CH}_2\text{P(CH}_2\text{CH}_2\text{PPh}_2)\text{)_2} + \text{LiAlH}_4 \rightarrow \text{PP}_2\text{N} \]

A solution containing 3.2 g of etp-CN (6.2 mmole) in 10 ml of benzene was added dropwise into a cooled, (0°C) stirred slurry containing 0.80 g of LiAlH\(_4\) and 40 ml of diethylether. After the foaming subsided, the flask was allowed to warm to room temperature, and the mixture was stirred for 24 hours. The solution was then carefully hydrolyzed with 0.8 ml of \( \text{H}_2\text{O} \), 0.8 ml of 10% NaOH, and finally with 0.24 ml of ml of \( \text{H}_2\text{O} \). The slurry was filtered through celite filter aid, and the remaining solid was rinsed with diethylether (3 x 30 ml). The solvents were removed from the resulting filtrate at 80°C in vacuo.

Yield: 91% (based on etp CN).

\[ ^{31}\text{P} \{^{1}\text{H}\} \text{ nmr (C}_6\text{H}_6\} : \delta = -22.6 \text{ ppm (t, PhP) } \]
\[ \delta = -13.5 \text{ ppm (d, Ph}_2\text{P-)} \]
\[ J_{\text{P-P}} = 25.3 \text{ Hz} \]

\[ ^{1}\text{H} \text{ nmr (C}_6\text{D}_6\} : \tau = 2.8 \text{ (m, phenyl) } \]
\[ \tau = 8.25 \text{ (m, CH}_2\text{) } \]
\[ \tau = 9.5 \text{ (br, NH}_2\text{) } \]

infrared (neat): 3350, 1585 cm\(^{-1}\) (NH\(_2\))

Mass: the parent ion \( M^+ \) occurs at m/e = 515

6. The Preparation of \( \text{PhP(CH}_2\text{CH}_2\text{S})\text{H}_2\text{N} \), \( \text{PS}_2\text{N}_2 \)

\[ \text{PhP(CH=CH}_2\text{)}\text{}/_2 + 2 \text{SHNH}_2 \rightarrow \text{PS}_2\text{N}_2 \]
A 100 ml Schlenk flask containing 3.0 of phenyldivinylphosphine (0.0185 mole), 4.8 g of phenylthiol (slightly > 2-fold molar excess) and 0.10 g of AIBN under constant stirring was heated to 110°C for 18 hours with 0.01 g of additional AIBN being added after 2 and 4-hour intervals. The resulting solution was then heated to 100°C for 6 hours in vacuo to remove any volatile components. The remaining colorless oil corresponded to the ligand (6.9 g, 90% yield).

\[ ^{31}P\{^1H\} \text{ nmr } (C_6H_6) : \delta -27.3 \text{ ppm} \]
\[ ^1H \text{ nmr } (C_6D_6) : \tau = 2.9 \text{ (m, PhP)}, \tau = 3.6 \text{ (m, } \bigcirc \text{)} \]
\[ \tau = 6.15 \text{ (br, } \text{NH}_2\text{)}, \tau = 8.25 \text{ (m, CH}_2\text{)} \]
\[ \tau = 7.49 \text{ (m, CH}_2\text{)} \]
\[ \text{infrared (neat): } 3450 \text{ cm}^{-1}, 3350 \text{ cm}^{-1}, 1650 \text{ cm}^{-1} (\text{NH}_2) \]

7. Preparation of \((C_6H_5)_2PCH_2CH_2CH_2Cl\)

\[ (C_6H_5)_2PH + n-BuLi \rightarrow (C_6H_5)_2PLi + n-BuH \]

\[ (C_6H_5)_2PLi + \text{excess } ClCH_2CH_2CH_2Cl \rightarrow (C_6H_5)_2PCH_2CH_2CH_2Cl + LiCl \]

A solution of 70.2 ml of \(n\)-BuLi (0.1613 mole in hexane) was added slowly to a solution containing 30 g of diphenylphosphate (0.1613 mole) dissolved in 800 ml of THF. After stirring this solution for 0.5 hour, it was transferred via a stainless steel needle into a pressure-equalizing dropping funnel. This solution was then added dropwise (over a period of 6 hours) into a cooled (0°C) 2-liter, three-neck flask containing 200 ml of 1,3-dichloropropane (10-fold excess) dissolved in 300 ml of diethylether. The red color of the
phosphide solution dissipated after each drop was added. After stirring this cloudy solution overnight, 50 ml of water was added, the reaction was stirred for one-half hour, and all solvents were removed in vacuo (< 0.1 torr). Water (150 ml) and diethylether (300 ml) were added to the flask and the product was extracted from the aqueous layer with diethylether (3 x 225 ml). All the extracts were transferred to a Schlenk flask, dried over Na₂SO₄, filtered, and the ether was removed in vacuo. The pale yellow product was finally heated to 65°C under vacuum for 1 hour to remove any remaining volatile material. Yield 99% based on Ph₂PH.

\[ ^{31}P \{^1H\} nmr (CHCl₃) : \delta = -17.9 \text{ ppm} \]

\[ ^1H nmr (CDCl₃) : \tau = 2.7 \text{ (m, phenyl), } \tau = 6.48 \text{ (t, R-CH₂Cl), } \tau = 7.9 \text{ (m, CH₂) } \]

These spectral data correspond exactly with the results of K. D. Tau, who used another route for this preparation.

8. Preparation of (C₆H₅)₂PCH₂CH₂CH₂P(H)C₆H₅, PPH

\[ C₆H₅PH₂ + Na \rightarrow NaP(H)C₆H₅ + 1/2 H₂ \]

\[ NaP(H)C₆H₅ + CIC₂H₂CH₂P(C₆H₅)₂ \rightarrow (C₆H₅)₂P(H)CH₂CH₂CH₂P(C₆H₅)₂ + NaCl \]

The procedure by K. D. Tau was followed to prepare this compound. Yield: quantitative.

\[ ^{31}P nmr (C₆H₆) : \delta = -54.5 \text{ ppm (d, } -P(C₆H₅) \text{)} \]

\[ \delta = -18.0 \text{ ppm } (-P(C₆H₅)₂) \]

\[ J_{P-P} = < 1 \text{ hz} \]

\[ J_{P-H} = 203 \text{ hz} \]
9. Preparation of \( \text{CH}_2[\text{CH}_2\text{P(Ph)}\text{CH}_2\text{CH}_2\text{NH}_2]^2 \), \( \text{P}_2\text{N}_2 \)

\[
\begin{align*}
\text{Ph} & \xrightarrow{\text{PCH}_2\text{CH}_2\text{NH}_2 + \text{n-BuLi}} \text{Ph} \& \text{Li} \xrightarrow{\text{PCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 + \text{n-BuH}} \\
\text{Ph} & \xrightarrow{\text{PCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 + \text{BrCH}_2\text{CH}_2\text{Br}} \xrightarrow{\text{P}_2\text{N}_2}
\end{align*}
\]

A solution containing 6.25 g of \( \text{PhCH}_2\text{CH}_2\text{NH}_2 \) (0.0374 mole) and 70 ml of THF was treated dropwise with 23.4 ml (1.6 mole) of \( \text{n-BuLi} \) (0.0374 mole) while stirring; the solution turned yellow. The color lightened after 3.78 g of \( \text{BrCH}_2\text{CH}_2\text{Br} \) was added dropwise, and the resultant solution was refluxed for 2 hours. Hydrolysis with 100 ml of \( \text{H}_2\text{O} \) and extraction with diethylether (150 ml) yielded a colorless solution. Removal of solvents in vacuo gave 6.5 g (92%) of the expected product, which is a colorless oil.

\[
\begin{align*}
\text{H} \text{nmr (C}_6\text{H}_6\text{)}: & \tau = 2.9 \text{ (m, phenyl), } \tau = 8.3 \text{ (m, CH}_2\text{),} \\
& \tau = 6.0 \text{ (dt, P-H, } J_{\text{P-H}} = 203 \text{ hz)} \\
\text{infrared (neat): } & 2290 \text{ cm}^{-1} \text{ P-H}
\end{align*}
\]

10. Preparation of \( \text{CH}_2(\text{CHSCH}_2\text{CH}_2\text{P}_2\text{S}_2\text{Ph}) \), \( \text{S}_2\text{P}_2 \)

\[
\text{PhPh}_2 + \text{n-BuLi} \xrightarrow{} \text{PhP(H)Li}
\]
A 1-l Grignard flask was equipped with a stirring motor, a pressure-equalizing dropping funnel, and gas inlets. It was charged with 12.43 g of PhPH₂ (0.113 mole) and 250 ml of high-boiling pet. ether. Dropwise addition of 100 ml of n-BuLi (2.4 M) to the stirred solution resulted in the evolution of heat and the formation of the dark yellow dilithium phenylphosphide. After refluxing this slurry for an hour, the solid was filtered and washed with 100 ml of pet. ether. The color changed to the characteristic canary yellow of lithium phenylphosphide after 300 ml of ethylether and 12.78 g of PhPH₂ were added to the solid. After stirring the mixture overnight, a solution containing 16.76 g of trimethylenesulfide in 100 ml diethylether was added, and the mixture was refluxed for 8 hours. The resulting light yellow solution was allowed to cool to room temperature, and a solution of 22.3 g of BrCH₂CH₂CH₂Br in 75 ml of diethylether was added dropwise over a 2-hour period. The color changed from yellow to white as the solution was refluxed for several hours. The resulting solution was treated with 100 ml of a 10% NH₄Cl-aqueous solution. The organic layer was removed and the aqueous layer was extracted with diethylether (3 x 50 ml). The organic layers were combined and dried over anhydrous Na₂SO₄. The solvent was removed at reduced pressure and the remaining clear solution was heated (150°C) in vacuo for 8 hours to remove any remaining volatile material. The yield of colorless oil was 39.5 g (86% based on PhPH₂).
$^{31}$P NMR ($C_6H_6$) : $\delta$ = -53.6 ppm (d, $J_{P-H} = 202$ Hz)

$^1$H NMR (CDCl$_3$) : $\tau$ = 2.7 (m, phenyl), $\tau$ = 7.5 (m, CH$_2$),
$\tau$ = 8.2 (m, CH$_2$), $\tau$ = 4.18 (t, 1/2P-H resonance, $^3J_{H-H} = 6$ Hz)

Infrared (neat) : 2290 cm$^{-1}$ (P-H)

11. Preparation of $Ph_2PCH_2CH_2P(Ph)CH_2CH_2N(CH_3)_2$, PPN

$Ph_2PCH_2CH_2P + CH_2=CH-CH_2N(CH_3)_2 \xrightarrow{hv} "PPN"$

A photolysis was carried out in a pyrex vessel containing a benzene solution of 11.85 g of 3-diphenylphosphinopropylphosphine (PPH) (0.035 mole) and 12 ml (excess) of N,N-dimethylallylamine. After 36 hours at 350 nm, the benzene was removed in vacuo and the remaining oil was then heated to 60°C for 3 hours. Yield: 90% (12.95 g) based on "PPH".

$^3$P $^1$H NMR ($C_6H_6$) : $\delta$ = -27.2 ppm (PhP )
$\delta$ = -18.2 ppm (Ph$_2$P-)
$J_{P-P} < 1$ Hz

$^1$H NMR (CDCl$_3$) : $\tau$ = 2.8 (m, phenyl)
$\tau$ = 7.88 (CH$_3$)
$\tau$ = 8.38 (m, CH$_2$)

12. Preparation of Bis-1,3(P,P'-Diphenylisopropylphosphinato)propane, $CH_2(CH_2P(O)(Oipr)Ph)_2$

$$2 \text{PhP(Oipr)}_2 + \text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br} \rightarrow \text{PhPCH}_2\text{CH}_2\text{CH}_2\text{PPh} + \text{Br-CH}_3$$
A three-neck flask equipped with a stirring bar, nitrogen inlets and a Claisen head containing a condenser was charged with 104.0 g (0.460 moles) of PhP(Oipr)$_2$ and 23.99 ml (46.47, 0.230 moles) BrCH$_2$CH$_2$CH$_2$Br. This mixture was heated to 145°C, where isopropylbromide began distilling off. After the distillation ceased, the viscous liquid was heated for an additional 1/2 hour, after which it was cooled and then stirred in vacuo overnight. The light yellow oil was used without further purification. Yield: 95.1 g, quantitative.

$^{31}$P ($^1$H) nmr (C$_6$H$_6$) : $\delta = 41.82$ ppm

$^1$H nmr (C$_6$H$_6$) : $\tau = 2.5$ (phenyl), $\tau = 5.47$ (m, CH) $\tau = 8.1$ (CH$_2$), $\tau = 8.85$ (dd, CH$_3$), $J_{H-H} = 6$ Hz

Infrared (neat) : 978 cm$^{-1}$ (P-O-C) 1222 cm$^{-1}$ (P=O)

13. Preparation of Bis-1,3(phenylphosphino)propane, pHpH

\[ \text{PhPCH}_2\text{CH}_2\text{CH}_2\text{PPh} + \text{LiAlH}_4 \rightarrow \text{PhPCH}_2\text{CH}_2\text{CH}_2\text{PPh} \]

A 500-ml, 3-neck flask which was equipped with nitrogen inlets and a dropping funnel, had 10.1 g of LiAlH$_4$ and 80 ml of Et$_2$O added. After stirring this slurry and cooling it to 0°C, the diphosphinate dissolved in 50 ml of Et$_2$O was added dropwise over a five-hour period. Foaming occurred, and a green slurry resulted after stirring overnight. An equal volume of dioxane was added, and the slurry was refluxed at 60°C for 6 hours. After cooling, 5 ml of THF was added, and the slurry
was stirred for an additional 12 hours. After cooling to 0°C, 10.1 g of H₂O was added dropwise followed by 10 ml of 15% NaOH and 30 ml of H₂O. The granular solid was filtered off using a Schlenk filter containing celite and was washed with Et₂O (150 ml). The solvent was removed in vacuo, and an oil remained. This oil was vacuum distilled and yielded two clear liquid fractions 1) 110°C → 130°C and 2) 130°C → 150°C. Fraction 2 was shown to be the desired product (15.3 g, 60% yield), and fraction 1 was a mixture of the product and PhP-PPh (see ligand preparation 14).

\(^1\)H nmr (C₆D₆) : \( \tau = 2.7 \) (phenyl), \( \tau = 8.2 \) \( (\text{CH}_2) \), \( \tau = 4.12 \) \( (\text{dm, P-H}) \)

Mass : parent ion observed at m/e = 260

---

14. Preparation of PhPP(Ph)CH₂CH₂CH₂

\[
\begin{align*}
\text{PhPCH₂CH₂CH₂PPh} + \text{PhSiH₃} & \rightarrow \text{PhP-PPh} \\
\text{Oipr} & \quad \text{Oipr}
\end{align*}
\]

A Schlenk flask was charged with 15 g of the diphosphinate and 19 ml of phenyl silane. This mixture was stirred for 2 hours and slowly heated to 110°C during the next 3 hours. The temperature was then raised to 180°C for 1.5 hours, cooled to 100°C, and finally vacuum distilled (0.3-0.4 torr) to yield 5.4 ml of product which came over at 168°C - 172°C. Yield: 57%.

\(^31\)P nmr (C₆H₆) : \( \delta = -8.4 \) ppm

\(^1\)H nmr (C₆D₆) : \( \tau = 8.2 \) \( (\text{m, CH}_2) \), \( \tau = 2.7 \) \( (\text{m, phenyl}) \)
Mass: parent ion at m/e 258 is observed as the most abundant ion.

Infrared (neat): shows the absence of a P-H stretch in the 2200 cm\(^{-1}\) region.

15. Preparation of PhAsCl\(_2\)

\[
\begin{align*}
\text{PhAs} & \xleftarrow{\text{OH}} \quad \text{OH} \\
+ \text{SO}_2 & \xrightarrow{\text{HCl}} \quad \text{PhAsCl}_2
\end{align*}
\]

A one-liter flask containing 20.2 g (0.1 mole) of benzenearsonic acid and 150 ml of H\(_2\)O under constant stirring had HCl (250 ml, conc.), H\(_2\)O (250 ml) and KI (1 g in 10 ml H\(_2\)O) added in sequence. After cooling the solution to 0°C, SO\(_2\) was slowly bubbled through the solution for 1.5 hours. The solution was allowed to warm to room temperature and, after sitting overnight, a yellow oil separated out. The oil was separated from the rest of the solution via separatory funnel and placed in a desiccator over NaOH. The oil was vacuum distilled and 15 ml (74–76°C at < 1 torr) of product was collected (67% yield).

Infrared: matches that of a genuine sample purchased from Columbia Organic Chemicals, Columbia, South Carolina.

16. Preparation of \(\text{CH}_2\left(\text{CH}_2\text{As}\right)\left(\text{H}_3\text{CS}\right)\_2\)

The published procedure of Dutta, Meek, and Busch was followed.\(^{111}\)
17. Preparation of \( \text{Ph}_2\text{P(CH}_2\text{)}_3\text{P(Ph)(CH}_2\text{)}_3\text{NH}_2, \text{PPNH}_2 \)

\[
\text{Ph}_2\text{P(CH}_2\text{)}_3\text{P(Ph)H} + \text{excess } \text{H}_2\text{C=CH}_2\text{NH}_2 \xrightarrow{\text{hv}} \text{PPH}_2
\]

The same procedure used for PPN \( \#11 \) was followed except that allylamine was substituted for \( \text{N,N dimethylallylamine} \). Yield: 99% based on \( \text{PPH} \).

\( ^{31}\text{P} \left( ^1\text{H} \right) \text{nmr (C}_6\text{D}_6 \right): \delta = -18.2 \text{ ppm (} \text{Ph}_2\text{P} \right)

\[
\delta = -27.2 \text{ ppm (} \text{PhP} \right)
\]

\( ^1\text{H} \text{nmr (C}_6\text{D}_6 \right): \tau = 2.8 \text{ (phenyl), } \tau = 8.35 \text{ (m, } \text{CH}_2 \right),

\[
\tau = 9.35 \text{ (} \text{NH}_2 \right)
\]

\( \text{infrared (neat): } \text{NH}_2, -350 \text{ cm}^{-1} \text{ (br) } \)

18. Preparation of \( \text{Ph}_2\text{P(CH}_2\text{)}_3\text{P(Ph)(CH}_2\text{)}_2\text{PPH}_2, \text{eptp} \)

\[
\text{Ph}_2\text{P(CH}_2\text{)}_3\text{P(Ph)H} + \text{H}_2\text{C=CH}_2\text{PPH}_2 \xrightarrow{\text{hv}} \text{eptp}
\]

The procedure of D. L. Dubois \( \#112 \) was followed. Yield: 99% based on \( \text{PPH} \).

Spectroscopic characterization is the same as that reported by Dubois.

19. Attempted Preparation of \( \text{PhP(CH}_2\text{CH}_2\text{CH}_2\text{PPH}_2}_2 \)

via the Free Radical Route

\[
2 \text{Ph}_2\text{PCH}_2\text{CH}=\text{CH}_2 + \text{PhPH}_2 \xrightarrow{\text{ttp}}
\]

Diphenylallylphosphine (2.1 g, 9.29 mmol) and diphenylphosphine were added to a 50 ml Schlenk flask under nitrogen. AIBN (0.0152 g) was added and the flask was placed in a photochemical reactor (350 nm) for 14 hours. The remaining thick oil was probably polymeric in nature.
$^{31}\text{P nmr}$: several peaks were present in each of the expected chemical shift areas; attempts at distillation or separation were unsuccessful.

E. Metal Complexes

1. Preparation of Rh(etp-CN)Cl

$$\{\text{Rh(COD)Cl}\}_2 + 2 \text{etp-CN} \xrightarrow{C_6H_6} 2 \text{Rh(etp-CN)Cl}$$

A Schlenk flask containing 0.2987 g (1.212 mmole Rh) of $\{\text{Rh(COD)Cl}\}_2$ and 15 ml benzene was stirred with a magnetic stirring bar. A benzene solution (3 ml) containing 1.212 mmoles of ligand was added dropwise, and the solution turned from an orange to a red color. After stirring this red solution for three hours, the volume of the solution was reduced to 1-2 ml, and diethylether was added to precipitate the desired product. The yellow solid was collected on a filter frit, washed with diethylether, and dried in vacuo. Yield: 0.638 g.

Analytical Data: calculated for $C_{32}H_{32}NCIP_{3}Rh$

C, 57.29; H, 4.97; P, 14.30; Cl, 5.45

Found: C, 56.95; H, 4.75; P, 14.57; Cl, 5.18

2. Preparation of Co(etp-CN)Cl$_2$

$$\text{Co(H}_2\text{O)}_6\text{Cl}_2 + \text{etp-CN} \xrightarrow{\text{EtOH}} \text{Co(etp-CN)}\text{Cl}_2$$

A Schlenk flask containing 0.9738 g of $\text{Co(H}_2\text{O)}_6\text{Cl}_2$ (4.093 mmole), 80 ml of ethanol, and 10 ml of stock ligand solution (4.093 mmole in benzene) was stirred and refluxed for two hours. During this
time a red solid precipitated. After cooling, the solid was collected on a frit, washed with ethanol (3 x 10 ml), and dried in vacuo. Yield: 2.05 g.

Analytical data: calculated for C₃₁H₃₂NCl₂P₃Co
C, 60.99; H, 5.29; N, 2.30; Cl, 11.60
Found: C, 60.57; H, 5.41; N, 2.08; Cl, 11.42

3. Preparation of Co(etp-CN)H(CO)

Co(etp-CN)Cl₂ + NaBH₄ $\xrightarrow{CO}$ Co(etp-CN)H(CO)

The procedure used for this synthesis was exactly the same as D. Dubois¹¹² used in preparing Co(etp)H(CO), except that etp-CN was used in place of etp. Yield: 0.75 g based on 1.33 g of Co(etp-CN)Cl₂ (60%).

4. Preparation of Supported etp-NH₂

Glycophase control-pore glass (600 mg) was placed in a 100 ml Schlenk flask, and the flask was evacuated to remove oxygen after being placed on a kugelrohr motor which had been turned to the vertical position. Sodium periodate (0.1284 g, 0.6 mmole) dissolved in 10 ml H₂O was added, and the motor was activated to give a constant rotating motion. After 5 minutes, a vacuum was pulled on the system in an attempt to pull trapped gases from the solid glass. The slurry was then
Figure 4. Apparatus Used for Supported Catalyst Hydrogenation Experiments rotated for an additional 1.5 hours. The glass was washed with 10 x 20 ml of H₂O, 5 x 20 ml of ethanol (with rotating) and, after adding 20 ml of ethanol, 0.6 mmole of etp-NH₂ in 5 ml of benzene was added. The suspension was rotated and at T=20 minutes and 40 minutes, ~10 mg of NaBH₄ was added. Rotation continued for two hours after the last addition of sodium borohydride. Then the glass was washed with water (10 x 20 ml) and ethanol (10 x 20 ml). After adding 10 ml of ethanol, CoCl₂·6H₂O (0.1428 g, 0.6 mmole) in 10 ml ethanol was added, and the solution was rotated for several hours. The glass was finally washed with ethanol (8 x 20 ml) to yield a greenish-blue product which was ready for further use.

5. Preparation of Rh(PPN)Cl

\[(\text{Rh(COD)Cl})_2 + 2 \text{PPN} \xrightarrow{\text{THF}} 2 \text{Rh(PPN)Cl}\]

A benzene solution (3 ml, 1.1595 mmole) of PPN was added dropwise into a solution of \{Rh(COD)Cl₂\} (0.2859 g, 1.1595 mmole) dissolved in 80 ml THF. After stirring for three hours, the volume was reduced to 3 ml, and 50 ml of diethylether was added. The resulting solid was filtered, washed with ether, and dried \textit{in vacuo}. Yield: 0.52 g.

Analytical Data: calculated for $C_{26}H_{33}NClP_2Rh$. 

C, 55.71: H, 5.95; P, 11.06; Cl, 6.33

Found: C, 55.93; H, 5.88; P, 11.21; Cl, 6.33

6. Preparation of Ir(PPN)Cl(COD)

\[
\text{(Ir(COD)Cl)}_2 + 2 \text{PPN} \rightarrow 2 \text{Ir(PPN)Cl(COD)}
\]

A Schlenk flask containing 0.2064 g (0.615 mmole) of \{Ir(COD)Cl\}_2 and 30 ml of benzene was stirred while 2 ml of ligand solution (0.615 mmole in benzene) was added dropwise. After the color of the solution changed from red to yellow, the solution was stirred for two hours, and the volume was reduced to 1.5 ml. Diethylether was added, the solid was collected on a frit, washed with ether, and dried in vacuo. Yield: 0.31 g.

Analytical Data: calculated for \(C_{34}H_{45}IrN_2P_2\)

C, 53.86; H, 5.99; Cl, 4.67; P, 8.17

Found: C, 54.39; H, 6.05; Cl, 4.93; P, 8.67

7. Preparation of Ir(PPN)Cl • EtOH

\[
\text{(Ir(COD)Cl)}_2 + 2 \text{PPN} \rightarrow 2 \text{Ir(PPN)Cl • EtOH}
\]

Ethanol (30 ml) and 0.3097 g (0.9228 mmole) of \{Ir(COD)Cl\}_2 were added respectively to a 100-ml Schlenk flask. Stock ligand solution (3 ml, 0.9228 mmole, in benzene) was added dropwise, and the solution was stirred for several hours. The volume was reduced to 2 ml, 30 ml of Et₂O was added, and the solution was placed in the refrigerator. After three days, a solid precipitate was then collected on a frit, washed with diethylether, and dried in vacuo. Yield: 0.50 g.
Analytical data: calculated for C_{28}H_{39}NCIO_{2}Ir
C, 48.37; H, 5.67; N, 2.02
Found: C, 48.56; H, 5.78; N, 1.73

8. Preparation of {Ni(PPN)Cl}BPh_{4}

\[
\text{Ni(H}_2\text{O)\_6\_Cl}_2 + \text{PPN} \xrightarrow{\text{NaBPh}_4} \{\text{Ni(PPN)Cl}\}_\text{BPh}_4 + \text{NaCl}
\]

Under nitrogen, 0.2194 g (0.9228 mmole) of NiCl_{2}\cdot6H_{2}O, and 20 ml ethanol were stirred, and 3 ml (0.9228 mmole) of PPN in benzene was added dropwise. Upon adding NaBPh_{4} (5 ml ethanol solution containing 0.3158 g), a peach color precipitate separated from solution. The solid was filtered, washed with water, ethanol, and diethylether, then dried in vacuo. Yield: 0.62 g.

Analytical data: calculated for C_{50}H_{53}NBCIQNiP_{2}
C, 71.92; H, 6.41; P, 7.42; Cl, 4.25
Found: C, 71.87; H, 6.14; P, 7.69; Cl, 4.37

9. Preparation of {Pd(PPN)Cl}BPh_{4}

\[
\text{Na}_2\text{PdCl}_4 + \text{PPN} \xrightarrow{\text{NaBPh}_4} \{\text{Pd(PPD)Cl}\}_\text{BPh}_4 + 3 \text{NaCl}
\]

Addition of 0.2715 g (0.9228 mmole) of Na_{2}PdCl_{4} to 25 ml of ethanol resulted in a red solution. When PPN (3 ml stock solution, 0.9228 mmole) was added dropwise to this solution, a yellow precipitate formed, which then redissolved to yield an orange solution. Addition of NaBPh_{4} (0.3158 g, 0.9228 mmole, in 5 ml ethanol) precipitated a yellow solid which was collected on a frit, washed with water, ethanol, diethylether, and then dried in vacuo. Yield: 0.70 g.
Analytical data: calculated for $C_{50}H_{53}NP_2Pd$

$C$, 68.03; $H$, 6.06; $P$, 7.02; $Cl$, 4.02

Found: $C$, 67.83; $H$, 5.79; $P$, 7.35; $Cl$, 4.45

10. Preparation of $\text{Pt(PPN)}Cl_2$

$$\text{Pt(COD)Cl}_2 + \text{PPN} \xrightarrow{C_6H_6} \text{Pt(PPN)}Cl_2$$

One mole (0.3740 g) of $\text{Pt(COD)Cl}$ was dissolved in 30 ml of benzene, and 3.25 ml of ligand solution (1.00 mmole in benzene) was added dropwise to yield a light yellow solution. After refluxing this solution for two hours, an oil separated which was then separated from solution by decantation. The oil was dissolved in $\text{CH}_2\text{Cl}_2$, and a white solid precipitated upon addition of diethylether. The white solid was collected on a frit, washed with diethylether, and dried in vacuo.

Yield: 0.57 g.

11. Preparation of $\{\text{Pt(PPN)}Cl\}_\text{AsF}_6$

$$\text{Pt(PPN)}\text{Cl}_2 + \text{NaAsF}_6 \xrightarrow{\text{EtOH}} \{\text{Pt(PPN)}\text{Cl}\}_\text{AsF}_6$$

A beaker containing 0.5000 g (0.728 mmole) of $\text{Pt(PPN)}\text{Cl}_2$ and 50 ml of ethanol had $\text{NaAsF}_6$ (0.1543 g, 0.728 mmole) dissolved in 5 ml of ethanol added slowly. A white precipitate immediately formed. After filtering this solid on a frit, it was washed with ethanol, diethylether, and was air dried. Yield (first crop): 0.45 g.

Analytical data: calculated for $C_{26}H_{33}N\text{AsClF}_6P_2\text{Pt}$

$C$, 37.13; $H$, 3.96; $N$, 1.67; $Cl$, 4.22

Found: $C$, 36.85; $H$, 3.73; $N$, 1.50; $Cl$, 4.50
12. In situ Preparation of Rh(PPN)(PPh₃)NO

\[
\text{Rh(PPh₃)₃NO} + \text{PPN} \rightarrow \text{Rh(PPN)(PPh₃)NO} + 2 \text{PPh₃}
\]

Equimolar amounts of Rh(PPh₃)₃NO (0.3634 g) and ligand (1 ml of stock solution, 0.3955 mmole) were added to a Schlenk flask containing 5 ml of benzene. This solution was stirred for one hour with heating. A $^{31}$P nmr spectrum was run on the in situ sample.

13. Attempted Preparation of Ir(PPN)(CO)Cl

\[
\text{Ir(PPN)Cl} + \text{CO} \xrightarrow{X} \text{Ir(PPN)(CO)Cl}
\]

After preparing Ir(PPN)Cl (see #6 above) in benzene, CO was bubbled through the solution for 15 minutes, followed by nitrogen for 10 minutes. The workup for this reaction was the same as for Ir(PPN)Cl (#6 above). Yield: 0.25 g (based on 0.2064 g of \{Ir(COD)Cl\}_2).

14. Attempted Preparation of Co(PPN)Cl₂

\[
\text{Co(H₂O)₆Cl₂} + \text{PPN} \xrightarrow{\text{EtOH}} \text{Co(PPN)Cl₂}
\]

A Schlenk flask was charged with 0.2759 g Co(H₂O)₆Cl₂ (1.1595 mmole), 80 ml of ethanol, and 3 ml of stock PPN solution (1.1595 mmole in benzene). After stirring the solution for one hour, the solution volume was reduced to 10 ml, and 80 ml of diethylether was added. The green solid was filtered, washed with ethanol and dried in vacuo. Yield: 0.35 g.

Analytical data: calculated for C_{26}H_{35}NCl₂CoP₂

C, 56.63; H, 6.04; P, 11.23; Cl, 12.87
15. Preparation of Pt(eptp)(CH$_3$)$_2$

\[
\begin{array}{c}
\text{Pt(COD)(CH$_3$)$_2$ + eptp} \\
\xrightarrow{\text{CH$_3$}} \\
\text{Pt(eptp)(CH$_3$)$_2$}
\end{array}
\]

A solution of Pt(COD)(CH$_3$)$_2$ (0.1667 g, 0.5 mmole), 0.81 ml of eptp (> 0.5 mmole) and 10 ml toluene was refluxed for 20 minutes. The volume was reduced to 1.5 ml and 5 ml of toluene-d$_8$ was added. This solution was used directly for $^{31}$P nmr studies. In order to obtain a pure sample, the solution had small amounts of Pt(COD)(CH$_3$)$_2$ added until excess $^{31}$P ligand resonances disappeared. The solvents were then removed _in vacuo_ and the remaining oil extracted with ether (~500 ml). After reducing the volume of ether to 80 ml, 20 ml of ethanol was added, and the volume of the solution was reduced to ~15 ml, and a white solid precipitated which was used directly for phosphorus-31 nmr studies.

16. Preparation of Pt(Ph$_2$PCH$_2$CH$_2$P(Ph)neoC$_{10}$$^\text{H}_{19}$)(CH$_3$)$_2$

\[
\begin{array}{c}
\text{Pt(COD)(CH$_3$)$_2$ + Ph$_2$PCH$_2$CH$_2$P(Ph)neoC$_{10}$$^\text{H}_{19}$} \\
\xrightarrow{\text{C$_6$H$_6$}} \\
\text{Pt(Ph$_2$PCH$_2$CH$_2$P(Ph)neoC$_{10}$$^\text{H}_{19}$(CH$_3$)$_2$}
\end{array}
\]

After 0.6426 g of ligand was added to 0.4650 g (1.395 mmole) of Pt(COD)(CH$_3$)$_2$ in 25 ml benzene, the solution was refluxed for three hours. After cooling, the volume was reduced to 5 ml, and 20 ml of high-boiling petroleum ether was added, and a white solid precipitated.
This solid was then collected on a frit, washed with pet. ether, and air dried. Yield (first crop): 0.5167 g.

Analytical data: calculated for C\textsubscript{32}H\textsubscript{34}P\textsubscript{2}Pt
\[ C, \text{56.04}\; \text{H, 6.48}\; \text{P, 9.03} \]

Found: C, 55.95; H, 6.53; P, 9.25

17. Preparation of Pt((CH\textsubscript{3})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2})(CH\textsubscript{3})\textsubscript{2}

\[
\text{Pt(COD)(CH}_3\text{)}\textsubscript{2} + \text{(CH}_3\text{)}\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2} \xrightarrow{\text{C}_6\text{H}_6} \text{Pt}((\text{Ph}_2PCH\textsubscript{2}CH\textsubscript{2}P(CH}_3\text{)}\textsubscript{2})(\text{CH}_3\textsubscript{2})
\]

A Schlenk flask containing 0.4012 g Pt(COD)(CH\textsubscript{3})\textsubscript{2} had 25 ml of benzene and 0.33 ml of pure ligand added. The solution was stirred and refluxed for three hours. After reducing the volume to 5 ml and adding 20 ml of petroleum ether, the flask was cooled. The white solid that formed was filtered, washed with pet. ether, and dried in vacuo. Yield: 0.60 g.

18. Preparation of Pd(As\textsubscript{2}S\textsubscript{2})(PF\textsubscript{6})\textsubscript{2}

\[
\text{Pd(CH}_3\text{CN)}\textsubscript{4}(PF\textsubscript{6})\textsubscript{2} + \text{SCH}_3\text{H}_3\text{CS}(\text{As(CH}_2\text{)}_3\text{As}) \xrightarrow{\text{CH}_3\text{CN}} \text{Pd(As}_2\text{S}_2)(PF\textsubscript{6})\textsubscript{2}
\]

The ligand (0.6343 g, 1.07 mmole) dissolved in 10 ml acetone was added dropwise into a 15 ml acetonitrile solution containing 0.600 g (1.07 mmole) of Pd(CH\textsubscript{3}CN)\textsubscript{4}(PF\textsubscript{6})\textsubscript{2}. After stirring this solution for six hours, the volume of the solution was reduced to 5 ml and ethanol (75 ml) was added. After cooling in the refrigerator, the yellow product was collected on a frit, washed with ethanol, diethylether, and dried in vacuo. Yield: 1.03 g.
Analytical data: calculated for C_{17}H_{20}As_{2}F_{12}P_{2}PdS_{2}
C, 35.22; H, 3.06; S, 6.48
Found: C, 35.44; H, 3.25; S, 6.33

19. Attempted Demethylation of Pd(As_{2}S_{2})(PF_6)

\[
Pd(As_{2}S_{2})(PF_6)_2 \xrightarrow{\text{butanol, DMF}} Pd^{2+}(As_{2}S_{2})^{2-}
\]

Butanol (10 ml) and DMF (10 ml) were added to a flask containing 0.2666 g Pd(As_{2}S_{2})(PF_6)_2. After refluxing the orange-yellow solution for four hours, it turned to a dark red color. The solution was reduced to 5 ml, and many attempts to obtain a solid were unsuccessful.
CHAPTER III

RESULTS AND DISCUSSION

A. Ligands

Both the free radical, 60, and coupling, 61, methods have been used in the preparation of polydentate ligands during this investigation.

\[
\text{R}_2\text{PH} \xrightarrow{\text{hv}} \text{R}_2\text{P}^* + \text{H}^* \\
\text{R}_2\text{P}^* + \text{H}_2\text{C} = \text{CR} \rightarrow \text{R}_2\text{PC} = \text{CR}^{60} \\
\text{R}_2\text{PC} = \text{CR}^* + \text{R}_2\text{PH} \rightarrow \text{R}_2\text{PCH}_2\text{CH}_2\text{R} + \text{R}_2\text{P}^* \\
\text{R}_2\text{PH} + \text{n-BuLi} \rightarrow \text{R}_2\text{PLi} + \text{n-BuH}^{61} \\
\text{R}_2\text{PLi} + \text{RCl} \rightarrow \text{R}_2\text{P}-\text{R} + \text{LiCl}
\]

Although each method is individually useful, combining them has usually resulted in attractive new routes to ligands which are tedious to prepare using standard techniques.

Two important compounds that were prepared as building blocks for the synthesis of other polydentate ligands are 3-chloropropyl-diphenylphosphine, 62, and diphenylphosphinopropylphenylphosphine, 63 (PPH). The former was originally prepared by Grimm\(^ {55} \) as shown in 64.
In this investigation a modification gave a compound of

\[
\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}
\]

\[
\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P(H)Ph}
\]

\[
\text{PPh}_3 + 2\text{Na} \rightarrow \text{Ph}_2\text{PNa} + \text{NaPh}
\]

\[
\text{Ph}_2\text{PNa} + 2\text{Cl(CH}_2\text{)_3Cl} \rightarrow \text{Ph}_2\text{P(CH}_2\text{)_3Cl} + \text{NaCl}
\]

equivalent purity in higher yield, and greatly simplified manipulations during the synthesis. The procedure is carried out at 0°C as described in 65. After the diphenylphosphide is generated by the

\[
\text{Et}_2\text{O}
\]

\[
\text{Ph}_2\text{PH} + \text{n-BuLi} \rightarrow \text{Ph}_2\text{PLi} + \text{n-Butane}
\]

\[
\text{Ph}_2\text{PLi} + \text{excess Cl(CH}_2\text{)_3Cl} \rightarrow \text{Ph}_2\text{P(CH}_2\text{)_3Cl} + \text{LiCl}
\]

addition of n-butyllithium, the reaction mixture can be easily transferred into a dropping funnel (via syringe) and added dropwise to a ten-fold molar excess of cold (0°C) 1,3-dichloropropane. Failure to add the diphenylphosphide slowly or use of less than a ten-fold excess of 1,3-dichloropropane causes formation of bis-1,3-diphenylphosphinopropane. Another factor to be considered is that the resulting compound is unstable at temperatures over 65°C. Above this temperature, the reaction product begins to color—probably due to intermolecular quarterization of the phosphines. Characterization data of \(\text{Ph}_2\text{P(CH}_2\text{)_3Cl}\) are listed in Table 13, and the proton nmr spectrum of this compound is shown in Figure 5. In the proton spectrum of nmr, the methylene protons adjacent to the electronegative chlorine atom are
deshielded and appear downfield as compared to other methylene protons present.

To insure purity and a complete reaction while preparing Ph₂P(CH₂)₃P(H)Ph, an excess of sodium (~7%) and of PhPH₂ (~15%) was used. This guarantees that after the reaction is completed, only PPH, sodium, and phenylphosphine remain. The sodium is removed as NaOH after hydrolysis and extraction, whereas the excess phenylphosphine is removed in the last step at 50°C (in vacuo). Both the ¹H (Figure 5) and ³¹P nmr spectra (Figure 6) suggest high purity (spectroscopic data listed in Table 14) and match with an authentic sample.²

The ligand PPH, in addition to being a useful intermediate for building polydentate ligands, has potential as an interesting ligand in its own right.²³,²⁴ Besides chelating as a neutral diphosphine, it deprotonates and behaves as an anionic ligand—thus creating the possibility of bridging to other metals through the new lone pair of electrons. As an intermediate, this ligand can be further utilized in the free radical and coupling schemes previously mentioned. Such reactions are illustrated in Figure 7. Although the coupling scheme with PPH has produced several new compounds, this investigation deals only with ligands produced via the free radical route.

Mono and disubstitution on primary phosphines can be controlled by varying the stoichiometry of the reactants (Figure 8). When photolyzing a 1:1 molar ratio of phenylphosphine and allyl amine, Ph(H)P(CH₂)₃NH₂, PHN is the major product, whereas a molar ratio of reagents greater than 2:1 produces the disubstituted product PhP(CH₂CH₂CH₂NH₂)₂, PN₂. Even though the latter ligand and several of
Figure 5. The Proton nmr Spectrum of $\text{Ph}_2P(\text{CH}_2)_3\text{Cl}$ and $\text{PPH}$
## TABLE 13

SPECTRAL DATA ON COMPOUNDS PREPARED via THE COUPLING METHOD

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{31}$P nmr Parameters $^a$</th>
<th>$^1$H nmr Parameters $^b$</th>
<th>Unique I.R. Features $(\text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_2$PCH$_2$CH$_2$CH$_2$Cl</td>
<td>$\delta_{P_a}$, ppm: -17.9</td>
<td>$\delta_{P_b}$, ppm: 2.7</td>
<td>$\tau_{PH}$: 2.7, $\tau_{CH^2}$: 7.9(m), CH$_2$Cl: 6.48(t)</td>
</tr>
<tr>
<td></td>
<td>$\delta_{P_a}$, ppm: -18.0</td>
<td>$\delta_{P_b}$, ppm: -54.5</td>
<td>$\tau_{PH}$: 2.9, $\tau_{CH^2}$: 8.3(m), PH: 6.0(d of t)</td>
</tr>
<tr>
<td></td>
<td>$\delta_{P_a}$, ppm: -53.4</td>
<td>$\delta_{P_b}$, ppm: -</td>
<td>$\tau_{PH}$: 2.7, $\tau_{CH^2}$: 7.5(m), PH: 4.18(1/2d)</td>
</tr>
</tbody>
</table>

$^a$ Phosphorus $^{31}$ chemical shifts are in ppm relative to 85% H$_3$PO$_4$ with negative values being upfield from the reference.

$^b$ Proton chemical shifts are in tau units, relative to TMS.

$^c$ The $^1J_{P-H}$ value is 203 Hz.

$^d$ The $^1J_{P-H}$ value is 202 Hz.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{31}$P nmr Parameters</th>
<th>$^1$H nmr Parameters</th>
<th>Unique I.R. Features</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta_{P_a}$, ppm</td>
<td>$\delta_{P_b}$, ppm</td>
<td>$J_{P-H}$, Hz</td>
</tr>
<tr>
<td>$\text{PhP} (\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2$</td>
<td>-25.6</td>
<td>-</td>
<td>2.6</td>
</tr>
<tr>
<td>$\text{Ph} \rightarrow \text{PCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$</td>
<td>-52.4</td>
<td>-</td>
<td>2.8</td>
</tr>
<tr>
<td>$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si(OEt)}_3$</td>
<td>-9.9</td>
<td>-</td>
<td>2.7</td>
</tr>
<tr>
<td>$\text{NCCH}_2\text{CH}_2\text{P} (\text{CH}_2\text{CH}_2\text{PPh})_2$</td>
<td>-21.0</td>
<td>-13.9</td>
<td>24.9</td>
</tr>
<tr>
<td>$\text{H}_2\text{N(CH}_2\text{)}_3\text{P} (\text{CH}_2\text{CH}_2\text{PPh})_2$</td>
<td>-22.6</td>
<td>-13.5</td>
<td>25.3</td>
</tr>
<tr>
<td>$\text{Ph}_2\text{P} (\text{CH}_2\text{)}_3\text{P} (\text{Ph}) (\text{CH}_2\text{)}_3 \text{N(CH}_3\text{)}_2$</td>
<td>-27.2</td>
<td>-18.2</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>$\text{PhP} (\text{CH}_2\text{CH}_2\text{N}(\text{H}_2\text{N}))_2$</td>
<td>-27.3</td>
<td>-</td>
<td>3.6</td>
</tr>
</tbody>
</table>

* Phosphorus $^{31}$P chemical shifts are in ppm relative to 85% H$_3$PO$_4$ with negative values being upfield from the reference.

* Proton chemical shifts are in tau units, relative to TMS.

* The $J_{P-H}$ value is 204 Hz.
Figure 6. The $^{31}$P nmr Spectra of PPH
Figure 7. Synthetic Uses of PPH
STOICHIOMETRIC CONTROL VIA THE FREE RADICAL METHOD

\[
\text{PhPH}_2 + \text{NH}_2 \xrightarrow{\text{hv}} \begin{array}{c}
\text{Ph(H)P} \cdots \text{NH}_2 \quad >65\% \\
\text{excess} \\
\text{PhP} \cdots \text{NH}_2 \quad >90\%
\end{array}
\]

Figure 8. Stoichiometric Control via the Free Radical Method
Its transition metal complexes have been previously synthesized and characterized, the chemistry of the former has not been investigated.

At first glance it would seem that PHN should act similarly to PPH, but the chemistry of the amine will dictate quite different chemistry than the tertiary phosphine. The use of this ligand as an intermediate in a coupling reaction will be discussed in a later section.

The bidentate ligand PHN was characterized by infrared, $^1$H nmr (Figure 9), and $^{31}$P nmr (Figure 10) spectroscopy (data listed in Table 13). The infrared stretches at 3350 cm$^{-1}$ and 3275 cm$^{-1}$ are consistent with those found for primary amines, whereas the 2270 cm$^{-1}$ peak is characteristic of a P-H stretch of a secondary phosphine. The $^1$H nmr spectrum shows resonances at $\tau = 2.8$ (phenyl), $\tau = 7.5$, 8.35 (CH$_2$), $\tau = 9.05$ (NH$_2$), and $\tau = 4.15$ (t, 1/2 of P-H, $^3$J$_{H-H} = 6.5$ Hz). Only half of the resonance for the proton bonded to phosphorus could be found, and coupling of this proton to the methylene protons adjacent to the phosphorus atom was observed ($^3$J$_{H-H} = 6.5$ Hz). Confirmation that the other half of this resonance which was masked by the methylene protons was made by calculating $J_{P-H}$ from the $^{31}$P nmr spectrum and extrapolating back to the proton spectrum. The NH$_2$ protons were assigned at $\tau = 9.05$ on the basis of an exchange that resulted after addition of D$_2$O. The $^{31}$P nmr spectrum of PHN is a doublet ($J_{P-H} = 204$ Hz) which collapsed to a singlet at $\delta = -52.4$ ppm upon irradiation with a broadband proton-decoupling frequency. The $^{31}$P-$^1$H nmr spectrum of PN$_2$ was not previously available for this compound: a single phosphorus resonance occurs at $\delta = -24.5$ ppm.
PLEASE NOTE:
Dissertation contains pages with small and indistinct print. Filmed as received.

UNIVERSITY MICROFILMS
Figure 9. The Proton nmr Spectrum of PHN
Figure 10. $^{31}$P nmr Spectra for PN$_2$ and PHN
Several ligands have been prepared to demonstrate that the free radical process could produce ligands with potential applications in the area of supported phosphine catalysis. These ligands are i) \((\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2\), ii) \(\text{H}_2\text{N(CH}_2\text{)}_3\text{P(Ph)(CH}_2\text{)}_3\text{PPh}_2;\text{(PPNH}_2\text{)}\), and iii) \(\text{H}_2\text{N(CH}_2\text{)}_3\text{P(CH}_2\text{CH}_2\text{PPh}_2\text{)}_2\), (etp-\text{NH}_2). The spectral data for these compounds are listed in Table 13.

The ligand \((\text{EtO})\text{CH}_3\text{CH}_2\text{PPh}_2\), which has been attached to a solid support by displacement of its ethoxy groups \((66)\), was previously prepared at 150°C using a free-radical reagent. With these extreme conditions, the reported maximum yield was only 55%. We have, however, been able to obtain a >75% yield after purification by photo-lyzing the reaction mixture at <45°C.

\[
\begin{align*}
\text{OH} + (\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2 & \rightarrow (\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2 + 3 \text{EtOH} \\
\text{OH} & \\
\end{align*}
\]

The \(^{31}\text{P}(^1\text{H})\) nmr spectrum of this phosphinosilane is a singlet \((\delta = -9.9 \text{ ppm})\); however, the \(^1\text{H} \text{nmr spectrum is more helpful for characterization. This product shows resonances corresponding to phenyl (} \tau = 2.7\text{), } -\text{CH}_2- (m, \tau = 7.86; q, \tau = 6.23; J = 7 \text{ Hz}); \text{ and } -\text{CH}_3 (t, \tau = 8.8, J = 7 \text{ Hz}) \text{ groups. Both } P-\text{H} \text{ and vinyl resonances from the starting materials are not observed.}

The ligand etp-\text{NH}_2 was supported in a different manner than the phosphinosilane. This method of support utilized a condensation between an aldehyde, which is already attached to a support, and the amine of
etp-NH₂ (Figure 11). Biochemists have for many years used this procedure to immobilize enzymes or glass beads, but they have not attempted to utilize this technology for supporting phosphines. Kagan's diop and Whitesides' PNP ligand are the only other reports of attempts to support polydentate phosphine-containing ligands.

The preparation of etp-NH₂ involves preparation of etp-CN by photolyzing 2-cyanoethylphosphine and two equivalents of diphenylvinylphosphine. Although this compound was prepared as an intermediate for etp-NH₂, investigations of several transition metal complexes of etp-CN were made both to characterize this intermediate and to see if the chemistry of these complexes parallels that of etp-containing complexes.

Spectroscopic methods used for characterizing etp-CN were infrared, mass, ¹H nmr and ³¹P nmr spectroscopy. An infrared absorption at 2260 cm⁻¹ was assigned to the C═N stretch. Two resonances occurred in the proton nmr spectrum: τ = 2.8 assigned to phenyl protons, and τ = 8.25 due to methylene protons. When a two-carbon chain separates phosphines in a polydentate ligand, a phosphorus-phosphorous coupling constant of ~25 Hz is observed. For etp-CN, the expected doublet (δ = -13.9 ppm, terminal phosphines) and triplet (-21.0 ppm, central phosphorus) patterns show coupling in this range (J_p-p = 24.9 Hz) (Figure 12). A molecular weight of 511 is confirmed by mass spectroscopy (m/e = 511).

After characterizing the etp-CN intermediate, the cyano group was reduced with LiAlH₄ to form a colorless oil. Infrared spectroscopy of the oil showed that the 2260 cm⁻¹ absorption band disappeared. Two new absorptions occurring at 3350 cm⁻¹ and 1585 cm⁻¹ were assigned to
Figure 11. The Method for Supporting \( \text{PP}_2\text{N} \) on a Solid Glass Support
$^{31}P\ (^{1}H)\ NMR\ OF\ \overset{1}{\text{N}=\overset{2}{\text{C}}\overset{2}{\text{P}}\left(\overset{2}{\text{CH}}_{2}\right)\overset{2}{\text{PPh}}_{2}\left(\overset{2}{\text{CH}}_{2}\right)\overset{2}{\text{PPh}}_{2}\left(\overset{2}{\text{CH}}_{2}\right)\overset{2}{\text{PPh}}_{2}\left(\overset{2}{\text{CH}}_{2}\right)\overset{2}{\text{PPh}}_{2}]}$  

$\delta P_1 = -21.0 \text{ ppm}$  

$\delta P_2 = -13.9 \text{ ppm}$  

$J_{P-P} = 24.9 \text{ Hz}$  

Figure 12. The $^{31}P\ (^{1}H)$ nmr Spectrum of etp-CN
the newly formed amino group. The $^{31}$P nmr spectrum of etp-NH$_2$ is similar to that of the etp-CN. Important changes were noticed in both the $^1$H nmr and mass spectra. Confirmation of the amine was seen in the $^1$H nmr spectrum at $\tau = 9.5$ where a new peak occurred. Exchange with D$_2$O confirmed this assignment. In addition, a parent peak at m/e = 515 confirmed the conversion of etp-CN to etp-NH$_2$.

This ligand was then attached to glass beads by the condensation reaction previously mentioned. Confirmation of this attachment was made using ESCA spectroscopy. Attempts were also made to compute the amount of ligand consumed by analyzing for the amount of ligand that remained in the wash solutions.

The ESCA data clearly display nitrogen Is and phosphorus 2s, 2p emissions in addition to those present for the pure aldehyde glass (Figures 13, 14). Attempts to assay the unreacted amine via standard ninhydrin or trinitrobenzenesulfonic acid tests were unsuccessful, probably due to interference from the phosphorus atoms. Although the amount of ligand present could not be determined exactly from these experiments, it could be inferred from a colorimetric difference determination of Co$^{2+}$ in the next step. Discussion of these results will appear in a subsequent section.

The third ligand prepared for use in supported catalysis is Ph$_2$P(CH$_2$)$_3$P(Ph)(CH$_2$)$_3$NH$_2$ (PPNH$_2$). The major difference between this ligand and etp-NH$_2$ is that the primary amine is now in the terminal position of a tridentate ligand instead of being connected to the central donor via an alkyl chain. The proton nmr spectrum of PPNH$_2$ shows resonances for phenyl ($\tau = 2.8$), methylene ($\tau = 8.35$), and amine
Figure 13. The ESCA Spectrum of the Aldehyde Glass
Figure 14. The ESCA Spectrum of the Aldehyde Glass plus $PP_2N^\text{+}$
(τ = 9.35) protons (Figures 15 and 16). The -NH₂ resonance was confirmed by D₂O addition. A broad peak at 3350 cm⁻¹ in the infrared spectrum shows the presence of the amine. Two singlets were present in the ³¹P nmr spectrum at δ = -18.2 and -27.2 ppm (Figure 17) which corresponded to the diphenyl- and phenylphosphino groups respectively. Table 13 lists all of the spectroscopic details.

After characterization, PPNH₂ was attached to a glass support via a condensation reaction. The amine formed from the condensation of the aldehyde attached to the support and the amine was reduced with NaBH₄. After attachment, a 10 mm nmr tube was filled with the supported material, benzene-d₆ was added, and the ³¹P nmr spectrum of the slurry was attempted. The resulting spectrum after 17,261 scans appears in Figure 18. Although the ligand was now part of a solid, the alkyl chain was long enough to permit solubility at the end of the ligand producing the resulting broad resonance. In order to obtain a better spectrum, the glass was dissolved using sodium methoxide. Sodium methoxide (400 mg) was added to the slurry from the previous nmr experiment, and it was allowed to sit overnight. After 18 hours, the liquid portion was decanted, and a ³¹P nmr spectrum was taken of this liquid (Figure 19). With the interference from the glass removed, sharper resonances could be seen. The presence of ligand on the surface of the glass beads was also supported by ESCA (Figure 20).

The ligand PPN was prepared to investigate the influence that a weakly bonded donor has on the rate enhancement for the homogeneous hydrogenation of olefins. To prepare PPN, a photolysis of PPH and N,N-dimethylallylamine was carried out under nitrogen. A dimethyl
Figure 15. The Proton nmr Spectrum of PPNH$_2$ (benzene d$_6$)
Figure 16. The Proton nmr Spectrum of PPNH₂ (benzene d₆ and D₂O)
Figure 17. The $^{31\text{P}}$-$^{1\text{H}}$ nmr Spectrum of PP$\text{NH}_2$
Figure 18. The $^{31}$P nmr Spectrum of PPNH$_2$ Supported on a Glass
Figure 19. The $^{31}$P nmr Spectrum of Supported PPNH$_2$
after Dissolving the Glass Support with NaOMe
Figure 20. The ESCA Spectrum of PPNH$_2$ Supported on Glass
substituted amine was chosen because nitrogen coordination to transition metals could be confirmed by the proton nmr spectrum. Observing the methyl resonances in the proton nmr has shown that coordination of the amine causes a downfield shift of 0.7 to 1.0 ppm, compared to the free ligand. Therefore, the -NMeg substituent allows more information to be obtained about the metal complexes of PPN.

Characterization of PPN was made by both $^1$H and $^{31}$P nmr data. The $^1$H nmr spectrum (Figure 21) shows three sets of peaks: i) $\tau = 2.8$ assigned to phenyl resonances, ii) $\tau = 7.88$ attributed to methyl groups on nitrogen, and iii) $\tau = 8.38$ assigned to the methylene protons. The $^{31}$P nmr spectrum shows two singlets observed at -18.2 (Ph2P-) and -27.2 (PhP<) ppm. Since a three-carbon alkyl chain connects the phosphines, $J_{P-P}$ is very small (<1 Hz).

The ligand PS2N2 was prepared by a one-step photochemical reaction incorporating divinylphenylphosphine and o-aminobenzenethiol. This ligand contains five potential donor atoms which can bond to a transition metal in various ways, although some combinations can be eliminated because of the constraints placed on both the nitrogen and sulfur which occupy ortho positions on a phenyl ring. Whereas coordination of the amine and phosphine can be detected by infrared and $^{31}$P nmr spectroscopic techniques, sulfide coordination is more difficult to detect spectroscopically.

The -NH2 moiety in PS2N2 can be detected by both infrared and proton nmr spectroscopy. In the infrared spectrum the two absorptions at 3410 cm$^{-1}$ and 3510 cm$^{-1}$ are consistent with the presence of the amino groups. A resonance at $\tau = 6.15$ in the $^1$H nmr spectrum is assigned to
Figure 21. The Proton nmr Spectrum of PPN
the NH₂ protons and was confirmed by the addition of D₂O. Two other
groups of resonances were observed in the ¹H nmr spectrum: 1) ² = 2.9
and 3.6 assigned to phenyl and o-phenylene groups, and ii) ² = 8.25,
7.42 assigned to the methylene groups. A single resonance at -27.3 ppm
in the ³¹P nmr spectrum is consistent with a dialkylphenylphosphine.

The coupling method for building polydentate ligands was used
to provide two linear tetradentates that have potential to be
cyclized, when situated in planar complexes, into macrocyclic
ligands.¹²⁵-¹²⁸ The first ligand, P₂S₂, has a trimethylene backbone
between each donor set and secondary phosphines in the terminal posi-
tions. Although P₂N₂ also has trimethylene connecting chains, it dif-
fers from P₂S₂ in composition and in the positioning of the donor atoms.
Positioning donors was accomplished by proper precursor selection—in
this case by using PHN (previously discussed).

In P₂S₂, an absorption at 2290 cm⁻¹ in the infrared region shows
the presence of a P-H bond. The proton nmr spectrum showed phenyl
(² = 2.7), methylene (² = 7.5, 8.2) and P-H (1/2 at ² = 4.18) reso-
nances. The ratio of integrations is 8.8:5.0 for phenyl:methylene
+ 1/2 P-H which shows that coupling did occur. The ³¹P nmr was a doub-
let (δ = -53.4 ppm) with Jₚ-H = 204 Hz.

The NH₂ group in P₂N₂, analogous to PN₂, had two absorptions in
the infrared spectrum at 3240 cm⁻¹ and 3320 cm⁻¹, and a resonance at
² = 9.3 (checked with D₂O) in the ¹H nmr spectrum. The central phos-
phorus in the ³¹P nmr resonates at δ = -25.9 ppm which is consistent
with other dialkylphenylphosphines of this type.
Early attempts to prepare phosphine ligands that could be precursors to macrocyclic ligands led to the preparation of phph. The ligand phph was prepared by reducing \( \text{CH}_2(\text{CH}_2\text{P}(\text{O})(\text{Oipr})\text{Ph})_2 \), which was easily prepared in quantitative yield via an Arbuzov reaction between \( \text{Br(}\text{CH}_2\text{)}_3\text{Br} \) and \( \text{PhP(Oipr)}_2 \). Reduction of this product with phenylsilane resulted in a compound which contained no evidence of a P-H in either the IR, \(^1\text{H nmr} \) or \(^{31}\text{P nmr} \). These results, coupled with the parent peak in the mass spectrum occurring at m/e = 258, led to the conclusion that there was formation of a phosphorus-phosphorus bond instead of complete reduction thus forming the cyclic compound \( \text{PhP}(\text{Ph})(\text{CH}_2)_3\text{CH}_2 \). The literature refers to this compound only once and no spectroscopic evidence was mentioned. Upon reviewing \(^{31}\text{P nmr} \) data for various other ligands containing 3-carbon backbones, it was found that the characteristic \( \delta = 8.4 \text{ ppm} \) resonance for this cyclic compound occurred as a small decomposition product. In fact Dubois found that when trying to distill the ligand \( \text{Ph}_2\text{P(}\text{CH}_2\text{)}_2\text{P(Ph)(}\text{CH}_2\text{)}_3\text{P(Ph)(}\text{CH}_2\text{)}_2\text{PPh}_2 \), a reverse of the free radical addition reaction occurred, and \( \text{PhP(PCCH}_2\text{CH}_2\text{CH}_2 \) was a major by-product.

Since PhSiH\(_3\) failed to reduce \( \text{CH}_2(\text{CH}_2\text{P}(\text{O})(\text{Oipr}))_2 \) completely, LiAlH\(_4\) was used. After reduction, phph was obtained as the major product and was characterized by the same methods used for the cyclic phosphine compound. It should be noted that the mass spectrum (m/e = 260), \(^1\text{H nmr} \), and \(^{31}\text{P nmr} \) spectra all showed strong evidence for complete reduction (Table 13).

Another ligand prepared as a precursor to a macrocyclic ligand was As\(_2\)S\(_2\). Although Meek et al. had looked at some palladium complexes
of this ligand previously, only dimeric compounds could be obtained. This ligand was reprepared in an attempt to make discrete monomeric species which could be demethylated, and, upon realkylation, could give a macrocyclic product. Before preparing As₂S₂, PhAsCl₂ was made via a reduction of PhAs(O)(OH)₂—a route which was previously used to prepare other chloroarsenic compounds.

B. Studies Using etp-CN and etp-NH₂

1. Synthesis of Metal Complexes

In this study both cobalt and rhodium complexes of etp-CN were prepared to investigate the similarity of etp-CN to etp in these metal complexes. Equations 67-69 show several methods for the preparation of complexes.

\[
\begin{align*}
(Rh(COD)Cl)_2 + 2 \text{etp-CN} & \rightarrow 2 \text{Rh(etp-CN)Cl} \quad 67 \\
\text{Co(H₂O)₆Cl₂} + \text{etp-CN} & \rightarrow \text{Co(etp-CN)Cl₂} \quad 68 \\
\text{Co(etp-CN)Cl₂} + \text{NaBH₄} + \text{CO} & \rightarrow \text{Co(etp-CN)H(CO)} \quad 69
\end{align*}
\]

These reactions take advantage of displacing a weak ligand such as water or a diolefin with a stronger chelating phosphine ligand. In the case of cobalt(II), after adding the phosphine, reduction to the cobalt(I) complex Co(etp-CN)H(CO) was accomplished by using sodium borohydride and carbon monoxide.
2. Characterization of Metal Complexes

The metal complexes were characterized by elemental analysis, infrared spectroscopy, proton and phosphorus-31 nuclear magnetic resonance spectroscopy. The infrared spectrum of Rh(etp-CN)Cl is almost identical to that of Rh(etp)Cl except for a weak, sharp C≡N stretch at 2250 cm\(^{-1}\). The \(^{31}\)P nmr spectra of both complexes also show great similarities (Figure 22, Table 15). A doublet of triplets is observed for the central phosphorus (P\(_1\) in \(\sim\)). This is due to the rhodium (doublet) and terminal phosphorus (triplet) coupling to this phosphorus atom.

![Diagram](image.png)

The doublet of doublets (Figure 22) arises from both rhodium and phosphorus coupling to the terminal phosphorus atom. A planar structure, \(\sim\), was chosen over five-coordinate square-pyramidal or trigonal-bipyramidal structures based on the infrared data which show no changes in the CN absorbance after formation of the metal complex.\(^{130}\)

A red crystalline powder was obtained after treating \(\text{Co(H}_2\text{O})_6\text{Cl}_2\) with etp-CN. The infrared spectrum of this compound was identical to that of Co(etp)Cl\(_2\) except for the presence of a C≡N stretch.
TABLE 15

PHOSPHORUS-31 DATA FOR Rh(etp)Cl AND Rh(etp-CN)Cl

<table>
<thead>
<tr>
<th>Compound</th>
<th>$P_1$ (ppm)</th>
<th>$P_2$ (ppm)</th>
<th>$J_{P_1-P_2}$ (Hz)</th>
<th>$J_{Rh-P_1}$ (Hz)</th>
<th>$J_{Rh-P_2}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(etp)Cl$^{a,b}$</td>
<td>108.3</td>
<td>39.3</td>
<td>-32.7</td>
<td>161.4</td>
<td>144.7</td>
</tr>
<tr>
<td>Rh(etp-CN)Cl$^{c}$</td>
<td>111.0</td>
<td>43.1</td>
<td>-29.3</td>
<td>159.9</td>
<td>144.0</td>
</tr>
</tbody>
</table>

$^{a}$P. R. Blum, Ph.D. Thesis, The Ohio State University, 1977.

$^{b}$Ph$_2$P(CH$_2$)$_2$P(Ph)(CH$_2$)$_2$PPh$_2$

$^{c}$Ph$_2$P(CH$_2$)$_2$P(Ph)$_2$(CH$_2$)$_2$PPh$_2$
Figure 22. The $^3\text{P}$ nmr spectrum of Rh(etp-CN)Cl
at 2250 cm$^{-1}$. Careful reduction of this compound with NaBH$_4$ in the presence of CO yielded Co(etp-CN)(CO)(H). The infrared spectra for both this compound and the etp analog$^{112}$ are similar in the hydride and carbonyl regions (Figure 23). Even though Co(I) has a quadrapole moment, a reasonable $^{31}$P spectrum can be obtained for this compound at 225$^\circ$K (Figure 24). The doublet and triplet patterns suggest that both terminal phosphines are in equivalent environments. The structure in Figure 24 is consistent with this fact. It should be also noted that the large downfield shift associated with two phosphorus atoms being confined to a five-member ring is observed for the central and terminal phosphine groups.

3. Discussion and Hydrogenation Results

Dubois and Meek have recently shown that Co(etp)H, which was prepared using Co(etp)Cl$_2$ and an appropriate reducing agent, was an extremely efficient homogeneous hydrogenation catalyst.$^{113}$ Industrial applications of this type of homogeneous catalyst, however, are limited by factors listed in the introduction. The aim of this investigation was to prepare a similar ligand, etp-NH$_2$, which could be supported on the surface of a polymer support, which would incorporate features of both hetero- and homogeneous catalysis.

Complexes of etp-CN were prepared to substantiate the hypothesis that etp-CN would act similarly to etp. The characterization data mentioned previously has shown this. When the characterization of the ligand (pure and supported) and of several complexes was completed, the supported ligand was reacted with cobalt(II) chloride to determine
Figure 23. A Comparison of the Infrared Spectra of Co(etc)Cl₂ (a) and Co(etc-CN)Cl₂ for the 1500-2000 cm⁻¹ Region
$^{31}P(^1H)$ NMR OF

$\text{Co(etp-CN)(CO)H}$

(225°K)

Figure 24. The $^{31}P(^1H)$ nmr Spectrum of Co(etp-CN)H(CO)
if a supported complex could be made (71). Analysis for the amount of

\[
\text{PPh}_2 \quad \text{PPh}_2 \quad + \text{CoCl}_2 \cdot 6\text{H}_2\text{O} \quad \rightarrow \quad \text{PPh}_2 \quad \text{Co}^{\text{II}} \quad \text{Cl} \quad \text{PPh}_2 \quad \text{Cl}
\]

cobalt taken up during the reaction was monitored using the 655 nm absorbance for cobalt(II) in the visible region (Figure 25). When absorbance from a standard solution and the support's wash solution were compared in ethanol, a 21.1% difference was found, indicating that 0.211 mmole of cobalt was bonded to the surface per gram of glass. An analysis utilizing ESCA confirmed the presence of the ligand and cobalt after the reaction (Figure 26). Although the Co(II) 2s and 2p ESCA peaks were masked by the auger peaks of oxygen (775 and 785 e.v.), an unmasked auger peak for cobalt was observed at 485 e.v. The chlorine peak at 200 e.v. was also observed.

Since the quantity of supported Co(etp-\text{NH}_2)\text{Cl}_2 was known, a screening test for the hydrogenation of terminal olefins could be attempted to determine the activity of the cobalt ligand hydride generated in situ. The experiment was set up using a modified gas inlet that would facilitate the stopcock addition of both OMH-1 and ethanol via syringe and under nitrogen (72). The results of the hydrogenation using 1-octene (500 : 1 olefin to catalyst ratio), 50 ml total of solution, 400 mg of glass support, and 1 ml of OMH-1 (29% in toluene) is shown in Figure 27. After addition of OMH-1, the color of
Figure 25. The 600-700 nm Visible Region of CoCl$_2$ (in Ethanol) Used for Comparing the Amount of CoCl$_2$ Bonded to Glass
Figure 26. The ESCA Spectrum of Glass-Supported Pp_2N + CoCl_2
CATALYTIC HYDROGENATION OF 1-OCTENE WITH SUPPORTED \( \text{Co(etp-NH}_2\text{)}\text{Cl}_2 + \text{OMH-1} \)

Figure 27. The Results of the Catalytic Hydrogenation of 1-Octene Using Supported \( \text{Co(etp-NH}_2\text{)}\text{Cl}_2 + \text{OMH-1} \)
the glass ligand lightened from blue-green to red. Upon agitation, catalysis proceeded. Several times during the experiment, rotation was stopped to see if the rate of catalysis would be affected. These results showed that when agitation was stopped, the rate of $H_2$ uptake decreased drastically, but upon reagitating, the rate of hydrogenation returned to normal. The product of the hydrogenation, as seen in Figure 27, is normal octane. Although this catalysis takes 15 hours to complete, the maximum turnover rate for catalysis was found to be 66.2% that of Rh(PPh$_3$)$_3$Cl.

4. Conclusions

Metal complexes of etp-CN were synthesized and characterized, and their chemistry was found to closely parallel that of complexes with etp. After these similarities were determined, the ligand etp-NH$_2$ was used to support a tridentate phosphine onto the surface of control-pore glass beads. Cobalt(II) chloride was reacted with this supported
ligand to give a supported analog of Co(etp)Cl₂, which is known to hydrogenate olefins homogeneously efficiently. After generating the cobalt-ligand hydride in situ, the supported catalyst was found to hydrogenate 1-octene efficiently with a maximum turnover rate of 66.2% that of Wilkinson's compound.

C. Studies Using Ph₂P(CH₂)₃P(Ph)(CH₂)₃N(CH₃)₂, PPN

Transition metals from both the nickel and cobalt triads were used to prepare complexes containing PPN. Examples of these preparations are shown in 73-77.

\[
\begin{align*}
\text{[Rh(COD)Cl]}_2 + 2 \text{PPN} & \rightarrow 2 \text{Rh(PPN)Cl} \quad 73 \\
\text{[Ir(COD)Cl]}_2 + 2 \text{PPN} & \rightarrow 2 \text{Ir(PPN)(COD)Cl} \quad 74 \\
\text{M(H₂O)}_6\text{Cl}_2 + \text{PPN} & \rightarrow \text{[M(PPN)Cl]BPh}_4 \quad \text{M=Ni,Pd} \quad 75 \\
\text{Pt(COD)Cl}_2 + \text{PPN} & \rightarrow \text{Pt(PPN)Cl}_2 \quad \text{NaAsF}_6 \quad \text{[Pt(PPN)Cl]AsF}_6 \quad 76 \\
\text{Rh(PPh₃)₃NO} + \text{PPN} & \rightarrow \text{Rh(PPN)(PPh₃)NO} + 2 \text{PPh₃ (in situ)} \quad 77
\end{align*}
\]

These compounds were characterized by elemental analysis, infrared spectroscopy, proton nmr spectroscopy, and phosphorus-31 nmr spectroscopy.

The series of compounds [Ni(PPN)Cl]⁺, [Pd(PPN)Cl]⁺, and [Pt(PPN)Cl]⁺ were prepared to investigate the effect that descending the nickel triad has on the phosphorus–phosphorus coupling constant. All three complexes were synthesized from ethanol solution of the appropriate metal starting materials and PPN, and precipitated from these alcoholic solutions upon adding the sodium salt of a large,
non-coordinating anion. After collecting the solids, washing them with water to remove sodium chloride, and drying, good analytical results were obtained for all three compounds. The proton nmr spectra for these complexes show downfield shifts for the dimethylamino resonances which are interpreted to indicate coordination of the nitrogen atom to the transition metal (Table 16). At some temperatures, two resonances are found for the methyl groups bonded to nitrogen, indicating that these methyl groups are not equivalent (78).

Phosphorus-31 nmr spectra for \( \{\text{M(PPN)Cl}\} \text{BPPh}_4 \), where \( \text{M} \) = Ni, Pd, and for \( \{\text{Pt(PPN)Cl}\} \text{AsF}_6 \) are shown in Figures 28-30 (data listed in Table 16). An unambiguous assignment of the chemical shifts for each phosphorus cannot be made in the nickel and palladium complexes, but an assignment can be made in the platinum complex. For the platinum complex, the metal-phosphorus coupling constant for the central phosphine in PPN will be different than the coupling constant obtained for the terminal \( \text{Ph}_2\text{P}^- \) group. This difference is caused by the ligand trans to each phosphorus atom. Generally, a weak trans-influencing ligand will result in large values of \( J_{\text{M-P}} \) for bonds trans to it, whereas a strong trans-influencing species will result in a much smaller \( J_{\text{M-P}} \). If the trans influence of a ligand is known relative to another ligand, a
**TABLE 16**

$^1\text{H}$ and $^{31}\text{P}$ NMR DATA FOR $[\text{M(PPN)}\text{Cl}]^+$ WHERE $\text{M} = \text{Ni, Pd, Pt}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1\text{H}$ nmr data (rel. to TMS)</th>
<th>$^{31}\text{P}$ nmr data (rel. to 85% $\text{H}_3\text{PO}_4$)</th>
<th>298$^\circ\text{K}$</th>
<th>254$^\circ\text{K}$</th>
<th>$\delta\text{Ph}_2\text{P}$ (ppm)</th>
<th>$\delta\text{PhP}&lt;\text{(ppm)}$</th>
<th>$J_{\text{P-P}}\text{(Hz)}$</th>
<th>$\Delta\text{Ph}_2\text{P}$</th>
<th>$\Delta\text{PhP}&lt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPN</td>
<td>2.8</td>
<td>8.38</td>
<td>7.88</td>
<td>-</td>
<td>-18.2</td>
<td>-27.2</td>
<td>&lt; 1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Ni(PPN)}\text{Cl}]^+$</td>
<td>7.0 P-Ph (br)</td>
<td>7.54$^a$</td>
<td>7.80$^a$</td>
<td>45.6$^b$</td>
<td>32.3$^b$</td>
<td>&lt; 1</td>
<td>63.8</td>
<td>59.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.45 B-Ph</td>
<td>(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Pd(PPN)}\text{Cl}]^+$</td>
<td>7.43 B-Ph (br)</td>
<td>7.28</td>
<td>7.17</td>
<td>8.42$^b$</td>
<td>4.46$^b$</td>
<td>22.1</td>
<td>26.6</td>
<td>31.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.37 P-Ph</td>
<td>(br)</td>
<td>7.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Pt(PPN)}\text{Cl}]^+$</td>
<td>7.39 (br)</td>
<td>7.64</td>
<td>7.64</td>
<td>-11.2</td>
<td>-13.0</td>
<td>27.2</td>
<td>7.0</td>
<td>14.2</td>
<td></td>
</tr>
</tbody>
</table>

$^a$These resonances were broad.

$^b$Not enough information is present for unambiguous assignment.
Figure 28. The $^{31}P\{^1H\}$ nmr Spectrum of {Ni(PPN)Cl}BPh$_4$ (254$^\circ$K)
Figure 29. The $^{31}_P\{^1H\}$ nmr Spectrum of $\{\text{Pd(PPN)}\text{Cl}\}\text{BPH}_4$ (254°K)
Figure 30. The $^{31}P^{1}H$ nmr Spectrum of $\{\text{Pt(PPN)Cl}\}_{6}\text{AsF}_6^-$
chemical-shift assignment can be made using the coupling constant argument. For \( \{\text{Pt(PPN)Cl}\}_6 \text{AsF}_6 \), two platinum-phosphorus coupling constants, 2964 Hz and 3436 Hz, were obtained.

In similar systems where the tridentate ligands etp, ttp, and eptp were used, the \( J_{\text{Pt-P}} \) assigned to the central phosphorus atom was in the range 2850 Hz to 3100 Hz. Since 2964 Hz lies in this range, the two satellites and the resonance about which they are symmetric were assigned to the central phosphorus in the bonded tridentate PPN.

Several researchers have recently investigated the effects that ring size and different metals have on cis phosphorus-phosphorus coupling constants. Their results are shown in Table 17.\(^{48,51,136} \) In general, the results in Table 17 show that upon descending the periodic chart in a certain triad (i.e., Cr → Mo → W), both the \( J_{\text{P-P}} \) and \( \Delta \) values (chemical shift differences) decrease. King\(^{51} \) found a disparity in some of his chemical-shift data for five-member rings (\( \Delta \text{Pd} > \Delta \text{Ni} > \Delta \text{Pt} \)) (Example A, Table 17). Although two modes of coupling are possible through a five-member metallocycle ring (Example A, Table 17), coupling occurs only through the metal with a three-carbon chain construction (B and C, Table 17). Since PPN has a three-carbon connecting chain between donor atoms, cis phosphorus-phosphorus coupling should have the same trends as were seen previously. Similar trends are noticed when comparing values for the nickel triad complexes of PPN with those found in Table 17. But the trend in the phosphorus-phosphorus coupling-constants is opposite those reported previously. These results raise the question of whether the coupling
# TABLE 17

CHEMICAL SHIFT AND $J_{P-P}$ DATA FOR VARIOUS UNSYMMETRICAL BIS-PHOSPHINE TRANSITION METAL COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>$J_{P-P}$(Hz)</th>
<th>$\Delta$(ppm)</th>
<th>$\Delta$(ppm) (Ph$_2$P–)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. $^a$</td>
<td>L = (CH$_3$)$_2$P(CH$_2$)$_2$PPh$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(L)Cl$_2$</td>
<td>76</td>
<td>103.4</td>
<td>94.7</td>
</tr>
<tr>
<td>Mo(L)Cl$_2$</td>
<td>10</td>
<td>74.7</td>
<td>70.6</td>
</tr>
<tr>
<td>W(L)Cl$_2$</td>
<td>2</td>
<td>56.3</td>
<td>55.7</td>
</tr>
<tr>
<td>Ni(L)(CO)$_4$</td>
<td>15</td>
<td>97.0</td>
<td>71.9</td>
</tr>
<tr>
<td>Pd(L)(CO)$_4$</td>
<td>7</td>
<td>107.0</td>
<td>78.0</td>
</tr>
<tr>
<td>Pt(L)(CO)$_4$</td>
<td>2</td>
<td>79.0</td>
<td>55.7</td>
</tr>
<tr>
<td>B. $^b$</td>
<td>L = Ph$_2$P(CH$_2$)$_3$P(Ph)(CH$_3$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(L)(CO)$_4$</td>
<td>40.8</td>
<td>56.9</td>
<td>58.3</td>
</tr>
<tr>
<td>Mo(L)(CO)$_4$</td>
<td>28.5</td>
<td>35.2</td>
<td>37.7</td>
</tr>
<tr>
<td>W(L)(CO)$_4$</td>
<td>22.6</td>
<td>12.8</td>
<td>17.2</td>
</tr>
<tr>
<td>C. $^c$</td>
<td>L = Ph$_2$P(CH$_2$)$_2$OOPh$_2$</td>
<td>(Ph)$_2$P–O–</td>
<td></td>
</tr>
<tr>
<td>Cr(L)(CO)$_4$</td>
<td>46.5</td>
<td>49.8</td>
<td>63.6</td>
</tr>
<tr>
<td>Mo(L)(CO)$_4$</td>
<td>35.0</td>
<td>30.0</td>
<td>44.8</td>
</tr>
<tr>
<td>W(L)(CO)$_4$</td>
<td>31.0</td>
<td>4.6</td>
<td>25.0</td>
</tr>
</tbody>
</table>


always increases upon descending a triad, or if this is true only for the chromium triad. In several monodentate phosphine cases, Nixon reported an increase in cis $J_{p-p}$ in going from Cr $\rightarrow$ Mo $\rightarrow$ W, but smaller absolute values were obtained because of the negative sign attributed to this coupling (Figure 31).

![Figure 31. $J_{p-M-p}$ for Group VIa Complexes (i.e., $M$(CO)$_4$L where $M$ = Cr, Mo, W)](image)

It is a possibility that in the complexes containing PPN, $J_{p-p}$ is increasing in value due to the positive nature of the $J_{p-p}$ values, whereas from Grimm's series, negative coupling constants are increasing to smaller absolute numbers. However, this explanation is in doubt. Goodfellow and Carty both determined that $J_{p-p}$ in cis monodentate and chelating phosphine systems decreased from palladium to platinum (i.e., $J_{pp} = -8.0$ Hz for cis-PdCl$_2$(PMe$_3$)$_3$, -18.9 Hz for cis-PtCl$_2$(PMe$_3$)$_3$). Although this $J_{pp}$ data is contrary to Grimm's results
for the chromium triad, it is consistent with values reported in this investigation.

In preparing Pt(PPN)Cl AsF₆, the intermediate Pt(PPN)Cl₂ was isolated and characterized. The ¹H nmr spectrum of this compound gave three resonances: i) τ = 2.63 for phenyl protons, ii) τ = 7.28 for -N-(CH₃)₂ protons, and iii) τ = 7.5 (m) assigned to methylene protons. The sharp singlet resonance for the methyl groups attached to the amine showed a 0.6 ppm downfield shift which strongly suggests nitrogen coordination to the platinum. Parts of the ³¹P{¹H} nmr spectrum of Pt(PPN)Cl₂ (Figure 32) are deceptively simple. Although this spectrum displays only a single central resonance, the satellites due to platinum coupling are each an AB portion of an ABX spin pattern. The downfield satellite shows a different deceptively simple pattern than is seen for the central resonance, and the upfield satellite shows a more typical AB portion of an ABX spin system. Although three types of AB patterns are seen, only the upfield satellite has enough information to determine a phosphorus-phosphorus coupling constant. Theoretical calculations ¹³⁸ (Figure 33) have shown how the features of an AB spectrum change with respect to \( \frac{J}{\Delta \nu} \).

The ³¹P nmr parameters based on the upfield satellite in the Pt(PPN)Cl₂ spectrum were calculated using the following formulae:

\[
\begin{align*}
\Delta &= (ab)^{1/2} \\
J_{ab} &= \frac{a-b}{2} \\
\nu_a &= \bar{\nu} + \frac{\Delta}{2} \\
\nu_b &= \bar{\nu} + \frac{\Delta}{2}
\end{align*}
\]

where a, b, and \( \bar{\nu} \) are defined above.
$^{31}$P($^1$H) NMR OF Pt(PPN)Cl$_2$

$J_{P-P} = 23$ hz

$J_{Pt-P} = 3517$ hz

$J_{Pt-P} = 3324$ hz

Figure 32. The $^{31}$P($^1$H) nmr Spectrum of Pt(PPN)Cl$_2$
Figure 33. Theoretical AB Type Spectra for Two Nuclei of Spin 1/2 Having $\nu_0\delta = 10$ c.p.s.\textsuperscript{a}

Evaluation of the $^{31}$P nmr spectrum of Pt(PPN)Cl$_2$ in CH$_3$CN gives the following values:

$\delta P_1 = P_2 = -5.91$ ppm
$J_{P-P} = 23$ Hz
$J_{Pt-P} = 3517$ Hz, 3324 Hz

An interesting solvent effect was noticed when CH$_2$Cl$_2$ was used to dissolve Pt(PPN)Cl$_2$. A single central resonance was still seen, but the AB patterns of the satellites are reversed due to slight chemical-shift differences. The nmr parameters of Pt(PPN)Cl$_2$ in CH$_2$Cl$_2$ were calculated to be:

$\delta J_p = \delta P_2 = -5.76$ ppm
$J_{P-P} = 22.6$ Hz
$J_{Pt-P} = 3503$ Hz, 3324 Hz

Rhodium and iridium complexes of PPN were prepared to investigate the catalytic activities that these compounds would have in the hydrogenation of olefins. Upon coordination, one would expect PPN to bond to rhodium(I) and to iridium(I) in a normal planar fashion (78), producing analogs to Wilkinson's compound. These low-valent complexes,
as postulated by Roundhill, would prefer π-acceptor ligands, since low-valent complexes are usually stabilized by π-acceptor ligands. The nitrogen donor could either dissociate or be displaced by an olefin to begin what might be the first step in a catalytic cycle for the hydrogenation of olefins (79).

The complex Rh(PPN)Cl was characterized by elemental analysis, $^1$H nmr spectroscopy, and $^{31}$P nmr spectroscopy. The proton nmr shows resonances at $\tau = 7.28 (-N(CH_3)_2)$, $\tau = 2.65$ (phenyl), and $\tau = 8.0$ (broad, $CH_2$). The chemical shift of the proton on the dimethylamino group strongly suggests that the nitrogen atom is coordinated to the rhodium atom. An eight-line pattern is seen for the $^{31}$P nmr spectrum of Rh(PPN)Cl (Figure 34) where $\delta_{P_1} = 29.0$ ppm, $\delta_{P_2} = 19.6$ ppm, $J_{P-P} = 64$ Hz, $J_{Rh-P_1} = 166$ Hz, and $J_{Rh-P_2} = 184.3$ Hz. Although the assignment of chemical shifts is not usually possible in ABX spin systems, this $^{31}$P nmr spectrum is different. The chemical shifts can be assigned using information known about other tridentate-phosphine rhodium(I) systems. Since $J_{Rh-P}$ for the central phosphorus atom in tridentate phosphine ligands trans to a chloride lie in the range 160-165 Hz, the four-line pattern containing the 166 Hz value
Figure 34. The $^{31}\text{P} \{^1\text{H}\}$ nmr Spectrum of Rh(PPN)Cl

$J_{\text{Rh-P}_1} = 166$ hz

$J_{\text{Rh-P}_2} = 184.3$ hz

$J_{\text{P-P}_1} = 63.5$ hz
was assigned to the central phosphorus atom. The remaining resonances have a $J_{\text{Rh-P}} = 184.3$ Hz, which is consistent with a value obtained for a phosphine atom trans to pyridine in a similar rhodium(I) complex.\textsuperscript{107}

Catalytic hydrogenations of 1-octene were attempted using Rh(PPN)Cl, and the results show no activity at room temperature 1 atm. of H$_2$. After carefully checking the experimental conditions and retesting, no activity was found. Activation of this complex was attempted by adding HBF$_4$·Et$_2$O during an experiment to "pull" the amine off the metal. No catalytic activity was found at room temperature and 1 atm. of H$_2$. The $^{31}$P nmr spectrum of the catalyst dissolved in THF with a 100:1 molar excess of 1-octene was identical to the spectrum of pure catalyst, thus confirming that the amine was coordinated and did not dissociate under these conditions. However, Rh(PPN)Cl could potentially be used as a catalyst if the chloride were replaced with a hydride ion. Dubois\textsuperscript{112} showed that NaAlEt$_2$H$_2$ (OMH-1) was a good agent for producing hydrides in cobalt(II) systems. A catalytic hydrogenation of 1-octene was attempted using the in situ combination of Rh(PPN)Cl, OMH-1 (1 ml, 29\% by gas analysis), and enough ethanol to cause a color change from yellow to redish-orange (~0.5 ml: if too much was added, a brown, inactive species formed). The olefin hydrogenation was completed in 8 hours, and the gas chromatographic analysis of the products shows only octane (Figure 35). Although it was originally thought that Rh(PPN)H, like Rh(ttp)H,\textsuperscript{112} was the catalytically-active species in this hydrogenation, recent $^{31}$P nmr experiments have shown other results. The addition of OMH-1 (0.1 ml) to 0.1 mole of Rh(PPN)Cl, 1.0 mole of 1-octene, and enough THF to bring the total
Figure 35. The Results of the Catalytic Homogeneous Hydrogenation of 1-Octene Using Rh(PPN)Cl
volume to 2 ml, produced a brown, homogeneous solution whose $^{31}\text{P nmr}$ spectrum showed only free, uncoordinated ligand. Hydrolysis with ethanol did not show the same color change that was observed in the olefin hydrogenation experiment, and the $^{31}\text{P nmr}$ spectrum of the brown solution after hydrolysis showed only two broad sets of resonances at approximately -2 to 8 ppm. The same conditions in both the actual hydrogenation experiment and in this experiment may not have been present, but exact experimental conditions could not be followed by $^{31}\text{P nmr}$ spectroscopy due to the relatively small amount of catalyst present in solution. Even though the species present and the mechanism for olefin hydrogenation is not known at present, a very efficient catalyst was produced for the hydrogenation of terminal olefins using Rh(PPN)Cl, OMH-1, and ethanol. The maximum turnover rate was the same as for Wilkinson's compound under the same experimental conditions.

From the data obtained in the Rh(PPN)Cl olefin hydrogenation experiments, it was found that the olefin did not displace the amine-donor atom. Hard and soft acid-base theory states that nitrogen is a hard-donor atom whereas rhodium(I) can be either hard or soft. To get a better combination, iridium(I), a soft atom, was used so that olefin displacement of the amine might be facilitated through the mismatch between the hard amine and the soft iridium(I) atoms.

The preparation of Ir(PPN)Cl was attempted by reacting $\{\text{Ir(COD)Cl}\}_2$ with two equivalents of PPN. The $^{31}\text{P nmr}$ spectrum showed an AB pattern with $\delta P_1 = -26.8$ ppm (central phosphorus), $\delta P_2 = -11.6$ ppm, and $J_{P-P} = 44.1$ Hz. The $^1\text{H nmr}$ spectrum of this complex showed resonances at $\tau = 2.7$ (phenyl), $\tau = 7.05$ (broad, coordinated COD),
\[ \tau = 2.05 \left(-N(CH_3)_2\right) \text{ and } \tau = 1.8 \left(\text{broad CH}_2\right). \] These results show that the nitrogen is not coordinated and that coordinated COD is present. The elemental analysis obtained corresponds to a complex with the composition Ir(PPN)(COD)Cl. Several structures are consistent with these facts, and at this time the correct structure has not yet been determined. Although it first seemed strange that the ligand PPN did not completely (or partially) displace 1.8-cyclooctadiene, precedent for this replacement has been well-documented in the literature.\(^{139,140}\) Crabtree\(^{140}\) found that a particular iridium complex, \{Ir(COD)(PMePh_2)_2\}_2PF_6, hydrogenated 1-methylcyclohexene at a rate 316 times as rapid as Wilkinson's compound. Although the amine is not displaced by olefin to generate an active catalytic species, an olefin hydrogenation was carried out to investigate how efficiently Ir(PPN)(COD)Cl would hydrogenate olefins. The results are shown in Figure 36. The maximum turnover rate is slightly greater than that for Wilkinson's compound (~5\%), and a G.C. analysis shows that >92\% of the olefin was hydrogenated with small amounts of isomerization occurring. Addition of HBF_4 during olefin hydrogenation led to an inactive species and a precipitate.

An attempt to prepare Ir(PPN)Cl in ethanol led to an Ir(III) complex which analyzes for Ir(PPN)Cl·EtOH. The proton nmr (254°K) shows resonances at \( \tau = 2.55 \) (phenyl), \( \tau = 2.90, 2.84; \tau = 2.41, 2.31 \) (\(-N(CH_3)_2\), \( J_{p-H} = 5.85, 8.79 \text{ Hz} \)), \( \tau = 2.4 \) (broad \( \text{CH}_2 \)), and \( \tau = 21.04, 21.17, 21.22, 21.35 \) (Ir-H, \( J = 16.6 \text{ Hz}, 11.72 \text{ Hz} \)). Two types of methyl peaks are present, and the chemical-shift data show that both
CATALYTIC HYDROGENATION
OF 1-OCTENE USING
Ir(PPN)Cl(COD)*

Figure 36. The Results of the Catalytic Homogeneous Hydrogenation of 1-Octene Using Ir(PPN)Cl(COD)

*G. C. Analysis shows >92% of 1-octene was converted to normal octane.
are bonded. The $^{31}$P$^1$H nmr spectrum gives a clean AB pattern with
$\delta_{P_1} = -24.3$ ppm, $\delta_{P_2} = -13.1$ ppm and $J_{P-P} = 28.6$ Hz. The infrared
spectrum shows an Ir-H stretch at 2270 cm$^{-1}$.

An in situ displacement reaction was attempted using
Rh(PPh$_3$)$_3$NO and PPN to investigate the effect that a chelating amine
would have in displacing PPh$_3$ in this rhodium(I) complex. The $^{31}$P nmr
spectrum showed four phosphorus resonances which are attributed to free
PPh$_3$, coordinated PPh$_3$, and two coordinated phosphine groups from PPN.
Each coordinated phosphine resonance consists of an eight-line pattern
due to coupling with two non-equivalent phosphines and the rhodium
atom. The $^{31}$P nmr parameters are as follows:

\[
\begin{align*}
\delta_{P_1} &= 18.65 \text{ ppm} & J_{\text{Rh-P}_1} &= 159.9 \text{ Hz} & J_{P_1-P_2} &= 51.55 \text{ Hz} \\
\delta_{P_2} &= 30.72 \text{ ppm} & J_{\text{Rh-P}_2} &= 161.1 \text{ Hz} & J_{P_2-P_3} &= 12.2 \text{ Hz} \\
\delta_{P_3} &= 52.40 \text{ ppm} & J_{\text{Rh-P}_3} &= 175.2 \text{ Hz} & J_{P_1-P_3} &= 19.53 \text{ Hz} \\
\delta_{P_4} &= -5.9 \text{ ppm} & & & & \\
\end{align*}
\]

where $P_1$ = the central phosphine in PPN
$P_2$ = the terminal phosphine in PPN
$P_3$ = the coordinated phosphine in PPh$_3$
$P_4$ = the free phosphine in PPh$_3$

Although the chelating phosphines displaced two triphenylphosphines, the
displacement of the third PPh$_3$ by the amine did not occur. Both the
chemical shifts and the coupling constants found in this $^{31}$P nmr spec-
trum are consistent with other data found on similar systems.$^{141}$

Attempts to displace the olefin in Ir(PPN)(COD)Cl with carbon
monoxide did not result in carbon monoxide addition. The infrared
spectrum of the solid resulting after workup showed no carbonyl
absorbances, and the $^{31}P$ nmr spectrum was identical to that of the starting material.

D. Studies of Pt(L)(CH$_3$)$_2$ where L = Bidentate or Tridentate Phosphines

Three platinum(II) dimethyl compounds were prepared to investigate further the exchange that occurs in Pt(Ph$_2$P(CH$_2$)$_3$P(Ph)(CH$_2$)$_2$PPh$_2$)(CH$_3$)$_2$.$^{113}$ Bidentate-phosphine complexes were prepared by adding the ligand to a toluene solution containing Pt(COD)(CH$_3$)$_2$.$^{134}$ 80, and refluxing the resulting solution for several hours. After reducing the volume of the solution and adding hexane, micro-crystalline solids were obtained.

$$\text{Pt(COD)}(\text{CH}_3)_2 + \text{L} \xrightarrow{\Theta \text{CH}_3} \text{Pt(L)}(\text{CH}_3)_2$$

$L = (\text{CH}_3)_2\text{P}($CH$_2$)$_2$PPh$_2$, Ph$_2$P($\text{CH}_2$)$_2$P(Ph)(neo-C$_{10}$H$_{19}$)$^{80}$

Preparation of the eptp complex, Ph$_2$P($\text{CH}_2$)$_2$P(Ph)($\text{CH}_2$)$_3$PPh$_2$, 81, was more difficult due to the possibility of trimer formation.$^{113}$ 82. To circumvent this problem, Pt(eptp)(CH$_3$)$_2$ was prepared using excess ligand. Although attempts to remove this excess ligand have been somewhat successful, a small amount of oxidized ligand or trimer, 82, still remains.
The phosphorus-31 nmr spectra of Pt(Me₂P(CH₂)₂PPh₂)(CH₃)₂, Pt(Ph₂P(CH₂)₂PPh(neo-C₁₀H₁₉)), and the free bidentate ligands used to make these compounds are shown in Figures 37, 38, 39, and 40. For Pt(Me₂P(CH₂)₂PPh₂)(CH₃), two sets of doublets are observed with each doublet having two satellites. The central peaks are the AM portion of an AMX spectrum where A and M are the phosphines, and X represents platinum. The phosphorus-phosphorus coupling constant is 3.6 Hz. The ³¹P nmr spectrum for Ph₂P(CH₂)₂P(Ph)(neo-C₁₀H₁₉), Figure 38, shows that two diastereomers are present in approximately a 1:1 ratio. The Ph₂P- group two carbons away from the chiral phosphine, has its chemical shift affected ~1 ppm depending on the chirality of the phosphine, in contrast to a 4.5 ppm shift difference for the two different chiral phosphines. In the dimethylplatinum(II) complex of this mixture of diastereomers, different chemical shifts are observed for each of the four different phosphorus environments. Each resonance is split further due to phosphorus-phosphorus coupling producing four doublets. Thirty-three percent of the platinum couples with each doublet, whereas 67% of the platinum isotopes do not couple. The final spectrum, as shown in Figure 40, consists of four central doublets—each with a set
Figure 37. The $^{31}\text{P}^1{\text{H}}$ nmr Spectrum of $(\text{CH}_3)_2P(\text{CH}_2)_2\text{PPh}_2$
Figure 38. The $^{31}\text{P}^{'\text{H}}$ nmr Spectrum of $\text{Ph}_2\text{P(CH}_2\text{)}_2\text{P(Ph)}_{\text{neo-C}}_{10}\text{H}_{19}$
Figure 39. The $^{31}$P{$^1$H} nmr Spectrum of Pt{(Ph)$_2$P(CH$_2$)$_2$P(CH$_3$)$_2$}(CH$_3$)$_2$
Figure 40. The $^{31}P\{^1H\}$ nmr Spectrum of Pt{$(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P(Ph)neoC}_{10} \text{H}_{19})\}^1\text{(CH}_3)^2$
Figure 41. The $^{31}\mathrm{P}^{1\mathrm{H}}$ nmr Spectrum of $\text{Ph}_2\text{P(CH}_2\text{)}_2\text{P(Ph) CH}_2\text{)}_3\text{PPh}_2$
of satellites caused by platinum coupling. The two phosphorus-phosphorus coupling constants for the five-member rings are 7.3 and 4.4 Hz. All of the $^{31}P$ nmr spectral parameters are listed in Table 18.

The $^{31}P\{^1H\}$ low-temperature-limiting nmr spectra (263°K) of Pt(eptp)(CH$_3$)$_2$ with and without excess ligand are shown in Figures 42 and 43. These results are consistent with a dangling Ph$_2$P(CH$_2$)$_3$-group (confirmed by its chemical shift) and with formation of a five-member metallocycle ring. The small phosphorus-phosphorus coupling constant of 3.7 Hz corresponds to coupling in a five-member ring. Small coupling is found in the two dimethylplatinum(II) compounds previously discussed and also in other platinum compounds discussed by Baird. This coupling constant information plus the chemical shift data that suggest a dangling Ph$_2$P(CH$_2$)$_3$-group confirm that the five-member chelate ring is more stable than the six-member chelate ring in Pt(eptp)(CH$_3$)$_2$ at 263°K. The $^{31}P\{^1H\}$ nmr spectrum of eptp is shown in Figure 41 for comparison.

As the temperature is increased from 263°K, a broadening of the resonances assigned to the bonded phosphines, of their satellites, and of the unbonded Ph$_2$P- group occurs (Figures 43-47). At 293°K, very broad resonances are observed, and at 303°K, a definite downfield shift for the non-bonded phosphine and an upfield shift for both of the bonded phosphines and their satellites are first noted. At 373°K, the highest temperature used with toluene, resonances for non-bonded and bonded phosphines have sharpened considerably.

If the exchange process for Pt(eptp)(CH$_3$)$_2$ involved either an associative or dissociative mechanism, one would expect, in these
<table>
<thead>
<tr>
<th>Compound</th>
<th>( \delta P_1 ) (ppm)</th>
<th>( \delta P_2 ) (ppm)</th>
<th>( J_{P-P} ) (Hz)</th>
<th>( J_{Pt-P_1} ) (Hz)</th>
<th>( J_{Pt-P_2} ) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ph}_2\text{P(CH}_2\text{)}_2\text{P(Ph)} )</td>
<td>-16.59</td>
<td>-51.52</td>
<td>26.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Ph}_2\text{P(CH}_2\text{)}<em>2\text{P(Ph)(neo-C}^{10}\text{H}</em>{19}) )</td>
<td>-15.68</td>
<td>-21.06</td>
<td>31.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isomer A</td>
<td>-15.68</td>
<td>-21.06</td>
<td>31.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isomer B</td>
<td>-15.83</td>
<td>-25.60</td>
<td>32.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Pt(Ph}_2\text{PCH}_2\text{CH}_2\text{P(Ph)_3(CH}_3\text{)}_2} )</td>
<td>47.19</td>
<td>26.80</td>
<td>3.6</td>
<td>1811.5</td>
<td>1738.3</td>
</tr>
<tr>
<td>Isomer A</td>
<td>48.27</td>
<td>45.1</td>
<td>4.4</td>
<td>1853.5</td>
<td>1723.6</td>
</tr>
<tr>
<td>Isomer B</td>
<td>49.83</td>
<td>43.04</td>
<td>7.3</td>
<td>1859.0</td>
<td>1704.1</td>
</tr>
</tbody>
</table>
Figure 42. The $^{31}\text{P}^{1\text{H}}$ nmr Spectrum of Recrystallized Pt(eptp)(CH$_3$)$_2$ at 263$^\circ$K
Figure 43. The $^{31}\text{P}^{1}\text{H}$ nmr Spectrum of Pt(eptp)(CH$_3$)$_2$ at 263°K ($x$ = impurity)
Figure 44. The $^{31}P^{1}H$ nmr Spectrum of Pt(eptp)(CH$_3$)$_2$ at 283$^\circ$K
($x$ = impurity)
Figure 45. The $^{31}\text{P-}^{1\text{H}}$ nmr Spectrum of Pt(eptp)(CH$_3$)$_2$ at 293°K
($x = \text{impurity}$)
Figure 46. The $^{31}P\left(^1H\right)$ nmr Spectrum of Pt(eptp)(CH$_3$)$_2$ at 303°K
(x = impurity)
Figure 47. The $^{31}\text{P}^{1}\text{H}$ nmr Spectrum of Pt(eptp)(CH$_3$)$_2$ at 373$^\circ$K
($x = \text{impurity}$)
limited, cases, to see the formation of new resonances (probably in the proximity of 0.0 ppm) some of which would retain satellites due to platinum coupling. If the exchange were fast compared to the $^{31}\text{P}$ nmr time scale, the spectrum would be expected to have phosphorus resonances at the weighted-average chemical shift for the two compounds $83$ and $84$. Slow exchange would produce resonances for two distinct compounds.

Since neither of these limiting cases was observed, it was hypothesized that intermolecular exchange with the free ligand might be competing during the exchange process. Several attempts to remove excess ligand by chromatography led to decomposition on the column (silica gel), but the ligand was finally removed by adding small amounts of Pt(COD)(CH$_3$)$_2$ to the original solution until the $^{31}\text{P}$ nmr spectrum showed the absence of ligand resonances. After recrystallizing the solid from diethyl-ether, variable-temperature $^{31}\text{P}$ nmr studies were again run. These new spectra were the same as before except the free ligand resonances were not present. These spectral results eliminated any possibility of free ligand interaction during the exchange process but still do not give an unambiguous interpretation for the exchange process.
Conclusion

From this spectral data, it can be concluded that at lower temperatures, the five-member metallocyclic ring is formed in preference to the six-member ring. Upon increasing the temperature, intramolecular bond-breaking takes place, and exchange begins. The exchange process and mechanism are not fully understood.
REFERENCES


108. R. Fagan, The Ohio State University, Dept. of Chemistry.


124. This ligand was prepared and supported in conjunction with T. J. Mazenec of The Ohio State University.

125. L. Horner, H. Kunz, and P. Walach, Phosphorus, 6, 63 (1975).


