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Synthesis and reactivity of homo- and heterobinuclear iron and ruthenium phosphido-bridged carbonyl complexes

Adams, Michael R., Ph.D.
The Ohio State University, 1990
Synthesis and Reactivity of Homo- and Heterobinuclear Iron and Ruthenium Phosphido-bridged Carbonyl Complexes

DISSERTATION

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

By

Michael R. Adams, B. A.

The Ohio State University

1990

Dissertation Committee:
Dr. Andrew Wojcicki
Dr. Eugene Schram
Dr. Bruce Bursten

Approved by

Dr. Andrew Wojcicki
Department of Chemistry
Dedicated to my sister Michele
and my parents
Acknowledgements

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VITA

September 14, 1961  Born - Presque Isle, Maine
1983  B. A. - Colby College, Waterville, Maine
1983 - 1989  Graduate Teaching Associate, The Ohio State University
             Columbus, Ohio
1987  Graduate Research Associate, The Ohio State University
           Columbus, Ohio
1990  Lecturer, The Ohio State University
           Columbus, Ohio
1990  Lecturer, Otterbein College
           Westerville, Ohio

Field of Study

Major Field: Chemistry, Inorganic and Organometallic
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Table 14: \textsuperscript{31}P{\textsuperscript{1}H} NMR Data for Reactions of Li_2[(CO)_3Fe(\mu-\text{PPh}_2)_2 Ru(CO)_3] with Alkyl iodides (R_I)
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<table>
<thead>
<tr>
<th>Abbreviation (Substituent)</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>Me</td>
<td>-CH₃</td>
</tr>
<tr>
<td>Et</td>
<td>-CH₂CH₃</td>
</tr>
<tr>
<td>α-Bu</td>
<td>-CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>t-Bu</td>
<td>-C(CH₃)₃</td>
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<td>s</td>
<td>strong (IR absorption intensities)</td>
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</tr>
<tr>
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<td>singlet (NMR data)</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>tr</td>
<td>triplet</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
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</table>
I. INTRODUCTION

A. General

The increasing importance of catalysis in the industrial world has led to a vast expansion\(^1\) of the study of polynuclear transition metal complexes in recent years. Many studies have centered on synthesis of new transition-metal clusters\(^2\) and examinations of reactions occurring at metal centers\(^3\) in these clusters. The rationale for these studies is that metal clusters, acting as homogeneous catalysts, can mimic transformations which take place at metal surfaces in heterogeneous catalyst systems.\(^4\) An example of this analogy is depicted in Figure 1.

![Diagram](image)

Figure 1

Information gained from these studies not only leads to the development of new
catalyst systems but provides a clearer understanding of known systems.

From a synthetic standpoint much of the recent work has focused on the specific design of cluster complexes. Binuclear transition metal complexes serve as a logical starting point for many of these designed syntheses. It is therefore necessary to develop syntheses of new binuclear complexes, and much of the work reported here will address this area. Moreover, studies of the reactivity of binuclear transition metal complexes can provide insight into the behavior of complexes of higher nuclearity.

An important consideration in the study of bimetallic complexes is obviously the role that metal-metal interaction plays in both the structure of the compound and its reactivity. The metal-metal bond can act to occupy a coordination site and provide electrons to a metal, thus stabilizing a particular complex, as in dimanganese decacarbonyl, shown in Figure 2. In this compound both metals display octahedral geometry and obey the effective atomic number rule.

![Figure 2](image)

Examples are also known of metals behaving as ligands via metal-metal bonding to dictate reactivity as shown in Equation 1 where one metal first acts
as an appropriately labile ligand to allow migration of H and then as the "incoming ligand", compensating for the reductive elimination of -PPh₂H.

\[ \begin{align*} 
\text{Ph}_2\text{P} & \quad \text{PPh}_2^- \\
\text{(CO)}_3\text{Fe} & \quad \text{Fe(CO)}_2 \\
\text{CHO} & \quad \rightarrow \\
\text{(CO)}_3\text{Fe} & \quad \text{Fe(CO)}_3 \\
\text{PPh}_2 & \quad \rightarrow \\
\text{Ph}_2\text{P} & \quad \text{CO}^- \\
\text{(CO)}_2\text{Fe} & \quad \text{Fe(CO)}_3 \\
\text{PPh}_2\text{H} & 
\end{align*} \]

(1)

B. Phosphido--Bridged Binuclear Complexes

A frequently encountered problem in reactivity studies of polynuclear systems is fragmentation of the metallic framework.¹⁴ A simplest case of this is the fragmentation of Mn₂(CO)₁₀ upon treatment with sodium as shown in equation 2.⁴³

\[ \text{(CO)}_5\text{Mn} \cdots \text{Mn(CO)}_5 + \text{Na} \rightarrow 2 \text{Na[Mn(CO)}_5] \]  (2)
It is thus desirable to keep the metals in close proximity throughout the course of reactions by using an appropriate bridging ligand. The diorganophosphido ligand, Figure 3, has been used extensively for this purpose.

![Figure 3](image)

It is generally resistant to disruption although exceptions are known. This versatile bridging ligand can be thought of as a neutral, three electron donor contributing one electron to one metal and two to the other as shown in Figure 4, and can bridge two metals in the presence or absence of metal-metal bonding.

![Figure 4](image)

The organo substituents on phosphorus can be widely varied and some studies have focused on effects of these substituents on structure and reactivity of binuclear complexes.

Much of the pioneering work concerning phosphido-bridged binuclear systems involved homobinuclear complexes. In the ensuing years
the family of homobinuclear complexes has grown to include many of the transition metals. A number of these complexes are shown in Table 1.

Table 1: Some Known Homobinuclear Phosphido--Bridged Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>ref.</th>
<th>Compound</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂(CO)₆(μ-PPh₂)₂</td>
<td>16</td>
<td>Cr₂(CO)₈(μ-PMe₂)₂</td>
<td>19</td>
</tr>
<tr>
<td>Ru₂(CO)₆(μ-PPh₂)₂</td>
<td>17</td>
<td>Mo₂(CO)₈(μ-PPh₂)₂</td>
<td>19</td>
</tr>
<tr>
<td>Os₂(CO)₆(μ-PPh₂)₂</td>
<td>18</td>
<td>W₂(CO)₈(μ-PPh₂)₂</td>
<td>19</td>
</tr>
<tr>
<td>Cp₄Ti₂(μ-PEt₂)₂</td>
<td>18c</td>
<td>Cp₂Co₂(μ-PPh₂)₂</td>
<td>21</td>
</tr>
<tr>
<td>Cp₄Zr₂(μ-PEt₂)₂</td>
<td>18c</td>
<td>Cp₂₂Rh₂(μ-PMe₂)₂</td>
<td>23</td>
</tr>
<tr>
<td>Cp₄Hf₂(μ-PEt₂)₂</td>
<td>18c</td>
<td>Ir₂(CO)₄(μ-P-t-Bu₂)₂</td>
<td>18b</td>
</tr>
<tr>
<td>Fe₂(CO)₆(μ-PPh₂)₂(μ-Cl)</td>
<td>20</td>
<td>Ni₂(CO)₃(μ-P-t-Bu₂)₂</td>
<td>25</td>
</tr>
</tbody>
</table>

It should be noted that the number of phosphido bridges contained in a particular compound can also vary, and the presence of multiple phosphido bridges can lend added stability to a compound.¹³ A particularly well-studied class of these compounds are the diiron carbonyl complexes, Fe₂(CO)₆(μ-PR₂)₂, in particular the diphenylphosphido analogue, Fe₂(CO)₆(μ-PPh₂)₂.²⁶,³¹,³² Much of the research reported herein will involve extensions of the studies of this and related compounds.

More recent synthetic work has been geared toward development of heterobinuclear phophido-bridged complexes, several examples of which are shown in Table 2.
Table 2: Some Known Heterobinuclear Phosphido-Bridged Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>ref.</th>
<th>Complex</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrMo(CO)$_6$(μ-PMe$_2$)$_2$</td>
<td>19</td>
<td>Cp$_2$Zr(μ-PPh$_2$)Fe(CO)$_4$</td>
<td>18c</td>
</tr>
<tr>
<td>CrW(CO)$_6$(μ-PMe$_2$)$_2$</td>
<td>19</td>
<td>Cp$_2$Ti(μ-PPh$_2$)$_2$W(CO)$_4$</td>
<td>18c</td>
</tr>
<tr>
<td>MoW(CO)$_6$(μ-PMe$_2$)$_2$</td>
<td>19</td>
<td>WOs(CO)$_7$(μ-PPh$_2$)$_2$</td>
<td>28</td>
</tr>
<tr>
<td>FeOs(CO)$_6$(μ-PPh$_2$)$_2$</td>
<td>24</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The presence of two distinct metal centers allows for flexibility in the reactivity of these complexes. Studies of reactivity, in terms of site selectivity, have been carried out$^{27}$ for a number of these compounds. In some cases reactions which are known for homobinuclear complexes are found to occur preferentially at one metal center$^{27a}$ in related heterobinuclear complexes, while in other cases these heterobinuclear complexes will undergo reactions$^{27b}$ not known at all for their homobinuclear counterparts. Equations 3$^{22a}$ and 4$^{27b}$ illustrate both of these points.

\[
\begin{align*}
(CO)_4\text{Fe}(\mu\text{-PPh}_2)\text{Co}(CO)_3 + \text{PPh}_3 & \rightarrow (CO)_4\text{Fe}(\mu\text{-PPh}_2)\text{Co}(CO)_2\text{PPh}_3 \\
\text{(3)} \\
(CO)_4\text{Ru}(\mu\text{-PPh}_2)\text{Co}(CO)_3 + \text{NaBH}_4 & \rightarrow (CO)_4\text{HRu}(\mu\text{-PPh}_2)\text{Co}(CO)_3^- \\
\text{(4)}
\end{align*}
\]

Again, one of the broad objectives of these studies is the application to cluster synthesis. The ability to selectively vary one metal in a polynuclear complex.
can assist in fine-tuning that complex to meet one's particular needs. This alteration could not only dictate the site of reactivity in a particular cluster but also enhance certain reactivity properties in general.

C. Synthetic Aspects

When beginning a study of phosphido-bridged bimetallic complexes a first consideration must be how to synthesize these particular compounds. A wide variety of synthetic routes to phosphido-bridged complexes have been developed over the years. Original syntheses of homobinuclear phosphido-bridged complexes, developed by Hayter\textsuperscript{29} and Thompson\textsuperscript{16}, among others, involve reactions of metal compounds, often carbonyls, with tetraalkyl- or tetraaryldiphosphines (e.g. Equation 5).\textsuperscript{29}

\[
\text{Fe(CO)}_5 + R_2\text{PPR}_2 \xrightarrow{\text{Ethylcyclohexane}} (\text{CO})_3\text{Fe(μ-PR}_2\text{)}_2\text{Fe(CO)}_3
\]

\[R = \text{Me, Ph}^{29}\text{, Ph}^{16}\]

Variations of this method are still widely employed, as in equation 6,\textsuperscript{30} although numerous better syntheses are now available for several of these compounds.

\[
2\text{Cp}_2\text{MCl}_2 + \text{Mg} + \text{Me}_2\text{PPMe}_2 \xrightarrow{\text{THF}} \text{CpM(μ-PMe}_2\text{)}_2\text{MCp} \quad M = \text{Zr, Hf}
\]

In particular, reactions of diorganohalophosphines with appropriate anionic metal complexes (Equations 7\textsuperscript{31} and 8\textsuperscript{33}) have proved quite successful.

\[
\text{Na}_2\text{Fe}_2(\text{CO})_8 + \text{PPh}_2\text{Cl} \xrightarrow{\text{THF}} (\text{CO})_3\text{Fe(μ-PPh}_2\text{)}_2\text{Fe(CO)}_3
\]

\[\text{R} = \text{Me, Ph}^{29}\text{, Ph}^{16}\]
Conversely, the reaction of an anionic diorganophosphide, obtained by deprotonation of a secondary phosphine, with a halogen-bearing metal species can also be employed successfully as shown in Equation 9.34

\[
\text{Fe}_2\text{NO}_4(\mu-X)_2 + 2\text{MPPh}_2 \xrightarrow{\text{THF}} \text{Fe}_2\text{NO}_4(\mu-\text{PPh}_2)
\]

\[X = \text{Cl}, \text{Br}, \text{I} \quad M = \text{Li}, \text{K}\]

These reactions are similar in that the driving force is the elimination of simple inorganic salts as side products. One advantage that these salt elimination methods afford over other general methods is that the nuclearity of the final product is often better controlled, i.e. higher nuclearity complexes as side products are often avoided.35

Only two of the general synthetic methods available have been discussed but both have been used extensively. A few examples of less common methods are illustrated in Equations 10-12.36-38

\[
\text{CoCl}_2\cdot\text{H}_2\text{O} + \text{PPh}_2\text{H} + \text{NaOMe} + \text{CO} \xrightarrow{\text{MeOH}} (\text{PPh}_2\text{H})(\text{CO})_2\text{Co} \xrightarrow{} \text{Co}(\text{CO})_2(\text{PPh}_2\text{H})
\]

(10)37
Many of the syntheses described thus far involve homobinuclear metal complexes as starting compounds. These methods, therefore, become less attractive when a heterobinuclear phosphido-bridged complex is the target, as there are not as many conveniently available heterobinuclear starting complexes. It is thus necessary to employ a method which not only introduces phosphido bridging ligands into a complex but also brings the two metal together. The so-called "bridge-assisted" method, usually involving salt elimination, is by far the most extensively used for this purpose. The procedure usually involves the reaction of a phosphido-bearing metal species with an appropriate halogen-containing metal complex. Several examples of this process are shown in Equations 13-15. Relatively high yields and good purity of products are often obtained from these reactions.
D. Reactions of Phosphido-bridged Complexes

As pointed out earlier, one reason for using phosphido-bridging ligands is to keep two metal centers in close proximity throughout the course of a reaction. In equation 2 a simple binuclear metal carbonyl was seen to fragment upon treatment with sodium. Equations 16\textsuperscript{32} and 17\textsuperscript{44} demonstrate the stabilizing effect of phosphido bridging ligands. In both cases, although bonding between the two metals is disrupted, the binuclear nature of the complex remains intact.
This allows further chemistry of the binuclear complexes to be carried out (equation 18).\(^\text{32}\)

By no means is this meant to imply that diorganophosphido bridges are completely resistant to reaction or disruption, however. Numerous cases of
reactivity of phosphido-bridging ligands, in which a phosphorus-metal bond is cleaved, have been reported in the literature. Equation 19\(^4\) is an example of this behavior.

\[
\begin{align*}
\text{(CO)}_4\text{Ru} & \hspace{1cm} \text{Co(CO)}_3 + \text{PhC} & \equiv & \text{CPh} \xrightarrow{\text{THF} \Delta} \text{(CO)}_3\text{Ru} \hspace{1cm} \text{Co(CO)}_2
\end{align*}
\]

(19)

The reaction shown in equation 21\(^4\) also involves cleavage of a phosphorus-metal bond. In this case the presence of two phosphido bridges allows disruption of one to take place while the other serves to maintain the integrity of the binuclear complex.

\[
\begin{align*}
\text{(CO)}_4\text{W} & \hspace{1cm} \text{RhH(CO)PPh}_3 + \text{H}_2\text{C} & \equiv & \text{CH}_2 \xrightarrow{} \text{(CO)}_4\text{W} \hspace{1cm} \text{Rh} \hspace{1cm} \text{CO} \hspace{1cm} \text{PPh}_2\text{Et}
\end{align*}
\]

(21)

Kyba, et. al., have also observed this behavior in the reactivity of the 1,2-phenylene-linked diphosphido complex depicted in equation 22\(^1\)\(^2\)

\[
\begin{align*}
\text{Ph} & \hspace{1cm} \text{Fe(CO)}_3 + \text{RLi} \xrightarrow{} \text{Ph} \hspace{1cm} \text{Fe(CO)}_3
\end{align*}
\]

(22)
There are also known cases of bridging phosphido ligands being involved in reactions but remaining in bridging positions as shown in equation 23.49

\[
\begin{align*}
\text{PhHP} & \quad \text{PPhH} \\
(CO)_3\text{Fe} & \quad \text{Fe(CO)}_3 + H_2\text{O} =\text{CHCO}_2\text{CH}_3 \quad \rightarrow (CO)_3\text{Fe} & \quad \text{Fe(CO)}_3 \\
\end{align*}
\]

(23)

The importance of phosphido-bridged bimetallic complexes as applied to catalysis has been demonstrated by Gelmani and Stephens50 who investigated the involvement of Cp₂Zr(μ-PPh₂)₂RhH(CO)(PPh₃) in the hydroformylation of 1-hexene. The absence of isomerization of the organic product, n-heptanal, to 2-methylhexanal is attributed by the authors to the chelating nature of the metalladiphosphide ligand on rhodium. This result contrasts that of the same reaction catalyzed by the mononuclear complex RhH(CO)(PPh₃)_3 where extensive isomerization is observed.51

E. Phosphorus-31 NMR

A convenient advantage in studying phosphido-bridged complexes versus other complexes is the availability of ³¹P NMR spectroscopy. The phosphorus-31 nucleus, with a nuclear spin of 1/2, occurs in 100% abundance and is thus observed by NMR quite easily. Not only does this assist in characterization of new compounds containing phosphido ligands, but it also allows the progress of a number of reactions of phosphido-bridged complexes
to be conveniently monitored. A full review of $^{31}$P NMR as it relates to phosphido-bridged complexes has been written by Carty, et al.\textsuperscript{18}

The chemical shift for a phosphorus bridging ligand can provide a wealth of information regarding the nature of the ligand. It has been shown\textsuperscript{18} that chemical shifts for phosphido ligands bridging two metals are often highly sensitive to the presence or absence of bonding interactions between the metals. In general the absence of a metal-metal bond in a particular complex results in a considerable upfield shift of the $^{31}$P NMR signal compared to a metal-metal bonded analogue. Several examples of this phenomenon are seen in Table 3.

Table 3. $^{31}$P Shifts for Metal-Metal Bonded Phosphido-bridged Complexes and Their Non-bonded Analogues.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$</th>
<th>Compound</th>
<th>$\delta$</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$(CO)$_6$(μ-PPh$_2$)$_2$</td>
<td>142.8</td>
<td>Na$_2$[Fe$_2$(CO)$_6$(μ-PPh$_2$)$_2$]</td>
<td>-60.0</td>
<td>32</td>
</tr>
<tr>
<td>W$_2$(CO)$_8$(μ-PPh$_2$)$_2$</td>
<td>180.9</td>
<td>Li$_2$[W$_2$(CO)$_8$(μ-PPh$_2$)$_2$]</td>
<td>-98.0</td>
<td>52</td>
</tr>
</tbody>
</table>

It should be noted that there are exceptions to this rule as evidenced by the last pair of compounds\textsuperscript{53} in Table 3.
Observed $^{31}$P chemical shifts for phosphido bridges are also dependent on the metals involved. For analogous homobinuclear complexes within a particular metal triad, a decrease in chemical shift is usually observed as atomic number of the metal increases. The two sets of data in Table 4 illustrate this point.

Table 4. Comparison of Phosphorus-31 NMR Shifts for Related Homobinuclear Complexes within the Same Triad.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$</th>
<th>ref</th>
<th>Compound</th>
<th>$\delta$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$(CO)$_6$((\mu)-PPh$_2$)$_2$</td>
<td>142.8</td>
<td>16</td>
<td>Cr$_2$(CO)$_6$((\mu)-PMe)$_2$</td>
<td>248.4</td>
<td>19</td>
</tr>
<tr>
<td>Ru$_2$(CO)$_6$((\mu)-PPh)$_2$</td>
<td>110.0</td>
<td>17</td>
<td>Mo$_2$(CO)$_6$((\mu)-PMe)$_2$</td>
<td>192.8</td>
<td>19</td>
</tr>
<tr>
<td>Os$_2$(CO)$_6$((\mu)-PPh)$_2$</td>
<td>14.5</td>
<td>18</td>
<td>W$_2$(CO)$_6$((\mu)-PMe)$_2$</td>
<td>133.7</td>
<td>19</td>
</tr>
</tbody>
</table>

The same effect is seen within a series of heterobinuclear complexes when one of the metals is varied (Table 5).

Table 5. Comparison of Phosphorus-31 NMR Data for the Complexes (CO)$_4$M(\(\mu\)-PMe)$_2$Fe(CO)$_3$ where M = Cr, Mo, W.

<table>
<thead>
<tr>
<th>M</th>
<th>$\delta$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>215.1</td>
<td>19</td>
</tr>
<tr>
<td>Mo</td>
<td>179.6</td>
<td>19</td>
</tr>
<tr>
<td>W</td>
<td>152.0</td>
<td>19</td>
</tr>
</tbody>
</table>

A third influence on chemical shift is that of the organo substituents on phosphorus. Some of the most dramatic effects are seen in complexes containing bridging di-$t$-butylphosphido ligands. Chemical shifts for these
ligands are generally far downfield (about 150 ppm)\textsuperscript{18} compared to dimethyl and diphenyl analogues. A downfield shift would be expected owing to the considerable electron-donating ability of the \textit{i}-butyl groups, an effect which is observed in the simple diphosphines \(\text{Ph}_2\text{PPh}_2\) (\(\delta = -15\)), \(\text{Me}_2\text{PPMe}_2\) (\(\delta = -59\)), and \(\text{^tBu}_2\text{PPh}_2\) (\(\delta = +40\)).\textsuperscript{54} Undoubtedly the size of the di-\textit{i}-butyl phosphido ligand leads to unusual geometries for many of these complexes which in turn can contribute to the considerable lowfield chemical shifts that are observed.

An equally important effect on the \(^{31}\text{P}\) chemical shift is that of the attendant ligands on the metals. Additionally, the disposition of these ligands will affect the overall pattern of the \(^{31}\text{P}\) NMR spectrum. This is best explained by considering the structures shown in Figure 5.\textsuperscript{26}

![Figure 5](image)

In complex A the hydride ligand is \textit{cis} to both phosphido ligands. Thus the phosphorus nuclei are equivalent and only a single resonance is observed in the \(^{31}\text{P}\) NMR spectrum. This signal appears upfield at -60.0 ppm owing to the absence of metal-metal bonding. On the other hand, the \(^{31}\text{P}\) NMR spectrum of complex B consists of two doublets, 159.6 ppm and 130.2 ppm, with an observed phosphorus-phosphorus coupling of 98 Hz. The formyl ligand must
be cis to one phosphorus and trans to the other to cause this observed inequivalence.

A combination of $^{31}$P NMR data with other spectroscopic data (e.g., infrared, $^{13}$C NMR, $^1$H NMR) can therefore lead to many conclusions concerning composition and structure of phosphido-bridged binuclear complexes. These methods are used extensively throughout the research reported here.

F. Goals

Complexes of the type $M_2L_x(\mu-PR_2)_2$ and their derivatives involve three variables. Direct comparisons of compounds where the attendant ligands, L, are varied have been carried out previously$^{31}$ and will not be considered extensively in this work. Variation of the organo substituents on the phosphido bridges involves two aspects: the electronic effects of the substituents and the steric effects. A portion of the research described herein involves the comparison of two compounds, $Fe_2(CO)_6(\mu-PPh_2)_2$ and $Fe_2(CO)_6[\mu-P(C_6H_4CF_3-2)_2]_2$, in which the organo substituents are sterically similar but should be electronically different. The focus of this study is on what effect, if any, the organo groups will have on the stabilities of anionic derivatives of these compounds.

A second aspect of this work also involves the organo substituents on the phosphido bridging ligands. Synthetic studies aimed at the development of complexes $Fe_2(CO)_6(\mu-PR_2)(\mu-PR'_2)$, bearing distinctly different phosphido bridges, are described and new complexes containing bridging di-1-butyl
phosphido ligands are reported. Problems concerning the steric effects of these ligands will be discussed.

The metals involved in these complexes are the third variable. The known compounds $\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)_2$ and $\text{Ru}_2(\text{CO})_6(\mu-\text{PPh}_2)_2$, and the new mixed-metal analogue $\text{FeRu}(\text{CO})_6(\mu-\text{PPh}_2)_2$ have been synthesized, and the effects on reactivity of varying the metals are described.
II. EXPERIMENTAL

A. Reagents and Chemicals

All chemicals used in this research were of reagent grade quality. Unless otherwise stated, chemicals were used as purchased or received without further purification.

Deuterated NMR solvents, including chloroform-d (CDCl₃), methylene chloride-d₂ (CD₂Cl₂), acetone-d₆ (CD₃COCD₃), and tetrahydrofuran-d₈ (THF-d₈), were purchased from Aldrich Chemical Co., Milwaukee, WI. Aldrich also supplied lithium triethylborohydride (Superhydride, supplied as a 1.0 M solution in THF), n-butyllithium (1.6 M solution in hexanes), methyl iodide-d₃ (CD₃I), allyl iodide (CH₂=CHCH₂I), sodium trimethoxyborohydride [NaB(OCH₃)₃H], benzyl iodide (C₆H₅CH₂I), n-butyl iodide (n-C₄H₉I), 1,3-diiodopropane (ICH₂CH₂CH₂I), methyl-p-toluenesulfonate (p-CH₃C₆H₄SO₃CH₃), trifluoroacetic acid (CF₃COOH), trifluoroacetic acid-d (CF₃COOD), and activated neutral alumina (Al₂O₃).
Florisil (activated magnesium silicate) and ethyl iodide (CH$_3$CH$_2$I) were obtained from Fisher Scientific Co., Fair Lawn, NJ. Sodium dispersion (40% in mineral oil), diethylaminodichlorophosphine [P(NEt$_2$)Cl$_2$] and trimethyloxonium tetrafluoroborate [(CH$_3$)$_3$OBF$_4$], were purchased from Alfa Chemical Co., Danvers, MA.

Strem Chemical Co., Newburyport, MA, was the supplier of iron pentacarbonyl [Fe(CO)$_5$], ruthenium trichloride (RuCl$_3$.nH$_2$O), diphosphine (PPh$_2$H), diphenylchlorophosphine (PPh$_2$Cl), diethylchlorophosphine (PEt$_2$Cl), and di-t-butylchlorophosphine (PtBu$_2$Cl).

Baker Chemical Co., Phillipsburg, NJ, supplied methyl iodide (CH$_3$I), and Columbia Organic Chemicals Co., Camden, SC, provided triethyloxonium hexafluorophosphate [(CH$_3$CH$_2$)$_3$OPF$_6$]. Diiodomethane (CH$_2$I$_2$) and 4-bromobenzotrifluoride (BrC$_6$H$_4$CF$_3$-2) were purchased from Sigma Chemical Co., St. Louis, MO.

Solvents were supplied by Mallinckrodt Chemical Co., St. Louis, MO., and purified according to methods described by Perrin, Amarego, and Perrin.55

B. Instrumentation

Infrared spectra were recorded on a Perkin-Elmer Model 283-B spectrophotometer and were calibrated using a polystyrene film. Solution spectra were obtained using matched sodium chloride cells (0.2 mm path length) whereas those of solid samples were taken as Nujol mulls between potassium bromide plates.
Proton and fluorine-19 nuclear magnetic resonance spectra were obtained on a Bruker AM-250 spectrometer with operating frequencies of 250.133 MHz and 235.36 MHz, respectively. Phosphorus-31 NMR spectra were recorded using a Bruker HX-90 spectrometer operating at 36.43 MHz or a Bruker AM-250 spectrometer operating at 101.256 MHz. Carbon-13 NMR spectra were obtained using a Bruker AM-250 spectrometer operating at 62.896 MHz or a Bruker AM-500 spectrometer with an operating frequency of 125.70 MHz. Deuterium NMR spectra were recorded by Dr. Charles Cottrell using a Bruker AM-500 spectrometer operating at 76.75 MHz. Values of phosphorus-31 chemical shifts are reported relative to 85% H₃PO₄ at 0.0 ppm. Fluorine-19 chemical shifts are relative to CFCI₃ at 0.0 ppm. Signals for deuterated solvents (carbon and residual proton) were used as internal standards for proton and carbon-13 spectra.

Elemental analyses (carbon and hydrogen) were performed by Galbraith Laboratories, Knoxville, TN, or M-H-W Laboratories, Phoenix, AZ. Samples were combusted in the presence of V₂O₅.

Mass spectra were obtained by Dr. David Chang and Mr. C. R. Weisenberger on a Kratos MS-30 or VG70-250-S mass spectrometer using either the Fast Atom Bombardment (FAB) or Electron Impact (EI) techniques. Melting points were determined by using a Thomas-Hoover melting point apparatus and are uncorrected.

Cyclic voltammograms were recorded using a hanging mercury-drop electrode as the working electrode. The electrode was constructed by imbedding a platinum wire in a glass rod, sanding the wire until it was flush with the glass surface and touching the clean end to a pre-formed mercury drop (Figure 6).
C. Experimental Procedures

Standard Schlenk techniques were employed for the handling of all oxygen- and moisture-sensitive compounds.\textsuperscript{56,57} Unless otherwise specified, reactions were carried out in an atmosphere of argon purified by passage through phosphorus(V) oxide and Chemical Dynamics Catalyst R3-11 oxygen scavenger. Syringes flushed with argon and stainless steel double-tipped
needles were used for transfers of solutions. When necessary, some reactions and manipulations of air-sensitive materials were carried out under nitrogen in a Vacuum Atmospheres HE43 drybox equipped with an MO-40 Dri-train purification system.

D. Preparations of Known Compounds

Tricarbonyldichlororuthenium(II) dimer was prepared by refluxing a solution of ruthenium trichloride in formic acid and hydrochloric acid. To purify the product recrystallization was carried out by treating a hot 1,2-dichloroethane solution with cold hexane.

Synthesis of tricarbonylbis(diphenylphosphine)iron involved photolysis of a hexane solution of iron pentacarbonyl and diphenylphosphine. While in some cases a 450 watt Hanovia medium-pressure mercury arc lamp was used, a simpler process involved carrying out the reaction in a quartz tube and photolyzing in a Rayonet photochemical reactor with 300-nm lamps.

Bis(α,α,α-trifluorotolyl)chlorophosphine, [P(C₆H₄CF₃-p)₂Cl], was produced by a literature method with the exception that the intermediate product, P(C₆H₄CF₃-p)₂N(CH₂CH₃)₂, was used without further purification by distillation. Hexacarbonylbis(diphenylphosphido)diiron was prepared according to the literature as was tetraphenylidiphosphine. Trirutheniumdodecacarbonyl, [Ru₃(CO)₁₂], was prepared by reaction of RuCl₃·nH₂O with carbon monoxide (750 psi) in methanol.
E. Preparation of Fe₂(CO)₆[µ-P(C₆H₄CF₃-O)₂]₂

A red slurry of Na₂Fe₂(CO)₈ was prepared by adding Fe(CO)₅ (5.25 ml, 39.4 mmole) dropwise to a stirred mixture of Na pieces (1.00 g, 41.7 mmole) and THF (100 ml) and stirring for 16 hours. To this slurry P(C₆H₄CF₃-O)₂Cl (14.50 g, 40.7 mmole) was added dropwise over a period of one hour. Evolution of carbon monoxide was observed and the solution gradually became a darker red color as stirring was continued for 20 hours. Solvent was removed under reduced pressure to leave a dark brown tar.

The remaining manipulations were carried out in air. A small amount of pentane (10 ml) was used to wash an oily red substance from the mixture (Note: The red oil was isolated but only partially characterized.). The now crumbly brown material was loaded on a 40 cm. x 4 cm. Grade III alumina column. Elution with a 5% diethyl ether / 95% pentane mixture moved a large, bright yellow band down the column. This band was collected and the solvent was removed by rotary evaporation leaving a bright yellow powder. This powder was washed with a minimum amount of pentane to remove trace amounts of the red oil, and the final product was collected on a frit. An additional amount of the yellow product was isolated by concentration of the pentane washings, cooling to -78 °C, and filtration to collect the resulting yellow precipitate. The compound was formulated as (CO)₃Fe[µ-P(C₆H₄CF₃-O)₂]₂Fe(CO)₃. Total yield = 7.44 grams (41%).

<table>
<thead>
<tr>
<th>Melting Point</th>
<th>265 °C</th>
</tr>
</thead>
</table>

³¹P¹H NMR (CDCl₃, 20 °C) δ 136.8 s
**1H NMR (CDCl₃, 20 °C) δ**

6.9-7.6 m

**19F NMR (CDCl₃, 20 °C) δ**

-64.2 s, -64.7 s

**IR (cyclohexane) v(CO), cm⁻¹**

2058 s, 2020 s, 1999 s, 1980 s, 1972 m

**Elemental Analysis**

<table>
<thead>
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<th></th>
<th>Calculated</th>
<th>Found</th>
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<tbody>
<tr>
<td>%C</td>
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<td>43.92</td>
</tr>
<tr>
<td>%H</td>
<td>1.75</td>
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</tr>
</tbody>
</table>

**F. Reactions of Fe₂(CO)₆[µ-P(C₆H₄CF₃-η₂)]₂**

1. Reaction With One Equivalent of LiBEt₃H

A solution of Fe₂(CO)₆[µ-P(C₆H₄CF₃-η₂)]₂ (100 mg., 0.11 mmole) in THF (2 ml) was prepared under argon. To this yellow solution 0.11 ml of 1.0 M LiBEt₃H in THF (0.11 mmole, 1.0 eq.) was added via syringe. The solution changed color from yellow to red. A sample of the solution was transferred under argon to a 10 mm NMR tube for spectroscopic analysis. Formation of Li[(CO)₃Fe[µ-P(C₆H₄CF₃-η₂)](µ-CO)Fe(CO)₂P(C₆H₄CF₃-η₂)₂H] was inferred from the spectroscopic data. No attempts were made to isolate a solid product from this reaction.

**31P{1H} NMR (THF, 20 °C) δ**

120.8 d, 51.0 d, ²Jp,p = 13.0 Hz
31P NMR (THF, 20 °C) δ

120.8 br. s,

50.9 d, 1Jp,H = 337 Hz

2. Reaction With Two Equivalents of LiBEt₃H

A similar reaction was carried out using 100 mg. of Fe₂(CO)₆[μ-
P(C₆H₄CF₃-p)₂]₂ (0.11 mmole), 2 ml THF, and two equivalents of 1.0 M LiBEt₃H (0.22 ml, 0.22 mmole). The yellow solution immediately turned dark red. Quantitative formation of Li₂[Fe₂(CO)₆[μ-P(C₆H₄CF₃-p)₂]₂], lacking a metal-metal bond, was inferred from 31P NMR spectral data.

31P{1H} NMR (THF, 20 °C) δ

-56.7 s

3. Reaction With Sodium

A 1% sodium amalgam was prepared in a Schlenk tube by adding sodium pieces (0.40 g) to 3 ml of mercury. The amalgam formed in this manner was covered with 10 ml of THF. In a separate vessel, a solution of Fe₂(CO)₆[μ-
P(C₆H₄CF₃-p)₂]₂ (0.25 g, 0.27 mmole) in THF (4 ml) was prepared and added to the amalgam. An immediate color change from yellow to dark red was observed. The solution was stirred for two hours and allowed to settle. A sample of the solution was transferred to an NMR tube for 31P NMR spectral analysis and an infrared spectrum of the solution, under argon, was also recorded. The product was formulated as Na₂[Fe₂(CO)₆[μ-P(C₆H₄CF₃-p)₂]₂]. No attempts were made to isolate a solid product from this reaction mixture.
\[
^{31}P\{^{1}H\} \text{NMR (THF, 20 °C)} \delta -55.01 \text{ s}
\]

IR (THF) \nu_{CO}, \text{cm}^{-1} 1942 \text{ m}, 1917 \text{ s}, 1856 \text{ s}, 1806 \text{ s}

G. Reactions of Anionic Derivatives of

\[\text{Fe}_2(\text{CO})_6[\mu-P(\text{C}_6\text{H}_4\text{CF}_3-\text{p})_2]_2.\]

1. Reaction of \( \text{Li}((\text{CO})_3\text{Fe}[\mu-P(\text{C}_6\text{H}_4\text{CF}_3-\text{p})_2]\)(\mu-\text{CO})\text{Fe}(\text{CO})_2P(\text{C}_6\text{H}_4\text{CF}_3-\text{p})_2H \) with \( \text{n-Butyllithium: Variable Temperature NMR Study.} \)

In a drybox a solution of \( \text{Fe}_2(\text{CO})_6[\mu-P(\text{C}_6\text{H}_4\text{CF}_3-\text{p})_2]_2 \) (100 mg, 0.11 mmole) in THF (2 ml) was prepared in a 10 mm NMR tube. A bar magnet was placed in the tube and 1.0 M \( \text{LiBEt}_3\text{H} \) in THF (0.11 ml, 0.11 mmole, 1.0 eq.) was added to form a red solution of \( \text{Li}((\text{CO})_3\text{Fe}[\mu-P(\text{C}_6\text{H}_4\text{CF}_3-\text{p})_2]\)(\mu-\text{CO})\text{Fe}(\text{CO})_2P(\text{C}_6\text{H}_4\text{CF}_3-\text{p})_2H \). The NMR tube and a coaxial insert (containing \( \text{D}_2\text{O} \) and \( (\text{Me}_3\text{O})_3\text{PO} \)) were placed in a large Schlenk tube which was then capped and removed from the drybox. Freshly distilled THF was added to the Schlenk tube to a level above those in the NMR tube and insert, and the entire apparatus was cooled to -78 °C (Figure 7).
Figure 7

- Serum cap
- Argon inlet
- 10 mm NMR tube
- Coaxial insert
- THF
- Dry ice/isopropyl alcohol
To the red solution, 1.6 M n-BuLi in hexanes (0.067 ml, 0.11 mmole, 1.0 eq.) was added causing a color change to purple. Keeping the purple solution cold, the magnet was removed and the insert placed in the NMR tube which was then removed from the Schlenk tube and placed in a Dry Ice/isopropyl alcohol bath. At -78 °C one product was observed in the $^{31}$P $^{1}$H NMR spectrum and is formulated as Li$_2$((CO)$_3$Fe[$\mu$-P(C$_6$H$_4$CF$_3$-$\pi$)$_2$]($\mu$-CO)Fe(CO)$_2$P(C$_6$H$_4$CF$_3$-$\pi$)$_2$).

$^{31}$P$^{1}$H NMR (THF, -78 °C) $\delta$ 133.1 d, 23.8 d, $^2$J$_{P,P}$ = 7.3 Hz

The solution was then warmed slowly, accompanied by a color change to dark red, and spectra were recorded at 10 °C intervals. Results of this study will be discussed in section III-C.

2. Reaction of Li$\{$(CO)$_3$Fe[$\mu$-P(C$_6$H$_4$CF$_3$-$\pi$)$_2$]($\mu$-CO)Fe(CO)$_2$P(C$_6$H$_4$CF$_3$-$\pi$)$_2$H$\}$ with n-BuLi at 20 °C

A THF solution (2 ml) of Li$\{$(CO)$_3$Fe[$\mu$-P(C$_6$H$_4$CF$_3$-$\pi$)$_2$]($\mu$-CO)Fe(CO)$_2$P(C$_6$H$_4$CF$_3$-$\pi$)$_2$H$\}$, prepared from (CO)$_3$Fe[$\mu$-P(C$_6$H$_4$CF$_3$-$\pi$)$_2$]$\_2$Fe(CO)$_3$, (100 mg, 0.11 mmole) and 1.0 M LiBEt$_3$H in THF (0.11 ml, 0.11 mmole, 1.0 eq.), was treated with 1.6 M n-BuLi in hexanes (0.067 ml, 0.11 mmole, 1.0 eq.). The resultant dark red solution was found, by $^{31}$P NMR, to contain Li$_2$((CO)$_3$Fe[$\mu$-P(C$_6$H$_4$CF$_3$-$\pi$)$_2$]$_2$Fe(CO)$_3$).

$^{31}$P$^{1}$H NMR (THF, 20 °C) $\delta$ -55.9 s
3. Reaction of Li₂{(CO)₃Fe[µ-P(C₆H₄CF₃-μ₂)]₂}₂Fe(CO)₃ with Oxygen

A solution of Li₂{(CO)₃Fe[µ-P(C₆H₄CF₃-μ₂)]₂}₂Fe(CO)₃, prepared as described previously, was exposed to air for five minutes. The color was observed to change from dark red to golden-brown. Analysis of the solution by ³¹P NMR spectroscopy indicated complete conversion of the dianion back to the neutral starting dimer, (CO)₃Fe[µ-P(C₆H₄CF₃-μ₂)]₂Fe(CO)₃.

³¹P{¹H} NMR (THF, 20°C) δ 136.0 s

The procedure was repeated using a solution of the sodium salt of the dianion, Na₂{(CO)₃Fe[µ-P(C₆H₄CF₃-μ₂)]₂}₂Fe(CO)₃, with a similar result being obtained.

4. Reaction of Li₂{(CO)₃Fe[µ-P(C₆H₄CF₃-μ₂)]}₂(µ-CO)Fe(CO)₂P(C₆H₄CF₃-μ₂) with CH₃I

A THF solution (5 ml) of Li[(CO)₃Fe[µ-P(C₆H₄CF₃-μ₂)]₂](µ-CO)Fe(CO)₂P(C₆H₄CF₃-μ₂)H was prepared from (CO)₃Fe[µ-P(C₆H₄CF₃-μ₂)]₂Fe(CO)₃ (200 mg, 0.22 mmole) and 1.0 M LiBE₃H (0.22 ml, 0.22 mmole, 1.0 eq.). Deprotonation with 1.6 M n-BuLi (0.14 ml, 0.22 mmole, 1.0 eq.) at -78 °C led to the formation of Li₂{(CO)₃Fe[µ-P(C₆H₄CF₃-μ₂)]}(µ-CO)Fe(CO)₂P(C₆H₄CF₃-μ₂), as noted in section II-G-1, which was subsequently reacted with methyl iodide (0.10 ml, 1.5 mmole, 7 eq.). The
solution was slowly warmed to 20 °C with stirring over a period of 16 hours. A gradual color change to burgundy was observed.

The following manipulations were carried out in air. Solvent was removed from the reaction mixture under reduced pressure and the resulting red tar was redissolved in a minimum amount of dichloromethane. Deactivated alumina (Grade III) was added to preadsorb the mixture, solvent was removed, and the product was loaded on a 30 cm x 2 cm Grade III alumina column. Elution with petroleum ether moved a red band closely followed by a yellow band. The red band was collected and upon solvent removal yielded a red solid formulated as \((\text{CO})_3\text{Fe}\{\mu-\text{P(C}_6\text{H}_4\text{CF}_3-\text{p})_2\}[\mu-\text{C(CH}_3)\text{O})\text{Fe(CO)}_2\text{P(C}_6\text{H}_4\text{CF}_3-\text{p})_2\text{CH}_3}\). Yield = 83 mg (40%).

\[^{31}\text{P}{}^{1}\text{H})\text{NMR (CDCl}_3, 20 \text{°C)} \delta \]

\[172.1 \text{ d, 41.8 d, } 2J_{\text{p,p}} = 71.6 \text{ Hz}\]

\[\text{IR (THF) } v_{\text{C=O}}, \text{ cm}^{-1} \]

\[2042 \text{ m, 1988 s, 1959 s, 1936 m}\]

\[v_{\text{C=O}}, \text{ cm}^{-1} \]

\[1462 \text{ w}\]

Elution with 2 % diethyl ether / petroleum ether allowed collection of the yellow band which yielded \((\text{CO})_3\text{Fe}[\mu-\text{P(C}_6\text{H}_4\text{CF}_3-\text{p})_2]_2\text{Fe(CO)}_3\) upon solvent removal.

\[^{31}\text{P}{}^{1}\text{H})\text{NMR (CDCl}_3, 20 \text{°C)} \delta \]

\[136.7 \text{ s}\]
5. Reaction of Na₂{(CO)₃Fe[μ-P(C₆H₄CF₃-p)₂]₂Fe(CO)₃} with Trifluoroacetic Acid

A solution of Na₂{(CO)₃Fe[μ-P(C₆H₄CF₃-p)₂]₂Fe(CO)₃} in THF (10 ml) was prepared from (CO)₃Fe[μ-P(C₆H₄CF₃-p)₂]₂Fe(CO)₃ (250 mg, 0.27 mmole) and a 1% sodium mercury amalgam (0.40 g Na, 3 ml Hg). The red dianion solution was decanted from the amalgam to a separate Schlenk flask. To this solution CF₃COOH (0.020 ml, 0.27 mmole, 1.0 eq.) was added. The volume of the solution was reduced and a sample was removed for spectroscopic analysis. Spectra indicated the formation of the sodium salt of the previously described monoanion, Na{(CO)₃Fe[μ-P(C₆H₄CF₃-p)₂]₂(μ-CO)Fe(CO)₂P(C₆H₄CF₃-p)₂H}.

\[ ^{31}P\{^1H\} \text{ NMR (THF, 20 °C)} \delta \quad 123.7 \text{ d}, 52.8 \text{ d}, \quad ^2J_{P,P} = 9.2 \text{ Hz} \]

\[ ^{31}P \text{ NMR (THF, 20 °C)} \delta \quad 123.6 \text{ br.}, 52.7 \text{ d}, \quad ^1J_{P,H} = 340 \text{ Hz} \]

H. Reactions of Li{(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(CO)₂PPh₂H}

1. Reaction With Diphenylchlorophosphine

A THF solution of Fe₂(CO)₆(μ-PPh₂)₂ (0.815 g, 1.25 mmole) was treated with 1.0 M LiBEt₃H (1.37 ml, 1.37 mmole, 1.1 eq.) to produce Li{(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(CO)₂PPh₂H}. To this solution diphenylchlorophosphine (2.3 ml, 13.7 mmole, 10 eq.) was added. The solution changed color from red to orange while stirring at 20 °C over a period of 72
hours. Solvent removal produced a sticky orange solid which was preadsorbed on activated Florisil and loaded on a 6 cm x 50 cm Florisil column. Elution with pentane moved two closely separated yellow bands down the column. The first band was collected and yielded a yellow solid identified by $^{31}$P NMR as $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Fe(\text{CO})}_3$. Yield = 398 mg (49%).

The second yellow band, eluted with 2% diethyl ether / 98% pentane, also yielded a yellow solid upon solvent removal. Analysis of this compound led to its identification as $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Fe(\text{CO})}_2\text{PPh}_2\text{H}$. Yield = 249 mg (24.7%)

$^{31}$P{[H]} NMR (CDCl$_3$, 20 °C), δ 143.4 s, 49.3 s

$^{31}$P NMR (CDCl$_3$, 20 °C), δ 143.4 br. s,

49.6 d, $^1$$J_{P,H}$ = 356 Hz

$^1$H NMR (CDCl$_3$, 20 °C) δ 6.6–7.5 m, 20 H

5.7 d, 1H, $^1$$J_{P,H}$ = 357 Hz

IR (cyclohexane) $\nu_{\text{CO}}$, cm$^{-1}$ 2045 w, 2013 m, 1977 s

1949 s, 1925 m

Mass Spectrum (FAB) 808 (M$^+$), 780 (M$^+$ - CO),

752 (M$^+$ - 2CO), 724 (M$^+$ - 3CO)

696 (M$^+$ - 4CO), 668 (M$^+$ - 5CO),

482 (M$^+$ - 5CO - PPh$_2$H)
No other products were isolated from this reaction.

2. Reaction with Di-t-butylchlorophosphine (excess)

A solution of Li[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$PPh$_2$H] was prepared in 40 ml of THF from (CO)$_3$Fe(μ-PPh$_2$)$_2$Fe(CO)$_3$ (650 mg, 1.0 mmole) and 1.0 M LiBEt$_3$H (1.1 ml, 1.1 mmole, 1.1 eq.). To this red solution di-t-butylchlorophosphine (0.9 g, 5 mmole, 5 eq.) was added. As stirring continued for 48 hours the color darkened to red-black. Solvent was removed leaving a dark red solid. The product mixture was preadsorbed on activated Florisil and loaded on a 50 cm x 4 cm Florisil column.

Elution was begun with pentane and five bands were observed on the column. The first band, blue-green in color, was eluted with pentane and yielded a trace amount of a green solid upon solvent removal. This product was identified as Fe$_2$(CO)$_5$(μ-P-t-Bu$_2$)$_2$ from its $^{31}$P NMR spectrum, and full characterization is discussed in sections II-J and III-H.

$^{31}$P $^{1}$H NMR (CDCl$_3$, 20 °C) δ 362.6 s

Continued elution with pentane next moved a large red band down the column. The band was collected and pentane removed under reduced pressure to yield a dark red, air-stable solid. Dark red crystals were obtained upon recrystallization from methylene chloride / hexane. This compound, the major product of the reaction, is formulated as (CO)$_3$Fe(μ-PPh$_2$)(μ-P-t-Bu$_2$)Fe(CO)$_3$. Yield = 264 mg (43.3 %).
Melting point 158 °C

$^{31}$P$^{(1)}$H NMR (CDC$_3$, 20 °C) $\delta$ 290.8 d, 173.3 d, $^2$J$_{P\cdot H}$ = 63 Hz

$^{31}$P NMR (CDC$_3$, 20 °C) $\delta$ 290.8 d of m, $^3$J$_{P\cdot H}$ = 14 Hz
173.9 d of tr, $^1$J$_{P\cdot H}$ = 11 Hz

$^1$H NMR (CDC$_3$, 20 °C) $\delta$ 7.62-7.28 m, 10 H
1.36 d, 18 H, $^1$J$_{P\cdot H}$ = 14 Hz

$^{13}$C$^{(1)}$H NMR (CDC$_3$, 20 °C) $\delta$ 214.0 tr, $^2$J$_{P\cdot C}$ = 5.5 Hz
127.8-142.0 m
44.27 d, $^1$J$_{P\cdot C}$ = 5.6 Hz
33.99 d, $^2$J$_{P\cdot C}$ = 1.9 Hz

IR (cyclohexane) $v_{CO}$, cm$^{-1}$ 2033 m, 1998 s, 1977 sh,
1965 s, 1959 s, 1948 m

Mass spectrum (EI) 582 (M$^+$ - CO), 554 (M$^+$ - 2CO), 526(M$^+$ - 3CO)
498(M$^+$ - 4CO), 470(M$^+$ - 5CO), 442(M$^+$ - 6CO)

Elemental analysis calculated found
% C 51.15 50.94
% H 4.59 4.80
A yellow band was next removed from the column using a 2 % diethyl ether / 98% pentane mixture as the eluent. Evaporation of solvent produced a yellow solid which proved to be (CO)$_3$Fe($\mu$-PPh$_2$)$_2$Fe(CO)$_3$. Yield = 71 mg (11 %).

$^{31}$P{$^1$H} NMR (CDCl$_3$, 20 °C) $\delta$ 142.0 s

A brown band was next collected from the column by continued elution with 2 % diethyl ether/98 % pentane. A red-brown solid was obtained upon solvent removal. Characterization of this somewhat air-sensitive solid led to its formulation as (CO)$_3$Fe($\mu$-PPh$_2$)($\mu$-P-t-Bu$_2$)Fe(CO)$_2$PPh$_2$H. Yield = 69 mg (9.0 %).

$^3$P{$^1$H} NMR (CDCl$_3$, 20 °C) $\delta$

$^1$H NMR (CDCl$_3$, 20 °C) $\delta$

$^{13}$C{$^1$H} NMR (CDCl$_3$, 20 °C) $\delta$ 212.6 s
The fifth original band was moved down the column with 5 % diethyl ether / 95 % pentane and produced a yellow solid. This product was subsequently found to be the previously described (Section II-H-1) (CO)$_3$Fe($\mu$-PPh$_2$)$_2$Fe(CO)$_2$PPh$_2$H. Yield = 26 mg (3.2 %).

Elution with a 50 % diethyl ether / 50 % pentane solution produced a sixth, and final, band. This yellow-orange band, upon solvent removal, yielded an orange solid identified as PPh$_2$H(CO)$_2$Fe($\mu$-PPh$_2$)$_2$Fe(CO)$_2$PPh$_2$H. Yield = 42 mg (4.3 %).

$^{31}$P($^1$H) NMR (CDCl$_3$, 20 °C) \(\delta\) 135.6 t, \(^2\)J$_{P\cdot P}$ = 12.5 Hz
52.5 t, \(^2\)J$_{P\cdot P}$ = 12.5 Hz

$^{31}$P NMR (CDCl$_3$, 20 °C) \(\delta\) 135.6 br. s
52.5 d of t \(^1\)J$_{P\cdot P}$ = 350 Hz

IR (cyclohexane) \(v_{CO}\) cm$^{-1}$ 1982 s, 1952 s, 1911 m
3. Reaction with One Equivalent of Di-1-butylchlorophosphine.

A similar procedure to that described above was employed in the reaction of Li[(CO)\(_3\)Fe(µ-PPh\(_2\))(µ-CO)Fe(CO)\(_2\)PPh\(_2\)H] with one equivalent of di-1-butylchlorophosphine. The same amounts of reagents were used except that only one equivalent of 1-Bu\(_2\)PCI (0.19 ml, 1.0 mmole) was added to the red solution of Li[(CO)\(_3\)Fe(µ-PPh\(_2\))(µ-CO)Fe(CO)\(_2\)PPh\(_2\)H] (1.0 mmole).

Chromatography of the product mixture produced the same six products previously described. However, the yields of di-1-butylphosphido-containing products were considerably lower than when excess di-1-butylchlorophosphine was used.

4. Reaction with Excess Diethylchlorophosphine.

A solution of Li[(CO)\(_3\)Fe(µ-PPh\(_2\))(µ-CO)Fe(CO)\(_2\)PPh\(_2\)H] (1.0 mmole) was prepared from (CO)\(_3\)Fe(µ-PPh\(_2\))\(_2\)Fe(CO)\(_3\) (650 mg, 1.0 mmole) and 1.0 M LiBEt\(_3\)H (1.05 ml, 1.05 mmole, 1.05 eq.) in 40 ml of THF. The red solution was treated with an excess amount of diethylchlorophosphine (0.61 ml, 5.0 mmole, 5.0 eq.) and an initial slight darkening of the solution was observed over the first hour of stirring. As stirring continued, though, the solution became lighter until after 48 hours of stirring at room temperature it had acquired an orange-yellow color. Solvent was removed under reduced pressure to leave a sticky orange solid.

The orange solid was dissolved in a minimum amount of methylene chloride and preadsorbed on activated Florisil. After solvent removal the solid
was loaded on a 45 cm x 4 cm Florisil column. Elution with pentane moved a number of very closely separated yellow bands onto the column. The first bright yellow band was collected, solvent was removed, and a bright yellow solid was obtained. This product was found to contain a number of compounds.

\[ ^{31}P\left(^{1}H\right)\text{ NMR (CDCl}_3, 20 \degree C\right) \delta 155.0 \text{ s, 20.7 s, -41.2 s,} \]
many minor signals

Continued elution with pentane allowed removal of a second yellow band. Upon solvent removal a yellow air-stable solid was obtained and subsequently identified as \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{PET}_2)\text{Fe(\text{CO})}_3\). Yield = 136 mg (24.5 %)

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<th>Melting Point</th>
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<td>[^{31}P\left(^{1}H\right)\text{ NMR (CDCl}_3, 20 \degree C\right) \delta</td>
<td>149.7 d, 145.1 d, (^2J_{P,P} = 124 \text{ Hz} )</td>
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<tr>
<td>[^{31}P\text{ NMR (CDCl}_3, 20 \degree C\right) \delta</td>
<td>149.7 d \text{ of tr, 145.1 d of m}</td>
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</table>
| \[^{13}C\left(^{1}H\right)\text{ NMR (CDCl}_3, 20 \degree C\right) \delta | 212.7 d \text{ of d, } \(^2J_{P,C} = 4.8 \text{ Hz} \)
127-140 m
25.84 d, 25.69 d, \(^1J_{P,C} = 20 \text{ Hz} \)
11.75 d, 11.36 d, \(^2J_{P,C} = 7 \text{ Hz} \)
| IR (cyclohexane) \(\nu_{\text{CO}}, \text{ cm}^{-1}\) | 2043 s, 2007 s, 1986 s, 1967 s, 1949 s, 1926 sh |
Mass Spectrum (El)  554 (M⁺), 526 (M⁺ - CO), 498 (M⁺ - 2CO)
  470 (M⁺ - 3CO), 442 (M⁺ - 4CO),
  414 (M⁺ - 5CO), 386 (M⁺ - 6CO)

Elemental Analysis

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<tr>
<td>% H</td>
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</table>

A third yellow band, also eluted with pentane and not well-separated from the second band, yielded a yellow solid identified by ³¹P as consisting mainly of (CO)₃Fe(μ-PPH₂)₂Fe(CO)₃. It was also determined spectroscopically that the solid contained a fair amount of the aforementioned second product. Total yield = 212 mg.

Elution with 1-10% diethyl ether/pentane mixtures produced more yellow to orange bands. Analysis by ³¹P NMR of the products contained in these bands showed no evidence of diethylphosphido- or diethylphosphine-containing products. The products were found to consist mainly of impure (CO)₃Fe(μ-PPH₂)₂Fe(CO)₂PPh₂H and PPh₂H(CO)₂Fe(μ-PPH₂)₂Fe(CO)₂PPh₂H in a total yield of less than 10%.

5. Reaction with Trimethylxonium Tetrafluoroborate

A solution of Li[((CO)₃Fe(μ-PPH₂)(μ-CO)Fe(CO)₂PPh₂H) was prepared in 10 ml of THF from (CO)₃Fe(μ-PPH₂)₂Fe(CO)₃ (200 mg, 0.31 mmole) and 1.0 M LiBEt₃H (0.33 ml, 0.33 mmole, 1.1 eq.). After 30 minutes of
stirring, the THF was removed and the resultant red oil was redissolved in 5 ml of methylene chloride. Trimethyloxonium tetrafluoroborate (148 mg, 0.34 mmole, 1.1 eq.) was added but no color change was observed. Spectroscopic analysis of the solution indicated the presence of only (CO)$_3$Fe(μ-PPh$_2$)$_2$Fe(CO)$_3$.

$^{31}$P{$^1$H} NMR (CH$_2$Cl$_2$, 20 °C) δ 141.9 s

6. Reaction With Triethyloxonium Hexafluorophosphate

In 10 ml of THF (CO)$_3$Fe(μ-PPh$_2$)$_2$Fe(CO)$_3$ (200 mg, 0.31 mmole) was treated with 1.0 M LiBEt$_3$H (0.33 ml, 0.33 mmole, 1.1 eq.) to produce Li[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$PPh$_2$H]. The solvent was removed under reduced pressure and the red oil was redissolved in 10 ml of methylene chloride. Addition of triethyloxonium hexafluorophosphate (0.367 mg, 0.34 mmole, 1.1 eq.) as a solid and 16 hours of stirring produced a yellow solution. This solution was found to consist of (CO)$_3$Fe(μ-PPh$_2$)$_2$Fe(CO)$_3$ as the main product.

$^{31}$P{$^1$H} NMR (CH$_2$Cl$_2$, 20 °C) δ 140.6 s
I. Reactions of \((\text{CO})_3 \text{Fe}(\mu-\text{PPh}_2)(\mu-\text{P-}1\text{-Bu}_2)\text{Fe(\text{CO})}_3\)

1. With Sodium

A suspension of sodium sand (50 mg, 0.22 mmole) was prepared in 5 ml of THF. In a separate vessel, \((\text{CO})_3 \text{Fe}(\mu-\text{PPh}_2)(\mu-\text{P-}1\text{-Bu}_2)\text{Fe(\text{CO})}_3\) (61 mg, 0.1 mmole) was dissolved in 5 ml of THF. This red solution was transferred to the sodium/THF suspension and stirred for 16 hours with a color change to very dark red being observed. Spectroscopic analysis of this solution indicated the formation of \(\text{Na}_2[(\text{CO})_3 \text{Fe}(\mu-\text{PPh}_2)(\mu-\text{P-}1\text{-Bu}_2)\text{Fe(\text{CO})}_3]\).

\[
^3\text{P} \left\{^1\text{H} \right\} \text{NMR (THF, 20 °C) } \delta \text{ ppm} \quad 19.2 \text{ s, } -20.2 \text{ s}
\]

\[
^3\text{P} \text{ NMR (THF, 20 °C) } \delta \quad 19.2 \text{ m, } -20.2 \text{ t}
\]

\[
\text{IR (THF) } \nu_{\text{CO, cm}^{-1}} \quad 1932 \text{ m, } 1903 \text{ s, } 1828 \text{ s, } 1780 \text{ s}
\]

J. Preparation of \((\text{CO})_2 \text{Fe}(\mu-\text{P-}1\text{-Bu}_2)_2\text{Fe(\text{CO})}_3\)

A slurry of \(\text{Na}_2 \text{Fe}_2(\text{CO})_8\) (7.9 mmole) was prepared by slowly dripping \(\text{Fe(CO)}_5\) (2.10 ml, 15.8 mmole) into a THF suspension (50 ml) of sodium pieces (400 mg, 17.4 mmole). The solution was stirred for 16 hours at which point it had formed the red slurry. To this slurry di-1-butylchlorophosphine (3.50 ml, 18.4 mmole, 2.4 eq.) was added dropwise over a period of 30 minutes. The resultant dark green solution was stirred at room temperature for 20 hours. Solvent was removed to leave a very dark green oil. The green oil was made
fluid by adding a minimum amount of methylene chloride; activated Florisil was added, and the methylene chloride was removed under reduced pressure. The product-containing Florisil was loaded on a 50 cm × 5 cm Florisil column and elution was begun with pentane. A dark green band moved down the column very quickly and upon collection and solvent removal produced a green oil. This green oil was shown to be a mixture of compounds by $^{31}$P NMR.

$^{31}$P $\{^{1}$H$\}$ NMR (CDCl$_3$, 20 °C) δ 362.2 s, 211.6 s, 84.5 s

$^{31}$P NMR (CDCl$_3$, 20 °C) δ

362.2 s, 211.6 s, 84.5 d, $^{1}$J$_{P-H}$ = 331 Hz

The green oil was dissolved in a minimum amount of pentane and this solution was cooled to -78 °C for 24 hours. Quick filtration of the solution at room temperature allowed collection of a dark green air-stable solid. Slow diffusion of hexane into a saturated methylene chloride solution of the green solid afforded dark green hexagonal crystals which were collected on a frit and washed with a minimal amount of cold hexane. The product was formulated as (CO)$_2$Fe(μ-P-t-Bu)$_2$Fe(CO)$_3$. Yield = 2.09 g (28%).

$^{31}$P$\{^{1}$H$\}$ NMR (CDCl$_3$, 20 °C) δ 362.2 s

$^{13}$C$\{^{1}$H$\}$ NMR (CDCl$_3$, 20 °C) δ 220.2 s

215.9 t, $^{2}$J$_{C-P}$ = 10 Hz
1H NMR (CDCl₃, 20 °C) δ 1.23 d, 3Jₚ-H = 14 Hz

IR (C₆H₁₂) νCO, cm⁻¹ 1998 m, 1950 s, 1945 s, 1911 m

Mass Spectrum (El) 542 (M⁺), 514 (M⁺ - CO), 486 (M⁺ - 2 CO)
458 (M⁺ - 3 CO), 430 (M⁺ - 4 CO)
402 (M⁺ - 5 CO)

Elemental Analysis

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<tr>
<td>% H</td>
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<td>6.66</td>
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</table>

The structure of the compound was determined by an X-ray diffraction study of one of the crystals. Details of this study and the resultant structure are discussed in Section III-H. It should be noted that crystals of good quality can also be obtained by subjecting the green oil directly to recrystallization by the procedure described above. The other two components of the green oil were found by 31P NMR to still exist in the decantate from the recrystallization but neither was isolated and fully characterized.

In the chromatography of the original product mixture continued elution with 2 % diethyl ether / 98 % pentane produced another green band. This band was collected and solvent was removed to yield a green-brown solid which is formulated as Fe(CO)₃(P-t-Bu₂H)₂. Yield = 153 mg (2.2 %).

31P(1H) NMR (CDCl₃, 20 °C) δ 100.9 s
31P NMR (CDCl₃, 20 °C) δ 100.9 d, ¹Jₚ,H = 330 Hz

¹³C{¹H} NMR (CDCl₃, 20 °C) δ 218.2 t, ²J₁₃C,H = 28 Hz

¹H NMR (CDCl₃, 20 °C) δ 4.77 d, ¹J₁H,P = 330 Hz
1.45 d, ³J₁H,P = 12.5 Hz

Mass Spectrum (El) 432 (M⁺), 376 (M⁺ - 2CO), 348 (M⁺ - 3CO)

K. Reactions of Fe₂(CO)₅(μ-P-t-Bu₂)₂.

1. Attempted Reaction with Carbon Monoxide (Trial 1)

A THF solution of Fe₂(CO)₅(μ-P-t-Bu₂)₂ (80 mg, 0.15 mmole) was prepared under a carbon monoxide atmosphere. Carbon monoxide was bubbled through the solution for 30 minutes with no observed color change. An infrared spectrum of the solution indicated that no reaction had taken place.

IR (THF) νCO, cm⁻¹ 1998 m, 1950 s, 1945 s, 1911 m

2. Attempted Reaction with Carbon Monoxide (Trial 2)

Under an atmosphere of carbon monoxide a 100 ml two-necked round-bottomed flask was charged with 20 ml THF. The flask was attached to a
manometer and solid Fe$_2$(CO)$_5$(μ-P-t-Bu)$_2$ (100 mg, 0.18 mmole) was added to form a green solution. This solution was allowed to stir for two hours at room temperature. No change in pressure was observed, i.e., no uptake of carbon monoxide is indicated.

L. Preparation of Ru$_2$(CO)$_6$(μ-PPh$_2$)$_2$

1. From Ru$_2$(CO)$_6$Cl$_4$

A solution of Ru$_2$(CO)$_6$Cl$_4$ (200 mg, 0.390 mmole) in THF (10 ml) was prepared under an atmosphere of carbon monoxide. In a separate vessel diphenylphosphine (0.136 ml, 0.78 mmole, 2.0 eq.) was dissolved in 10 ml of THF. Deprotonation of the phosphine was carried out by using 1.6 M n-BuLi (0.488 ml, 0.78 mmole, 2.0 eq.) to form a red solution of PPh$_2$Li. Both solutions were cooled to -78 °C, and the PPh$_2$Li solution was added dropwise to the yellow Ru$_2$(CO)$_6$Cl$_4$ solution. Stirring was continued accompanied by slow warming to room temperature over a 16 hour period. The resultant orange solution was then transferred quickly to a flask containing a previously prepared suspension of sodium (18 mg, 0.78 mmole, 2.0 eq.) in THF (10 ml). The solution remained orange as it was stirred for 24 hours.

Solvent removal left an orange solid which was chromatographed in air on a 35 cm x 4 cm Grade III alumina column. Elution with pentane moved a yellow band which upon collection and solvent removal yielded a dark yellow air-stable solid identified as the desired (CO)$_3$Ru(μ-PPh$_2$)$_2$Ru(CO)$_3$.\textsuperscript{17} Yield = 21 mg (7.3 %)
$^{31}$P $^1$H NMR (CDCl$_3$, 20 °C) $\delta$ 108.5 s

IR (cyclohexane) $v_{\text{CO}}$, cm$^{-1}$ 2067 s, 2035 s, 2002 s, 1985 s, 1974 m

Mass Spectrum (El) 740 (M$^+$), 712 (M$^+$ - CO), 684 (M$^+$ - 2CO), 656 (M$^+$ - 3CO), 628 (M$^+$ - 4CO), 600 (M$^+$ - 5CO), 572 (M$^+$ - 6CO)

Three additional yellow products were obtained through further chromatography but none were fully characterized.

2. From Ru$_3$(CO)$_{12}$ and Ph$_2$PPPPh$_2$

The reaction of Ru$_3$(CO)$_{12}$ with Ph$_2$PPPPh$_2$ has been reported to produce Ru$_2$(CO)$_6$(μ-PPPh$_2$)$_2$ in low to moderate yield. The procedure used here is similar to that used by Carty, et. al., with only minor variations in the chromatographic methods.

A xylene (50 ml) solution of trirutheniumdodecacarbonyl (1.3 g, 2.0 mmole) and tetraphenyldiphosphine (1.35 g, 3.6 mmole, 1.8 eq.) was prepared and heated to reflux for 1.5 hours. A color change from orange to dark red was observed. The volume of the solution was reduced to 20 ml, pentane (100 ml) was added, and the solution was decanted from a small amount of precipitate which had formed. The decantate was evaporated to dryness and the residue was loaded as a methylene chloride solution onto a silica gel column. Elution
with hexane moved a large yellow band which eventually yielded a yellow solid identified as \((\text{CO})_3\text{Ru}(\mu-\text{PPh}_2)_2\text{Ru(\text{CO})}_3\). Yield = 468 mg (21 %)

\[
^{31}\text{P}^1\text{H} \text{ NMR (CDCl}_3, 20^\circ \text{C}) \delta \quad 109.0 \text{ s}
\]

M. Reactions of \((\text{CO})_3\text{Ru}(\mu-\text{PPh}_2)_2\text{Ru(\text{CO})}_3\).

1. Attempted Reaction With LiBEt$_3$H

A solution of \((\text{CO})_3\text{Ru}(\mu-\text{PPh}_2)_2\text{Ru(\text{CO})}_3\) (80 mg, 0.11 mmole) was prepared in THF (3 ml) and cooled to -78 °C. Lithium triethylborohydride (0.13 ml of 1.0 M solution, 0.13 mmole, 1.2 eq.) was added, and the solution was warmed to room temperature with no observable color change. Spectroscopic analysis \((^{31}\text{P} \text{ NMR})\) of the solution indicated that no reaction had taken place.

\[
^{31}\text{P}^1\text{H} \text{ NMR (THF, 20}^\circ \text{C}) \delta \quad 109.1 \text{ s}
\]

This reaction was attempted under varying conditions of temperature (e.g., 50 °C) and solvent (Et$_2$O) but no reaction was ever seen to occur.
2. Attempted Reaction with n-BuLi

A THF solution of \((\text{CO})_3\text{Ru}(\mu-\text{PPh}_2)_2\text{Ru(\text{CO})}_3\). (100 mg, 0.14 mmole) was cooled to -78 °C and treated with 1.6 M n-BuLi (0.10 ml, 0.16 mmole, 1.2 eq.). The solution was warmed to room temperature with a slight darkening from yellow to orange being observed. Analysis by \(^{31}\text{P}\) NMR, however, revealed the presence of only unreacted starting material, \((\text{CO})_3\text{Ru}(\mu-\text{PPh}_2)_2\text{Ru(\text{CO})}_3\).)

\[^{31}\text{P}\{^1\text{H}\}\text{ NMR (THF, 20 °C)}\delta\quad 109.0\text{ s}\]

3. Reaction With Sodium

A solution of \((\text{CO})_3\text{Ru}(\mu-\text{PPh}_2)_2\text{Ru(\text{CO})}_3\) (50 mg, 0.07 mmole) in THF (2 ml) was transferred to a Schlenk tube containing a previously prepared 1 % sodium amalgam. After two hours of stirring an aliquot of the resultant red-brown solution was removed for phosphorus-31 NMR analysis. Formation of \(\text{Na}_2[(\text{CO})_3\text{Ru}(\mu-\text{PPh}_2)_2\text{Ru(\text{CO})}_3]\) was indicated as was the presence of a small amount of unreacted \((\text{CO})_3\text{Ru}(\mu-\text{PPh}_2)_2\text{Ru(\text{CO})}_3\).

\[^{31}\text{P}\{^1\text{H}\}\text{ NMR (THF, 20 °C)}\delta\quad -92.5\text{ s}\]

IR (THF) \(v_{\text{CO}}\text{, cm}^{-1}\)

| 2010 s | 1955 s
| 1930 sh | 1888 m |

No attempts were made to isolate a solid product from this reaction.
N. Preparation of \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(\text{CO})}_3\)

Under a carbon monoxide atmosphere a yellow solution of \(\text{Ru}_2(\text{CO})_6\text{Cl}_4\) (0.63 mg, 1.22 mmole) in THF (50 ml) was prepared. In a separate flask, also under carbon monoxide, bis(diphenylphosphine)tricarbonyliron (1.25 g, 2.44 mmole, 1.0 eq. to Ru) was dissolved in 20 ml of THF and 1.6 M \(\text{n-BuLi}\) (3.06 ml, 4.88 mmole, 2.0 eq.) was added to form a red solution of \(\text{Li}_2[\text{Fe(\text{CO})}_3(\text{PPh}_2)_2]\). This red solution was transferred to the yellow \(\text{Ru}_2(\text{CO})_6\text{Cl}_4\) solution and the resulting mixture was heated to reflux for 2.5 hours. Progress of the reaction was followed by infrared spectroscopy. Upon cooling the solution to room temperature and solvent removal an orange solid was obtained. The following manipulations were carried out in air. Pentane was added to the residue, and washing was continued until the pentane extracts were colorless. The yellow pentane washings were passed through neutral activated alumina and solvent was removed to yield a bright yellow powder formulated as \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(\text{CO})}_3\). Recrystallization from methylene chloride/hexane afforded dark yellow crystals of the product. Yield = 643 mg (38 %)

**Melting point**

144 °C

\(^{31}\text{P}(\text{H})\) NMR (CDCl\(_3\), 20 °C) δ 124.1 s

\(^1\text{H}\) NMR (CDCl\(_3\), 20 °C) δ 6.7-7.6 m
\[ \text{\textsuperscript{13}C\textsuperscript{1}H} \text{ NMR (CDCl}_3, 20^\circ C) \delta \]

- 213.4 br. s (Fe-CO)
- 198.5 br. s (Ru-CO)
- 127-145 m

IR (THF) \( v_{\text{CO}} \), cm\(^{-1} \)

- 2062 s, 2020 s, 2001 s
- 1981 s, 1959 m

Mass spectrum, m/e (FAB) 695 (M\(^+\)), 668(M\(^+\) - CO + H),
  - 639 (M\(^+\) - 2CO), 612 (M\(^+\) - 3CO + H)
  - 583 (M\(^+\) - 4CO), 556 (M\(^+\) - 5CO + H)
  - 527 (M\(^+\) - 6CO)

Analysis

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<tr>
<td>% H</td>
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<td>2.83</td>
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O. Reactions of \((\text{CO})_3\text{Fe(\mu-PPh}_2)_2\text{Ru(CO)}_3\)

1. With Sodium Amalgam

A yellow THF solution (2 ml) of \((\text{CO})_3\text{Fe(\mu-PPh}_2)_2\text{Ru(CO)}_3\) (25 mg, 0.036 mmole) was prepared and transferred to a vessel containing a previously prepared 1 % amalgam of sodium (133.5 mg Na, 1.0 ml Hg). An immediate darkening of the solution to a deep red color was observed. After 30 minutes of stirring samples were removed for spectroscopic analysis. The solution was
found by $^{31}$P NMR and IR spectroscopy to contain only $\text{Na}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru}($CO$)_3]$.

$^{31}$P($^1$H) NMR (THF, 20 °C) δ
-86.6 s

IR (THF, 20 °C) ν$_\text{CO}$, cm$^{-1}$
1943 s, 1915 s, 1863 s,
1850 s, 1805 w

2. With One Equivalent LiBEt$_3$H

A solution of $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru}($CO$)_3$ (100 mg, 0.144 mmole) in THF (10 ml) was cooled to -78 °C. With stirring, 1.0 M LiBEt$_3$H (0.145 ml, 0.145 mmole, 1.0 eq.) was added. The solution turned red-orange immediately and gas evolution was observed. The solution was warmed to room temperature and a sample was transferred to a 5 mm NMR tube. Phosphorus-31 NMR analysis showed that the solution contained approximately equal amounts of $\text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru}($CO$)_3]$ and unreacted starting material, $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru}($CO$)_3$.

$^{31}$P($^1$H) NMR (THF, 20 °C) δ
124.1 s
-85.4 s

The same reaction, when repeated at room temperature or on a different scale, produced the same result.
3. With Two Equivalents LiBEt$_3$H

A THF solution (10 ml) of (CO)$_3$Fe(μ-PPh$_2$)$_2$Ru(CO)$_3$ (100 mg, 0.144 mmole) was cooled to -78 °C and treated with 1.0 M LiBEt$_3$H (0.290 ml, 0.290 mmole, 2.0 eq.). An immediate darkening to red, accompanied by gas evolution, was observed. Spectral analysis indicated a complete conversion to Li$_2$[(CO)$_3$Fe(μ-PPh$_2$)$_2$Ru(CO)$_3$].

$^31$P($^1$H) NMR (THF, 20 °C) δ -85.4 s

IR (THF, 20 °C) v CO, cm$^{-1}$ 1946 s, 1906 s, 1873 s, 1855 s, 1812 w

4. With One Equivalent Na(MeO)$_3$BH

A yellow solution of (CO)$_3$Fe(μ-PPh$_2$)$_2$Ru(CO)$_3$ (100 mg, 0.144 mmole) in THF (10 ml) was prepared under argon. At room temperature sodium trimethoxyborohydride (17 mg, 0.144 mmole, 1.0 eq.) was added with no observable color change or gas evolution. The yellow solution was stirred for 6 hours and a sample was removed for NMR analysis. Spectroscopic data indicated that no reaction had taken place.

$^31$P($^1$H) NMR (THF, 20 °C) δ 124.2 s
5. With \( \text{n-Butyllithium} \)

A solution of \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(}\text{CO})_3\) (150 mg, 0.216 mmole) in THF (10 ml) was cooled to -78 °C. With stirring, 1.6 M \text{n-BuLi} (0.16 ml, 0.26 mmole, 1.2 eq.) was added causing an immediate color change to red. The reaction solution was removed from the cold bath, stirred for 1.5 hours, and a sample was removed for IR analysis. Solvent was removed leaving a red air-sensitive tar which was redissolved in THF-\(\text{d}_8\) (1.0 ml). This solution was transferred to a 5 mm NMR tube. The NMR and IR data obtained led to the formulation of the product as \(\text{Li[(CO)}_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(}\text{CO})_2\text{COC}_4\text{H}_9]\).

\[ ^{31}\text{P}[^1\text{H}] \text{NMR (THF-}d_8, 20 \degree \text{C} \delta \quad 124.5 \text{ d} \]
\[ \quad 84.8 \text{ d } J_{p,p} = 90 \text{ Hz} \]

\[ ^{13}\text{C}[^1\text{H}] \text{NMR (THF-}d_8, 20 \degree \text{C} \delta \]
\[ \quad 207.2 \text{ br. t } (\text{Ru-}\text{CO}) \]
\[ \quad 220.7 \text{ br. s } (\text{Fe-}\text{CO}) \]
\[ \quad 127-142 \text{ m} \]

\[ \text{IR (THF) } \nu_{\text{CO}}, \text{ cm}^{-1} \]
\[ \quad 2002 \text{ s}, 1955 \text{ s}, 1938 \text{ s}, 1924 \text{ s}, 1893 \text{ s}, 1550 \text{ w} \]

Numerous attempts at isolating the product as a solid were carried out. Attempted metathesis with \text{PPNCl}, \text{Ph}_4\text{AsCl}, \text{n-Bu}_4\text{NI}, and \text{Ph}_4\text{PCl}, as well as treating the lithium salt with various mixed solvent systems all led to decomposition of the product to \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(}\text{CO})_3\). Typically one equivalent of one of the above mentioned salts was added as a THF
suspension to the reaction solution. Solvent removal and $^{31}\text{P}$ NMR spectroscopic analysis of the resulting crude tar consistently indicated that decomposition had taken place. Alternatively, reducing the volume of the original reaction solution and transferring this solution (under argon) to a frit filter covered with hexane allowed collection of a brown solid subsequently shown by $^{31}\text{P}$ NMR to be $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru( CO)}_3$.

P. Reactions of $[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru( CO)}_3]^2^-$.

1. With Methyl Iodide

A solution of $\text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru( CO)}_3]$ was prepared by treating a THF solution (5 ml) of $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru( CO)}_3$ (150 mg, 0.216 mmole) with 1.0 M LiBEt$_3$H (0.43 ml, 0.43 mmole, 2.0 eq.) at room temperature. The resultant red dianion solution was cooled to -78 °C and $\text{CH}_3\text{I}$ (14 μl, 0.216 mmole, 1.0 eq.) was added. The reaction vessel was removed from the cold bath and the contents were stirred at room temperature for 24 hours. A slow darkening of the solution to red-black was observed. Samples of the solution were removed for IR and NMR investigation. Results of this study are discussed in Section III-N.

$^{31}\text{P}^{(1)}\text{H)} \text{ NMR (THF, 20 °C)} \delta$ 139.3 d, 110.3 d,

$J_{p,p} = 105 \text{ Hz}$

119.2 d, 91.2 d,

$J_{p,p} = 86 \text{ Hz}$
A similar reaction was carried out using the sodium salt (100 mg (CO)₃Fe(μ-PPh₂)₂Ru(CO)₃, 0.144 mmole; 1 % Na/Hg) as the dianion source. The solution of Na₂[(CO)₃Fe(μ-PPh₂)₂Ru(CO)₃] was transferred from the amalgam, cooled to -78 °C, and treated with CH₃I (9.2 μl, 1.05 eq.). The solution was warmed to room temperature with an accompanying darkening to red-black over a period of 24 hours. Spectral data from analysis of the reaction solution proved to be similar to those obtained from the reaction of Li₂[(CO)₃Fe(μ-PPh₂)₂Ru(CO)₃] with methyl iodide. In this case, though, none of the minor product was seen; however, a substantial amount of Na₂[(CO)₃Fe(μ-PPh₂)₂Ru(CO)₃]I remained in the solution.

\[ \text{IR (THF, 20 °C) } v_{CO}, \text{ cm}^{-1} \]
\[ 1998 \text{ s, 1968 s, 1950 s, 1920 s, 1885 sh, 1583 w } \]

\[ ^{31}P{^1H} \text{ NMR (THF, 20 °C) } \delta \]
\[ 141.1 \text{ d, 110.4 d, } \]
\[ J_{p,p} = 104.5 \text{ Hz } \]
\[ -60.0 \text{ s } \]

\[ \text{IR (THF, 20 °C) } v_{CO}, \text{ cm}^{-1} \]
\[ 1998 \text{ m, 1967 s, 1945 sh, 1922 s, 1870 w,br, 1583 w } \]

All attempts at isolation of these products by methods described in II-O-5 resulted in decomposition to (CO)₃Fe(μ-PPh₂)₂Ru(CO)₃.
2. Reaction with CD₃I

A red solution of Li₂[(CO)₃Fe(μ-PPh₂)₂Ru(CO)₃] (0.29 mmole) was prepared in THF (3 ml) from (CO)₃Fe(μ-PPh₂)₂Ru(CO)₃ (200 mg, 0.288 mmole) and 1.0 M LiBEt₃H (0.58 ml, 0.58 mmole, 2.0 eq.). The solution was stirred for one hour, cooled to -78 °C, and CD₃I (38 μl, 0.60 mmole, 2.0 eq.) was added. The reaction vessel was removed from the cold bath and the mixture was stirred for 20 hours. A sample of the resultant red-black solution was transferred to a 5 mm NMR tube for investigation by ²H NMR. Solvent was removed and the resultant red oil was redissolved in acetone-d₆ for ¹³C and ³¹P NMR studies. Results of these studies will be discussed in Section III-N.

³¹P{¹H} NMR (CD₃COCD₃, 20 °C) δ

140.5 d, 111.7 d
²J_P,P = 105 Hz
120.5 d, 92.4 d
²J_P,P = 92 Hz

²H NMR (THF, 20 °C) δ

1.61 s

¹³C{¹H} NMR (CD₃COCD₃, 20 °C) δ

218.6 t, ²J_P,C = 4.9 Hz
208.5 d, ²J_P,C = 6.2 Hz
127-142 m
3. Reaction with Methyl-$\text{p}$-toluenesulfonate

A THF solution (2 ml) of $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Ru}(\text{CO})_3$ (100 mg, 0.144 mmole) was treated with 1.0 M LiBEt$_3$H (0.31 ml, 0.31 mmole, 2.2 eq.) to form Li$_2[/(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Ru}(\text{CO})_3]$. The red solution was cooled to $-78 \, ^\circ\text{C}$ and CH$_3$OSO$_2$C$_6$H$_4$CH$_3$-$\text{p}$ (28 mg, 0.14 mmole, 1.0 eq.) was added as a solid. The solution was warmed to room temperature over a period of 16 hours. A sample of the resultant dark red solution was transferred to a 5 mm NMR tube for $^{31}$P NMR analysis. Results of this study will be discussed in Section III-N.

$^{31}$P($^1$H) NMR (THF, 20 $^\circ$C) $\delta$

120.1 d, 92.0 d

$^2$J$_{P-P} = 89.4$ Hz

4 Reaction with Allyl Iodide

A red solution of Li$_2[/(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Ru}(\text{CO})_3]$ (0.14 mmole) was prepared from $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Ru}(\text{CO})_3$ (100 mg, 0.144 mmole) and 1.0 M LiBEt$_3$H (0.31 ml, 0.31 mmole, 2.2 eq.) in THF (2 ml). The solution was cooled to $-78 \, ^\circ\text{C}$ and treated with allyl iodide (13 $\mu$l, 0.14 mmole, 1.0 eq.). The reaction vessel was removed from the cold bath, and the solution was stirred at room temperature for 16 hours with a gradual color change to dark red. The solution was analyzed by $^{31}$P NMR, the results of which will be discussed in Section III-N.
5. Reaction with Benzyl Iodide

A red solution of Li$_2$[(CO)$_3$Fe($\mu$-PPh$_2$)$_2$Ru(CO)$_3$] (0.12 mmole) was prepared by treatment of a THF solution (4 ml) of (CO)$_3$Fe($\mu$-PPh$_2$)$_2$Ru(CO)$_3$ (80 mg, 0.12 mmole) with 1.0 M LiBEt$_3$H (0.25 ml, 0.25 mmole, 2.1 eq.). This solution was stirred for 30 minutes, cooled to -78 °C, and treated with 15 µl of C$_6$H$_5$CH$_2$I (0.12 mmole, 1.0 eq.). The solution was then slowly warmed to room temperature over a period of 14 hours. A sample of the resultant black solution was transferred to a 5 mm NMR tube for analysis by $^{31}$P NMR spectroscopy. Results of this study are discussed in Section III-N.

$^{31}$P($^1$H) NMR (THF, 20 °C) δ 139.6 d, 110.6 d  
2$\text{J}_{P-P}$ = 105 Hz

6. Reaction with 1,3-Diodopropane

A red solution of Li$_2$[(CO)$_3$Fe($\mu$-PPh$_2$)$_2$Ru(CO)$_3$] (0.086 mmole) was prepared from (CO)$_3$Fe($\mu$-PPh$_2$)$_2$Ru(CO)$_3$ (60 mg, 0.086 mmole) and 1.0 M LiBEt$_3$H (0.172 ml, 0.172 mmole, 2.0 eq.) in THF (4 ml). The solution was stirred for 30 minutes, cooled to -78 °C, and 1,3-diodopropane (10 µl, 0.086
mmole, 1.0 eq.) was added. The solution was warmed to room temperature over a period of 16 hours at which point it was very dark red. A sample was transferred to a 5 mm NMR tube for analysis by $^{31}$P NMR spectroscopy, the results of which are discussed in Section III-N.

$$^{31}\text{P} \{^1\text{H}\} \text{ NMR (THF, } 20 \, ^\circ\text{C}) \delta$$

\vspace{1cm}

7. Reaction with $\mathbf{\text{p-Butyl iodide}}$

A red solution of Li$_2$[(CO)$_3$Fe($\mu$-PPH$_2$)$_2$Ru(CO)$_3$] (0.14 mmole), prepared from (CO)$_3$Fe($\mu$-PPH$_2$)$_2$Ru(CO)$_3$ (100 mg, 0.144 mmole) and 1.0 M LiBEt$_3$H (0.288 ml, 0.288 mmole, 2.0 eq.), was cooled to -78 °C. The solution was treated with $\mathbf{\text{p-butyl iodide}}$ (16 μl, 0.15 mmole, 1.1 eq.) and slowly warmed to room temperature. After 16 hours a sample of the dark red solution was transferred to a 5 mm NMR tube for analysis by $^{31}$P NMR. Results of this study are discussed in Section III-N.
\[ ^{31}\text{P} \{ ^{1}\text{H} \} \text{ NMR (THF, 20 °C) } \delta \]
\[
139.3 \text{ d, 110.3 d}
\]
\[
^{2}J_{P,H} = 105 \text{ Hz}
\]
\[
123.5 \text{ d, 96.1 d}
\]
\[
^{2}J_{P,H} = 81 \text{ Hz}
\]

8. Reaction with Trifluoroacetic Acid

In a drybox (CO)\(_3\)Fe(μ-PPh\(_2\))\(_2\)Ru(CO)\(_3\) (100 mg, 0.144 mmole) was dissolved in THF (2 ml) and treated with 1.0 M LiBEt\(_3\)H (0.31 ml, 0.31 mmole, 1.2 eq.) to form Li\(_2\)((CO)\(_3\)Fe(μ-PPh\(_2\))\(_2\)Ru(CO)\(_3\)) (0.14 mmole). After 30 minutes of stirring CF\(_3\)COOH (12 μl, 0.16 mmole, 1.1 eq.) was added. The solution darkened considerably and was analyzed by \(^{31}\text{P} \text{ NMR spectroscopy} after 5 hours.

\[ ^{31}\text{P} \{ ^{1}\text{H} \} \text{ NMR (THF, 20 °C) } \delta \]
\[
136.1 \text{ d, 112.9 d} \quad ^{2}J_{P,H} = 99 \text{ Hz}
\]
\[
120.0 \text{ d, 91.8 d} \quad ^{2}J_{P,H} = 84 \text{ Hz}
\]
\[
97.0 \text{ d, 85.1 d} \quad ^{2}J_{P,H} = 117 \text{ Hz}
\]
\[-76.0 \text{ s}
\]

The above procedure was repeated using CF\(_3\)COOD (12 μl, 0.16 mmole, 1.1 eq.). Spectroscopic data for the reaction solution (\(^{31}\text{P} \text{ and } ^{2}\text{H NMR}) are presented below.
\[
^{31}\text{P} \{^{1}\text{H}\} \text{NMR (THF, } 20 \degree \text{C)} \delta \\
140.1 \text{ d, } 110.2 \text{ d, } J_{P-P} = 101 \text{ Hz} \\
120.2 \text{ d, } 91.7 \text{ d, } J_{P-P} = 83 \text{ Hz}
\]

\[
^{2}\text{H} \text{NMR (THF, } 20 \degree \text{C)} \delta \\
3.78 \text{ s, } 1.92 \text{ s, } -3.32 \text{ s, } -16.86 \text{ s}
\]

Results of these studies are discussed in Section III-N.

Q. Electrochemical Reduction of (CO)\textsubscript{3}Fe(\mu\text{-}PPh\textsubscript{2})\textsubscript{2}Ru(CO)\textsubscript{3}

A cyclic voltammetry experiment involving (CO)\textsubscript{3}Fe(\mu\text{-}PPh\textsubscript{2})\textsubscript{2}Ru(CO)\textsubscript{3} was carried out under a nitrogen atmosphere in a drybox by the following procedure. A solution of (CO)\textsubscript{3}Fe(\mu\text{-}PPh\textsubscript{2})\textsubscript{2}Ru(CO)\textsubscript{3} was prepared in acetonitrile with tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Ferrocene was added as an internal standard. A cyclic voltammogram was recorded using a hanging mercury-drop electrode and an Ag/AgCl reference electrode (0.197 V vs. NHE). The resultant two electron reduction was quasi-reversible with \(E_{p}^c = -1.92\) V vs. ferrocene. The cyclic voltammogram is shown in Figure 8.

An identical procedure was used to study the reduction of (CO)\textsubscript{3}Fe(\mu\text{-}PPh\textsubscript{2})\textsubscript{2}Fe(CO)\textsubscript{3}.\textsuperscript{32} The cyclic voltammogram obtained in this experiment is shown in Figure 9. A reversible two electron reduction is indicated with \(E_{1/2} = -1.65\) V vs. ferrocene.
$\text{(CO)}_3\text{Fe(\mu-PPh}_2\text{)}_2\text{Ru(CO)}_3 \xleftrightarrow{+2e^+} \text{(CO)}_3\text{Fe(\mu-PPh}_2\text{)}_2\text{Ru(CO)}_3^{2-}$

$E_p^c = -1.92V \text{ vs. ferrocene}$

Figure 8: Cyclic Voltammogram of FeRu(CO)$_6$(\mu-PPh$_2$)$_2$
Figure 9: Cyclic Voltammogram of $\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)_2$
III. DISCUSSION

A. Synthesis of \( \text{Fe}_2(\text{CO})_6[\mu-\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\text{Ph})_2]_2 \)

The family of bis(diorganophosphido)hexacarbonyldiiron complexes has grown extensively since the synthesis of the first member, \( \text{Fe}_2(\text{CO})_6(\mu-\text{PMe}_2)_2 \), in 1964 by Hayter.\textsuperscript{29} Since that time the diphenylphosphido\textsuperscript{16} and diethylphosphido\textsuperscript{72} analogues as well as several others\textsuperscript{68} have been added and a vast number of new related compounds have been derived from these simple dimers.\textsuperscript{26,31,32} One of the most extensively studied members of the family has been the bis(diphenylphosphido) complex\textsuperscript{16,32} and numerous comparisons of reactivity and properties of this complex with other analogues have been made.\textsuperscript{26}

One goal of the research reported herein was to develop a new member of the family in which a significant electronic difference but subtle geometric change from the bis(diphenylphosphido) complex had been introduced. A complex containing para-trifluoromethyl groups on the phenyl rings appeared to be a good candidate for this study. A number of anionic derivatives of \( \text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)_2 \) are known but some are thermally unstable\textsuperscript{31} and it was hoped that the presence of the electron-withdrawing trifluoromethyl groups would help to stabilize these derivatives.
In developing a synthesis of the trifluoromethyl-substituted compound a number of routes could have been chosen but the best of these appeared to be one completely analogous to the best available synthesis of Fe$_2$(CO)$_6$(μ-PPPh)$_2$. The reaction of Na$_2$Fe$_2$(CO)$_8$ with PPh$_2$Cl produces Fe$_2$(CO)$_6$(μ-PPPh)$_2$ in moderate yield (53%), and a similar result is obtained when Na$_2$Fe$_2$(CO)$_8$ is reacted with P(C$_6$H$_4$CF$_3$-μ)Cl to produce Fe$_2$(CO)$_6$[μ-P(C$_6$H$_4$CF$_3$-μ)]$_2$ (41% yield). While the yield is slightly lower, the simplicity of the procedure and the purity of the product thus obtained indicate that it is probably the best method to employ. The product was obtained as a yellow powder, similar in appearance to Fe$_2$(CO)$_6$(μ-PPPh)$_2$. It is sparingly soluble in pentane but readily soluble in more polar organic solvents such as THF and acetone.

Characterization of this compound is based on comparisons of spectral data with those of related known complexes. In Table 6 $^{31}$P NMR and IR spectral data for this complex and the bis(diphenylphosphido) and bis(dimethylphosphido) analogues are compared. The infrared spectra of Fe$_2$(CO)$_6$[μ-P(C$_6$H$_4$CF$_3$-μ)]$_2$ and Fe$_2$(CO)$_6$(μ-PPPh)$_2$ are depicted in Figure 10 to illustrate the similarity between the two. It is immediately observed that a five band carbonyl absorption pattern is seen in both cases. The pattern is typical of complexes of the type Fe$_2$(CO)$_6$(μ-PR)$_2$, and it should be noted in these two cases that the intensities of the absorptions are also similar.

The phosphorus-31 NMR shift for the fluorinated complex is, as expected, slightly upfield from that of the non-fluorinated compound owing to the electronic effect of the CF$_3$ groups. Additionally, the electron-withdrawing effect of the CF$_3$ groups is evidenced by the shift of the carbonyl frequencies in the IR to slightly higher energy.
Figure 10: Infrared Spectra of Fe$_2$(CO)$_6$(μ-P(C$_6$H$_4$CF$_3$-O)$_2$) and Fe$_2$(CO)$_6$(μ-PPh$_2$)$_2$
Table 6
Spectral Data For Fe$_2$(CO)$_6$(μ-PR$_2$)$_2$

<table>
<thead>
<tr>
<th>R</th>
<th>C$_6$H$_4$CF$_3$-R</th>
<th>Ph$^{31}$</th>
<th>Me$^{26}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{31}$P $^{1}$H NMR, δ$^a$</td>
<td>136.0</td>
<td>141.0</td>
<td>120.0</td>
</tr>
<tr>
<td>IR v$_{CO}$, cm$^{-1}$$^b$</td>
<td>2058 s, 2020 s, 1999 s, 1980 s, 1972 m</td>
<td>2058 s, 2019 s, 1997 s, 1970 s, 1952 m</td>
<td>2050 s, 2010 vs, 1977 vs, 1961 s</td>
</tr>
</tbody>
</table>

$^a$CDCl$_3$, 20 °C, $^bcyclohexane$

The structure of the bis(diphenylphosphido) complex is known to have a folded ("butterfly") Fe$_2$P$_2$ core$^{32}$ rather than a planar arrangement. Although an X-ray crystallographic study of Fe$_2$(CO)$_6$[P(C$_6$H$_4$CF$_3$-Q)$_2$]$_2$ was not carried out, this complex is presumed to also exist in a folded form, and there are some data to support this assumption. The appearance of two signals in the $^{19}$F NMR spectrum (Figure 11) of the complex indicates non-equivalent CF$_3$ groups. A folded structure would have two of the substituted phenyl rings oriented toward the fold (endo) and two pointing away (exo) and thus the inequivalence of the CF$_3$ groups. A planar geometry would not account for this difference (Figure 12). Additionally, the IR pattern in the carbonyl region suggests a geometry (C$_{2v}$ symmetry) similar to that of Fe$_2$(CO)$_6$(μ-PPh$_2$)$_2$. 
Figure 11: $^{19}$F NMR Spectrum of Fe$_2$(CO)$_6$[μ-P(C$_6$H$_4$CF$_3$-p)$_2$]$_2$
B. Reduction of Fe₂(CO)_₆[µ-P(C₆H₄CF₃-p)₂]₂

As stated previously one goal of this research was to study the reduction of Fe₂(CO)_₆[µ-P(C₆H₄CF₃-p)₂]₂ and determine the stability of the so derived anionic species. Additionally, some reactivity studies of the anionic derivatives were carried out.

A number of metal-metal bonded binuclear transition metal complexes are known in which reduction by two electrons results in a loss of metal-metal bonding interaction due to addition of the electrons to molecular orbitals that are metal-metal antibonding in character. The family of bis(diorganophosphido)hexacarbonyldiiron systems generally undergo this type of reduction, and that result was obtained in the sodium reduction of Fe₂(CO)_₆[µ-P(C₆H₄CF₃-p)₂]₂ (Equation 24). The conversion is indicated by ^{31}P NMR to be quantitative, and the resultant dianionic complex produces a deep red color in solution.
The sodium salt of the dianion was identified as such by its spectroscopic similarity to related compounds. Upon reduction to the dianion, the bis(diphenylphosphido) complex adopts a planar geometry for the Fe₂P₂ core, and it is likely that a similar geometric change takes place in the above reaction. The ³¹P{¹H} NMR spectrum exhibits only one high-field signal at -55.0 ppm, indicating equivalent phosphido groups and the absence of a metal-metal bond in the compound. Additionally, the IR spectrum of Na₂{Fe₂(CO)₆[μ-P(C₆H₄CF₃-p)₂]₂} has a pattern resembling that of Na₂{Fe₂(CO)₆(μ-PPh₂)₂}, with terminal carbonyl stretching absorptions at low energies confirming the anionic nature of the complex. Pertinent data for both dianions are contained in Table 7.

While thermally quite stable, the dianionic product is easily converted back to the original neutral complex upon exposure to oxygen for short periods of time (< 5 min.). From ³¹P NMR spectroscopic analysis it is estimated that the oxidation to Fe₂(CO)₆[μ-P(C₆H₄CF₃-p)₂]₂ is essentially quantitative.
A different, more indirect method of forming the two-electron reduction product, involving two steps, has also been found. When a solution of \( \text{Fe}_2(\text{CO})_6[\mu-\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\text{p})_2]_2 \) is treated with two or more equivalents of \( \text{LiBE}_3\text{H} \) the corresponding lithium dianion, \( \text{Li}_2\{\text{Fe}_2(\text{CO})_6[\mu-\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\text{p})_2]_2 \} \), is produced as the only product. It is advantageous at this point to first discuss the reaction of \( \text{Fe}_2(\text{CO})_6[\mu-\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\text{p})_2]_2 \) with less than two equivalents of \( \text{LiBE}_3\text{H} \).

When the starting neutral dimer is treated with one equivalent of \( \text{LiBE}_3\text{H} \) a monoanionic complex with a terminal phosphine ligand, \( \text{Li}\{(\text{CO})_3\text{Fe}[\mu-\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\text{p})_2](\mu-\text{CO})\text{Fe}(\text{CO})_2\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\text{p})_2\text{H}\} \), is formed.

### Table 7

Comparative Spectroscopic Data for \( \text{Na}_2[\text{Fe}_2(\text{CO})_6(\mu-\text{PR}_2)_2] \)
\[
R = \text{C}_6\text{H}_4\text{CF}_3-\text{p}, \text{C}_6\text{H}_5
\]

<table>
<thead>
<tr>
<th></th>
<th>( \text{C}_6\text{H}_4\text{CF}_3-\text{p} )</th>
<th>( \text{Ph}^{31,32} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{31}\text{P} {^1\text{H}} \text{ NMR, } \delta )</td>
<td>-55.0</td>
<td>-62.4</td>
</tr>
<tr>
<td>IR ( \nu_{\text{CO}, \text{cm}^{-1}} )</td>
<td>1942 m, 1917 s, 1856 s, 1806 s</td>
<td>1930 sh, 1905 s, 1845 s, 1825 sh, 1800 s</td>
</tr>
</tbody>
</table>

* THF, 20 °C
The product is formulated as such based on comparisons of $^{31}$P NMR data with those of the known compound, Li[(CO)$_3$Fe($\mu$-PPh$_2$)($\mu$-CO)Fe(CO)$_2$PPh$_2$H].$^{47}$ This information is contained in Table 8 and the $^{31}$P NMR spectrum of Li[(CO)$_3$Fe[$\mu$-$P$($C_6H_4CF_3$-$p$)$_2$][$\mu$-CO]Fe(CO)$_2$P($C_6H_4CF_3$-$p$)H] is shown in Figure 13. The signal downfield at 120.8 ppm is assigned to the phosphorus of the bridging phosphido group while the signal at 50.9, with phosphorus-proton coupling of 337 Hz, can be assigned to the phosphorus of the terminal phosphine ligand. A mechanism for formation of Li[(CO)$_3$Fe($\mu$-PPh$_2$)$_2$($\mu$-CO)Fe(CO)$_2$PPh$_2$H] has been proposed by Wojcicki and Shyu.$^{11}$ Although a low temperature NMR study was not carried out to follow the reaction of Fe$_2$(CO)$_6$[$\mu$-$P$(C$_6$H$_4$CF$_3$-$p$)$_2$] with LiBEt$_3$H the formation of the monoanion is presumed to occur by a similar mechanism, shown in equation 25.

$$\text{(CO)}_3\text{Fe} + \text{LiBEt}_3\text{H} \xrightarrow{\text{THF}, 78^\circ C} \text{Li[(CO)}_3\text{Fe}_2\text{Fe(CO)}_2\text{]}$$

$$\xrightarrow{\text{warm}} \text{Li[(CO)}_3\text{Fe}_2\text{Fe(CO)}_3\text{]}$$

$$\text{Li[(CO)}_3\text{Fe}_2\text{Fe(CO)}_2\text{]} \xrightarrow{20^\circ C} \text{Li[(CO)}_3\text{Fe}_2\text{Fe(CO)}_3\text{]}$$

$\text{Ph'} = C_6H_4CF_3$-$p$
### Table 8: Comparison of $^{31}P$ NMR Data for Li[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$PPh$_2$H] and

$^1$Li[(CO)$_3$Fe[μ-P(C$_6$H$_4$CF$_3$-p)$_2$](μ-CO)Fe(CO)$_2$[P(C$_6$H$_4$CF$_3$-p)$_2$H]]

<table>
<thead>
<tr>
<th></th>
<th>PB$_2$</th>
<th>C$_6$H$_4$CF$_3$-p</th>
<th>Ph$_{31}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{31}P$ ($^1$H) NMR δ</td>
<td>120.8 d, 51.0 d</td>
<td>122.5 d, 51.3 d</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^2$J$_{P,H}$ = 13.0 Hz</td>
<td>$^2$J$_{P,P}$ = 12 Hz</td>
<td></td>
</tr>
<tr>
<td>$^{31}P$ NMR δ</td>
<td>120.8 br. s, 50.9 d</td>
<td>122.5 br. s, 51.3 br. d</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^1$J$_{P,H}$ = 337 Hz</td>
<td>$^1$J$_{P,P}$ = 334 Hz</td>
<td></td>
</tr>
</tbody>
</table>
Figure 13: $^{31}P(^1H)$ NMR Spectrum of
\[ \text{Li}((\text{CO})_3\text{Fe}[\mu-P(\text{C}_6\text{H}_4\text{CF}_3-p)_2](\mu-\text{CO})\text{Fe}(\text{CO})_2[P(\text{C}_6\text{H}_4\text{CF}_3-p)_2\text{H}]) \]
At room temperature addition of a second equivalent of LiBEt$_3$H to Li[(CO)$_3$Fe($\mu$-PPh$_2$)$_2$(\(\mu$-CO)Fe(CO)$_2$PPh$_2$H)] produces no further reaction.$^{31}$ Treatment of Li[(CO)$_3$Fe($\mu$-P(C$_6$H$_4$CF$_3$-p)$_2$)(\(\mu$-CO)Fe(CO)$_2$P(C$_6$H$_4$CF$_3$-p)$_2$H)] with an additional equivalent of LiBEt$_3$H, however, produces the lithium dianion Li$_2$[(CO)$_3$Fe($\mu$-P(C$_6$H$_4$CF$_3$-p)$_2$)$_2$Fe(CO)$_3$] readily. It is assumed that the second equivalent of LiBEt$_3$H serves as a deprotonating agent to form H$_2$ and the dianion Li$_2$[(CO)$_3$Fe($\mu$-P(C$_6$H$_4$CF$_3$-p)$_2$)$_2$Fe(CO)$_3$], which quickly rearranges to the final product (equation 26).

\[
\text{Ph'} = \text{C}_6\text{H}_4\text{CF}_3\text{-p}
\]

(26)

A reasonable explanation for the differences in behavior of the fluorinated and non-fluorinated systems is that the presence of the CF$_3$ groups tends to increase the acidity of the phosphine hydrogen through the increased electron withdrawing ability. A similar deprotonation can be carried out using \(\eta^2\)-BuLi. Details of this reaction are discussed in the following section.
C. Thermal Conversion of Li$_2$((CO)$_3$Fe[μ-P(C$_6$H$_4$CF$_3$-p)$_2$](μ-CO)Fe(CO)$_2$[P(C$_6$H$_4$CF$_3$-p)$_2$]) to Li$_2$((CO)$_3$Fe[μ-P(C$_6$H$_4$CF$_3$-p)$_2$]$_2$Fe(CO)$_3$).

Deprotonation of Li[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$H)] at low temperature (-78 °C) using n-BuLi leads to formation of Li$_2$((CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$)).$^{31}$ It has been shown that this product is thermally unstable and rearranges to the more symmetrical dianion, Li$_2$((CO)$_3$Fe(μ-PPh$_2$)$_2$Fe(CO)$_3$), upon warming to -33 °C. One goal of this research was to develop a compound similar to (CO)$_3$Fe(μ-PPh$_2$)$_2$Fe(CO)$_3$ which would mimic its chemistry somewhat but allow isolation of Li$_2$((CO)$_3$Fe(μ-PR$_2$)(μ-CO)Fe(CO)$_2$(PR$_2$)) at room temperature. It was presumed that if this dianion could easily be isolated, a considerable amount of chemistry aimed at formation of new products could be carried out using the dianion as a starting material.

As indicated in the previous section, deprotonation of Li[(CO)$_3$Fe[μ-P(C$_6$H$_4$CF$_3$-p)$_2$](μ-CO)Fe(CO)$_2$[P(C$_6$H$_4$CF$_3$-p)$_2$H)] with n-BuLi at -78 °C does in fact lead to formation of Li$_2$((CO)$_3$Fe[μ-P(C$_6$H$_4$CF$_3$-p)$_2$](μ-CO)Fe(CO)$_2$[P(C$_6$H$_4$CF$_3$-p)$_2$]) producing a purple color in THF. In order to examine the stability of this product a variable temperature $^{31}$P NMR study was carried out. Spectra were recorded at 10 °C intervals and are depicted in Figure 14. At -78 °C two signals are observed in the $^{31}$P NMR spectrum. The bridging phosphido group produces the signal at 133.1 ppm, indicating the presence of a metal-metal bond, while the terminal phosphido ligand is indicated by the signal at 23.8 ppm. Additionally, the upfield signal does not exhibit a one-bond phosphorus-proton coupling, thus confirming the deprotonation of the original phosphine ligand.
Figure 14: Variable Temperature $^{31}$P NMR Study of the Conversion of Li$_2$((CO)$_3$Fe[$\mu$-P(C$_6$H$_4$CF$_3$-p)$_2$]($\mu$-CO)Fe(CO)$_2$[P(C$_6$H$_4$CF$_3$-p)$_2$]) to Li$_2$((CO)$_3$Fe[$\mu$-P(C$_6$H$_4$CF$_3$-p)$_2$)$_2$Fe(CO)$_3$]
As the solution is warmed, these doublets begin to broaden and diminish in intensity while a new signal at -55.0 ppm appears. This upfield resonance indicates the formation of \( \text{Li}_2[(\text{CO})_3\text{Fe}[\mu-(\text{C}_6\text{H}_4\text{CF}_3-\mu)_2]_2\text{Fe}(\text{CO})_3] \), the dianionic complex described in the previous section. The data indicate that the conversion begins to occur at approximately -43 °C and is essentially complete at -33 °C. The conversion temperature in the rearrangement of \( \text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PPH}_2)] \) to \( \text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPH}_2)_2\text{Fe}(\text{CO})_3] \) is -43 °C to -33 °C, and therefore it can be concluded that the presence of the trifluoromethyl groups has not altered the thermal stability of the unsymmetrical dianion, \( \text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PR}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PR}_2)] \), to any significant extent. This thermal instability precluded an in-depth investigation of the chemistry of \( \text{Li}_2[(\text{CO})_3\text{Fe}[\mu-(\text{C}_6\text{H}_4\text{CF}_3-\mu)_2](\mu-\text{CO})\text{Fe}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\mu)_2]] \) but some work was carried out as described in the next section.

D. Reaction of \( \text{Li}_2[(\text{CO})_3\text{Fe}[\mu-(\text{C}_6\text{H}_4\text{CF}_3-\mu)_2](\mu-\text{CO})\text{Fe}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\mu)_2]] \) with Methyl Iodide.

While the goal of forming \( \text{Li}_2[(\text{CO})_3\text{Fe}[\mu-(\text{C}_6\text{H}_4\text{CF}_3-\mu)_2](\mu-\text{CO})\text{Fe}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\mu)_2]] \) at room temperature was not realized it was still decided to investigate some reactivity and compare the results with those obtained from the non-fluorinated system. Alkylation of \( \text{Li}_2[(\text{CO})_3\text{Fe}[\mu-(\text{C}_6\text{H}_4\text{CF}_3-\mu)_2](\mu-\text{CO})\text{Fe}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\mu)_2]] \) by treatment at -78 °C with excess methyl iodide has been found to produce an air-stable compound containing a bridging acetyl ligand, \( (\text{CO})_3\text{Fe}[\mu-(\text{C}_6\text{H}_4\text{CF}_3-\mu)_2][\mu-(\text{C}(\text{CH}_3)\text{O})\text{Fe}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\mu)_2\text{CH}_3]] \) (Figure 15). This complex is obtained as a red powder, the characterization of which involved comparisons of \(^{31}\text{P}\)
NMR and IR spectroscopic data to those of the analogous compound, (CO)$_3$Fe($\mu$-PPh$_2$)[μ-C(CH$_3$)O]Fe(CO)$_2$(PPh$_2$CH$_3$). Data for both complexes are contained in Table 9.

![Figure 15](image)

As expected, two doublets ($^{2}J_{P\cdot P} = 71.6$ Hz) are observed in the $^{31}$P NMR spectrum, one downfield at 172.1 ppm owing to the bridging phosphido group and the other farther upfield at 41.8 ppm arising from the terminal phosphine ligand. The bridging acetyl ligand is evidenced by a weak absorption at 1462 cm$^{-1}$ in the infrared spectrum. The absorptions assigned to the terminal carbonyl ligands appear in an expected pattern similar to that of (CO)$_3$Fe($\mu$-PPh$_2$)[μ-C(CH$_3$)O]Fe(CO)$_2$(PPh$_2$CH$_3$).

One aspect of this reaction which differs significantly from that of the non-fluorinated compound is that the yield of (CO)$_3$Fe($\mu$-P(C$_6$H$_4$CF$_3$-d)$_2$)[μ-C(CH$_3$)O]Fe(CO)$_2$[P(C$_6$H$_4$CF$_3$-d)$_2$CH$_3$] is substantially lower. A yield of 90% has been reported$^{31}$ for the synthesis of (CO)$_3$Fe($\mu$-PPh$_2$)[μ-C(CH$_3$)O]Fe(CO)$_2$(PPh$_2$CH$_3$) while (CO)$_3$Fe($\mu$-P(C$_6$H$_4$CF$_3$-d)$_2$)[μ-C(CH$_3$)O]Fe(CO)$_2$[P(C$_6$H$_4$CF$_3$-d)$_2$CH$_3$] has been produced only in a yield of 40%.
Table 9: Spectroscopic Data for (CO)$_3$Fe(μ-PR$_2$)[μ-C(CH$_3$)O]Fe(CO)$_2$(PR$_2$CH$_3$)

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<thead>
<tr>
<th>R</th>
<th>C$_6$H$_4$CF$_3$-p</th>
<th>Ph$^{31}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{31}$P ($^1$H) NMR $^a$</td>
<td>172.1 d, 41.8 d</td>
<td>174.1 d, 39.7 d</td>
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<tr>
<td>$^2$J$_{P,p}$ = 71.6 Hz</td>
<td></td>
<td>$^2$J$_{P,p}$ = 55 Hz</td>
</tr>
</tbody>
</table>

| IR $v_{C=O}$ cm$^{-1}$ $^b$ | 2042 m, 1988 s            | 2039 m, 1981 s, 1951 s, 1934 m, 1928 m |
|                            | 1959 s, 1936 m            |                                      |

| $v_{C=O}$ cm$^{-1}$         | 1462 w                      | 1483 w                       |

$^a$THF, 25 °C  
$^b$cyclohexane
E. Reaction of \( \text{Li}_2\{(\text{CO})_3\text{Fe}[\mu-\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\text{a})_2]\text{Fe}(\text{CO})_3}\) with Trifluoroacetic Acid.

A considerable amount of chemistry has also been derived from \( \text{M}_2\{(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe}(\text{CO})_3\}\) (\( \text{M} = \text{Li} \) or \( \text{Na} \)). For example, protonation with one equivalent of trifluoroacetic acid leads to formation of \( \text{M}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PPh}_2\text{H})]\) via an initially-formed metal hydride complex whereas alkylation by alkyl halides results in the initial formation of metal alkyl complexes, \( \text{M}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe}(\text{CO})_3\text{R}] \), which thermally rearrange to metal acyl complexes, \( \text{M}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe}(\text{CO})_2\text{COR}] \). In this study protonation of \( \text{Na}_2\{(\text{CO})_3\text{Fe}[\mu-\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\text{a})_2]\text{Fe}(\text{CO})_3\} \) using trifluoroacetic acid was investigated.

When carried out at room temperature in THF the reaction proceeds smoothly to give a product analogous to that obtained in the bis(diphenylphosphido) system, viz. \( \text{Na}_2\{(\text{CO})_3\text{Fe}[\mu-\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\text{a})_2]\text{Fe}(\text{CO})_3\}[(\mu-\text{CO})\text{Fe}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\text{a})_2\text{H}]] \), as the only product indicated by \( ^{31}\text{P} \) NMR. This product is simply the sodium analogue of the previously-described lithium salt obtained by the reaction of \( (\text{CO})_3\text{Fe}[\mu-\text{P}(\text{C}_6\text{H}_4\text{CF}_3-\text{a})_2]\text{Fe}(\text{CO})_3 \) with one equivalent of \( \text{LiBEt}_3\text{H} \). Therefore the \( ^{31}\text{P} \) NMR spectrum appears essentially the same. A doublet at 123.7 ppm is assigned to the bridging phosphido group while the terminal phosphine ligand appears at 52.8 ppm.

The probable pathway for formation of this product involves initial attack of \( \text{H}^+ \) at one of the metal centers to form a metal hydride species which then, as mentioned earlier, undergoes reductive elimination of the hydride and a phosphido ligand to give the final product (Scheme 1). This is the same type of mechanism that has been proposed for the bis(diphenylphosphido) system.
$\text{Na}_2[(\text{CO})_3\text{Fe}]$ + $\text{H}^+$ $\rightarrow$ $\text{Na}[(\text{CO})_3\text{Fe}]$

$\text{Ph}^' = \text{C}_6\text{H}_4\text{CF}_3\cdot\text{O}$

Scheme 1
F. Reactions of $[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(CO)}_2\text{PPh}_2\text{H}]]^-$ with Diorganochlorophosphines: Preparation and Characterization of "Mixed-Bridge" Bisphosphido Hexacarbonyl Diiron Complexes.

1. $\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)(\mu-\text{P-1-Bu}_2)$

As with the dianionic diiron complexes discussed in the previous sections, the monoanionic species $[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(CO)}_2\text{PPh}_2\text{H}]]^-$ can serve as a starting point for formation of new compounds. Studies of this anionic compound have been carried out previously\textsuperscript{31,67} leading to the formation of several new products. The research undertaken in this study involved further investigations of the reactivity of $\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(CO)}_2\text{PPh}_2\text{H}]$ with a goal of forming more new products. In particular, reaction with diorganochlorophosphines, $\text{PR}_2\text{Cl}$, has led to the formation of new "mixed-bridge" complexes, $\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)(\mu-\text{PR}_2)$, a class of compounds for which there are very few reports in the literature.\textsuperscript{68}

Treatment of a THF solution of $\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(CO)}_2\text{PPh}_2\text{H}]$ with excess di-1-butylchlorophosphine and subsequent chromatography on Florisil leads to the isolation of several binuclear phosphido-bridged products. The major product of this reaction has been identified as $\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)(\mu-\text{P-1-Bu}_2)$. This dark red solid, obtained in moderate yield (43 %), can be obtained as crystals by slow diffusion of hexane into a methylene chloride solution saturated with the compound. The red solid is somewhat more soluble in hydrocarbon solvents than is the bis(diphenylphosphido) analogue, an expected consequence of replacement of two phenyl groups with bulky alkyl groups.
The proton-decoupled phosphorus-31 NMR spectrum of this new compound (Figure 16) exhibits two doublets with phosphorus-phosphorus coupling of 63 Hz. The signal at 290.8 ppm is assigned to the bridging di-1-butyl phosphido group, while the diphenylphosphido bridging ligand gives rise to the signal at 173.3 ppm. The relative downfield position of both signals indicates that the phosphido ligands are bridging iron centers involved in metal-metal bonding. Two pieces of information have allowed assignment of these signals. First, the substantial difference in chemical shift must be considered. When surveying the literature of di-1-butylphosphido-bridged complexes it is found that the phosphorus atoms of the bridges exhibit $^{31}$P NMR signals with considerable downfield shifts. The $^{31}$P NMR data for two of these complexes and related diphenylphosphido complexes are contained in Table 10.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta(\mu-P)$</th>
<th>Complex</th>
<th>$\delta(\mu-P)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Co}_2(\text{CO})_4$($\mu$-P-1-Bu$_2$)$_2$</td>
<td>331.4</td>
<td>$\text{Co}_2(\text{CO})_6$($\mu$-PPh$_2$)$_2$</td>
<td>114</td>
</tr>
<tr>
<td>$\text{Rh}_3(\text{CO})_3$($\mu$-P-1-Bu$_2$)$_3$</td>
<td>369.5</td>
<td>$\text{Rh}_3(\text{CO})_3$($\mu$-PPh$_2$)$_3$(PPh$_3$)</td>
<td>269</td>
</tr>
</tbody>
</table>
Figure 16: $^{31}\text{P}(\text{IH})$ NMR Spectrum of Fe$_2$(CO)$_6$(µ-PPh$_2$)(µ-P-1-Bu$_2$)
This information supports the assignment of the downfield signal to the di-t-butylphosphido ligand. This assignment is confirmed upon examination of the proton-coupled $^{31}$P NMR spectrum shown in Figure 17. The signal at 173.3 ppm appears as a doublet of triplets with phosphorus-proton coupling of 11 Hz. This signal is typical for bridging diphenylphosphido ligands, with the phosphorus coupling to two protons in the ortho positions. The signal for the di-t-butylphosphido ligand, on the other hand, should appear as a doublet of decets, with phosphorus coupling to nine equivalent methyl protons. In fact, it appears as an overlapping doublet of multiplets with phosphorus-proton coupling of 14 Hz.

The presence of one di-t-butylphosphido bridge and one diphenylphosphido bridge is confirmed by the $^1$H NMR spectrum, Figure 18. A multiplet in the region from 7.28 ppm to 7.62 ppm is assigned to the ten phenyl protons. The eighteen methyl protons of the t-butyl groups give rise to a doublet at 1.36 ppm with proton-phosphorus coupling of 14 Hz, the same value as that observed in the $^{31}$P NMR spectrum. Furthermore, with the assignment of the phenyl region to ten protons, the methyl signal integrates to eighteen protons.

Further support for the assignment of this structure is provided by the $^{13}$C($^1$H) NMR spectrum which is shown in Figure 19. Assuming that the carbonyl ligands are equivalent, a doublet of doublets, owing to the inequivalence of the bridging phosphido ligands, would be expected for the carbonyl resonance in the downfield region of the spectrum. In fact, the carbonyl signal appears as a triplet with carbon-phosphorus coupling of 5.5 Hz. This is assumed to arise from coincidental overlap of the expected two doublets, i.e. the carbonyls are coupled to each phosphorus nucleus by 5.5 Hz.
Figure 17: $^{31}$P NMR Spectrum of $\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)(\mu-\text{P-1-Bu}_2)$
Figure 18: $^1$H NMR Spectrum of Fe$_2$(CO)$_6$(μ-Ph$_2$)(μ-Ph$_{-}$Bu$_2$)
Figure 19: $^{13}$C($^1$H) NMR Spectrum of Fe$_2$(CO)$_6$(μ-PPh$_2$)(μ-P-1-Bu$_2$)
In the aromatic region of the $^{13}$C-$^1$H NMR spectrum the expected signals for the phenyl carbons are seen. Further upfield two doublets are observed and are assigned to the $t$-butyl carbons. At 44.27 ppm a signal with carbon-phosphorus coupling of 5.6 Hz is observed. This signal is assigned to the quaternary carbons of the $t$-butyl groups because of the significant carbon-phosphorus coupling, the intensity of the signal, and the chemical shift of the signal. This assignment becomes clearer when considering the other signal in the aliphatic region, a doublet at 33.99 ppm with carbon-phosphorus coupling of only 1.9 Hz. Assignment of this signal to the methyl carbons of the $t$-butyl groups is supported by comparisons to the other aliphatic signal: this upfield signal is much more intense owing to the fact that it arises from primary carbons and the carbon-phosphorus coupling is relatively smaller ($^2J_{C-P}$ vs. $^1J_{C-P}$). Additionally, the methyl carbons of $t$-butyl groups bonded to phosphorus generally appear upfield from the quaternary carbon.

The terminal carbonyl stretching region of the infrared spectrum, obtained in cyclohexane, is shown in Figure 20. Compounds of the type $\text{Fe}_2(\text{CO})_6(\mu-\text{PR}_2)_2$ with a folded $\text{Fe}_2\text{P}_2$ core and $C_{2v}$ symmetry generally display a five band absorption pattern in this region. The asymmetry introduced by the inequivalence of the phosphido bridges in $\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)(\mu-P-t-\text{Bu}_2)$, however, gives rise to an observed pattern of six distinct carbonyl stretching absorptions. The relative low energy [vs. $\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)_2$] of the absorptions is an expected consequence of the electron-donating ability of the $t$-butyl groups.

Although crystals of this compound can be obtained, a determination of the structure by X-ray diffraction was not carried out. Some comments on the geometry of the complex can be made, though. A number of
Figure 20: Infrared Spectrum of Fe₂(CO)₆(μ-PPh₂)(μ-P-1-Bu₂)
complexes of the type $\text{Fe}_2(\text{CO})_6(\mu-\text{PR}_2)_2$ have been shown by X-ray crystallographic studies to contain folded $\text{Fe}_2\text{P}_2$ cores. However, in the broader category of binuclear complexes containing bridging di-1-butylphosphido ligands unusual and perhaps unexpected geometries have been observed.\textsuperscript{25} The size of the di-1-butylphosphido group often forces a planar geometry of the $\text{M}_2\text{P}_2$ core for complexes which might have been predicted to have folded geometries (Figure 21).

In the complex reported here a folded geometry would likely result in inequivalence of the 1-butyl groups as shown in Figure 22, structure A. Inequivalence of the 1-butyl groups is not indicated by the $^{13}\text{C}$($^1\text{H}$) and $^1\text{H}$ NMR spectra as only one methyl signal is observed in each spectrum. A planar arrangement (Figure 22, structure B), on the other hand, would account for this equivalence. The infrared spectrum does not confirm or rule out either of these possibilities, although the pattern is very similar to those obtained for related folded complexes with $C_{2v}$ symmetry. Obviously an X-ray crystallographic determination of the structure would be the only certain way of solving this dilemma.

The reaction of $\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2\text{PPh}_2\text{H}]$ with excess di-1-butylchlorophosphine also produced a number of minor side products. Two of these were shown spectroscopically to simply be diphenylphosphine-substituted derivatives of $\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)_2$, specifically a monosubstituted compound, $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe}(\text{CO})_2\text{PPh}_2\text{H},^{31,72}$ and the disubstituted complex, $(\text{PPh}_2\text{H})(\text{CO})_2\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe}(\text{CO})_2(\text{PPh}_2\text{H}).^{31,72}$ Both have been reported previously and have been fully characterized. A third product was identified as the original starting material, $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe}(\text{CO})_3$. Although produced in fairly low yields (3.2, 4.3, and 11
Figure 21: Planar Di-1-butylphosphido-bridged Complexes
Figure 22: Planar vs. Folded Geometry for Fe$_2$(CO)$_6$(μ-PPh$_2$)(μ-P-1-Bu$_2$)
%, respectively), these compounds by their presence suggest that the chemistry involved in the reaction is indeed quite complicated. It should be noted, however, that the diphenylphosphine-substituted complexes may have formed during the chromatographic workup as a $^{31}$P($^1$H) NMR spectrum (Figure 23) of the reaction solution recorded prior to chromatography indicates the presence of only $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{P-t-Bu}_2)\text{Fe}(\text{CO})_3$, $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe}(\text{CO})_3$, diphenylphosphine (-41 ppm), and di-t-butylchlorophosphine.

Another new compound, produced in 9.0 % yield, has been characterized as $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{P-t-Bu}_2)\text{Fe}(\text{CO})_2\text{PPh}_2\text{H}$. A pattern of three signals is observed in the $^{31}$P($^1$H) NMR spectrum. A triplet downfield at 292.1 ppm is assigned to the bridging di-t-butylphosphido ligand. A doublet of doublets would be expected owing to coupling to two distinct phosphorus nuclei, but the values of these couplings are similar and result in overlap of the doublets to produce the triplet with an observed phosphorus-phosphorus coupling of 55 Hz. The diphenylphosphido bridge gives rise to a signal at 166.6 ppm which is split into a doublet of doublets with couplings of 47.7 Hz and 56.0 Hz. This reflects separate coupling to the di-t-butylphosphido ligand and the terminal diphenylphosphine ligand. Finally, the terminal diphenylphosphine ligand, which should also appear as a doublet of doublets, is seen as a triplet at 45.8 ppm with an observed coupling of 48.0 Hz. Examination of the proton-coupled $^{31}$P NMR spectrum confirms these assignments. The triplet at 45.8 ppm becomes a doublet of multiplets with phosphorus-proton coupling of 357 Hz, a value in the range for a proton directly bonded to a phosphorus atom. Additionally, the downfield signal at 292.1 ppm appears as a multiplet while, as expected, the signal at 166.6 ppm is seen as a triplet of triplets.
Figure 23: $^{31}P(^1H)$ NMR Spectrum of Crude Reaction Solution of Li[(CO)$_3$Fe(μ-PPh$_2$)$_2$] with P-1-Bu$_2$Cl
The $^1$H NMR spectrum (Figure 24) of this compound also supports the assignment discussed above. The signal for the phenyl protons, observed as a multiplet at 6.7-7.4 ppm, and that for the $t$-butyl protons, 1.36 ppm, integrate to 20 protons and 18 protons, respectively. In other words, this confirms the presence of two diphenyl phosphorus groups and only one di-$t$-butyl phosphorus group. The resonance for the terminal phosphine proton is seen as a doublet centered at 5.46 ppm with proton-phosphorus coupling of 360 Hz. The $^{13}$C ($^1$H) NMR spectrum produces no surprising results except that the carbonyl ligands appear as a singlet at 212.6 ppm thus suggesting fluxionality of these carbonyls.

One final product from this reaction must be mentioned. When the product mixture is subjected to chromatography on a Florisil column, the first substance obtained in a trace amount is a green solid. The phosphorus-$^{31}$ NMR spectrum of this solid consists of only one signal, a singlet at 362.6 ppm. Based on this spectrum the compound appears to be Fe$_2$(CO)$_5$(μ-P-$t$-Bu)$_2$, a compound which has been synthesized independently by the reaction of Na$_2$Fe$_2$(CO)$_8$ with $t$-Bu$_2$PCl. Details of this reaction and full characterization of the compound are discussed in section III-H.

The variety of products obtained in this reaction suggest that the chemistry involved is complicated. In an effort to gain some insight into this chemistry the reaction was repeated using only one equivalent of di-$t$-butylchlorophosphine. This reaction also produced the same six products discussed above. However, the most abundant product is (CO)$_3$Fe(μ-PPh$_2$)$_2$Fe(CO)$_3$ (ca. 35 %), while the yield of the di-$t$-butylphosphido-containing product, (CO)$_3$Fe(μ-PPh$_2$)(μ-$t$-Bu$_2$)Fe(CO)$_3$ was significantly lower (22 %). This substantially lower yield of what was previously the major product suggests
Figure 24: $^1$H NMR Spectrum of Fe$_2$(CO)$_5$(μ-Ph$_2$)(μ-P-$t$-Bu$_2$)PPh$_2$H
that it is likely not the initial compound formed in this reaction. As stated earlier, though, it is seen as a component of the reaction solution prior to chromatography. Determining the mechanism of the reaction will likely require an in-depth study involving low temperature NMR to follow the progress of the reaction.

2. \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{PET}_2)\text{Fe}(\text{CO})_3\)

In light of the result obtained in the reaction of \(\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2\text{PPh}_2\text{H}]\) with di-\(\text{t}\)-butylchlorophosphine it was decided that an investigation of the generality of the reaction should be undertaken. What products would be obtained if a diorganochlorophosphine other than di-\(\text{t}\)-butylchlorophosphine were used? In order to answer this question a solution of \(\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2\text{PPh}_2\text{H}]\) was treated with an excess amount of diethylchlorophosphine. The product mixture was chromatographed on activated Florisil and yielded a number of products. The major product of this reaction is a yellow solid identified as \((\text{CO})_3\text{Fe}(\mu-\text{PET}_2)(\mu-\text{PPh}_2)\text{Fe}(\text{CO})_3\) which was obtained in an isolated yield of 24.5%. Although the yield of this new mixed-bridge complex is substantially lower than that of \((\text{CO})_3\text{Fe}(\mu-\text{P-1-Bu}_2)(\mu-\text{PPh}_2)\text{Fe}(\text{CO})_3\), it is apparent that both reactions involve similar chemistry.

Characterization of the air-stable \((\text{CO})_3\text{Fe}(\mu-\text{PET}_2)(\mu-\text{PPh}_2)\text{Fe}(\text{CO})_3\) involved IR and NMR analysis as well as mass spectroscopy and elemental analysis. The proton-decoupled phosphorus-31 NMR spectrum of the compound, shown in Figure 25, produces the two expected doublets. The signals have similar chemical shifts thus appearing as an AB pattern, and assignment of the signals could therefore only be confirmed by examining the
Figure 25: $^{31}$P($^1$H) NMR Spectrum of Fe$_2$(CO)$_6$(µ-PPh$_2$)(µ-PEt$_2$)
proton-coupled spectrum (Figure 26). The doublet centered at 149.7 ppm becomes a doublet of triplets upon proton coupling and thus is assigned to the bridging diphenylphosphido ligand. Consequently, the doublet centered at 145.1 ppm is assigned to the bridging diethylphosphido ligand. In the proton-coupled spectrum this signal necessarily appears as a doublet of multiplets as it is coupling to the methylene protons and the methyl protons of the ethyl groups. Interestingly, the phosphorus nuclei are coupled to each other by 124 Hz, a relatively large value when compared to \((\text{CO})_3\text{Fe}(\mu-\text{P-1-Bu}_2)(\mu-\text{PPh}_2)\text{Fe(\text{CO})}_3\). This suggests a significant geometric difference between the two compounds, perhaps an increased folding of the \(\text{Fe}_2\text{P}_2\) core in \((\text{CO})_3\text{Fe}(\mu-\text{PET}_2)(\mu-\text{PPh}_2)\text{Fe(\text{CO})}_3\) owing to the smaller size of the diethylphosphido ligand.

The carbon-13 NMR spectrum of \((\text{CO})_3\text{Fe}(\mu-\text{PET}_2)(\mu-\text{PPh}_2)\text{Fe(\text{CO})}_3\) is shown in Figure 27. The carbonyl ligands are coupled to two phosphorus nuclei and thus appear as an overlapping doublet of doublets, resembling a triplet, at 212.7 ppm. The value of this coupling, 4.8 Hz, is typical for terminal carbonyl ligands in compounds of this type. Further upfield the expected resonances arising from the phenyl carbons appear in the region between 127 ppm and 140 ppm. In the aliphatic region of the spectrum an interesting pattern is observed. Two doublets, each with carbon-phosphorus coupling of 20 Hz, appear at 25.85 ppm and 25.69 ppm. These signals are assigned to the methylene carbons of the ethyl groups by virtue of their chemical shift and their coupling to phosphorus, the value of which is typical for carbon directly bonded to phosphorus. At 11.75 ppm and 11.36 ppm an additional two doublets appear. Both signals exhibit carbon-phosphorus coupling of 7 Hz and thus are assigned to the methyl carbons of the ethyl groups. These assignments were further confirmed by recording the DEPT carbon-13 NMR spectrum of the
Figure 26: $^{31}P$ NMR Spectrum of $\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)(\mu-\text{PEt}_2)$
Figure 27: $^{13}$C($^1$H) NMR Spectrum of Fe$_2$(CO)$_6$(μ-PPh$_2$)(μ-PEt$_2$)
compound. Both signals at 25.85 ppm and 25.69 ppm are found to arise from secondary carbons, i.e. the methylene groups, while the signals at 11.75 ppm and 11.36 ppm correspond to primary carbons, the methyl groups. These data indicate that the ethyl groups of the diethylphosphido ligand are inequivalent. A further discussion of this result will follow the description of the $^1$H NMR spectrum.

In the $^1$H NMR spectrum (Figure 28) the expected signals due to the phenyl protons appear as a multiplet in the region between 7.2 ppm and 7.8 ppm. Further upfield between 0.7 ppm and 2.3 ppm a number of signals are observed. Integration of the spectrum and assignment of the phenyl region to ten protons leads to an assignment of these upfield signals to ten ethyl protons. Particular assignments of these signals to methyl or methylene protons is not intuitively obvious, and thus a carbon-hydrogen correlation NMR experiment was carried out (Figure 29). As expected, the quintet centered at 2.26 ppm is found to correspond to the carbon signals at 25 ppm, and thus can be assigned to methylene protons. A doublet of triplets appearing at 1.30 ppm correlates to the $^{13}$C signal at 11.75 ppm. It is therefore apparent that this signal arises from the protons of one of the methyl groups, with coupling to phosphorus of 16 Hz to produce the doublet and further coupling (8 Hz) to two methylene protons to produce triplets. A less well-resolved signal at about 0.81 ppm correlates to the $^{13}$C NMR signal at 11.36 ppm and therefore is also assigned to a methyl group.

As stated above, the $^{13}$C NMR and $^1$H NMR data indicate inequivalence of the ethyl groups. This result suggests that the Fe$_2$P$_2$ core of this complex exists in a folded geometry, Figure 30. This folding would result in having an exo ethyl group (A) and an endo ethyl group (B).
Figure 28: $^1$H NMR Spectrum of Fe$_2$(CO)$_6$(μ-PPh$_2$)(μ-PEt$_2$)
Figure 29: Carbon-Hydrogen Correlation NMR Spectrum of Fe$_2$(CO)$_6$(μ-PPh$_2$)(μ-PEt$_2$)
The infrared spectrum of $(\text{CO})_3\text{Fe}(\mu-\text{PET}_2)(\mu-\text{PPh}_2)\text{Fe(\text{CO})}_3$ (Figure 31) closely resembles that of $(\text{CO})_3\text{Fe}(\mu-\text{P-1-Bu}_2)(\mu-\text{PPh}_2)\text{Fe(\text{CO})}_3$. Six absorptions are seen in the terminal carbonyl stretching region.

As in the case of di-1-butylchlorophosphine reacting with $\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(\text{CO})}_2\text{PPh}_2\text{H}]$, a number of minor side products were also obtained from the analogous reaction with diethylchlorophosphine. The first band removed from the column was found by $^{31}\text{P}$ NMR to consist of a mixture of products. Some of the components were identified as phosphines (e.g., diphenylphosphine) and phosphine oxides while others remain unidentified. It is possible that one component is $(\text{CO})_3\text{Fe}(\mu-\text{PET}_2)_2\text{Fe(\text{CO})}_3$, a known compound\textsuperscript{72} for which $^{31}\text{P}$ NMR data have not been reported. As this entire mixture was obtained only in a small amount no attempts at further separation were carried out. Small amounts of $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe(\text{CO})}_2\text{PPh}_2\text{H}$ and $\text{PPh}_2\text{H(\text{CO})}_2\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe(\text{CO})}_2\text{PPh}_2\text{H}$ (identified by $^{31}\text{P}$ NMR as previously described in section III-F-1) were also isolated from this reaction, but no
Figure 31: Infrared Spectrum of Fe₂(CO)₆(μ-PPH₂)(μ-PEt₂)
evidence of phosphine-substituted mixed-bridge compounds of the type Fe₂(CO)₅(μ-PR₂)(μ-PR'₂)PR₂H was seen.

Binuclear complexes containing two distinctly different diorganophosphido bridging ligands, although not unknown, are rarely encountered in the literature. One recent example⁷⁴ is the dirhodium complex Cp₂Rh₂(μ-PPh₂)(μ-PMe₂) prepared by the reaction of Cp₂Rh₂(μ-PPh₂)(μ-Cl) with LiPMe₂. Owing to the paucity of these types of complexes virtually no in-depth studies of their reactivity, particularly concerning preferential reactivity of one phosphido ligand over the other, have been conducted. The apparent generality of the synthetic method reported here should lead to increased study of compounds of this type in the near future.

G. Reduction of (CO)₃Fe(μ-P-ι-Bu₂)(μ-PPh₂)Fe(CO)₃ with Sodium

In order to determine if the reduction properties of the mixed-bridge compound, (CO)₃Fe(μ-P-ι-Bu₂)(μ-PPh₂)Fe(CO)₃, would mimic those of other bis(μ-phosphido) diiron complexes a THF solution of the compound was treated with a 1% sodium amalgam. The ³¹P{¹H} NMR spectrum (Figure 32) of the resultant dark red solution exhibits two signals shifted significantly upfield from those in the neutral starting complex. The infrared spectrum (Figure 33) exhibits absorptions at relatively low energies in the terminal carbonyl stretching region. Both of these results suggest that the reduction has proceeded in the same fashion as for other bis(μ-phosphido) complexes and that Na₂[(CO)₃Fe(μ-P-ι-Bu₂)(μ-PPh₂)Fe(CO)₃] has been formed.
Figure 32: $^{31}\text{P}({}^1\text{H})$ NMR Spectrum of Na$_2$[Fe$_2$(CO)$_6$(μ-PPh$_2$)(μ-P-1-Bu$_2$)]
Figure 33: Infrared Spectrum of Na₂[Fe₂(CO)₆(μ-PPh₂)(μ-P-1-Bu₂)]
H. Reaction of Na$_2$Fe$_2$(CO)$_6$ with P-1-Bu$_2$Cl: Preparation, Characterization and X-Ray Crystal Structure of Fe$_2$(CO)$_5$(μ-P-1-Bu$_2$)$_2$

The bulk of work in the area of di-1-butylphosphido bridged compounds has been conducted by Jones and coworkers.$^{25,53,69}$ Their studies have led to the formation of a number of new compounds, many of which possess unusual geometries owing to the steric bulk of the di-1-butylphosphido group. It is interesting, however, that the diiron hexacarbonyl compound, (CO)$_3$Fe(μ-P-1-Bu$_2$)$_2$Fe(CO)$_3$, has not been prepared. It was therefore decided to explore the possibility of developing a synthesis of this compound. It was expected that if the compound could be prepared it would likely have a more planar Fe$_2$P$_2$ core than analogous known diiron complexes of the type Fe$_2$(CO)$_6$(μ-PR$_2$)$_2$. All complexes of this type which have been structurally determined by X-ray crystallography$^{66}$ have been found to possess significantly folded Fe$_2$P$_2$ cores. Additionally, reactivity studies of Fe$_2$(CO)$_6$(μ-P-1-Bu$_2$)$_2$ in regards to behavior of the phosphido bridges could provide interesting results for comparison with the bis(μ-diphenylphosphido) system.

In setting out to develop a synthesis of the bis(di-1-butylphosphido) complex it was decided to employ a procedure completely analogous to the best available synthesis for Fe$_2$(CO)$_6$(μ-PPh$_2$)$_2$. A THF solution of Na$_2$Fe$_2$(CO)$_6$ was treated with two equivalents of di-1-butylchlorophosphine. Preliminary spectroscopic ($^{31}$P NMR) investigation of the reaction solution indicated the presence of several products and it was only through chromatography and slow recrystallization from methylene chloride / hexane that the major product of the reaction, a green solid, was obtained. Subsequent
examination of spectroscopic data for this compound, however, showed that it was not the desired compound but, rather, it was Fe₂(CO)₅(μ-P-t-Bu₂)₂ (Figure 34). This assignment has been confirmed by an X-ray crystallographic determination of the structure.

The phosphorus-31 NMR spectrum of the complex, shown in Figure 35, exhibits only a singlet very far downfield at 362 ppm. This signal indicates that all phosphido bridges are equivalent but provides no evidence as to the number of phosphido ligands contained in the complex. The chemical shift is in the range expected for a bridging di-t-butylphosphido ligand as was pointed out in Section III-F.

The ¹H NMR spectrum of the complex (Figure 36) indicates the presence of only methyl protons appearing as a doublet at 1.23 ppm with coupling to phosphorus of 14 Hz. As with the ³¹P NMR no indication as to the number of phosphido ligands is provided by the ¹H NMR spectrum.

The carbon-13 NMR spectrum is shown in Figure 37 and provides some very interesting information. In addition to the expected signals for the t-butyl groups (44 ppm and 23 ppm) two distinct signals are seen in the carbonyl region above 200 ppm. Both signals appear as triplets with very small carbon-phosphorus coupling and it is easily seen that the intensities of these signals are different. The more intense signal at 220 ppm is assigned to the three carbonyl ligands on one iron while the less intense signal at 215 ppm can be attributed to the two carbonyls on the other iron. The appearance of these signals as triplets indicates the presence of two equivalent phosphido bridges.
Figure 34: Structure and Numbering Scheme for

\[ \text{Fe}_2(\text{CO})_5(\mu-\text{P-1-Bu}_2)_2 \]
Figure 35: $^{31}\text{P}^{(1}\text{H})$ NMR Spectrum of Fe$_2$(CO)$_5$(μ-P-1-Bu$_2$)$_2$
Figure 36: $^1$H NMR Spectrum of Fe$_2$(CO)$_5$(μ-η-P$_2$-Bu)$_2$
Figure 37: $^{13}$C($^1$H) NMR Spectrum of Fe$_2$(CO)$_5$(μ-P-1-Bu$_2$)$_2$
The initial indication that the product was, in fact, not Fe₂(CO)₆(μ-P-
₁-Bu₂)₂ was provided by the infrared spectrum. Inspection of the IR spectrum
(Figure 38) clearly shows that it does not have the same pattern as IR spectra
for known compounds of the type Fe₂(CO)₆(μ-PR₂)₂ with folded Fe₂P₂ cores.
As pointed out previously, these complexes generally show five distinct
absorption bands with two or three appearing above 2000 cm⁻¹. Only four
strong absorptions are observed for Fe₂(CO)₅(μ-P-₁-Bu₂)₂ with a slight shoulder
appearing at 1950 cm⁻¹. A further discussion of the IR spectrum will follow the
description of the x-ray determination of the structure.

Strong evidence for the assignment of the product as having one
less carbonyl ligand than expected is provided by the mass spectrum. No peak
is seen at 570 m/e but the M⁺ peak is observed at 542 m/e. Consecutive loss of
only five carbonyl ligands is observed.

In light of the spectroscopic indications that an unusual compound
had been obtained, it was decided to determine the structure of the complex by
a single crystal X-ray diffraction study. Green crystals of the complex can be
grown at -10 °C by slow diffusion of hexane into a saturated solution of the
complex in methylene chloride.

An ORTEP drawing of Fe₂(CO)₅(μ-P-₁-Bu₂)₂ is shown in Figure 39.
It is immediately observed that the Fe₂P₂ core is essentially planar. This
planarity of the core is highly unusual, and, in fact, has not previously been
observed for neutral bis(μ-phosphido) diiron carbonyl complexes. Equally
unusual and interesting is the presence of only two carbonyl ligands on Fe(2)
(see Figure 34 for the numbering scheme used in the following discussion).
Both of these results are undoubtedly due to the bulkiness of the di-₁-
butylphosphido ligands.
Figure 38: Infrared Spectrum of $\text{Fe}_2(\text{CO})_5(\mu-P-\text{t-Bu}_2)_2$
Figure 39: ORTEP Drawing of Fe₂(CO)₅(μ-P-1-Bu₂)₂
Figure 40: ORTEP Drawing of Fe$_2$(CO)$_5$(μ-P-1-Bu$_2$)$_2$
A different perspective of the structure is shown in Figure 40. It should be noted that the molecule does contain a plane of symmetry. A structure of this type with $C_5$ symmetry would be predicted to exhibit five absorption bands in the terminal carbonyl stretching region of the infrared spectrum. In fact, four distinct absorptions are observed (see Figure 38) with the fifth appearing as a slight shoulder at 1950 cm$^{-1}$, and thus the spectrum is consistent with the structure.

The perspective shown in Figure 40 also indicates that the phosphido ligands are equivalent but are not symmetrically located in their bridging positions. An average Fe(2)-P bond distance of 2.137 Å is observed while the Fe(1)-P bond distances (avg. = 2.368 Å) are significantly longer. Comparative bond distance values for this and related complexes are contained in Table 11. Also contained in Table 11 are values for iron-iron bond distances in Fe$_2$(CO)$_5$($\mu$-P-t-Bu$_2$)$_2$ and related complexes. It is observed that the iron-iron bond distance in this new compound, 2.487 Å, is significantly short. Complete bond distance and bond angle data for Fe$_2$(CO)$_5$($\mu$-P-t-Bu$_2$)$_2$ are contained in Appendix A.

On the basis of the short Fe-Fe bond distance and in order to satisfy the EAN rule, the complex is formalized as having an iron-iron double bond. Additionally, the asymmetry of the phosphido-bridging ligands suggests that both are contributing two electrons to Fe(2) and only one each to Fe(1). This bonding description of Fe$_2$(CO)$_5$($\mu$-P-t-Bu$_2$)$_2$ is illustrated below in Figure 41. Multiple metal-metal bonding has been observed previously in other di-t-butylphosphido-bridged binuclear complexes such as the dimolybdenum complex, (P-t-Bu$_2$)Mo($\mu$-P-t-Bu$_2$)$_2$Mo(P-t-Bu$_2$)$_2$, reported by Jones to have a molybdenum-molybdenum bond order of four.
Table 11: Comparative Bond Distance and Angle Data for Fe$_2$(µ-PR$_2$)$_2$(CO)$_n$ Complexes

<table>
<thead>
<tr>
<th></th>
<th>Fe$_2$(µ-P-1-Bu$_2$)$_2$(CO)$_5$</th>
<th>Fe$_2$(µ-PPh$_2$)$_2$(CO)$_6^{32}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$P$_2$ Torsion Angle</td>
<td>179°</td>
<td>100°</td>
</tr>
<tr>
<td>P-Fe(2) Distance</td>
<td>2.137 Å</td>
<td>2.24 Å</td>
</tr>
<tr>
<td>P-Fe(1) Distance</td>
<td>2.368 Å</td>
<td>2.23 Å</td>
</tr>
<tr>
<td>Fe-Fe Distance</td>
<td>2.487 Å</td>
<td>2.623 Å</td>
</tr>
</tbody>
</table>
Some preliminary studies of the chemistry of this interesting complex have been conducted. It was of course of interest to see if $\text{Fe}_2(\text{CO})_5(\mu-\text{P-t-Bu}_2)_2$ could be converted to the original target molecule, $\text{Fe}_2(\text{CO})_6(\mu-\text{P-t-Bu}_2)_2$. Treatment of solutions of the compound with carbon monoxide under various conditions have produced no change in the structure, i.e., no uptake of a sixth CO ligand is observed. For the future it will perhaps be more interesting to look at reactions of this compound in the presence of carbon monoxide. For example, treatment with sodium may produce a dianion in which the iron-iron bond has been disrupted as in the case of $\text{Na}_2[\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)_2]$. If a similar reduction product were to be obtained from $\text{Fe}_2(\text{CO})_5(\mu-\text{P-t-Bu}_2)_2$, the probable increase in the iron-iron distance may allow the complex to add a sixth carbonyl ligand as the bulk surrounding Fe(1) would presumably be less.
I. Preparation and Characterization of Ru₂(CO)₆(µ-PPh₂)₂

Although preparation of bis(µ-diphenylphosphido)hexacarbonyl diruthenium has been reported previously,¹⁷ a high yield synthetic method has not been developed thus far. Rather, the complex has usually been seen as a minor side product of a number of reactions. Many of these reactions involved higher nuclearity clusters as additional products. It was therefore decided to concentrate some efforts on developing a convenient synthesis of the diruthenium compound. This would then allow reactivity studies of the system to be carried out and results compared to those of the diiron system.

The process which was investigated involved treatment of Ru₂(CO)₆(µ-Cl)₂Cl₂ with LiPPh₂ to replace the chloride bridges with diphenylphosphido bridges and subsequent reaction with sodium to form the final product (Scheme 2). The isolated yield of the desired product, however, was very low (7.3%).

Scheme 2
The product was characterized by $^{31}$P NMR, infrared, and mass spectroscopy. In the $^{31}$P NMR spectrum only a single resonance is observed, a singlet at 108.5 ppm. This value is, as expected, upfield from that for the corresponding diiron complex (142 ppm) but downfield from the shift for the diosmium analogue (14 ppm).\textsuperscript{18}

The infrared spectrum in the carbonyl region (1600-2100 cm$^{-1}$, Figure 42) appears very similar to that of Fe$_2$(CO)$_6$(μ-PPh$_2$)$_2$. Five absorption bands are observed with intensities similar to those for the diiron compound. The identity of the compound was confirmed by the mass spectrum which exhibits a parent peak at 740 with an observed consecutive loss of six carbonyl ligands.

While this work was in progress it was learned that Carty and his coworkers\textsuperscript{64} were also working on the development of a synthetic route to the diruthenium complex. Their process involves the reaction of triruthenium dodecacarbonyl with tetraphenyl diphosphine in refluxing xylene. Unfortunately, this procedure also produces the desired compound only in relatively low yield. Carty reports that the product can be obtained in 10-30 % yield, and when the synthesis was repeated here Ru$_2$(CO)$_6$(μ-PPh$_2$)$_2$ was obtained in 21 % yield. While this is certainly higher than the 7 % yield obtained from the process starting with Ru$_2$(CO)$_6$Cl$_4$, it is still not great enough to warrant large scale production of the diruthenium compound by this method.

It is not entirely surprising that a high yield synthesis of Ru$_2$(CO)$_6$(μ-PPh$_2$)$_2$ has not been developed at this point. It has been pointed out previously that diruthenium complexes in general have not been as widely reported\textsuperscript{76} as might be expected and several researchers have encountered difficulties in studying these systems.\textsuperscript{64}
Figure 42: Infrared Spectrum of Ru$_2$(CO)$_6$(μ-PPh$_2$)$_2$
J. Reactions of Ru₂(CO)₆(μ-PPh₂)₂

The intended purpose for developing a synthesis of Ru₂(CO)₆(μ-PPh₂)₂ was to allow reactivity studies to be carried out and the results compared to those known for the diiron system. In each separate reaction which was studied the goal was to determine whether the change from iron to ruthenium would enhance or inhibit reactivity, or, in fact, result in completely different behavior.

One of the first reactions attempted was with Superhydride, LiBEt₃H. It is known that in the diiron system hydride attack on a bound carbonyl produces a formyl complex, Li[(CO)₃Fe(μ-PPh₂)₂Fe(CO)₂CHO], as the initial product. As discussed previously, this formyl complex subsequently rearranges to a terminal phosphine complex, Li[(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(CO)₂PPh₂H], via a metal hydride intermediate. When the reaction of LiBEt₃H with Ru₂(CO)₆(μ-PPh₂)₂ was attempted, however, no reaction was observed to occur, even at temperatures above 20 °C. This is somewhat perplexing in that one would expect the carbonyl ligands in Ru₂(CO)₆(μ-PPh₂)₂ to be susceptible to nucleophilic attack by hydride as the infrared spectrum does not indicate that they differ greatly in π bonding with metal from those in the diiron compound.

This surprising inertness toward nucleophilic attack was also observed when a THF solution of the diruthenium compound was treated with n-BuLi. Again, no reaction was observed to occur, and the expected product, in this case an acyl complex, Li[(CO)₃Ru(μ-PPh₂)₂Ru(CO)₂C(C₄H₉)O], was not obtained.

One reaction of Ru₂(CO)₆(μ-PPh₂)₂ which did produce an expected result was the apparent formation of Na₂[Ru₂(CO)₆(μ-PPh₂)₂] upon treatment
with sodium. The $^{31}$P NMR spectrum of this reaction solution (in THF) exhibits only one signal, a singlet at -92.5 ppm. This upfield shift confirms the absence of metal-metal bonding and is completely analogous to the diiron case. Observed low energies of terminal carbonyl stretching frequencies in the infrared spectrum support the assignment of the product as the dianion.

K. Preparation and Characterization of (CO)$_3$Fe(µ-PP$_2$)$_2$Ru(CO)$_3$

Most known heterobinuclear phosphido-bridged complexes have been prepared by the bridge-assisted method$^{39}$ involving reaction of an anionic terminal phosphido metal complex with an appropriate halogen-bearing metal species. In order to synthesize (CO)$_3$Fe(µ-PP$_2$)$_2$Ru(CO)$_3$, a procedure similar to that used by Geoffroy to prepare (CO)$_3$Fe(µ-PP$_2$)$_2$Os(CO)$_3$ was employed. Reaction of Li[Fe(CO)$_3$(PP$_2$)$_2$] with [Ru(CO)$_3$Cl$_2$]$^*$ in THF and subsequent workup allowed isolation of (CO)$_3$Fe(µ-PP$_2$)$_2$Ru(CO)$_3$ as a yellow powder in moderate yield (38%). The product is sparingly soluble in hydrocarbon solvents but very soluble in more polar solvents such as THF and acetone. Extensive chromatography is necessary to separate the product from small amounts of (CO)$_3$Ru(µ-PP$_2$)$_2$Ru(CO)$_3$ and (CO)$_3$Fe(µ-PP$_2$)$_2$Fe(CO)$_3$, which are formed as minor side products and are equally soluble in the solvents used to extract the desired product.

$^*$Note: [Ru(CO)$_3$Cl$_2$]$_2$ is fairly easily cleaved by THF to yield two monomeric units, Ru(CO)$_3$Cl$_2$·THF. This solvated complex is the probable reactive species in the reaction.
The product was characterized by a combination of spectroscopic and analytical data. The $^{31}$P{$^1$H} NMR spectrum (Figure 43) exhibits only a singlet indicating that the phosphido bridges are equivalent. The chemical shift of this signal, 124 ppm, is, as expected, midway between those of the diiron analogue, 142 ppm, and the diruthenium compound, 109 ppm. A similar shift would be predicted when comparing the diiron compound, the mixed iron-ruthenium compound, and the mixed iron-osmium compound (85 ppm). The carbon-13 NMR spectrum, shown in Figure 44, contains the expected signals for the phenyl carbons (145-127 ppm) and two downfield signals in the terminal carbonyl region. The appearance of the downfield triplets, with phosphorus-carbon coupling of <5 Hz, indicates the presence of two equivalent phosphido bridges. The triplet appearing at 213.4 ppm is assigned to the three carbonyl ligands on iron while the triplet at 198.5 ppm arises from the three carbonyl ligands on ruthenium. These assignments are based on comparisons to carbon-13 NMR data for known related compounds. In general signals for carbonyl ligands on ruthenium are shifted somewhat upfield (10-20 ppm) from signals for analogous carbonyls on iron.

The infrared spectrum for this compound (2100-1500 cm$^{-1}$) is shown in Figure 45. The pattern is very similar to the infrared spectra of (CO)$_3$Fe(μ-PPh$_2$)$_2$Fe(CO)$_3$ and (CO)$_3$Ru(μ-PPh$_2$)$_2$Ru(CO)$_3$ and suggests that the geometry of the compound consists of a folded FeRuP$_2$ core with C$_{2v}$ symmetry. The energies of the absorptions are slightly lower than those for the diruthenium complex but nearly the same as those in the diiron case.

The mass spectrum of the compound exhibits a molecular ion peak at 695 m/e and signals corresponding to consecutive loss of six carbonyl units.
Figure 43: $^{31}\text{P}^{(1}\text{H})$ NMR Spectrum of FeRu(CO)$_6$(μ-PPh$_2$)$_2$
Figure 44: $^{13}\text{C}(1\text{H})$ NMR Spectrum of FeRu(CO)$_6$(µ-PPh$_2$)$_2$
Figure 45: Infrared Spectrum of FeRu(CO)$_6$(μ-PPh$_2$)$_2$
Finally, the formulation of the compound as \((\text{CO})_3\text{Fe} (\mu-\text{PPh}_2)_2\text{Ru} (\text{CO})_3\) was confirmed by carbon and hydrogen analytical data.

L. Reduction of \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru} (\text{CO})_3\)

The diiron complex, \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe} (\text{CO})_3\) and the diruthenium complex, \((\text{CO})_3\text{Ru}(\mu-\text{PPh}_2)_2\text{Ru} (\text{CO})_3\), both readily undergo reduction by two electrons to form the dianionic compounds \([(\text{CO})_3\text{M}(\mu-\text{PPh}_2)_2\text{M} (\text{CO})_3)^{2-}\) in which metal-metal bonding no longer exists. In the diiron case Collman\(^{32}\) has reported the electrochemical reduction to be a single two-electron process and has explained the non-existence of a one-electron reduction product. Additionally it has been shown that upon this two-electron reduction of the diiron compound, the \(\text{Fe}_2\text{P}_2\) core adopts a planar arrangement.\(^{66}\) It was therefore of interest to investigate the reduction behavior of \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru} (\text{CO})_3\).

Treatment of a THF solution \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru} (\text{CO})_3\) with 1 % sodium amalgam caused an immediate reaction to occur as evidenced by a color change from yellow to red, and it was subsequently shown by \(^{31}\text{P}\) NMR and IR spectroscopy that the complex had been completely converted to the corresponding dianion, \(\text{Na}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru} (\text{CO})_3]\). The phosphorus-31 NMR spectrum, Figure 46, exhibits only one signal, a singlet at -86.6 ppm. This represents a shift upfield by 210 ppm from the original neutral complex and is explained by the absence of metal-metal bonding. Furthermore, the carbonyl region of the infrared spectrum (Figure 47) is very similar to that of \(\text{Na}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe} (\text{CO})_3]\) (Figure 48), with absorptions occurring at relatively low energies owing to the anionic nature of the complex.
Figure 46: $^{31}$P($^1$H) NMR Spectrum of Na$_2$[FeRu(CO)$_6$(μ-PPh$_2$)$_2$]
Figure 47: Infrared Spectrum of Na$_2$[FeRu(CO)$_6$(μ-PPh$_2$)$_2$]
Figure 48: Infrared Spectrum of $\text{Na}_2\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)_2$
As stated above, an X-ray crystallographic determination of the structure of Na₂[(CO)₃Fe(μ-PPh₂)₂Fe(CO)₃]⁶₆ has shown that upon reduction the Fe₂P₂ core adopts a planar arrangement. No attempts were made to isolate a solid sample of Na₂[(CO)₃Fe(μ-PPh₂)₂Ru(CO)₃] but it is presumed, based on spectroscopic data, that a similar flattening of the FeRuP₂ core occurs.

The cyclic voltammogram of the reduction of (CO)₃Fe(μ-PPh₂)₂Fe(CO)₃, which was determined by Collman,⁶² indicated a single reversible two-electron reduction at -1.26 V vs. SCE. A similar investigation of the reduction of (CO)₃Fe(μ-PPh₂)₂Ru(CO)₃ was carried out in this study. Cyclic voltammograms of (CO)₃Fe(μ-PPh₂)₂Ru(CO)₃ and (CO)₃Fe(μ-PPh₂)₂Fe(CO)₃ were recorded using a mercury drop electrode. The result obtained here for (CO)₃Fe(μ-PPh₂)₂Fe(CO)₃ is in agreement with that reported by Collman.⁴ A single reversible two-electron reduction is observed at -1.65 V vs. ferrocene. In the case of (CO)₃Fe(μ-PPh₂)₂Ru(CO)₃ a single two-electron reduction is also observed although it is only quasi-reversible under the conditions of the experiment.

The reduction occurs at -1.92 V vs. ferrocene and thus is 0.27 V more cathodic than the reduction of (CO)₃Fe(μ-PPh₂)₂Fe(CO)₃. The experiment was also attempted using several other electrodes but in all cases the reduction was irreversible.

*Note: Although the electrochemical reduction of (CO)₃Fe(μ-PPh₂)₂Fe(CO)₃ was previously reported, the experiment was repeated here in order to compare both systems under the exact same conditions.
As only one reduction wave is observed it is presumed to involve two electrons based on the result obtained in the sodium reduction experiment. Unequivocal assignment of the electrochemical reduction as being a two electron process could be accomplished if an appropriate electrode at which the reduction is reversible would become available.

M. Reactions of \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru}(\text{CO})_3\) with Nucleophiles

The behavior of \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe}(\text{CO})_3\) toward nucleophilic reagents has been investigated extensively by Collman\textsuperscript{32} and Wojcicki\textsuperscript{11}. It has been found that, in general, nucleophiles, such as alkyl anions and hydride, will initially attack the carbon of a bound carbonyl ligand to form, in the two cases mentioned, metal acyl or formyl products. It has further been shown by Wojcicki\textsuperscript{11} that the formyl compound, \([(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe}(\text{CO})_2\text{CHO}]^+\), is not thermodynamically stable and decomposes to a hydride complex and subsequently to a monoanionic terminal phosphine complex. It was therefore of interest to investigate the behavior of \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru}(\text{CO})_3\) toward these same reagents to see if, in fact, similar reactions would occur. If they did it would also be interesting to determine if there would be any selectivity in terms of which metal would be involved.

The reaction of \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru}(\text{CO})_3\) with one equivalent of \(n\)-butyllithium in THF was observed to occur immediately to form a red compound. Subsequent study of the reaction solution by NMR and IR spectroscopy has led to the formulation of the product as the metal acyl complex, \(\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru}(\text{CO})_2\text{C}(\text{C}_4\text{H}_9-\text{H})_0]\), the acyl ligand being on ruthenium.
The initial indication that a metal acyl complex had been formed came from the infrared spectrum (Figure 49). In the region from 2100 cm$^{-1}$ to 1800 cm$^{-1}$ expected absorptions are seen for the terminal carbonyl ligands, the energies being lower than those of the original neutral starting compound owing to the anionic nature of the product. Additionally, a weak absorption is seen at 1550 cm$^{-1}$ and is assigned to the carbonyl group of the acyl ligand. The overall pattern and energies of the absorptions are quite similar to those of related diiron complexes. Data for some of these compounds are included in Table 12.

Evidence for assignment of the acyl ligand to ruthenium is provided by the $^{13}$C($^1$H) NMR spectrum. In the downfield region (> 180 ppm) of the spectrum the iron carbonyl ligands remain as a relatively sharp singlet at 220.7 ppm (coupling of the carbonyl carbons to phosphorus is apparently too small to be resolved). On the other hand, the signal for the ruthenium carbonyls, when compared to $\text{(CO)}_3\text{Fe(μ-PPPh}_2\text{)}_2\text{Ru(CO)}_3$, has become less intense and appears as a very broad triplet centered at 207.2 ppm. This result indicates a severe disruption of the chemical environment for the ruthenium carbonyls and thus suggests the presence of the new acyl ligand on ruthenium. The $^{13}$C($^1$H) NMR spectrum is shown in Figure 50.

Finally, the $^{31}$P($^1$H) NMR spectrum must also be considered. The room temperature (20 °C) $^{31}$P($^1$H) NMR spectrum of the analogous diiron acyl complex, $\{\text{Li[(CO)}_3\text{Fe(μ-PPPh}_2\text{)}_2\text{Fe(CO)}_2\text{C(C}_4\text{H}_9\text{-n)}\text{]}\}$, consists only of a broad singlet at 120 ppm indicating equivalence of the phosphido bridging ligands. For the mixed iron-ruthenium complex, however, two sharp doublets are observed in the $^{31}$P ($^1$H) NMR spectrum (Figure 51). This first indicates that the
Figure 49: Infrared Spectrum of Li[(CO)_3Fe(μ-PPh_2)_2Ru(CO)_2C(C_4H_9)_2]
Table 12: Infrared Spectroscopic Data for Li[(CO)$_3$Fe($\mu$-PPh$_2$)$_2$Ru(CO)$_2$C(C$_4$H$_9$)O] and Related Dilron Complexes

<table>
<thead>
<tr>
<th></th>
<th>M = Ru, R = n-Bu</th>
<th>M = Fe, R = i-pr (Na$^+$ salt)</th>
<th>M = Fe, R = Me (Na$^+$ salt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>v$_{CO}$, cm$^{-1}$</td>
<td>2002 s, 1955 s, 1938 s</td>
<td>2000 s, 1945 s, 1915 sh</td>
<td>1995 s, 1940 s, 1905 sh</td>
</tr>
<tr>
<td></td>
<td>1924 s, 1893 s</td>
<td>1880 sh</td>
<td>1885 sh</td>
</tr>
<tr>
<td>v$_{C=O}$, cm$^{-1}$</td>
<td>1550 w</td>
<td>1565 w</td>
<td>1570 w</td>
</tr>
</tbody>
</table>
Figure 50: $^{13}$C($^1$H) NMR Spectrum of Li[(CO)$_3$Fe(μ-PPh$_2$)$_2$Ru(CO)$_2$C(C$_4$H$_9$)O]
Figure 51: $^{31}P(^1H)$ Spectrum of Li[(CO)$_3$Fe($\mu$-PPh$_2$)$_2$Ru(CO)$_2$C(C$_4$H$_9$)O]
structure of the complex is rigid at room temperature. Two of the more probable geometric possibilities for the complex are shown in Figure 52.

In structure A the acyl ligand is cis to both phosphido-bridging ligands. This would result in equivalence of the phosphorus nuclei and only one signal in the $^{31}$P NMR spectrum would be observed. In structure B the arrangement of the acyl ligand as cis to one phosphorus nucleus and trans to the other results in inequivalence of the phosphorus nuclei and thus the observed two doublets in the $^{31}$P NMR spectrum. The observed phosphorus-phosphorus coupling of 90 Hz is in the range of values normally seen for similar diiron complexes having inequivalent phosphido bridges and a non-planar Fe$_2$P$_2$ core.

The fluxional process proposed for the diiron acyl complex involves rotation of the carbonyl ligands about a pseudo C$_3$ axis on one metal center as well as exchange of the carbonyl ligands between the two metals. The increased size of ruthenium vs. iron likely prevents any exchange between the
metals in the mixed iron-ruthenium acyl complex. It is interesting that the "rotor-like" motion of the ligands on ruthenium is also apparently prevented, though.

The reaction of \((CO)_3Fe(\mu-PPh_2)_2Ru(CO)_3\) with hydride was also attempted to determine if a stable formyl complex could be formed or if this product would rearrange to the terminal hydride or terminal phosphine complex as in the diiron case. The result obtained in this study proved to be quite surprising.

Upon treatment of a THF solution of \((CO)_3Fe(\mu-PPh_2)_2Ru(CO)_3\) with one equivalent of LiBEt_3H at -78 °C a reaction occurred immediately. The phosphorus-31 NMR spectrum (Figure 54) of the reaction solution consists of two signals. The lowfield signal at 124.1 ppm can be attributed to unreacted \((CO)_3Fe(\mu-PPh_2)_2Ru(CO)_3\). The high field signal at -85.4 ppm caused some initial confusion. Of the three expected possible products, only a hydride of the type shown in Figure 53 would produce a singlet far upfield, as it is the only possibility in which both phosphorus nuclei are equivalent and no metal-metal bonding exists. However, upon recording a proton-coupled 31P NMR spectrum, no coupling of the phosphorus nuclei to a hydride ligand was observed. For the diiron analogue a phosphorus-proton coupling of 30 Hz has been reported.26

![Figure 53](image-url)
Figure 54: $^{31}\text{P}(^1\text{H})$ Spectrum of Reaction of FeRu(CO)$_6$(μ-PPh$_2$)$_2$ with One Equivalent of LiBE$_3$H
This problem was solved by investigating the reaction of \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(CO)}_3\) with two equivalents of \(\text{LiBEt}_3\text{H}\). In this case the \(^{31}\text{P}\{^{1}\text{H}\}\) NMR spectrum exhibits only the signal at -85.4 ppm, again with no coupling to a hydride ligand observed in the proton-coupled spectrum. The infrared spectrum of the reaction solution confirmed that the product was, in fact, \(\text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(CO)}_3]\). Characterization of the sodium analogue of this dianion was described in Section III-L. It was by comparison of the spectroscopic data for the sodium salt with those obtained here that the product was determined to be the lithium dianion. Spectroscopic data (\(^{31}\text{P}\) NMR and IR) for both are contained in Table 13. Additionally, the infrared spectrum of the lithium dianion is shown in Figure 55, and it should be noted how similar the pattern is to that of the sodium dianion (Figure 47).

Still unanswered at this point is why \(\text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(CO)}_3]\) is formed and not one of the expected products. It is possible that one of these products is initially formed but is rapidly deprotonated by a second equivalent of \(\text{LiBEt}_3\text{H}\) to form \(\text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(CO)}_3]\). The nature of the first-formed product remains unknown as no intermediates were ever observed spectroscopically.

The attempted reaction of \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(CO)}_3\) with a different source of hydride did not provide a better result. In fact, when a THF solution of \((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(CO)}_3\) was treated with \(\text{NaB(OC\text{H}_3)}_3\text{H}\) no reaction was observed to occur at all.
Table 13: Comparative Spectroscopic Data for $M_2[(CO)_3Fe(\mu-PPh_2)_2Ru(CO)_3$  
$M = Li, Na$

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<td>1946 s, 1906 s, 1873 s, 1855 s, 1812 w</td>
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Figure 55: Infrared Spectrum of Li₂[FeRu(CO)₆(μ-PPh₂)₂]
N. Reactions of [(CO)₃Fe(μ-PPPh₂)₂Ru(CO)₃]²⁻ with Electrophiles

A considerable amount of chemistry has been carried out involving reactions of [(CO)₃Fe(μ-PPPh₂)₂Fe(CO)₃]²⁻. In particular, it has been shown that reaction of this dianion with alkyl halide reagents initially produces metal alkyl complexes via direct attack of iron on the electrophilic alkyl group. These metal alkyl complexes subsequently undergo rearrangement to the more thermodynamically favored metal acyl complexes, [(CO)₃Fe(μ-PPPh₂)₂Fe(CO)₂C(R)O]⁻, (R = alkyl). Treatment of the dianion with acid also involves initial attack of proton on iron to form a metal hydride complex but this product rearranges to the terminal phosphine complex as discussed previously in Section III-L. It was therefore of some interest to investigate the reactivity of [(CO)₃Fe(μ-PPPh₂)₂Ru(CO)₃]²⁻ toward electrophilic reagents to see if there would be a preference as to which metal would be attacked or if completely different chemistry would take place. In most attempted reactions the lithium salt of the dianion was used as it can be easily produced via reaction of (CO)₃Fe(μ-PPPh₂)₂Ru(CO)₃ with LiBEt₃H and used in situ.

Solutions of Li₂[(CO)₃Fe(μ-PPPh₂)₂Ru(CO)₃] prepared in THF were treated with various alkyl halides and the solutions analyzed by phosphorus-3¹ NMR and infrared spectroscopy. The following discussion will focus on the results obtained using methyl iodide and will be followed by a brief description of the results obtained using other alkyl halides.

The solution of Li₂[(CO)₃Fe(μ-PPPh₂)₂Ru(CO)₃] was treated with one equivalent of methyl iodide and allowed to react for sixteen hours. Progress of the reaction was monitored by ³¹P NMR by observing the disappearance of the dianion. The phosphorus-3¹ NMR spectrum of the resultant black solution at
sixteen hours is shown in Figure 56. The spectrum exhibits two sets of doublets in the region from 80 ppm to 140 ppm. A large doublet of doublets appear at 139.3 ppm and 110.3 ppm with phosphorus-phosphorus coupling of 105 Hz. A smaller set of doublets appears at 119.2 ppm and 91.2 ppm with phosphorus-phosphorus coupling of 86 Hz. Signals are also observed for (CO)$_3$Fe(μ-PPh$_2$)$_2$Ru(CO)$_3$ (124 ppm), (CO)$_3$Fe(μ-PPh$_2$)$_2$Fe(CO)$_3$ (141 ppm), and (CO)$_3$Ru(μ-PPh$_2$)$_2$Fe(CO)$_3$ (109 ppm). No evidence for unreacted Li$_2$[(CO)$_3$Fe(μ-PPh$_2$)$_2$Ru(CO)$_3$] is seen in the spectrum.

The chemical shifts of the signals suggest that the phosphorus nuclei have remained in bridging positions and that metal-metal bonding is intact. This result rules out the possibility that a metal alkyl complex of the type Li[(CO)$_3$M(μ-PPh$_2$)$_2$M'(CO)$_3$CH$_3$] has been obtained as this complex would lack a ruthenium-iron bond. What is indicated by the data is the formation of two products.

The infrared spectrum of the crude reaction solution is complicated owing to the presence of more than one metal carbonyl compound. However, after discounting weak absorptions arising from (CO)$_3$Fe(μ-PPh$_2$)$_2$Ru(CO)$_3$, strong absorptions are observed at 1998, 1968, 1950, and 1920 cm$^{-1}$ with a weaker absorption seen at 1885 cm$^{-1}$. These low energies indicate that one of the products (presumably the major product observed in the $^{31}$P [$^1$H] NMR spectrum) is anionic in nature. Additionally, a weak absorption is observed at 1583 cm$^{-1}$ suggesting that perhaps a metal acyl complex has been formed. Unfortunately the product (or products) could not be isolated as decomposition to (CO)$_3$Fe(μ-PPh$_2$)$_2$Ru(CO)$_3$ occurred in all attempts. Additionally, carbon-13 NMR data have been inconclusive as the spectra are, as expected, very complicated.
Figure 56: $^{31}P\{^{1}H\}$ Spectrum of Reaction of $\text{Li}_2[\text{FeRu(CO)}_6(\mu\text{-PPh}_2)_2]$ with One Equivalent of CH$_3$I
In an effort to clarify the nature of the major product formed the reaction was repeated using CD$_3$I as the alkylating agent. Subsequent investigation of the reaction mixture by $^{31}$P{$_1^H$} NMR again indicated the formation of two products in a ratio similar to that obtained in the previous experiment. The $^2$H NMR spectrum exhibits as the major signal a singlet at 1.61 ppm. This chemical shift is in the range reported for metal acyl complexes and, again, does not suggest the formation of a metal alkyl complex as the final product. As before, difficulty was encountered when recording the carbon-13 NMR spectrum. Neither an acyl carbon signal nor a CD$_3$ signal could be conclusively located.

The inability to isolate products from these reactions and to obtain better spectroscopic data has prevented conclusive identification of the products. The results, however, warrant some comment. It is apparent that two products are being formed and that both may be metal acyl complexes. The $^{31}$P NMR data suggest that the two products are related, and it is quite possible that what is being observed is the formation of both an iron acyl complex and a ruthenium acyl complex. If, in fact, metal acyl complexes are not being formed there is still the possibility that similar chemistry is taking place at both metal centers.

In order to gain more insight into the chemistry discussed above the dianion Li$_2$[(CO)$_3$Fe(µ-PPh$_2$)$_2$Ru(CO)$_3$] was treated with a variety of alkyl halides (allyl iodide, benzyl iodide, d-butyl iodide) in a series of reactions. In all cases the $^{31}$P{$_1^H$} NMR spectra again indicate the formation of two products. The major product in each case appears as a set of doublets at about 139 ppm and 110 ppm with phosphorus-phosphorus coupling of 105 Hz. A set of doublets corresponding to a minor product appears at about 120 ppm and 90
ppm with phosphorus-phosphorus coupling of about 84 Hz. These data are completely analogous to results obtained using methyl iodide and indicate that the chemistry in all cases is similar. Complete $^{31}\text{P}^{(1\text{H})}$ NMR data for each reaction are contained in Table 14.

A similar reaction was also carried out using 1,3-diiodopropane as the alkylating agent. Collman$^{32}$ has reported that treatment of the corresponding diiron dianion, $[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe}(\text{CO})_3]^2^-$, with 1,3-diiodopropane produces a neutral carbene complex. A proposed mechanism (Scheme 3)$^{32}$ for this reaction involves initial attack of metal at one of the electrophilic centers of $\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}$ to form an iron-alkyl complex which subsequently undergoes alkyl migration to give an acyl intermediate. Intramolecular alkylation of the acyl oxygen produces the final product.

![Scheme 3](image-url)
Table 14: $^{31}$P($^1$H) NMR Data for Reactions of Li$_2$[(CO)$_3$Fe(μ-PPh)$_2$Ru(CO)$_3$] with Alkyl Iodides (Rl)

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<td>84</td>
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J$_{p.p} = 87$ Hz
It was hoped that a similar reaction might occur with the mixed metal system which would allow isolation and full characterization of a neutral product. The results, however, were similar to those obtained in previously attempted alkylation reactions. In fact, in this case the $^{31}$P($^1$H) NMR data indicate the formation of three products and provide no added evidence as to the nature of the alkylation products. While the desired carbene complex would produce a $^{31}$P NMR signal similar to any of the observed sets of doublets, attempted isolation of a product from the mixture resulted in decomposition to $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(/CO)}_3$.

A complicating factor in each alkylation reaction was the formation of large amounts of neutral starting material, $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(/CO)}_3$. Whether this arises from oxidation of $\text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(/CO)}_3]$ or decomposition of one of the products is unknown. In an attempt to avoid possible oxidation of $\text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(/CO)}_3]$ an alkylation agent other than an alkyl halide was employed. When a solution of $\text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(/CO)}_3]$ is treated with methyl-$p$-toluenesulfonate a black solution is formed over a period of sixteen hours. The phosphorus-$^{31}$ NMR spectrum proved quite interesting. Only one set of doublets is observed with signals appearing at 120.1 ppm and 92.0 ppm ($J_{\text{P-P}} = 89.4$ Hz). These signals correspond to the minor product obtained when the reaction was carried out using CH$_3$I. No signals indicative of the previous major product are observed. The original intent of avoiding formation of $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(/CO)}_3$ was not realized, however, and, in fact, considerably more $(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(/CO)}_3$ is obtained in this case.

Complicated results were also obtained when protonation of $\text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Ru(/CO)}_3]$ with CF$_3$COOH was attempted. The $^{31}$P($^1$H)
NMR spectrum of the crude reaction solution consists of three sets of doublets in the region from 80 ppm to 140 ppm. A fourth product is indicated by a singlet far upfield at -76.0 ppm. A similar result is obtained when the dianion is treated with CF₃COOD. The ²H NMR spectrum of the reaction solution indicates a variety of products. A likely initial product of the reaction is a metal hydride complex of the type Li[(CO)₃M(µ-PPh₂)₂M'(CO)₃H] which might explain the phosphorus signal at -76.0 ppm and a deuterium signal at -3.32 ppm. One would not expect this hydride to rearrange to a formyl complex, and no definite conclusions can be made concerning the nature of the other observed products. As with the alkylation reactions, a considerable amount of (CO)₃Fe(µ-PPh₂)₂Ru(CO)₃ was also formed in these reactions.
APPENDIX
Data Collection and Refinement

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References


   b) *ibid.*, ref. 112.
   c) *ibid.*, ref. 48.


   


64. Carty, A. J.; personal communication.


73. e. g., $^1$Jp-C for PEt$_2$Cl is 27.1 Hz.


