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STUDIES ON BINUCLEAR IRON CARBONYL AND NITROSYL COMPLEXES CONTAINING BRIDGING DIPHENYLPHOSPHIDE

The Ohio State University

Ph.D. 1983

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STUDIES ON BINUCLEAR IRON CARBONYL
AND NITROSYL COMPLEXES CONTAINING BRIDGING
DIPHENYLPHOSPHIDE

DISSERTATION

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

By
Yuan-Fu Yu, M.S.

* * * * *

The Ohio State University
1983

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THE AUTHOR DEDICATES THIS DISSERTATION
TO HIS MOTHER

Mrs. Hseuh-Wen Lu Yu
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VITA

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PUBLICATIONS

Y.-F. Yu, J. Gallucci and A. Wojcicki, "Novel Mode of
Reduction of Phosphido-Bridged, Metal-Metal-Bonded Binuclear
Complexes. Synthesis and Reactivity of an Unsymmetrical
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Y.-F. Yu and A. Wojcicki, "New Binuclear Iron Carbonyl and
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Meeting of the American Chemical Society, Washington, D.C.,
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Y.-F. Yu and A. Wojcicki, "Reduction of [Fe(CO)₃(µ-PPh₂)]₂
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[(CO)₃Fe(µ-PPh₂)(µ-CO)Fe(CO)]₂(PPh₂)]++. Paper presented to
the 1983 15th Central Regional Meeting of the American

Y.-F. Yu, A. Wojcicki, G. Nardin and M. Calligaris, "Crystal
Structures of [Fe₂(NO)₄(µ-PPh₂)(µ-CH₂PPh₂)] and
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FIELDS OF STUDY

Major Field: Inorganic Chemistry, Professor Andrew Wojcicki
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<td>Ph</td>
<td>( C_6H_5 )</td>
</tr>
<tr>
<td>Me</td>
<td>( CH_3 )</td>
</tr>
<tr>
<td>Et</td>
<td>( C_2H_5 )</td>
</tr>
<tr>
<td>n-Pr</td>
<td>( CH_3CH_2CH_2 )</td>
</tr>
<tr>
<td>i-Pr</td>
<td>( (CH_3)_2CH )</td>
</tr>
<tr>
<td>sec-Bu</td>
<td>( CH_3CH(CH_3)_2 )</td>
</tr>
<tr>
<td>COD</td>
<td>( 1,5-C_8H_{12} )</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

A. General

Binuclear transition metal complexes have been the subject of intense recent research activity.1-7 These compounds find extensive use in the designed synthesis of metal clusters8-11 and in studies related to catalysis by adjacent metal sites.12-16

A major drawback of the use of metal cluster compounds as homogeneous catalysts is the fragmentation of the metal framework under conditions appropriate for effective catalysis.17-24 Many high nuclearity carbonyl clusters such as HRu3Co(CO)13 and [Ru3Co(CO)13]− were found to completely fragment when placed under pressure of CO or in the presence of Lewis bases.25

One way to retard such fragmentation is to use stable but flexible supporting bridging ligands to assist in holding adjacent metals together while allowing facile metal-metal bond cleavage and reformation. Bridging phosphido ligands are attractive in that they resemble the PR3 ligands found in many mononuclear catalysts and they are not easily displaced from their polynuclear framework. The
presence of PR₂ ligands enhances the stability of polynuclear systems with respect to the dissociation to mononuclear fragments. Investigations of various cooperative reactions involving metal-metal bond formation and cleavage are therefore feasible. The phosphido bridge is capable of supporting a wide range of bonding and nonbonding M-M distances with metal-phosphorus-metal bond angles ranging from less than 70°C through values close to the tetrahedral angle and even beyond 120°C in situations where a single bridge supports two non-interacting metal fragments. A further important feature is the availability of phosphorus-31 NMR spectroscopy, which can be used extensively to provide data concerning the bonding character of the bridging phosphido group and the metal-metal interaction.

B. Synthesis of Organometallic Compounds with Phosphido Bridged Ligands

The organophosphide ligand PR₂ can be considered either as an anionic four-electron donor or a neutral three-electron donor. It can act as a terminal or a bridging ligand.

Four-Electron Donor

\[
\begin{align*}
\text{R} & \quad \text{P}^- \\
\text{R} & \quad \text{R}
\end{align*}
\]

Three-Electron Donor

\[
\begin{align*}
\text{R} & \quad \text{P}^- \\
\text{R} & \quad \text{R}
\end{align*}
\]
Synthetic methods for phosphido-bridged complexes can be classified into the following categories based on the source of phosphido-bridged ligand: (1) salt elimination; (2) dehydrogenation of secondary phosphines; (3) P-P bond cleavage of the biphosphines \( R_2PPR_2 \); (4) miscellaneous reactions.

1. Salt Elimination

The salt elimination reactions are widely used to obtain binuclear phosphido-bridged compounds. One method involves the reaction of chlorodialkyl- or chlorodiaryl-phosphine with alkali metal salts of transition metal complexes which proceeds with elimination of lithium, sodium, or potassium chloride. Some examples are given below.\(^{26,27,28}\)

\[
\text{Na}[(C_5H_5)\text{Fe(CO)}_2] + PR_2Cl \xrightarrow{\text{THF}} [(C_5H_5)\text{Fe(\mu-PR}_2)(\text{CO})]_2 + 2\text{NaCl} + 2\text{CO}
\]

\( R = \text{Me, Ph} \)  

\[ (1) \]

\[ 2\text{Na}[(C_5H_5)\text{Mo(CO)}_3] + 2\text{PMe}_2\text{Cl} \xrightarrow{\text{THF}} [C_5H_5\text{Mo(\mu-PMe}_2)(\text{CO})]_2 + 2\text{CO} + 2\text{NaCl} \]

\[ (2) \]

\[ \text{Na}_2\text{Fe(CO)}_4 + \text{Fe(CO)}_5 + 2\text{PPh}_2\text{Cl} \xrightarrow{\text{THF}} [\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2 + 2\text{NaCl} + 3\text{CO} \]

\[ (3) \]
Another method of salt elimination involves the reaction of alkali metal phosphides with organometallic halide complexes. Examples are:

\( \text{TiCl}_2(C_5H_5)_2 + 2\text{LiPEt}_2 \rightarrow [(C_5H_5)_2\text{Ti}(\mu-\text{PEt}_2)]_2 + 2\text{LiCl} \) (4)

\( 2\text{Re(CO)}_5\text{Cl} + 2\text{KPR}_2 \rightarrow [(\text{CO})_4\text{Re}(\mu-\text{PPh}_2)]_2 + 2\text{CO} + 2\text{KCl} \) (5)

\[
\begin{array}{c}
\text{Ph}_2 \\
\text{P}
\end{array}
\]

\( \left[\text{Fe(NO)}_2\text{I}_2 + \text{KPPPh}_2 \rightarrow \left(\begin{array}{c}
\text{NO} \\
\text{Fe}
\end{array}\right)_{2\text{Fe}} \left(\begin{array}{c}
\text{NO} \\
\text{Fe}
\end{array}\right)_2 + 2\text{KCl} \) (6)

\[
\begin{array}{c}
\text{Ph}_2 \\
\text{P}
\end{array}
\]

\( \left[\text{M(COD)}_2\text{Cl}_2 + 2\text{LiPPh}_2 \rightarrow \left(\begin{array}{c}
\text{COD} \\
\text{M}
\end{array}\right)_{2\text{M}(\mu-\text{PPh}_2)_2} \right] \)

\( \text{M} = \text{Rh}, \text{Ir} \) (7)

\( (\text{Me}_3\text{P})_2\text{NiCl}_2 + 2\text{LiP(SiMe}_3)_2 \rightarrow [(\text{Me}_3\text{P})_2\text{Ni(Cl)(\mu-P(SiMe}_3)_2]_2 + 2\text{LiCl} \) (8)

The products obtained from the above two methods are almost always binuclear compounds and the yield is generally reasonable.

A third method of salt elimination involves the reaction of coordinated phosphine or phosphido ligand with organometallic complexes.\(^{34,35}\)

\( \text{Li[Fe(CO)}_4\text{(PPh}_2)_2] + \text{trans-IrCl(CO)(PPh}_3)_2 \rightarrow \)

\( \text{LiCl} + \text{FeIr(\mu-PPh}_2)(\text{PPh}_3)_2(\text{CO})_5 \) (9)
Fe(CO)$_4$PMeCl + NaFe(CO)$_2$(C$_5$H$_5$) + [Fe$_2$(CO)$_6$(μ-PMe$_2$)(C$_5$H$_5$)] + NaCl  \hspace{1cm} (10)

Recently, this method has been used to prepare mixed-metal bimetallic phosphido-bridged compounds with great success.

### 2. Dehydrogenation of Secondary Phosphines

Phosphido-bridged complexes are sometimes obtained by reaction of secondary phosphines with organometallic complexes. The dehydrogenation can occur by loss of hydrogen gas, by coupling of hydrogen with small unsaturated organic ligands, or by the formation of hydrogen halides.

Generally, secondary phosphines react directly with transition metal carbonyls to form phosphido-bridged complexes accompanied by hydrogen gas evolution.$^{36,37,38}$

\[
\text{Co}_2(\text{CO})_8 + 2\text{PPh}_2\text{H} \xrightarrow{\text{toluene}} [\text{Co}(\mu-\text{PPh}_2)(\text{CO})_3]_x + 2\text{CO} + \text{H}_2 \hspace{1cm} (11)
\]

\[
3\text{Fe}(\text{CO})_5 + 2\text{PPh}_2\text{H} \xrightarrow{100^\circ\text{C}} \text{decalin} \hspace{1cm} \text{Fe}_3(\text{CO})_9(\mu-\text{PPh})_2 + \text{H}_2 + 6\text{CO} \hspace{1cm} (12)
\]

\[
2\text{V}(\text{CO})_6 + 2\text{PMe}_2\text{H} \xrightarrow{} [\text{V}(\text{CO})_4(\mu-\text{PMe}_2)]_2 + \text{H}_2 + 4\text{CO} \hspace{1cm} (13)
\]

A second method involves loss of small organic molecules by coupling of hydrogen of a secondary phosphine with coordinated unsaturated organic ligands such as $\eta^3$-allyl and $\eta^5$-C$_5$H$_5$. Some examples are given below.$^{39,40,10}$
Fe(CO)$_4$PPh$_2$H + (n$^3$-C$_3$H$_5$)Co(CO)$_3$ +
\[
\begin{array}{c}
\text{(CO)$_4$Fe} \\
\text{P} \\
\text{(CO)$_3$Co} \\
\text{PPh$_2$H} \\
\text{(CO)$_3$Co + C$_3$H$_6$}
\end{array}
\] (14)

(CO)$_3$NiPMe$_2$H + (n$^3$-C$_3$H$_5$)Co(CO)$_3$ +
\[
\begin{array}{c}
\text{(CO)$_3$Ni} \\
\text{P} \\
\text{(CO)$_3$Co} \\
\text{PMe$_2$H} \\
\text{(CO)$_3$Co + C$_3$H$_6$}
\end{array}
\] (15)

2Co(n$^5$-C$_5$H$_5$)$_2$ + 2PMe$_2$H + [(C$_5$H$_5$)Co(μ-PMe$_2$)]$_2$ + 2C$_5$H$_6$ (16)

As can be seen from equations 14 and 15, a coordinated secondary phosphine can be used to synthesize phosphido-bridged heterobimetallic products.

Transition metal halides react with secondary phosphines to form phosphido-bridged compounds with elimination of hydrogen halide, for example,\textsuperscript{41,42,43}

\[
\begin{array}{c}
\text{[Rh(CO)$_2$Cl]$_2$ + 2PPh$_2$H} \\
\text{C$_6$H$_6$}
\end{array}
\rightarrow
\text{[Rh$_3$(μ-PPh$_2$)$_3$(CO)$_5$] + HCl}
\] (17)

K$_2$MCl$_4$ + 2PPh$_2$H $\xrightarrow{\text{EtOH}}$ [MCl(μ-PPh$_2$)(HPPh$_2$)]$_2$ + 2KCl + HCl

M = Pd, Pt (18)
Again, as can be seen from equation 19, coordinated secondary phosphine was used to prepare mixed-metal complexes.

3. Phosphorus-Phosphorus Bond Cleavage of Biphosphines

Reaction of transition metal complexes with biphosphines, \( R_2P-PR_2 \), at elevated temperature leads to cleavage of the P-P bond of the biphosphines and the formation of compounds with bridging phosphido ligands. Examples include \( ^{44,45,27} \)

\[
\text{Fe(CO)}_5 + \text{Ph}_2P-P\text{Ph}_2 \xrightarrow{220^\circ C} [\text{Fe(CO)}_3(\mu-P\text{Ph}_2)]_2 \quad (20)
\]

\[
\text{M(CO)}_6 + R_2P-PR_2 \xrightarrow{240^\circ C} [\text{M(CO)}_4(\mu-PR_2)_2]_2 \quad (21)
\]

\( R = \text{Me, Ph} \quad \text{M=Mo, W, Cr} \)

\[
\text{Co}_2(\text{CO})_8 + \text{Ph}_2P-P\text{Ph}_2 \xrightarrow\Delta [\text{Co}(\mu-P\text{Ph}_2)_2(\text{CO})_3]_2 + 2\text{CO} \quad (22)
\]

In some cases, cyclic biphosphines have been used to react with metal carbonyls. \( ^{46} \)

\[
2\text{Fe(CO)}_5 + \text{PhP} \xrightarrow{\Delta} (\text{OC})_3\text{FeFe(CO)}_3 \quad (23)
\]
Complexes containing coordinated biphosphine also can be used to synthesize mixed-metal cluster compounds with phosphido bridges.47

\[
\text{Fe(CO)}_4(\text{Ph}_2\text{P-PPh}_2) + \text{Co}_2(\text{Cu})_8 \xrightarrow{A} \]

Cleavage of the P-P bond in biphosphines was used extensively44,45,27 in the early sixties to prepare binuclear phosphido-bridged complexes. The formation of undesired by-products of the type M-PR$_2$-PR$_2$-M has severely restricted general application of this method. Such thermal reactions generally give low yields and are often complicated by the high temperature required.

4. Miscellaneous Reactions

Besides the methods described above, there are some other methods which have been used to synthesize metal complexes containing phosphido-bridged ligands. These methods mainly involved cleavage of phosphorus-heteroatom bonds of various phosphines.

One common method involves thermal cleavage of the phosphorus-carbon bond of the triphenylphosphine ligand coordinated to transition metals. Examples are48,49

\[
\text{Fe(CO)}_4(\text{Ph}_2\text{P-PPh}_2) + \text{Co}_2(\text{Cu})_8 \xrightarrow{A} \]

\[
\begin{align*}
\text{Fe} & \quad \text{Ph}_2\text{P} \\
\text{PPh}_2 & \quad \text{Fe} \\
\text{(CO)}_2\text{Co} & \quad \text{Co(Cu)}_3
\end{align*}
\]
These thermal cleavage reactions generally are of little synthetic utility because of low yields of the products. As can be seen from equations 25 and 26, another drawback of this method is the unpredictable product stoichiometry.

Carty and co-workers\textsuperscript{17} have developed a method that involves cleavage of the phosphorus-carbon bond of phosphinoacetylenes followed by the addition of the cleaved ligands to a bimetallic species or a cluster. One of the examples is given below:\textsuperscript{17}

$$\text{Fe}_2(\text{CO})_9 + \text{PH}_2\text{PC} \rightleftharpoons \text{CR} \rightarrow (\text{CO})_3\text{Fe} \rightarrow \text{Ph}_{\text{P}}$$

Under mild conditions, silylphosphines react with metal halides to produce phosphido-bridged compounds. In these
cases, the silicon-phosphorus bond cleavage occurred.\textsuperscript{50,51,52}

\[ 2\text{M(CO)}_5\text{Br} + 2\text{Me}_3\text{SiPH}_2 + [\text{M(CO)}_4(\mu-\text{PPh}_2)]_2 + 2\text{Me}_3\text{SiBr} + 2\text{CO} \]
\[ \text{M} = \text{Mn} \text{ and Re} \]

\[ [\text{Pt}_2\text{Cl}_2(\mu-\text{Cl})_2\text{L}_2] + 2\text{Me}_3\text{SiPH}_2 + \]
\[ + \text{Me}_3\text{SiCl} \quad \text{L} = \text{triorganophosphine} \]

\[ \text{P(SiMe}_3)_3 + 2\text{Mn(CO)}_5\text{Br} \rightarrow [\text{(CO)}_4\text{Mn(\mu-Br)(\mu-P(SiMe}_3)_2]_2 \]
\[ + \text{Me}_3\text{SiBr} + 2\text{CO} \]

Only in few instances were primary phosphines, \( \text{RPH}_2 \), used to prepare phosphido-bridged complexes. Some tri-nuclear phosphido-bridged complexes were prepared at reflux condition.\textsuperscript{53,37}

\[ \text{Fe}_3(\text{CO})_{12} + \text{PhPH}_2 \xrightarrow{100 \degree \text{C} \text{12 hr}} (\text{CO})_3\text{Fe} \quad \text{Fe(} (\text{CO})_3 + 3\text{CO} \]

\[ \text{Fe}_2(\text{CO})_9 + \text{RPH}_2 \xrightarrow{78 \degree \text{C}} [\text{Fe(} (\text{CO})_3(\mu-\text{PRH))]_2 \]
\[ \text{R} = \text{Me, Ph} \]
C. The Phosphorus Nuclear Magnetic Resonance Spectroscopy

The $^{31}$P chemical shift values of the phosphido-bridged phosphorus with a metal-metal interaction are sometimes hundreds ppm downfield from those of the same phosphido-bridged ligand with no metal-metal interaction. In order to illustrate this effect, some phosphorus-$^{31}$ chemical shift values of $\mu$-PPh$_2$ group with or without metal-metal interaction are listed in Table 1.

The distinct differences in these chemical shift values provide very useful information about the extent of metal-metal interaction in phosphido-bridged complexes. Ring contribution effects have been used to explain these large downfield shifts.$^{54}$ A phosphido ligand bridging over a metal-metal bond produces a three-member ring which is expected to show a large downfield coordination chemical shift. On the other hand, a four-membered ring will result with two phosphido-bridged ligands and two metal centers that do not interact.

The bond angles, $\angle M$-$P$ (phosphido bridge)-$M$, have also been correlated with the variation in chemical shift values of bridging phosphorus nucleus.$^{56}$ Although the relationship is not well understood, it appears that the chemical shift of the $^{31}$P nucleus (bridge) moves increasingly downfield as $\angle M$-$P$-$M$ angles increase for those phosphido ligands bridging over a metal-metal bond. On the other hand, the chemical shift of the $^{31}$P nucleus (bridge) of phosphido ligands bridging over nonbonded $M$-$\cdots$-$M$ systems will move
Table 1. P-31 Chemical Shift Data for the \(\mu\)-PPh\(_2\) Ligand in Some Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta) (ppm)(^a)</th>
<th>Metal-Metal Bond</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([Fe_2(CO)_6(\mu-Cl)(\mu-PPh_2)])</td>
<td>142.7</td>
<td>Fe-Fe bond</td>
<td>17</td>
</tr>
<tr>
<td>([Fe_2(CO)_6(\mu-C_2C_6H_5)(\mu-PPh_2)])</td>
<td>148.4</td>
<td>Fe-Fe bond</td>
<td>17</td>
</tr>
<tr>
<td>([Fe_2(CO)_6(\mu-PPh_2)]_2)</td>
<td>142.8</td>
<td>Fe-Fe bond</td>
<td>54</td>
</tr>
<tr>
<td>([W(CO)_4(\mu-PPh_2)]_2)</td>
<td>180.0</td>
<td>W-W bond</td>
<td>55</td>
</tr>
<tr>
<td>([W(CO)_4(\mu-PPh_2)]^-)K(_2)</td>
<td>-63.5</td>
<td>no W-W bond</td>
<td>55</td>
</tr>
<tr>
<td>([Cu_3(CO)_6(\mu-PPh_2)]_3)</td>
<td>44.0</td>
<td>Co-Co bond</td>
<td>58</td>
</tr>
</tbody>
</table>

\(^a\)Relative to \(H_3PO_4\) as external reference standard. Positive values are downfield from reference.
upfield as the $\angle M-P-M$ angles increase. The following two complexes will serve as examples to illustrate this phenomenon.\textsuperscript{17}

\begin{align*}
\text{Fe-P-Fe} &= 71.64^\circ \\
\delta \text{ $\mu$-PPh}_2 &= 148.4 \text{ ppm}
\end{align*}

\begin{align*}
\text{Fe-P-Fe} &= 75.6^\circ \\
\delta \text{ $\mu$-PPh}_2 &= 198.5 \text{ ppm}
\end{align*}

Phosphorus-31 NMR spectroscopy has been used recently to investigate the structure and bonding of phosphido-bridged compounds. Phosphorus-31 is the only naturally occurring phosphorus isotope. It possesses a nuclear spin of $\frac{1}{2}$. The three significant aspects of a $^{31}\text{P}$ NMR spectrum are the spectral patterns, the chemical shifts, and the coupling constants of phosphorus nuclei in different environments.

There are several factors that affect the chemical shift, $\delta$, of phosphorus nucleus.\textsuperscript{57} The most important factor is the nature of different substituents which provide different electron density at the phosphorus nucleus. An electron-withdrawing group decreases the electron shielding effect of the phosphorus atom which makes the chemical shift of phosphorus further downfield relative to that caused by substituents of electron-donating character. For example,\textsuperscript{58}
The phosphorus-31 NMR spectra of complexes with phosphido-bridged ligands are very useful for obtaining structural information when both the resonance positions and the coupling patterns are considered. Efforts have been made to correlate the $^{31}\text{P}$ chemical shift values of the phosphido-
bridged ligands with the existence of metal-metal interaction and the variations in metal-phosphorus-metal bond angles. The $^{31}$P chemical shift values of the phosphido-bridged ligands depend not only on the substituents on the phosphorus nuclei but also on the metals to which the phosphorus atom is coordinated. Therefore, a comparison of the relative chemical shift values of the phosphido-bridged ligands will only be meaningful if the discussion is restricted to the same type of phosphido-bridged ligands.$^{54}$

It has been pointed out that not enough data have been accumulated to allow unequivocal structural assignments to be made on these bases.$^{54}$ For example, the expected large downfield shift of the phosphorus resonance of the $\mu$-$\text{P}(t\text{-Bu})_2$ ligand was not observed in the formation of metal-metal bond of the dimeric rhodium compound.$^{61}$

\[
\delta \mu$-$\text{P}(t\text{-Bu})_2 = 402.8 \text{ ppm} \quad \delta \mu$-$\text{P}(t\text{-Bu})_2 = 402.8 \text{ ppm}
\]

The two compounds give identical $^{31}$P{${}^1$H} spectra although one compound has a Rh-Rh bond while the other one does not.

Still, this large downfield chemical shift may serve as a criterion for the determination of the presence of a metal-metal bond and be extremely useful in structural
characterization of organometallic compounds with phosphido-bridged ligands.

D. Reactions of Metal-Metal Bonded-Phosphido-Bridged Compounds

There have been relatively few detailed reactivity studies on phosphido-bridged compounds compared to the number of synthetic efforts. These reactions can be classified as (1) reaction of terminal ligands, (2) metal-metal bond cleavage reaction and (3) metal-phosphorus (phosphido bridge) bond cleavage reaction.

1. Reaction of Terminal Ligands

Phosphido-bridged ligands are more inert toward common reagents than terminally coordinated ligands such as carbonyl and phosphine ligands. The replacement of one or more ligands of the phosphido-bridged compounds is not as common as the substitution reactions of the sulfido- and nitrido-bridged compounds.

Terminal carbonyl ligands of complexes with $\mu$-PR$_2$ ligands can be substituted by triorganophosphines. For example, the dimeric iron compound, [Fe(CO)$_3$(μ-PPPh)$_2$]$\ell_2$, undergoes photochemically initiated carbonyl substitution reactions at room temperature. Both mono and disubstituted derivatives result.$^{62,63}$

In one particular case, terminal carbonyl ligands were substituted by a phosphido-bridged compound, [Fe(CO)$_3$-
(μ-PPhH)\(_2\), to form a capped phosphido-bridged higher
nuclearity cluster.\(^{64}\)

\[
[\text{Fe(CO)}\(_3\)(μ-PPhH)\(_2\)]_2 + L \xrightarrow{\text{hv}} \text{(CO)}\(_3\)\text{Fe} \quad \text{Fe(CO)}\(_2\)\text{L} +
\]

\[L = \text{P(OEt)}\(_3\), \quad \text{P(Me)}\(_2\)\text{Ph}, \quad \text{P(Me)}\text{Ph}_2\]

\[
[\text{V(CO)}\(_4\)(μ-PMe}\(_2\))]_2 + \text{PR}_3 \rightarrow \text{(CO)}\(_4\)\text{V} \quad \text{V(CO)}\(_3\)\text{PR}_3
\]

\[R = \text{PMe}_3, \quad \text{PBu}_3, \quad \text{PHMe}_2\]

\[
[\text{Fe(CO)}\(_3\)(μ-PPhH)]_2 + \text{Co}_2(\text{CO})\(_8\) \xrightarrow{-3\text{CO}} \quad \text{H}_2 \rightarrow
\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

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\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

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\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]

\[
\text{(CO)}\(_3\)\text{Fe} \quad \text{Co(CO)}\(_2\) \quad \text{Co(CO)}\(_2\)\text{Fe}\]
Coordinated tertiary phosphine ligands, PR$_3$, can also be substituted by carbon monoxide.\textsuperscript{65, 36} The reaction described in equation 39 not only involved the substitution of phosphine ligands but also the formation of higher nuclearity cluster.

\[
\text{RuCo(µ-PPh}_2\text{)}_2\text{(CO)}_5\text{(PPh}_3\text{)} \overset{2\text{CO}}{\longrightarrow} \text{RuCo(µ-PPh}_2\text{)}_2\text{(CO)}_7
\]  

\[
\text{MeOH} \quad \text{[(C}_5\text{H}_5\text{)(CO)}_4\text{Fe}_2(µ-PPh}_2\text{)]}^+ + 2\text{MeOH} \quad \text{MeOH} \quad \text{[(C}_5\text{H}_5\text{)(CO)}_4\text{Fe}_2(µ-\text{P(OMe)}_2\text{)]}^+ \quad (40)
\]

Substitution of coordinated 1,5-cyclooctadiene (COD) of [(COD)Rh(µ-PPh$_2$)]$_2$ with monodentate phosphines gives products with two different stereochemistries around the rhodium atoms. The rhodium atom surrounded by four phosphorus atoms adopts a tetrahedral arrangement while the rhodium atom bonded to COD is nearly planar.\textsuperscript{67}
Another type of reaction involves direct addition to the terminal carbonyl ligand. Collman and co-workers have reported that the addition of phenyllithium or methyllithium to the bimetallic $\text{[Fe(CO)}_3(\mu-\text{PPh}_2)]_2$ results in the formation of an acyl complex. X-ray structure indicated that the folded arrangement of the $M_2P_2$ core remains in the product. A similar experiment has been reported by Geoffroy and co-workers. Reactions of the heterobimetallic complex $[(\text{CO})_4\text{W(μ-PPh}_2)_2\text{IrH(CO)(PPh}_3)]$ with LiR lead to the formation of acyl complexes. In this case, the MMP$_2$ core of the acyl anion has a folded arrangement in contrast to the planar arrangement of the neutral dimer.
2. Metal-Metal Bond Cleavage Reaction

Cleavage of the metal-metal bond is a very common reaction pathway for bi- and polynuclear complexes with phosphido-bridged ligands. Some theoretical studies on bi-nuclear phosphido-bridged metal-metal-bonded complexes have led to the conclusion that the metal-metal bonds are quite weak relative to most metal-ligands bonds and are often the ones most directly affected in reactions. Cleavage of the metal-metal bond can generally be achieved either by electrochemical reduction or chemically.

On addition of electrophiles to the dimeric complex $[C_5H_5Co(\mu-PMe_2)]_2$ the Co-Co bond breaks with the formation of two new metal-electrophile bonds.
Alkynes with strong electron withdrawing groups such as CF$_3$ or COOCH$_3$ will insert into the metal-metal bond of [(CO)$_3$Fe($\mu$-PMe$_2$)]$_2$ under photolytic condition.$^{74}$

$$[(CO)_3Fe(\mu-PMe_2)]_2 + RC=CR \xrightarrow{hv} (CO)_3Fe \quad R = CF_3, COOCH_3$$

No reaction was observed when $R = \text{Ph}$ or $H$. However, the addition of disubstituted alkynes into the Fe-Ni bond of $C_5H_5\text{Ni}(\mu-\text{CO})(\mu-\text{PPh}_2)\text{Fe(CO)}_3$ is not restricted to strong electron-withdrawing disubstituted alkynes.$^{75}$

$$C_5H_5\text{Ni} + RC=CR \xrightarrow{hv} C_5H_5\text{Ni} \text{Fe(CO)}_3 + RC=CR$$

$R = \text{Ph, Me, H}$

$R' = \text{Ph, Me, COOCH}_3$
Metal-metal bond cleavage also occurred when phosphido-bridged complexes were attacked by a metal electrophile, AgClO₄.⁷⁶

\[
\begin{align*}
\text{Me}_2\text{N}^+\text{C} & \quad \text{Ph} \\
\text{Me}_2\text{N}^+\text{C} & \quad \text{Ph} \\
\text{Me}_2\text{N}^+\text{C} & \quad \text{Ph} \\
\text{Me}_2\text{N}^+\text{C} & \quad \text{Ph} \\
\end{align*}
\]

In one case (eq. 48), a reversible metal-metal bond cleavage and formation have been observed. Addition of a substrate molecule leads to the cleavage of the metal-metal bond. Elimination of the modified substrate molecule then reforms the metal-metal bond.⁷⁷

In a systematic theoretical investigation via the non-parametrized Fenske-Hall MO model of representative Fe₂(CO)_₆(μ-PR₂)₂, Dahl and co-workers indicated that the HOMO in each neutral dimeric species mainly corresponds to the Fe-Fe bond and the LUMO is of predominantly antibonding diiron character. Electrochemical reduction will put two
electrons into the LUMO and lead to the cleavage of the metal-metal bond.\textsuperscript{69}

In 1968, Dessy and co-workers reported that $[\text{Fe(CO)}_3(\mu-\text{PMe}_2)]_2$ undergoes an electrochemically reversible two-electron reduction to $[\text{Fe(CO)}_3(\mu-\text{PMe}_2)]_2^{2-}$.\textsuperscript{62} The diphenylphosphido-bridged compound, $[\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2$, also undergoes a two-electron reversible reduction to the symmetrical dianion, $[\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2^{2-}$.\textsuperscript{62}

\[
[\text{(CO)}_3\text{Fe}(\mu-\text{PR}_2)]_2 \xrightarrow{2e^-} [\text{(CO)}_3\text{Fe}(\mu-\text{PR}_2)]_2^{2-} \tag{50}
\]

3. Metal-Phosphorus (Phosphido-Bridge) Bond Cleavage Reaction

In all of the examples of the above-discussed reactivity of phosphido-bridged compounds, the phosphido bridge remained intact although the nature of the bridge did change. Only in a few cases is there evidence to indicate that the reaction might occur at the metal-phosphorus bond of a phosphido bridge.

The reaction of $\text{Fe}_2(\text{CO})_6(\mu-^2\eta-\text{C}≡\text{CBu}^t)(\mu-\text{PPh}_2)$ with disubstituted acetylenes results in a cleavage of the

\[
\begin{align*}
\text{(CO)}_3\text{Fe} & \quad \xrightarrow{\text{Bu}} \quad \text{(CO)}_3\text{Fe} \\
\text{Ph}_2 & \quad \xrightarrow{\text{Bu}} \quad \text{Ph}_2
\end{align*}
\]

\[
\begin{align*}
\text{R}^2 &= \text{Me}, \quad \text{R}^3 &= \text{Ph}
\end{align*}
\]
Fe-PPh$_2$ bond and the generation of phosphine-containing products via acetylide-acetylene coupling.$^{17}$

It has been claimed that the cobalt-phosphido bonds must be broken in the course of the hydroformylation reaction with [Co(μ-PPh$_2$)(CO)$_3$]$_x$ as a catalyst.$^{36}$

$$[\text{Co(μ-PPh}_2\text{)(CO)}_3]_x + \text{1-hexene + H}_2 \rightarrow \left(\frac{x}{2}\right)\text{Co}_2(\text{CO})_6(\text{PPh}_2(\text{C}_6\text{H}_{11}))_2$$  \hspace{1cm} (52)

The irreversible transformation of bridging PPh$_2$ ligands into the terminal PPh$_2(\text{C}_6\text{H}_{11})$ ligands under hydroformylation conditions illustrates the lability of a phosphido-bridged ligand.

Disruption of the dimeric complexes in solution must occur to account for the quantitative synthesis of [Rh$_2$(μ-PPh$_2$)(μ-Cl)(COD)$_2$] from the reaction of [Rh$_2$(μ-PPh$_2$)$_2$(COD)$_2$] with [Rh$_2$(μ-Cl)$_2$(COD)$_2$]$^{78}$ at 60°C.

$$[\text{Rh}_2(\mu-\text{Cl})_2(\text{COD})_2] + [\text{Rh}_2(\mu-\text{PPh}_2)_2(\text{COD})_2] \xrightarrow{\Delta} 2[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{PPh}_2)(\text{COD})_2]$$ \hspace{1cm} (53)

When [Rh(μ-PPh$_2$)$_2$(COD)]$_2$ is treated with Ph$_2$PCH$_2$CH$_2$CH$_2$PH (PPH) in THF, diphenylphosphine is found in the solution.$^{32}$ The only source of diphenylphosphine in this solution is the diphenylphosphido bridge in [Rh(μ-PPh$_2$)(COD)]$_2$. This implies that the μ-diphenylphosphido group was displaced, presumably by the secondary phos-
As can be seen from the above examples, the phosphido bridge is not as chemically inert as it had been assumed.

E. Application of MBR$_3$H Reagents to Organometallic Chemistry

Throughout this research, the alkali metal trialkylborohydride reducing agents with the common formula MBR$_3$H have been used extensively for the reduction reaction of [Fe(CO)$_3$(μ-PPh$_2$)]$_2$ and [Fe(NO)$_2$(μ-PPh$_2$)]$_2$. Therefore it is proper to review the chemistry of these complex reducing agents with organometallic compounds and their specific reduction capabilities.

Among these reagents, lithium triethylborohydride, "Super Hydride", is known to be a very powerful nucleophile.

The other widely used reagent is K-Selectride, which is a more stereoselective reducing agent.
Known reactions of these reducing agents with organo-metallic compounds can be classified into the following categories:

1. Cleavage of Metal-Metal Bond

One of the first useful reactions observed was the cleavage of metal carbonyl dimers to metal carbonyl anions, which may be readily alkylated, acylated, or metalated by reaction with an appropriate electrophile (eq. 54-55). Examples are:

\[(\text{CO})_n M-M(\text{CO})_n + 2\text{LiBEt}_3\text{H} \rightarrow 2\text{Li}[M(\text{CO})_n] + 2\text{BEt}_3 + \text{H}_2\]  \hspace{1cm} (54)

- \(M = \text{Co}, n = 4\)
- \(M = \text{Mn}, n = 5\)

\[\left[(\text{C}_5\text{H}_5M(\text{CO})_n\right)_2 + 2\text{LiBEt}_3\text{H} \rightarrow 2\text{Li}[\text{C}_5\text{H}_5M(\text{CO})_n] + 2\text{BEt}_3 + \text{H}_2\]  \hspace{1cm} (55)

- \(M = \text{Fe}, n = 2\)
- \(M = \text{Mo}, n = 3\)

These metal carbonyl anions can also be prepared by sodium amalgam reduction of metal carbonyl dimers. However, the use of LiBEt_3H provided a rapid, one-flask synthesis of metal anions in near quantitative yield under homogeneous conditions.

2. Preparation of Metal Formyl Complexes

At lower temperature, (ca. -20°C), the addition of one equivalent of LiBEt_3H to Mn_2(CO)_10 leads to the formation of an anionic formyl compound (eq. 56) which decomposed rapidly at room temperature to the monomeric metal anion.
\[
M_2(\text{CO})_{10} + \text{LiBEt}_3\text{H} \rightarrow \text{Li}[(\text{CO})_5^\text{M} - \text{M(}\text{CO})_5] + \text{BEt}_3 \\
(56)
\]

\[
M = \text{Mn}, \; t^\circ \text{C} = -20^\circ \text{C} \\
M = \text{Re}, \; t^\circ \text{C} = \text{room temperature}
\]

However, the reaction of \(\text{Re}_2(\text{CO})_{10}\), which has a stronger metal-metal bond, with \(\text{LiBEt}_3\) leads to the formation of a similar anionic formyl compound that is stable at room temperature for days.

The reactions of \(\text{LiBEt}_3\text{H}\) with metal carbonyl clusters such as \(\text{Os}_3(\text{CO})_{12}, \text{Ir}_4(\text{CO})_{12}, \text{Ru}_3(\text{CO})_{12}\) and \(\text{Rh}_4(\text{CO})_{12}\) have been studied by spectroscopic methods. \(^{81}\)

\[
M_x(\text{CO})_n + \text{LiBEt}_3\text{H} \rightarrow [M_x(\text{CO})_{n-1}(\text{CHO})]^\text{−}\text{Li}^+ \\
(57)
\]

\[
M = \text{Os, Ru, } X = 3, \; n = 12 \\
M = \text{Ir, Rh, } X = 4, \; n = 12
\]

The results suggested that anionic metal formyl complexes were formed. Addition of a second equivalent of \(\text{LiBEt}_3\text{H}\) produced biformyl complexes.

3. Reaction with Organosulfur Compounds

Lithium triethylborohydride is known to react with organosulfur compounds. It reacts with elemental sulfur to give \(\text{Li}_2\text{S}\) or \(\text{Li}_2\text{S}_2\). It also reacts rapidly with organic disulfides, \(\text{RSSR}\), to give \(\text{RSLi}\). \(^{79}\)

An organometallic analogue of organic disulfides is the bimetallic iron compound, \(\text{S}_2\text{Fe}_2(\text{CO})_6\), which contains \(\text{S-S}\) and \(\text{Fe-Fe}\) bonds. This compound reacts rapidly with one equivalent of \(\text{LiBEt}_3\text{H}\) at \(-78^\circ \text{C}\) to form a monoanionic species by nucleophilic cleavage of the \(\text{S-S}\) bond. \(^{82}\)
a second equivalent of LiBEt$_3$H resulted in the formation of the corresponding dianion. Throughout these reactions, the metal-metal bond remained intact.

\[
\begin{align*}
\text{(Cu)}_3\text{Fe} & \quad \text{Fe(CO)}_3 + \text{LiBEt}_3\text{H} \rightarrow \text{(Cu)}_3\text{Fe} - \text{Fe(CO)}_3 + \text{Li}^+ \text{S-S-H} \\
& \quad \text{LiBEt}_3\text{H} \quad \text{Li}_2\left[\text{(Cu)}_3\text{Fe} - \text{Fe(CO)}_3\right]
\end{align*}
\]

F. Research Objective

The major goal of this dissertation was to study redox chemistry of binuclear metal-metal-bonded complexes containing phosphido-bridged ligands with different reducing agents. Of additional interest was the chemistry of such reduced bimetallic species toward various organic reagents.

In this dissertation, the results of the reactions of [Fe(CO)$_3$(μ-PPh$_2$)]$_2$ and [Fe(NO)$_2$(μ-PPh$_2$)]$_2$ with various reducing agents are reported. Results of the protonation and alkylation of these reduced species are also presented.
II. EXPERIMENTAL

A. Reagents and Chemicals

The chemicals used in this research were of reagent grade quality and were used without further purification unless stated otherwise.

1. Phosphines

Chlorodiphenylphosphine (PPh₂Cl) was purchased from Aldrich Chemical Company, Milwaukee, Wisconsin. Diphenylphosphine (PPh₂H) was obtained from Strem Chemicals, Newburyport, Massachusetts.

2. Reducing Agents

The alkali metal trialkylborohydride reducing agents, LiBEt₃H (Super Hydride, 1 M in THF solution), LiB(sec-Bu)₃H (L-Selectride, 1 M in THF solution), NaBEt₃H (1 M in THF solution), NaB(sec-Bu)₃H (N-Selectride, 1 M in THF solution), KBEt₃H (1 M in THF solution), KB(secBu)₃H (K-Selectride, 1 M in THF solution), and LiBEt₃D (Super Deuteride, 1 M in THF solution) were purchased from Aldrich Chemical Company. Aldrich was also the source of NaAlH₂-(OCH₂CH₂OMe)₂ (Red-Al or Vitride, 70% in toluene solution), (i-Bu)₂AlH (DIBAL-H, 1 M solution in hexane), lithium aluminum hydride (LiAlH₄, 1 M in THF solution) and potassium
30-
hydride (KH, 35% in mineral oil). Sodium dispersion (40% in
mineral oil) and sodium cyanoborohydride (NaB(CN)H₃) were
obtained from Alfa Products (Ventron), Danvers,
Massachusetts. Potassium hydride and sodium dispersion were
washed with hexane to remove mineral oil and were stored in
the solid form inside a dry box. Sodium borohydride
(NaBH₄) was obtained from Fisher Scientific.

3. Alkylating and Protonating Reagents

Methyl iodide (CH₃I) was obtained from EM Science,
Cincinnati, Ohio. Ethyl iodide (C₂H₅I) was purchased from
Chemical Company supplied diiodomethane (CH₂I₂), 1,3-
diiodopropane (ICH₂CH₂CH₂I). 1-iodopropane (ICH₂CH₂CH₃),
ioodoacetonitrile (ICH₂CN) and deuterated methyl iodide
(CD₃I). Benzyl iodide (ICH₂C₆H₅) was purchased from ICN
(ClCH₂C₆H₅) and 2-bromopropane (CH₃CHBrCH₃) were obtained
from J. T. Baker Chemical Company, Phillipsburg, New
Jersey. Allyl iodide (CH₂CHCH₂I) was purchased from Alfa
Products. Trifluoroacetic acid (CF₃COOH), deuterated
trifluoroacetic acid (CF₃COOD) and tetrafluoroboric acid
were provided by Aldrich Chemical Company. Carbon-13
labeled methyl iodide (¹³CH₃I, 90% enriched) was purchased
from Merck, Sharpe, and Dohme Isotopes, Montreal, Canada.

4. Other Reagents

Iron pentacarbonyl (Fe(CO)₅) was obtained from Alfa
Products. Triethylamine (N(C₂H₃)₃) was purchased from J. T.
Baker Chemical Company, and Proton Sponge \( \text{C}_{10}\text{H}_8\text{N(C}_3\text{H}_3\text{)}_2 \) and \( n\)-butyllithium \( (n\)-BuLi, 1.64 M in hexane) were purchased from Aldrich Chemical Company. Bis(triphenylphosphine)-iminium chloride \( \text{PPNCl} \) was obtained from Alfa Products. Carbon-13 labeled carbon monoxide gas (90% enriched) was purchased from Merck, Sharpe, and Dohme Isotopes, Montreal, Canada.

5. Solvents

All solvents were reagent grade, and most were purified and/or dried by methods described by Perrin, et al. Tetrahydrofuran (THF) was distilled from sodium and benzophenone under a nitrogen atmosphere immediately before use. Dichloromethane was distilled from \( P_4\text{O}_{10} \) and stored over 4Å molecular sieves. Hexane was distilled from sodium and stored over 4Å molecular sieves. Methanol was distilled from \( P_4\text{O}_{10} \) immediately before use. Anhydrous diethyl ether, petroleum ether (low boiling, 30°C - 60°C) and cyclohexane were used as received without further purification.

6. NMR Solvents and Standards

Deuteriated dichloromethane \( (\text{CD}_2\text{Cl}_2) \), deuteriated chloroform \( (\text{CDCl}_3) \), deuteriated acetone \( (\text{CD}_3\text{COOD}_3) \), deuteriated benzene \( (\text{C}_6\text{D}_6) \), deuteriated tetrahydrofuran \( (\text{C}_4\text{D}_8\text{O}) \), and tetramethylsilane \( ((\text{CH}_3)_4\text{Si}) \) were purchased from Aldrich Chemical Company and were used to prepare samples for proton and carbon-13 NMR spectra.
7. Chromatographic Materials

Activated magnesium silicate ("Florisil", 60-100 mesh) was supplied by J. T. Baker Company and used as received. Activated neutral alumina was purchased from Aldrich Chemical Company and deactivated by addition of 3% (Grade II), 6% (Grade III) and 9% (Grade IV) by weight of water.

B. Instrumentation and Physical Measurements

Infrared spectra were recorded on either a Perkin-Elmer 337 or a Perkin-Elmer 283B Grating Spectrophotometer from 4000 to 400 (P.E. 337) or to 200 (P.E. 283B) cm$^{-1}$. Spectra were calibrated against a sharp peak (1601.4 cm$^{-1}$) of polystyrene film. Solution spectra were recorded in a NaCl solution cell with a path length of 0.2 mm. Some samples were examined as pressed KBr pellets or Nujol mulls between KBr plates.

Continuous-wave proton NMR spectra were collected on a Varian EM-360 or EM-390 spectrometer. Fourier transfer-mode proton NMR spectra were collected on either Bruker HX-90 spectrometer operating at 90 MHz or a Bruker WM-300 spectrometer operating at 300 MHz. Spectra were obtained by using deuteriated solvents, and they were standardized against internal TMS ($\delta = 0$ ppm). All reported $^1$H chemical shifts are given in ppm relative to TMS.

Phosphorous-31 spectra were run in 10 mm tubes using THF as solvent on the Bruker HX-90 spectrometer operating at 36.43 MHz in the Fourier transform mode with a Bruker B-NC
12 data system. Phosphorous-31 NMR spectra were proton noise decoupled except when $^{31}\text{P}-^{1}\text{H}$ coupling constants were desired to be observed. These spectra were standardized through the use of coaxial insert tubes. The coaxial insert tube contained deuteriated acetone and a secondary standard, trimethylphosphate, ($\delta = 58.09$ Hz relative to $\text{H}_3\text{PO}_4$) and was placed in the sample tube throughout the collection of data. The phosphorous-31 spectra generally are reproducible to ±0.1 ppm for chemical shifts and ±1.0 Hz for coupling constants. Concentration and temperature effects can also cause chemical shifts to vary. Chemical shifts are reported with positive values as downfield from the standard.

Room temperature carbon-13 NMR spectra were recorded on a Bruker WP-80 spectrometer operating at 20.11 MHz. Spectra were obtained by using deuteriated solvents and standardized against internal TMS ($\delta = 0$ ppm) or against C-13 resonances of deuteriated solvents. Spectra were recorded both in the broadband-noise $^{1}\text{H}$-decoupled mode and in off-resonance mode. Variable temperature carbon-13 NMR spectra were recorded on a Bruker HX-90 spectrometer operating at 22.63 MHz. In a few cases, THF was used as solvent.

Deuterium NMR spectra were recorded on a Bruker WM-300 spectrometer operating at 46.072 Hz. Tetrahydrofuran was used as solvent for all the samples. The spectra were standardized against the absolute frequency of the instrument.
Boron-11 NMR spectra were collected on a Bruker HX-90 spectrometer operating at 28.87 MHz. Spectra were recorded both in the proton coupled mode and broadband decoupled mode. The boron spectra were standardized relative to boron trifluoride in diethyl ether ($\delta = 0.0$ Hz).

Line shape analysis and computer simulation of experimental spectra were performed by using the DNMR III program of G. Binsch and D. A. Klein of the University of Notre Dame.\textsuperscript{84}

Mass spectra were obtained by Mr. C. R. Weisenberger with a Kratos MS-30 mass spectrometer. These spectra were acquired using Fast Atom Bombardment (FAB) techniques. The bombarding gas was xenon and fluorinated kerosene was used as reference. The samples were dissolved in THF and mixed in the matrix of tetraglyme.

Melting points were determined in glass capillaries in a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

C. General Experimental Procedures

Standard techniques for the manipulation of air-sensitive compounds were used for all reactions unless otherwise specified.\textsuperscript{85} Frequently, a Vacuum Atmospheres HE43 dry box equipped with an MO-40 catalyst system purged with argon was utilized for handling compounds or conducting
reactions which were sensitive to air or moisture. A manifold with a two-way stopcock, one of which led to the vacuum system and the other to the source of dried nitrogen, was used in this work. Schlenk vessels and Schlenk filters (with sintered glass frits) were used for most reactions of air-sensitive compounds. Solutions of air-sensitive reagents were transferred between reaction vessels by using syringes flushed with nitrogen or double tip stainless steel needles. All reactions were carried out under an atmosphere of high purity nitrogen. The nitrogen gas was prepurified by passing through a drying sequence composed of concentrated H$_2$SO$_4$, KOH pellets and CaSO$_4$ column. Solvents were purged with nitrogen for 10 minutes prior to use. A general purpose vacuum line was used in some cases where the reactions involved evolution and collection of gases.

Photoreactions were conducted by using a Hanovia UV Ultraviolet lamp (medium pressure Hg arc lamp) with a water cooling system.

D. Preparations of Known Compounds

Reaction of iron pentacarbonyl (Fe(CO)$_5$) with iodine in ether at 0°C afforded Fe(CO)$_4$I$_2$ as a deep purple microcrystalline solid which is thermally unstable.$^{86}$ The compound was characterized by its infrared spectrum: the carbonyl stretching frequencies are consistent with the reported literature values.$^{87}$
Reaction of Fe(CO)$_4$I$_2$ with nitric oxide in diethyl ether at room temperature afforded the corresponding nitrosyl compound, [Fe(NO)$_2$I]$_2$.$^{88}$ The dark brown compound was further purified by sublimation at 110°C.$^{89}$ The compound was characterized by its infrared spectrum, with the nitrosyl stretching frequencies being consistent with the reported literature values.$^{89}$ The nitric oxide gas used in this experiment was prepared by adding dilute sulfuric acid into sodium nitrite (NaNO$_2$).$^{90}$ The gas formed was dried by passage through concentrated KOH solution (10 M) and then directly bubbled into the Fe(CO)$_4$I$_2$ solution.

The preparation of 2-iodopropane from 2-bromopropane was accomplished by using the halogen exchange reaction according to a published method.$^{91}$ The alkyl iodide was characterized by its proton NMR spectrum, and the chemical shifts are comparable to the literature values.

E. Preparation and Characterization of Starting Materials

1. Preparation of [Fe(CO)$_3$(μ-PPh$_2$)]$_2$

To a suspension of Na (7.50 g, 0.326 mole) in 300 ml of THF in a 500 ml three-neck flask under N$_2$, Fe(CO)$_5$ (40 ml, 0.300 mole) was added dropwise. Reaction occurred immediately and the CO gas evolved and was released through an oil bubbler. The solution was stirred at room temperature overnight as the reddish slurry of Na$_2$Fe$_2$(CO)$_8$ was formed. To that slurry, chlorodiphenylphosphine (54.0 ml, 0.300 mole) was added dropwise over a two hour period.
Upon addition of the phosphine ligand the solution changed color from red to deep dark brown. The reaction is highly exothermic with vigorous CO gas evolution. The resulting solution was stirred at room temperature for two days. The solvent was removed by rotary evaporation. The dark brown residue was extracted with portions of petroleum ether or pentane (~ 4 l was used) until the washings were nearly colorless. The yellowish extracts were then passed through a medium porority glass filter packed with neutral alumina as filter aid. The volume of the filtrate solution was reduced to about 30 ml by rotary evaporation. Yellow microcrystals then spontaneously precipitated from the solution and were collected on a frit. The yield is 51.6 g (53%).

Melting point 179-180°C (uncorrected)

$^1$H NMR(CDC$_3$)δ 7.2, multiplet

IR (Cyclohexane) ν(C=O) 2058(s), 2019(s), 1997(s), 1970(s), 1961(s), cm$^{-1}$

(THF) ν(C=O) 2050(s), 2005(s), 1988(s), 1966(s), 1950(sh) cm$^{-1}$

$^{13}$C{$^1$H} NMR(CDC$_3$, 25°C)δ 212.8, triplet, $J_{P-C}$=6 Hz
$J_{P-C}$ = 6 Hz
127.5-133.2, multiplet

$^{31}$P{$^1$H} NMR(THF, 25°C)δ 142.5, singlet

Mass spectrum (70 ev, electron impact) Calc. 650 for $M^+$

<table>
<thead>
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<th>m/e</th>
<th>intensity(%)</th>
<th>ion</th>
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<td>510</td>
<td>33.58</td>
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</tr>
<tr>
<td>482</td>
<td>30.29</td>
<td>$M^+$-6CO</td>
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2. Preparation of \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\)

A solution of diphenylphosphine, \(\text{PPh}_2\text{H}\) (2.20 ml, 12.4 mmole) in 10 ml of THF was treated with 7.5 ml of \(n\)-butyl lithium (1.64 M, 12.2 mmole) under nitrogen. The solution underwent color change from colorless to bright red. This solution was transferred via stainless steel needle to a flask containing 3.0 g of \([\text{Fe(NO)}_2\text{I}]_2\) (6.2 mmole) in 40 ml of THF under nitrogen. The solution was stirred at room temperature for two days. Reddish microcrystalline solid precipitated from the solution. The product was collected on a fritted glass filter. The volume of the filtrate solution was reduced by rotary evaporation to about 10 ml and additional solid was precipitated by the addition of 50 ml of methanol. The two crops were combined and washed with 10 ml of ether and then washed with 10 ml of methanol three times. The yield was 3.25 g (87.2%).

IR(THF) \(v(\text{N=O})\) 1762(s), 1748(s) cm\(^{-1}\)

IR(KBr) \(v(\text{N=O})\) 1760(s), 1740(s), 1695(w) cm\(^{-1}\)

\(^{31}\text{P}(\text{H})\) NMR(THF, 125°C)\(\delta\) 261.5, singlet

Mass spectrum (70 ev, EI) Calc. 602 for \(M^+\)

<table>
<thead>
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<th>ion</th>
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<tr>
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<td>100</td>
<td>(M^+-\text{NO})</td>
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<td>(M^+-2\text{NO})</td>
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<tr>
<td>512</td>
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<td>(M^+-3\text{NO})</td>
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This compound, \([\text{Fe(NO)}_2(\mu-P\text{Ph}_2)]_2\), can also be prepared by the reaction of \([\text{Fe(NO)}_2\text{Br}]_2\) with LiP\text{Ph}_2 in comparable yield.

3. Carbon-13 Monoxide Enrichment of \([\text{Fe(CO)}_3(\mu-P\text{Ph}_2)]_2\)

Enrichment was achieved by dissolving 2.6 g of \([\text{Fe(CO)}_3(\mu-P\text{Ph}_2)]_2\) in 100 ml of THF in a 500 ml Pyrex flask. The experiment was performed on a vacuum line. After the solvent was frozen at liquid nitrogen temperature and the flask was evacuated, carbon-13 monoxide gas was admitted. The solution was stirred and externally irradiated by the Hanovia 450-W medium-pressure mercury arc lamp for 24 hours. The solution was filtered through a short alumina column, and solvent removal by rotary evaporation afforded pure enriched material. Mass spectral analysis revealed enrichment to be approximately 50%. The mass spectra of the enriched sample and unenriched sample of the region around the parent ion (m/e = 650) are shown in Figure 1.

P. Reduction of \([\text{Fe(CO)}_3(\mu-P\text{Ph}_2)]_2\) and \([\text{Fe(NO)}_2(\mu-P\text{Ph}_2)]_2\)

1. Reduction of \([\text{Fe(CO)}_3(\mu-P\text{Ph}_2)]_2\)

a. Reaction with LiB\text{Et}_3\text{H} (Super Hydride)

A 100 ml Schlenk flask equipped with serum cap and a magnetic stirring bar was charged with 0.26 g (0.40 mmole) of \([\text{Fe(CO)}_3(\mu-P\text{Ph}_2)]_2\) and then evacuated and flushed with nitrogen. THF (30 ml) was added by syringe. To the resulting yellow solution, 0.40 ml (0.40 mmole) of 1 M LiB\text{Et}_3\text{H} in
Figure 1. Mass Spectra of $[\text{Fe(CO)}_3(\mu\text{-PPh}_2)]_2$ and $^{13}\text{CO}$ enriched $[\text{Fe(CO)}_3(\mu\text{-PPh}_2)]_2$
THF solution was added slowly by syringe. The solution immediately changed color from yellow to deep orange red. The reaction solution was stirred at room temperature for 10 minutes; the solvent was removed under reduced pressure and gave a deep orange red oil. Attempts to obtain solid samples of the product failed. Quantitative formation of the product monoanion was estimated from P-31 NMR measurements.

\[
\text{IR(THF)} v(C=O) \quad 1992(s), 1941(s), 1905(s), 1887(s) \text{ cm}^{-1}
\]

\[
v(C=O) \quad 1645 \text{ cm}^{-1}
\]

\[
^{31}P\{^1H\} \text{ NMR(THF, 25°C)} \delta \quad 122.5, \text{ doublet}
\]

\[
51.3, \text{ doublet } J_{P-P} = 12 \text{ Hz}
\]

\[
^{31}P \text{ NMR(THF, 25°C)} \delta \quad 122.5, \text{ broad singlet}
\]

\[
51.3, \text{ broad doublet } J_{P-H} = 334 \text{ Hz}
\]

\[
^{13}C \text{ NMR(THF)} \text{ (carbonyl region, 25°C)} \delta \quad 234.8, \text{ broad singlet}
\]

b. Reaction with LiBEt$_3$D (Super Deuteride)

A solution of 0.26 g (0.40 mmole) of [Fe(CO)$_3$(μ-PPh$_2$)$_2$]$_2$ in 30 ml of THF in a 100 ml Schlenk flask equipped with a serum cap was treated with 0.40 ml of 1 M LiBEt$_3$D in THF (0.40 mmole, 1 equivalent) by syringe. Upon addition of the Super Deuteride, the color of the solution changed from yellow to deep orange red. No attempts were made to isolate solid product. Quantitative formation of the product monoanion was estimated from P-31 NMR measurements.

\[
\text{IR(THF)} v(C=O) \quad 1994(s), 1940(s), 1905(s), 1890(s) \text{ cm}^{-1}
\]

\[
v(C=O) \quad 1648(m) \text{ cm}^{-1}
\]
\[ ^{31}\text{P}\{^1\text{H}\} \text{NMR}(\text{THF}, 25^\circ\text{C}) \delta \]

122.5, doublet  
52.3, triplet of doublets  
\[ J_{\text{P}-\text{P}} = 12 \text{ Hz} \]  
\[ J_{\text{P}-\text{D}} = 51 \text{ Hz} \]

\[ ^{2}\text{H} \text{NMR}(\text{THF}, 25^\circ\text{C}) \delta \]

6.3, doublet  
\[ J_{\text{P}-\text{D}} = 51 \text{ Hz} \]

c. Reaction with LiB(sec-Bu)_3H (L-Selectride)

The procedure for this reaction was similar to that described for the LiBEt_3H reduction. A solution containing 0.26 g (0.40 mmole) of \( \left[ \text{Fe(CO)}_3(\mu-\text{PPh}_2) \right]_2 \) in 30 ml of THF was treated with 0.40 ml of 1 M LiB(sec-Bu)_3H in THF (0.40 mmole, 1 equivalent). The yellow solution changed to deep orange red immediately. Removal of solvent under reduced pressure resulted in deep red oil. No attempts were made to obtain a solid sample. Quantitative formation of the monoanion was estimated from the P-31 NMR and IR spectral measurements.

IR(THF) \( \nu(\text{C=O}) \)

1992(s), 1939(s), 1901(s), 1888(sh) cm\(^{-1}\)

\( \nu(\text{C=O}) \)

1645(m) cm\(^{-1}\)

\[ ^{31}\text{P}\{^1\text{H}\} \text{NMR}(\text{THF}, 25^\circ\text{C}) \delta \]

122.5, doublet  
52.3, doublet  
\[ J_{\text{P}-\text{P}} = 11 \text{ Hz} \]

\[ ^{31}\text{P} \text{ NMR}(\text{THF}, 25^\circ\text{C}) \delta \]

122.5, singlet  
52.3, broad doublet  
\[ J_{\text{P}-\text{H}} = 336 \text{ Hz} \]

d. Reaction with NaBEt_3H

The procedure for this reaction was similar to that described for the LiBEt_3H reduction. The product monoanion solution was prepared by the addition of 0.40 ml (0.40
mmole) of a 1 M solution of NaBEt₃H to a solution of 0.40 mmole of [Fe(CO)₃(μ-PPh₂)]₂ (0.26 g) in 30 ml of THF at room temperature. Immediately, a dark red solution was formed. The solvent was removed under reduced pressure to give a dark red oil. No attempts were made to isolate a solid sample. Quantitative formation of the monoanion was estimated from its P-31 NMR and IR spectral measurements.

IR(THF) v(C=O)  
1986(s), 1933(s), 1880(s) cm⁻¹  
v(C=O)  
1669(m) cm⁻¹  

3¹P{¹H} NMR(THF, 25°C)δ  
126.6 ppm, doublet  
51.7 ppm, doublet  
Jₚₚ = 12 Hz  

3¹P NMR(THF, 25°C)δ  
126.6, broad singlet  
51.7, broad doublet  
Jₚ₋ₜ = 340 Hz

e. Reaction with KBET₃H

The procedure for this reaction was similar to that described for the LiBEt₃H reduction. When 0.40 ml of KBET₃H (0.40 mmole, 1 M in THF solution) was added to a solution of [Fe(CO)₃(μ-PPh₂)]₂ (0.26 g, 0.40 mmole) in 30 ml of THF, the yellow color was discharged immediately to give a deep orange red solution. The solvent was removed under reduced pressure to give a dark red oil. No attempts were made to isolate solid samples of the product. Yield was estimated from the P-31 NMR spectrum to be quantitative.

IR(THF) v(C=O)  
1983(s), 1932(s), 1900(s) cm⁻¹  
v(C=O)  
1672(m) cm⁻¹  

3¹P{¹H} NMR(THF, 25°C)δ  
127.1, doublet  
51.6, doublet  
Jₚ₋ₜ = 10 Hz
31P NMR(THF, 25°C)δ
127.1, broad singlet
51.6, broad doublet
\( J_{P-H} = 331 \text{ Hz} \)

f. Reaction with NaB(sec-Bu)₃H

The procedure for this reaction was similar to that described for the LiBEt₃H reduction. A solution containing 0.26 g (0.40 mmole) of \([\text{Fe(CO)}₃(\mu-PPh₂)]₂\) in 30 ml of THF was treated with 0.40 ml of NaB(sec-Bu)₃H (1 M in THF solution, 0.40 mmole). The yellow solution changed color to deep orange red immediately. Removal of solvent under reduced pressure resulted in deep red oil. No attempts were made to isolate solid samples of the product. Quantitative formation of the monoanion was estimated from P-31 NMR measurements.

\[
\text{IR(THF)\nu(C=O)} \quad 1982(s), 1933(s), 1890(s) \text{ cm}^{-1} \\
\quad 1665(m) \text{ cm}^{-1}
\]

31P\{1H\} NMR(THF, 25°C)δ
126.4, doublet
50.7, doublet
\( J_{P-P} = 11 \text{ Hz} \)

31P NMR(THF, 25°C)δ
126.4, broad singlet
50.7, broad doublet
\( J_{P-H} = 336 \text{ Hz} \)

g. Reaction with KB(sec-Bu)₃H (K-Selectride)

The procedure for this reaction was similar to that described for the LiBEt₃H reduction. The product monoanion solution was prepared by the addition of 0.40 ml (0.40 mmole) of a 1 M solution of KB(sec-Bu)₃H to a solution of 0.40 mmole of \([\text{Fe(CO)}₃(\mu-PPh₂)]₂\) (0.26 g) in 30 ml of THF at room temperature. Immediately, a dark red solution was
formed. The solvent was removed under reduced pressure to give a dark red oil. Attempts to prepare solid samples failed. Yield was estimated to be quantitative from the P-31 NMR spectral measurements.

\[
\begin{align*}
\text{IR (THF) } v(C=O) & \quad 1989(s), 1938(s), 1900(s) \\
\text{ } & \quad 1674(m) \text{ cm}^{-1} \\
\text{P-31 NMR (THF, 25°C) } \delta & \quad 127.2, \text{ doublet} \\
\text{ } & \quad 52.1, \text{ doublet} \\
\text{ } & \quad J_{p-p} = 10 \text{ Hz} \\
\end{align*}
\]

h. Reduction with Two Equivalents of Complex Boron Hydride Reducing Agents, LiBEt$_3$H, NaBEt$_3$H, KBEt$_3$H, LiB(sec-Bu)$_3$H, NaB(sec-Bu)$_3$H and KB(sec-Bu)$_3$H

The procedures for these reduction reactions were analogous to the procedures described in the above sections 1 through 7, except that two equivalents of complex reducing agents were employed instead of one equivalent. The results of these reductions using two equivalents of reducing agents are identical to those obtained from one equivalent reductions. These conclusions were drawn by comparing the P-31 NMR and IR spectra of the reduced species.

i. Reduction with LiAlH$_4$

The procedure for this reaction was similar to that described for the LiBEt$_3$H reduction. A 100 ml Schlenk flask equipped with a serum cap and a magnetic stirring bar was
charged with 0.26 g (0.40 mmole) of $[\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2$ and then was evacuated and filled with nitrogen. THF (30 ml) was added by syringe. To the resulting yellow solution, 0.80 ml (two equivalents) of 1 M LiAlH$_4$ (0.40 mmole) in THF solution was added slowly by syringe. Immediately, a dark brown solution was formed and gas evolution was observed. The gas was later identified as dihydrogen. No attempts were made to isolate solid samples of the product. The product was formulated as $\text{Li}_2[\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2$ by comparing the IR spectrum of the product with the reported IR spectral data of $\text{Na}_2[\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2$.

$$\text{IR(THF)} \nu(\text{CO}) \quad 1931(\text{sh}), \ 1908(\text{s}), \ 1850(\text{s}), \ 1771(\text{s}) \ \text{cm}^{-1}$$

$$31\text{P}^1(\text{H}) \text{NMR(THF, 25°C)} \delta \quad -63.9, \text{singlet}$$

This reaction was also performed at $-78^\circ C$ (Dry Ice/isopropyl alcohol) and monitored by $31\text{P}$ NMR spectroscopy. The product $\text{Li}_2[\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2$ formed as the dark brown solution was warmed to room temperature gradually. The IR and $31\text{P}$ NMR spectra data revealed that the product is identical with the product obtained from the room temperature reaction.

### j. Reaction with Vitride

The procedure for this reaction was similar to that for the LiB$\text{Et}_3$H reaction. To a solution of $[\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2$ (1.0 g, 1.5 mmole) in 30 ml of THF at room temperature was added 1 ml of Vitride (two equivalents, 70% in toluene).
which caused a color change to deep brown. The solvent was removed under reduced pressure to give dark brown oil. No attempts were made to isolate solid samples of the product. The compound was identified as Na₂[Fe(CO)₃(μ-PPh₂)]₂ from its P-31 NMR spectrum, and quantitative formation of the dianion was also estimated from the P-31 NMR spectrum.

\[ ^{31}P\{^1H\} \text{NMR(THF, 25°C)} \delta -61.6, \text{singlet} \]

**k. Reaction with Sodium Dispersion**

A 100 ml Schlenk flask equipped with a serum cap and a magnetic stirring bar was charged with 1.0 g (1.5 mmole) of [Fe(CO)₃(μ-PPh₂)]₂ and 0.069 g (3.0 mmole) of sodium dispersion inside a dry box. THF (30 ml) was added by syringe and the solution was stirred at room temperature overnight. The yellow solution gradually changed color to brown. The IR spectrum is consistent with the published result on the dianion in Na₂[Fe(CO)₃(μ-PPh₂)]₂. No attempts were made to obtain a solid sample of the product.

\[ \text{IR(THF)} v(C≡O) \]
\[ 1930(\text{sh}), 1905(\text{s}), \]
\[ 1845(\text{s}), 1825(\text{sh}), 1800(\text{s}) \text{ cm}^{-1} \]

\[ ^{31}P\{^1H\} \text{NMR(THF, 25°C)} \delta -62.4, \text{singlet} \]

**l. Reaction with Sodium Amalgam**

A 100 ml, three-neck, round-bottom flask equipped with a serum cap, two nitrogen inlet adapters and a magnetic stirring bar was charged with 1% sodium amalgam solution which was prepared by adding 1.34 g (0.058 mole) of sodium into 10 ml of mercury under nitrogen. The amalgam thus
prepared was covered with 50 ml of freshly distilled THF by syringe. To the amalgam was added 1.0 g (1.5 mmole) of \([\text{Fe(Cu)}_3(\mu-\text{PPh}_2)]_2\) in 10 ml of THF by a stainless steel needle. Immediately, reaction occurred and a brown solution was formed. The reaction mixture was stirred at room temperature for 3 hours with monitoring by IR spectroscopy. No attempts were made to isolate a solid sample of the product.

\[
\begin{align*}
\text{IR(THF)} & \nu(C=O) \\
& 1930(\text{sh}), 1905(\text{s}), \\
& 1845(\text{s}), 1825(\text{sh}), 1800(\text{s}) \text{ cm}^{-1}
\end{align*}
\]

\[
\begin{align*}
\text{31P}^{[1H]} \text{NMR(THF, 25°C)} & \delta \\
& -62.8, \text{ singlet}
\end{align*}
\]

m. Reaction with Potassium Hydride

The procedure for this reaction was similar to that described for the Na dispersion reduction. The product dianion solution was prepared in a 100 ml Schlenk flask from 0.65 g (1.0 mmole) of \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2\) and 0.090 g (42 mmole) of KH. The reaction mixture was stirred for 68 hours at room temperature with monitoring by IR spectroscopy. The infrared spectrum showed a mixture of unreacted \([\text{Fe(Cu)}_3(\mu-\text{PPh}_2)]_2\) and \(K_2[\text{Fe(Cu)}_3(\mu-\text{PPh}_2)]_2\).

\[
\begin{align*}
\text{IR(THF)} & \nu(C=O) \\
& 1930(\text{s}), 1905(\text{s}), 1845(\text{s}), 1825(\text{s}) \text{ cm}^{-1}
\end{align*}
\]

n. Attempted Reaction with NaBH₄

A 100 ml Schlenk flask equipped with a serum cap and a magnetic stirring bar was charged with 0.26 g (0.40 mmole) of \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2\) and then was evacuated and filled with nitrogen. THF (30 ml) was added by syringe. To the resulting yellow solution was added NaBH₄ (0.2 g, excess) as
a solid against a counterflow of nitrogen. The solution was then stirred at room temperature for three days. The reaction was monitored by infrared spectroscopy from time to time and no reaction was observed to occur. The yellow solution was then heated at reflux THF temperature for an additional three days and no reaction occurred. The experiment was repeated with ethanol as a solvent at reflux temperature and no reaction could be observed.

o. Attempted Reaction with [(CH$_3$)$_2$CHCH$_2$)$_2$AlH
(DIBAL-H)

The procedure for this reaction was similar to that described for the LiBEt$_3$H reduction. A solution containing 0.50 g (0.76 mmole) of [Fe(CO)$_3$(μ-PPPh$_2$)]$_2$ in 30 ml of THF was treated with 3.0 ml of DIBAL-H (1.16 M in hexane). The solution was stirred at room temperature for three days with constant monitoring by IR spectroscopy. The infrared spectrum showed only unreacted [Fe(CO)$_3$(μ-PPPh$_2$)]$_2$.

p. Attempted Reaction with NaB(CN)H$_3$

In a glove box, a 100 ml Schlenk flask equipped with a serum cap and a magnetic stirring bar was charged with 0.50 g (0.76 mmole) of [Fe(CO)$_3$(μ-PPPh$_2$)]$_2$ and 0.50 g (8.0 mmole) of NaBH$_3$CN. THF (30 ml) was added by syringe, and the reaction mixture was stirred to effect solution. The reaction mixture was stirred at room temperature for three days with monitoring by IR spectroscopy from time to
time. The infrared spectrum showed only unreacted [Fe(CO)₃(μ-PPh₂)]₂.

2. Reduction of [Fe(NO)₂(μ-PPh₂)]₂

a. Reduction of [Fe(NO)₂(μ-PPh₂)]₂ with LiBEt₃H

A 100 ml Schlenk flask equipped with serum cap and a magnetic stirring bar was charged with 0.30 g (0.50 mmole) of [Fe(NO)₂(μ-PPh₂)]₂ and then evacuated and filled with nitrogen. THF (30 ml) was added by syringe and the reaction solution was cooled to -24°C (Dry Ice/carbon tetrachloride). By syringe, 0.5 ml of 1 M LiBEt₃H in THF solution was added. The reaction solution was stirred at -24°C for 30 minutes to ensure completeness of the reduction. The reaction solution turned from the red suspension of [Fe(NO)₂(μ-PPh₂)]₂ to a dark brown solution. The dark brown solution was then filtered through a fritted filter with filter aid under nitrogen. Attempts made to obtain solid samples of the product by adding organic solvents such as hexane, benzene, and ether to the THF solution failed. Yield was estimated from P-31 NMR spectrum to be quantitative.

IR(THF) ν(N=O)            1704(m), 1660(s) cm⁻¹
ν(N=O)                      1420(w) cm⁻¹

3¹P{¹H} NMR(THF, 25°C)δ    164.6, doublet
                          43.4, doublet
                          Jₚ-ₚ = 19.6 Hz

3¹P NMR(THF, 25°C)δ        164.6, broad singlet
                          43.4, broad doublet
                          Jₚ-Η = 338 Hz
b. Reduction of $[\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2$ with Li$\text{BEt}_3\text{D}$

The procedure for this preparation was similar to that described for the Li$\text{BEt}_3\text{H}$ reduction. When 0.30 g (0.50 mmole) of $[\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2$ in 30 ml of THF was treated with 0.5 ml (one equivalent) of Li$\text{BEt}_3\text{D}$ (1 M in THF) at $-24^\circ\text{C}$ (Dry Ice/carbon tetrachloride bath), the reddish suspension gradually disappeared to form a dark brown solution. Removal of solvent under reduced pressure after stirring at $-24^\circ\text{C}$ for 30 minutes gave a dark brown oil. No attempts were made to isolate solid samples of the product. Quantitative formation was estimated from the $^3\text{P} \{^1\text{H}\}$ NMR spectral measurements.

$^3\text{P} \{^1\text{H}\} \text{NMR}\text{(THF, 25°C)} \delta$

- 164.0, doublet
- 42.2, doublet of triplets
  $J_{p-p} = 20 \text{ Hz}$
  $J_{p-D} = 50 \text{ Hz}$

$^2\text{H} \text{NMR}\text{(THF)} \delta$

- 6.0, doublet
  $J_{p-D} = 50 \text{ Hz}$


c. Reduction of $[\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2$ with Na$\text{BEt}_3\text{H}$

A 100 ml Schlenk flask equipped with serum cap and a magnetic stirring bar was charged with 0.30 g of $[\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2$ and then was evacuated and filled with nitrogen. THF (30 ml) was added by syringe and the reaction solution was cooled to $-24^\circ\text{C}$ (Dry Ice/CCl$_4$ bath). By syringe, 0.5 ml (one equivalent) of 1 M Na$\text{BEt}_3\text{H}$ in THF solution was added. The reaction solution was stirred at $-24^\circ\text{C}$ for 30 minutes to ensure the completeness of the reduction. The reaction mixture turned to dark brown. No
attempts were made to obtain solid samples of the product.

Quantitative formation of the product was estimated from P-31 NMR spectral measurements.

\[
\text{IR(THF) } \nu(N=O) \quad 1696(s), 1656(s) \text{ cm}^{-1} \\
\nu(N=O) \quad 1435(w) \text{ cm}^{-1}
\]

\[
^{31}P\{^1H\} \text{ NMR(THF, 25°C)} \delta \quad 161.4, \text{ doublet} \\
44.0, \text{ doublet} \\
J_{P-P} = 20 \text{ Hz}
\]

d. Reduction of \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\) with KBEt$_3$H

The procedure for this reaction was similar to that described for the LiBEt$_3$H reduction. A reddish slurry containing 0.30 g of \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\) (0.50 mmole) in 30 ml of THF was treated with 0.5 ml of KBEt$_3$H (1 M in THF solution). The reaction mixture was stirred at -24°C (Dry Ice/CCl$_4$ bath) for 30 minutes and dark brown solution was formed. No attempts were made to obtain solid samples of the product. The yield was estimated to be quantitative from P-31 NMR spectral measurements.

\[
\text{IR(THF) } \nu(N=O) \quad 1696(m), 1660(s) \text{ cm}^{-1} \\
\nu(N=O) \quad 1435(w) \text{ cm}^{-1}
\]

\[
^{31}P\{^1H\} \text{ NMR(THF, 25°C)} \delta \quad 161.5, \text{ doublet} \\
43.3, \text{ doublet} \\
J_{P-P} = 20 \text{ Hz}
\]

e. Reduction of \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\) with Li(sec-Bu)$_3$BH

A 100 ml Schlenk flask equipped with serum cap and a magnetic stirring bar was charged with 0.30 g (0.50 mmole) of \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\) and then was evacuated and filled with nitrogen. THF (30 ml) was added by syringe and the reaction
solution was cooled to 0°C (ice-water bath). By syringe, 0.50 ml of 1 M Li(sec-Bu)_3BH in THF (0.50 mmole, one equivalent) was added. THF reaction solution turned from the red suspension of [Fe(NO)_2(μ-PPPh_2)]_2 to a dark brown solution. The reaction solution was stirred at 0°C for 30 minutes to ensure the completeness of the reduction. The dark brown solution was then filtered through a fritted filter with filter aid under nitrogen.

\[ \text{IR(THF) } \nu(\text{N=U}) \quad 1673(\text{s, broad}) \text{ cm}^{-1} \]

\[ ^{31}P(\text{H}) \text{ NMR(THF, 25°C)} \delta \quad \text{unable to observe signal after long data collecting time.} \]

f. Reduction of [Fe(NO)_2(μ-PPPh_2)]_2 with Two Equivalents of Reducing Agents, LiBEt_3H, NaBEt_3H and KBEt_3H

The procedures for these reduction reactions were analogous to the procedures described in the above sections except that two equivalents of reducing agents were employed instead of one equivalent. The results of these reductions are identical to those obtained from one equivalent reduction reactions.

g. Reduction of [Fe(NO)_2(μ-PPPh_2)]_2 with LiAlH_4

A 100 ml Schlenk flask equipped with serum cap and a magnetic stirring bar was charged with 0.30 g (0.50 mmole) of [Fe(NO)_2(μ-PPPh_2)]_2 and then was evacuated and filled with nitrogen. THF (30 ml) was added by syringe. To that reddish slurry was added 1.0 ml of LiAlH_4 solution (1 M in THF)
by syringe at room temperature. The reddish slurry gradually disappeared and turned to a dark brown solution over a five minute period. Attempts to obtain a solid sample by adding hexane, benzene, ether or ethanol to the THF solution failed. Quantitative formation of the product was estimated from P-31 NMR spectral measurements. The reduction reaction was also repeated at -78°C. The reaction solution turned dark brown after stirring at -78°C for 30 minutes. The P-31 NMR spectrum of the solution is identical with that for the room temperature reaction.

\[ \text{IR(THF)} \nu(N=O) \quad 1673(s) \text{ cm}^{-1} \]

\[ ^{31}P(\text{H}) \text{ NMR(THF, 25°C)} \delta \quad -34.6, \text{ singlet} \]

**h. Reduction of \([\text{Fe(NO)}_2(\mu-PPh_2)]_2\) with Na Dispersion**

A 100 ml Schlenk flask fitted with serum cap and a magnetic stirring bar was charged with 0.30 g (0.50 mmole) of \([\text{Fe(NO)}_2(\mu-PPh_2)]_2\) and 0.030 g (1.3 mmole) of sodium dispersion inside a dry box. THF (30 ml) was added by syringe and the solution was stirred at room temperature for 5 hours. The reddish slurry gradually changed to a dark brown solution. Excess sodium dispersion was collected on a fritted filter under nitrogen. The filtrate was concentrated to about 5 ml under reduced pressure. No attempts were made to obtain a solid sample of the product.

\[ \text{IR(THF)} \nu(N=O) \quad 1672(s) \text{ cm}^{-1} \]

\[ ^{31}P(\text{H}) \text{ NMR(THF, 25°C)} \delta \quad -32.9, \text{ singlet} \]
i. Reaction of \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\) with \(\text{KB(sec-Bu)}_3\text{H}\)

The procedure for this reaction was similar to that described for the \(\text{LiBEt}_3\text{H}\) reduction. To a slurry of \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\) (0.30 g, 0.50 mmole) in 30 ml of THF was added 1.0 ml of \(\text{KB(sec-Bu)}_3\text{H}\) (1 M in THF), which caused a color change to deep brown. The solution was filtered through a fritted filter. The volume of the solution was decreased to about 5 ml under reduced pressure. The \(^{31}\text{P}\) NMR spectra of the concentrated brown solution showed no signal after long data accumulation time.

\[ ^{31}\text{P}\{^1\text{H}\} \text{ NMR(THF, 25°C)} \delta \]

No signal can be observed after long data collection time.

j. Reaction of \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\) with Vitride

The procedure for this reaction was similar to that described for the \(\text{LiBEt}_3\text{H}\) reduction. To a slurry of \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\) (0.30 g, 0.50 mmole) in 30 ml of THF was added 0.14 ml of Vitride (70% in toluene) which caused a color change to deep brown over a 30 minute period. The solution was filtered through a fritted filter. The volume of the solution was decreased to about 5 ml under reduced pressure. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra of the solution showed only a brown solution showed no signal after long data accumulation time.

\[ \text{IR(THF) } \nu(\text{N=O}) \quad 1670(\text{s}) \text{ cm}^{-1} \]

\[ ^{31}\text{P}\{^1\text{H}\} \text{ NMR(THF, 25°C)} \delta \quad -32.9, \text{ broad singlet} \]
3. Study of the Conversion of the Carbonyl and Nitrosyl Monoanions to the Dianions by P-31 NMR Spectroscopy

The carbonyl and nitrosyl monoanions \([(CO)_3Fe(\mu-PPH_2)(\mu-CO)Fe(CO)_2(PPh_2H)]^-\) and \([(NO)_2Fe(\mu-NO)(\mu-PPH_2)Fe(NO)(PPh_2H)]^-\) with different counterions (Li^+, Na^+, K^+) were prepared by the method described in the above section by use of one or two equivalents of the reducing agent. The monoanion solutions were heated at 65°C for 2 minutes. The P-31 NMR spectra of the monoanion solution before and after heating were recorded and compared. The results will be discussed in detail in a later section (section III-C and section III-e).

G. Reactions of the Diphenylphosphine-Substituted Monoanions \([(CO)_3Fe(\mu-PPH_2)(\mu-CO)Fe(CO)_2(PPh_2H)]^-\) and \([(NO)_2Fe(\mu-NO)(\mu-PPH_2)Fe(NO)(PPh_2H)]^-\)

1. Reactions of \([(CO)_3Fe(\mu-PPH_2)(\mu-CO)Fe(CO)_2(PPh_2H)]^-\)

a. Reaction with Methyl Iodide

A solution of Li\([(CO)_3Fe(\mu-PPH_2)(\mu-CO)Fe(CO)_2(PPh_2H)]\) was prepared from 3.0 g (4.6 mmole) of \([Fe(CO)_3(\mu-PPH_2)]_2\) and two equivalents (9.0 ml) of LiBEt_3H solution (1 M in THF) in 30 ml of THF at 0°C. The procedure for this monoanion preparation was identical to that described for the LiBEt_3H reduction of \([Fe(CO)_3(\mu-PPH_2)]_2\). To this solution was added 2 ml of MeI (tenfold excess) at -78°C. After the mixture had been stirred for 3 hours at -78°C, it was gradually warmed to room temperature while being stirred an
additional 3 hours. Solvent was removed from the dark red solution on a rotary evaporator, leaving a dark red oil which was then dissolved in a minimum amount of CH₂Cl₂. Alumina was added to the CH₂Cl₂ solution and the solvent was rotary evaporated. The residue was added on top of a grade III alumina-petroleum ether column. Elution with petroleum ether moved a yellow band down the column which yielded 0.96 g of recovered [Fe(CO)₃(μ-PPh₂)]₂ (32%). The yellow material was identified by infrared spectroscopy. When the eluting solvent was changed to 3% ether/petroleum ether, two orange bands were eluted down the column. After collection of the first orange band and removal of solvent by rotary evaporation, a reddish brown material was collected and identified as [(Cu)₃Fe(μ-PPh₂)(μ-C(Me)U)Fe(CO)₂(PPh₂Me)]. Yield = 0.83 g (26%).

Melting Point

Analytical Data

<table>
<thead>
<tr>
<th>% of carbon</th>
<th>calc.</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
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<td>56.00</td>
</tr>
<tr>
<td>56.85</td>
<td>3.87</td>
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</table>

¹H NMR (CDCl₃)δ

IR (Cyclohexane)

| ν(C≡U) | 2039(m), 1981(s), 1951(s), 1934(m), 1928(m), cm⁻¹ |
|        | 1483(w) cm⁻¹ |

¹³C{¹H} NMR (d₆-Acetone), 25°C)δ

299.6, doublet, Jp-C=21 Hz
219.5-214.8, multiplet
140.9-128.3, multiplet
47.8, singlet
15.3, doublet, J<sub>P-C</sub> = 55 Hz

<sup>31</sup>P{<sup>1</sup>H} NMR (THF, 25°C) δ
174.1 ppm, doublet
39.7 ppm, doublet
J<sub>P-P</sub> = 55 Hz

Mass Spectrum (tetraglyme, FAB)
Calc. 680 for M⁺
m/e Ion
680 Parent ion, M⁺
624 M⁺-2CU
540 M⁺-5CU

When 5% ether/petroleum ether mixed solution was used for elution, the second orange band passed down the column. Evaporation of the solvent from the collected fraction yielded 0.14 g (4%) of an orange solid which was identified as [(CO)₃Fe(μ-PPh₂)₂Fe(CO)₂(PPh₂Me)], one of the carbonyl ligands of the neutral dimer [Fe(CO)₃(μ-PPh₂)]₂ having been substituted by methyldiphenylphosphine. The compound was recrystallized from CH₂Cl₂-hexane at 5°C.

Melting Point 165°C decomposed

Analytical Data Calc. for Fe₂P₃O₃C₄₂H₃₃
% of carbon
61.38 61.37
calc. Found
% of hydrogen 4.05 4.15

<sup>1</sup>H NMR (CDCl₃) δ
1.6, doublet, 3 H,
J<sub>P-H</sub> = 9 Hz
7.2, multiplet, 30 H
IR (Cyclohexane)  
$\nu (C=O)$  
2038(s), 1980(s), 1972(sh),  
1953(s), 1918(w), cm$^{-1}$

$^{13}\text{C}[^1\text{H}]$ NMR  
($d_6$-Acetone), 25°C$\delta$  
215.1, multiplet  
127.5-133.9, multiplet  
17.2, doublet,  
$\text{J}_{p-C} = 26 \text{ Hz}$

$^{31}\text{P}[^1\text{H}]$ NMR(THF, 25°C$\delta$)  
138.7 ppm, doublet  
46.3 ppm, triplet  
$\text{J}_{p-p} = 10 \text{ Hz}$

Mass Spectrum  
(tetraglyme, FAB)  
Calc. 822 for $M^+$

\begin{center}
\begin{tabular}{c c c}
\hline
m/e & Ion & \text{Calc.} \text{ of} $M^+$
\hline
822 & Parent ion, $M^+$ & -
794 & $M^+-\text{CO}$ & -
766 & $M^+-2\text{CO}$ & -
738 & $M^+-3\text{CO}$ & -
710 & $M^+-4\text{CO}$ & -
682 & $M^+-5\text{CO}$ & -
\hline
\end{tabular}
\end{center}

Continued elution with 10% ether/petroleum ether resulted in a faint red band passing down the column. Only a trace amount of red powder was obtained after the solvent was removed. No further characterizations were performed.

Identical experimental procedures as described above were used to prepare a solution of Li[$(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)$-$(\mu-\text{CO})\text{Fe(CO)}_2(\text{PPh}_2\text{H})]$ from 3.0 g (4.6 mmole) of [Fe(CO)$_3$-$(\mu-\text{PPh}_2)$]$_2$ and one equivalent (4.5 ml) of Li$\text{BEt}_3$H solution. To the resulting solution was added 2 ml of MeI (tenfold excess) at -78°C. The work-up procedure of the reaction mixture is analogous to that described above. The reaction yielded 1.4 g of recovered [Fe(CO)$_3$(\mu-\text{PPh}_2)]$_2$ (47%) and 0.38 g (12%) of [[(\text{Cu})$_3$\text{Fe}(\mu-\text{PPh}_2))(\mu-\text{C(Me})\text{O})\text{Fe(CO)}_2(\text{PPh}_2\text{Me})]]

A general procedure for the separation of reaction mixture by column chromatography is illustrated as follows:
after the solvent of reaction solution was removed by rotary evaporation, a minimum amount of THF or CH$_2$Cl$_2$ was added to redissolve the residue. Just enough grade III alumina was added to cover the solution. The solvent was removed by rotary evaporation again. The dry alumina was then transferred to the top of a grade III alumina column packed with petroleum ether. Throughout this research, three different size columns were most frequently used: a 2 x 20 cm column was used for reactions with less than 1.0 g of [Fe(CO)$_3$(μ-PPh$_2$)$_2$]$_2$ as starting material. A 2.5 x 25 cm column was used for reactions starting with 2.0 g of [Fe(CO)$_3$(μ-PPh$_2$)$_2$]$_2$. A 3 x 30 cm column was used for reactions with more than 2.0 g of [Fe(CO)$_3$(μ-PPh$_2$)$_2$]$_2$ as starting material.

b. Reaction with Ethyl Iodide

A solution of Li[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$H)]$_2$ was prepared from 1.00 g (1.54 mmole) of [Fe(CO)$_3$(μ-PPh$_2$)$_2$]$_2$ and two equivalents (3.0 ml) of LiBEt$_3$H solution (1 M in THF) in 30 ml of THF at 0°C (ice-water bath). The dark red monoanion solution was cooled to -78°C (Dry Ice/isopropyl alcohol) and 1.0 ml (tenfold excess) of EtI was added by syringe. After the reaction mixture had been stirred at -78°C for three hours, it was gradually warmed to room temperature while being stirred an additional three hours. Solvent was removed from the dark red solution on a rotary evaporator which was then dissolved in a minimum amount of CH$_2$Cl$_2$. Alumina was added to the CH$_2$Cl$_2$ solution and the
solvent was again rotary evaporated. The residue was added on top of a grade III alumina-petroleum ether column. Elution with petroleum ether resulted in the appearance of several bands. The major, yellow band was eluted down the column with petroleum ether, collected, and the solvent was removed by rotary evaporation. The yellow compound was identified as \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2\) \((0.46 \text{ g, 46\%})\) by infrared spectroscopy. When 3\% ether/petroleum ether mixed solution was used for elution, an orange band passed down the column. Evaporation of the solvent from the collected fraction yielded a dark orange red oil. Attempts to obtain a solid sample by addition of hexane or ether to the CH\(_2\)Cl\(_2\) solution of oil failed to initiate crystallization. The compound was identified as \([(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C(\text{Et})U})-\text{Fe(CO)}_2(\text{PPh}_2\text{Et})]\). Yield = 0.06 g (5\%).

\(^1\text{H NMR (CDCl}_3\)\(\delta\) 7.3, multiplet, 20 H
2.3, multiplet, 4 H
1.1, multiplet, 3 H
0.1, triplet, 3 H,
\(J = 7.0\) Hz

IR (Cyclohexane)
\(\nu(\text{C=O})\) 2023(m), 1970(s), 1942(m),
1924(m) cm\(^{-1}\)
1482(w) cm\(^{-1}\)

\(^{13}\text{C}\{^1\text{H}\} \text{NMR(CDCl}_3\)\(\delta\) 304.9, doublet, \(J_{P-C} = 17\) Hz
214.1, multiplet
127.5-133.9, multiplet
73.7, singlet
54.7, singlet
24.6, doublet, \(J_{P-C} = 23\) Hz
8.1, doublet, \(J_{P-C} = 13\) Hz

\(^{31}\text{P}\{^1\text{H}\} \text{NMR(THF, 25°C)\(\delta\) 171.6, doublet
53, doublet
\(J_{P-P} = 49\) Hz
A second orange band was eluted down the column by using 10% ether/petroleum ether mixed solution. The solvent was removed by rotary evaporation, leaving an orange solid which was shown to be a mixture of two compounds by P-31 NMR spectroscopy. The orange solid was dissolved in 10% ether/hexane and crystallized by a slow evaporation process. One compound crystallized from the solution as a red orange solid with irregular crystal shape while the other compound crystallized in yellow-orange needles. The red-orange compound was identified as \([(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe(CO)}_2(\text{PPh}_2\text{Et})]\) (0.07 g, 5%).

Melting Point 183°C

Analytical Data

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<th>% of carbon</th>
<th>calc.</th>
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<tbody>
<tr>
<td>% of hydrogen</td>
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<td>59.62</td>
</tr>
<tr>
<td>6.22</td>
<td>4.68</td>
<td></td>
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</tbody>
</table>

$^1$H NMR (CDCl$_3$)δ

- 7.1, multiplet, 20 H
- 2.0, multiplet, 2 H
- 1.2, multiplet, 3H

IR(Cyclohexane)

\(\nu(\text{C=O})\)

- 2021(s), 1974(s), 1960(s), 1951(s), 1916(sh), 1905(m) cm$^{-1}$

$^{31}$P[1H] NMR(THF, 25°C)δ

- 138.2, doublet
- 58.9, doublet

$J_{P-P} = 10$ Hz
The orange needles were later identified as \([(\text{CO})_3\text{Fe}-(\mu\text{-PPh}_2)_2\text{Fe(CO)}_2\text{(PPh}_2\text{H})]\). The characterization of this diphenylphosphine-substituted compound will be described in Section III-G-1-d.

c. Reaction with Allyl Iodide

A THF solution of Li[\((\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)\text{(\mu}\text{-Cu})\text{Fe(CO)}_2\text{-(PPh}_2\text{H})]\) was prepared from 2.0 g (3.1 mmole) of \([\text{Fe(CO)}_3\text{-(\mu}\text{-PPh}_2)]_2\) and two equivalents of LiEt\(_3\) solution (1 M in THF) at 0°C (ice water). The monoanion solution was cooled to -78°C and 0.6 ml of allyl iodide (6.6 mmole) was added. The solution was stirred at -78°C for three hours and was warmed to room temperature gradually while being stirred an additional three hours. Solvent was removed from the dark red solution on a rotary evaporator, leaving a dark red oil which was then dissolved in a minimum amount of CH\(_2\)Cl\(_2\). Alumina was added to the CH\(_2\)Cl\(_2\) solution and the solvent was rotary evaporated. The residue was added on top of a grade III alumina-petroleum ether column. Elution with petroleum ether resulted in several bands. A yellow band was eluted down the column first by petroleum ether. Removal of the solvent yielded the yellow neutral dimer \([\text{Fe(CO)}_3(\mu\text{-PPh}_2)]_2\) (0.62 g, 31%) which was identified by infrared spectro-
-64-
scopy. When the eluting solution was changed to 3% ether/petroleum ether, a long red band started to move down the column. When the solvent was switched to 5% ether/petroleum ether, the red band was collected. The solvent was removed by rotary evaporation to give a purple red solid. The compound was identified as the \( \eta^3 \)-allyl complex \([(\text{CO})_2(\eta^3-\text{C}_3\text{H}_5)-\text{Fe}(\mu-\text{PPh}_2)\text{Fe(CO)}_3(\text{PPh}_2\text{C}_3\text{H}_5)] \). Yield = 0.55 g (26%).

Melting Point 149-150°C

Analytical Data

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<th>Calc. for ( \text{C}<em>{36}\text{H}</em>{30}\text{Fe}_2\text{O}_6\text{P}_2 )</th>
<th>Found</th>
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<tr>
<td>% of carbon</td>
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<td>59.22</td>
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<tr>
<td>% of hydrogen</td>
<td>4.13</td>
<td>4.20</td>
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</table>

\(^1\text{H} \text{NMR (CDCl}_3\)\( \delta \)

- 7.4, multiplet, 20 H
- 5.5, multiplet, 1 H
- 5.0, multiplet, 2 H
- 4.3, heptet, 1 H, \( J = 7 \) Hz
- 3.3, doublet of doublets,
  - 2 H, \( J = 7 \) Hz, \( J = 10 \) Hz
- 2.4, doublet, 2 H,
  - \( J = 10 \) Hz
- 2.0, doublet, 2 H,
  - \( J = 13 \) Hz

IR(Cyclohexane)

\( \nu(\text{C}=\text{O}) \)

- 2018(m), 1972(s), 1960(m),
- 1950(sh), 1920(w), cm\(^{-1}\)

\(^{13}\text{C}\{^1\text{H}\} \text{NMR (d}_6\text{-Acetone)}\( \delta \) 221.9-215.7, multiplet

- 143.7, doublet,
  - \( J_{\text{P}-\text{C}} = 29 \) Hz
- 128.2-138.9, multiplet
- 121.0, doublet,
  - \( J_{\text{P}-\text{C}} = 11 \) Hz
- 92.8, singlet
- 49.9, singlet
- 38.6, doublet, \( J_{\text{P}-\text{C}} = 27 \) Hz

\(^{31}\text{P}\{^1\text{H}\} \text{NMR(THF, 250°C)}\( \delta \)

- 180.54, doublet
- 53.95, doublet
  - \( J_{\text{P}-\text{P}} = 16 \) Hz
Mass Spectrum
(tetraglyme, FAB)

Calc. 704 for M+
m/e = 704 (100%) for parent ion. No fragments observed.

The tail portion of the long red band was collected separately. It was found to contain a trace amount of allyldiphenylphosphine-substituted complex \([(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2^{-}\text{Fe(\text{CO})}_2(\text{PPh}_2\text{C}_3\text{H}_5})\]}. The preparation and characterization of this allyldiphenylphosphine complex will be described in detail in Section III-G-1-d.

\textbf{d. Reaction with Benzyl Iodide}

A solution of Li\([(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{Cu})\text{Fe(\text{Cu})}_2(\text{PPh}_2\text{H})]\] was prepared from 2.0 g (3.1 mmole) of \([\text{Fe(\text{Cu})}_3(\mu-\text{PPh}_2)]_2\] and two equivalents (6.2 ml) of Li\text{B}E\text{t}_3\text{H} (1 M in THF) in 30 ml of THF at 0°C. To the dark red solution was added 0.8 ml of benzyl iodide (ICH$_2$Ph). The reaction mixture was stirred for two days at room temperature with no reaction occurring. The solution was then heated at reflux while being stirred an additional 24 hours. The reaction was monitored by infrared spectroscopy. The solvent was removed by rotary evaporation to leave a deep red oil. A minimum amount of CH$_2$Cl$_2$ was added to dissolve the oil. Alumina was added to the CH$_2$Cl$_2$ solution and the solvent was rotary evaporated. The residue was added on top of a grade III alumina-petroleum ether column. Elution with petroleum ether moved a yellow band down the column, which yielded 0.74 g (37%) of yellow \([\text{Fe(\text{Cu})}_3(\mu-\text{PPh}_2)]_2\), identified by infrared spectroscopy.
Continued elution with 3% ether/petroleum ether mixed solution moved an orange band down the column. Evaporation of the solvent from the collected fraction yielded an orange-yellow solid which was identified as \( [(CO)_3Fe(\mu-PPh_2)_2Fe(CO)_2(PPh_2H)] \). The compound can be recrystallized by slow diffusion of hexane into a \( CH_2Cl_2 \) solution. Yield = 0.26 g (10%).

Melting Point 190°C

Analytical Data

| % of carbon | calc. 60.92 | found 60.59 |
| % of hydrogen | 3.87 | 4.14 |

\(^1\text{H} \text{NMR (CDCl}_3\text{)}\delta 7.2, \text{ multiplet 40 H}
5.4, \text{ singlet, 1/2 H}
\text{ (half of the doublet, the other half under phenyl peaks)}

IR(Cyclohexane)

\( \nu(C=O) \)

\( 2024(s), 1979(s), 1967(s), 1951(s), 1928(m), \text{ cm}^{-1} \)

\(^{31}\text{P}\{^1\text{H}\} \text{NMR(THF, 25°C)}\delta 143.4, \text{ doublet}
49.8, \text{ triplet}
\( J_{p-H} = 4 \text{ Hz} \)

\(^{31}\text{P} \text{NMR(THF, 25°C)}\delta 143.4, \text{ broad singlet}
49.8, \text{ broad doublet}
\( J_{p-H} = 354 \text{ Hz} \)

Mass Spectrum (70 ev, EI)

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<th>m/e Intensity</th>
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<td>752</td>
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<td>796</td>
<td>11</td>
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<tr>
<td>668</td>
<td>100%</td>
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Finally, elution with 5% ether/petroleum ether solution moved a red-orange band down the column. Rotary evaporation of the
solvent afforded an orange red solid which was identified as

\[ ([\text{CO}]_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe(CO)}_2(\text{PPh}_2\text{C}_3\text{H}_5)) \]. Yield = 0.18 g (6%).

**Melting Point**

- 205-206°C (decomposed)

**Analytical Data**

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<td>63.74</td>
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<td>4.15</td>
<td>4.24</td>
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</table>

**\(_1^H\) NMR (CDCl\(_3\))\(\delta\)**

- 7.2, multiplet, 35 H
- 3.6, doublet, 2 H
- \(J_{P-H} = 3\) Hz

**IR (Cyclohexane)**

- \(\nu(\text{C}≡\text{O})\)
- 2026(s), 1981(s), 1960(s), 1953(s), 1932(w), \(\text{cm}^{-1}\)

**\(^{13}C\{^1H\}\) NMR (CDCl\(_3\))\(\delta\)**

- 214.2-219.5 multiplet
- 126.3-135.9, multiplet
- 38.8, doublet
- \(J_{P-C} = 15\) Hz

**\(^{31}P\{^1H\}\) NMR (THF, 25°C)\(\delta\)**

- 138.3, doublet
- 63.9, triplet
- \(J_{P-P} = 9\) Hz

The complex \([([\text{CO}]_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe(CO)}_2(\text{PPh}_2\text{C}_3\text{H}_5))\) was used to prepare \([([\text{CO}]_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe(CO)}_2(\text{PPh}_2\text{C}_3\text{H}_5))\) in good yield as described below.

### i. Preparation of \([([\text{CO}]_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe(CO)}_2(\text{PPh}_2\text{C}_3\text{H}_5))\)

An orange red solution of \([([\text{CO}]_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe(CO)}_2(\text{PPh}_2\text{C}_3\text{H}_5))\) (0.30 g, 0.37 mmole) in 30 ml of THF was treated with 0.23 ml of n-BuLi (0.37 mmole, 1.64 M in hexane solution). The solution immediately turned deep red as \(\text{Li}([([\text{CO}]_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe(CO)}_2(\text{PPh}_2)))\) was formed.

To that deep red solution, 0.20 ml (2.2 mmole) of
allyl iodide was added. It was then stirred at room temperature for one hour as the color changed to light red. Solvent was removed on a rotary evaporator, leaving a dark red oil which was chromatographed on a grade III alumina-petroleum ether column. Elution of the column with 3% ether/petroleum ether mixed solution resulted in an orange-red band. The band was collected and the solvent was evaporated from it to yield an orange-red solid which was identified as \([(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe}(	ext{CO})_2\text{PPh}_2\text{C}_3\text{H}_5)]\).

Yield = 0.26 g (84%).

Melting Point 175°C (decomposed)

Analytical Data

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<td>4.16</td>
<td>4.22</td>
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\(^1\text{H} \text{NMR (CDCl}_3\text{)}\delta\)

- 7.4, multiplet, 30 H
- 5.7, multiplet, 1 H
- 5.0, doublet, 1 H
- \(J_{	ext{H-H}} = 10 \text{ Hz}\)
- 4.8, doublet, 1 H,
  \(J_{	ext{H-H}} = 15 \text{ Hz}\)
- 2.7, triplet, 2 H, \(J = 8 \text{ Hz}\)

\(\text{IR(THF)} \nu(\text{C=O})\)

- 2020(s), 1972(s), 1958(m), 1944(m), 1915(w), cm\(^{-1}\)

\(\text{\text{^13C}[^1\text{H}]} \text{NMR(CDCl}_3\text{)}\delta\)

- 215.0, multiplet,
- 127.2-135.3, multiplet
- 119.3, doublet,
  \(J_{\text{P-C}} = 10 \text{ Hz}\)
- 38.5, doublet, \(J_{\text{P-C}} = 22 \text{ Hz}\)

\(\text{\text{^31P}[^1\text{H}]} \text{NMR(THF, 25°C)}\delta\)

- 138.3, doublet
- 54.9, triplet
  \(J_{\text{P-P}} = 9 \text{ Hz}\)

Mass Spectrum
(tetraglyme, FAH)

Calc. 848 for \(\text{M}^+\)
m/e Intensity  Ion
848     3  Parent ion, M⁺
820     4  M⁺-CO
792     67  M⁺-2CO
764       8  M⁺-3CO
736     36  M⁺-4CO
708     81  M⁺-5CO
622     77  M⁺-PPh₂CH₂CHCH₂
510   100  M⁺-PPh₂CH₂CHCH₂-4CO

e. Attempted Reaction with 1-Iodopropane and 2-Iodopropane

The experimental procedure for these two reaction was similar to that described for the methylation reaction. A THF solution of the carbonyl monoanion was prepared from 3.0 g (4.6 mmole) of [Fe(CO)₃(μ-PPh₂)]₂ by using two equivalents of LiBEt₃H (9.2 ml). To this solution was added 0.45 ml of n-PrI at -78°C. After the mixture had been stirred for 3 hours at -78°C, it was gradually warmed to room temperature. Infrared monitoring showed that no reaction had occurred after overnight stirring. The reaction solution was then heated at 40°C and stirred an additional five hours. Only unreacted Li[(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(CO)₂(PPh₂H)] could be observed in the infrared spectrum.

The alkylation with i-PrI was performed in a similar fashion. No reaction was observed after the mixture had been heated at 40°C for ten hours.

f. Attempted Reaction with CH₂I₂, I(CH₂)₂I and I(CH₂)₃I

A solution of Li[(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(CO)₂(PPh₂H)] was prepared by the addition of 3.0 ml of 1 M solution of
LiBEt$_3$H (two equivalents) to a solution of 1.5 mmole of $[\text{Fe(CO)₃(µ-PPh₂)}]_₂$ (1.0 g) in 60 ml of THF at room temperature. The solution was cooled to -78°C and 0.3 ml of CH$_2$I$_2$ was added. The reaction mixture was stirred at -78°C for two hours and was then gradually warmed to room temperature while being stirred an additional two hours. Gas evolution was observed. Solvent was removed by rotary evaporation leaving an orange oil which was chromatographed on a grade III alumina-petroleum ether column. Only a yellow band was eluted down the column; it was collected and evaporated to give a yellow solid. The compound was identified as $[\text{Fe(CO)₃(µ-PPh₂)}]_₂$ from its infrared and P-31 NMR spectra.

The procedure for the reactions with I(CH$_₂$)$_₂$I and I(CH$_₂$)$_₃$I was similar to that described for the IOH$_2$I reaction. After the addition of the diiodoalkane, the monoanion decomposed back to the neutral dimer $[\text{Fe(CO)}₃$-(µ-PPh₂)]$_₂$.

### g. Reaction with CF$_3$COOH

A solution of Li[(CO)$_₃$Fe(µ-PPh$_₂$)(µ-CO)Fe(CO)$_₂$(PPh$_₂$H)] was prepared by addition of two equivalents (0.8 ml) of a 1 M solution of LiBEt$_3$H to a solution of 0.26 g (0.40 mmole) of $[\text{Fe(CO)}₃(µ-PPh₂)]_₂$ in 1.0 ml of THF at room temperature. To this solution was added 0.10 ml (1.3 mmole) of CF$_3$COOH. Immediately, the reaction solution turned from dark red to orange red. After stirring at room temperature for 10 minutes, solvent was removed under reduced pressure, leaving an orange oil. The residue was extracted with 10 ml of
benzene, and evaporation to dryness afforded an air-sensitive orange solid. Attempts to further purify this material by recrystallization from benzene failed. The complex was formulated as \[\{(\text{Cu})_3 \text{Fe}(\mu-P\text{Ph}_2)\text{Fe}(\text{Cu})_3(\text{P}_2\text{Ph}_2\text{H}_2)\}\].

**1H NMR (C\text{D}_6)δ**
-9.45, doublet of doublet

\[2J_{\text{P}(1)-\text{H}(1)} = 51 \text{ Hz}\]

\[3J_{\text{P}(2)-\text{H}(1)} = 4.0 \text{ Hz}\]

**IR(THF) \nu(C=O) 2057(m), 2014(s), 1995(s), 1955(sh) cm\(^{-1}\)**

**31P NMR(THF, 50°C)δ**
172.3, doublet
37.4, doublet
\[J_{\text{P}(1)-\text{P}(2)} = 17 \text{ Hz}\]

**1J_{\text{P}(1)-\text{P}(2)} = 17 \text{ Hz}\**

2\[J_{\text{P}(1)-\text{H}(1)} = 50 \text{ Hz}\]
37.4, broad doublet
1\[J_{\text{P}(2)-\text{H}(2)} = 380 \text{ Hz}\]

**h. Reaction with \text{CF}_3\text{COOD}\**

The corresponding deuteriated complex was prepared by the exact procedure described above except that Li\text{BET}_3D and \text{CF}_3\text{COOD} were used. The complex, Li\[\{(\text{Cu})_3\text{Fe}(\mu-P\text{Ph}_2)(\mu-\text{Cu})-\text{Fe}(\text{Cu})_2(\text{PPh}_2\text{D})\}\], was prepared by the addition of 0.4 ml (one equivalent) of a 1 M solution of Li\text{BET}_3D to a solution of 0.26 g (0.4 mmole) of \[\text{Fe}(\text{Cu})_3(\mu-P\text{Ph}_2)\] in 1.0 ml of THF at room temperature. To this solution was added 0.1 ml (1.3 mmole) of \text{CF}_3\text{COOD}. Immediately, the dark red solution turned orange red. No attempts were made to obtain solid samples of
this air-sensitive product. The complex was identified as

\[ \left( \text{CO}\right)_3\text{D}_1\text{Fe}(\mu-\text{PPh}_2)\text{Fe(CO)}_3(\mu_2\text{PPh}_2\text{D}_2) \] .

\[^{31}\text{P}\{^1\text{H}\} \text{ NMR(THF, 25°C)} \delta 172.9, \text{ quintet (possibly a doublet of triplets with two peaks overlapping each other)} \]

\[ J_{P(1)-P(2)} = 18 \text{ Hz} \]

\[ 2J_{P(1)-D(1)} = 8 \text{ Hz} \]

\[ 38.5, \text{ doublet of triplets} \]

\[ J_{P(1)-P(2)} = 18 \text{ Hz} \]

\[ J_{P(2)-D(2)} = 58.5 \text{ Hz} \]

i. Reaction with \((\text{Ph}_3\text{P})_2\text{N}^+\text{Cl}^-\)

A solution of \(\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(CO)}_2(\text{PPh}_2\text{H})]\)
was prepared by the addition of 2.0 ml (one equivalent) of a 1 M solution of \(\text{LiBEt}_3\text{H}\) to a solution of 1.3 g (2.0 mmole) of \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2\) in 30 ml of THF. To this solution was added 1.2 g (2.0 mmole) of \([(\text{Ph}_3\text{P})_2\text{N}^+\text{Cl}^-]\) as a solid under a flow of nitrogen. The solution immediately changed color
from deep orange red to dark red. It was then stirred at room temperature for three hours. The volume of the solution
was reduced to about 5 ml under reduced pressure. Slow
addition of ethanol (30 ml) to the concentrated solution
afforded purple solid. The purple solid slurry was then
transferred via a stainless steel needle to a Schlenk filter.
It was collected on a frit and washed with 10 ml of ethanol followed by 10 ml of ether four times. The complex
was formulated as \((\text{Ph}_3\text{P})_2\text{N}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(CO)}_2(\text{PPh}_2\text{H})]\). The yield was 2.1 g (89%).
$^{1}H$ NMR (d$_{6}$-acetone)$\delta$
- 7.6, multiplet, 50 H
- 4.2, doublet, $1/2$ H
(the other resonance with $1/2$ H intensity is probably under phenyl resonance)
$^{3}J_{P-H} = 6$ Hz

IR(THF) $v$(C=O) 1990(s), 1938(s)
- 1900U(bs) cm$^{-1}$
- 1710U(m) cm$^{-1}$

$^{31}P$[${^1}H$] NMR(THF, 25°C)$\delta$
- 129.8, broad singlet
- 56.3, broad singlet
- 20.7, singlet

$^{31}P$ NMR(THF, 25°C)
- 129.8, broad singlet
- 56.3, broad doublet
$J_{P-H} = 316$ Hz
- 20.7, singlet

Analytical Data
Calc. for C$_{66}$H$_{51}$Fe$_{2}$O$_{6}$P$_{4}$N

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<td>4.32</td>
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j. Reaction with n-BuLi (Preparation of Li$_2$[(CO)$_3$Fe($\mu$-PPh$_2$)]$_2$)

A solution of Li[(CO)$_3$Fe($\mu$-PPh$_2$)]$_2$ in 1.0 ml of THF was prepared by the addition of 0.4 ml (one equivalent) of a 1 M solution of LiBEt$_3$H to a solution of 0.26 g (0.40 mmole) of [Fe(CO)$_3$(μ-PPh$_2$)$_2$]$_2$ in 1.0 ml of THF in a 10 mm NMR tube inside a Schlenk tube at room temperature. The dark orange red solution was cooled to -78°C and 0.25 ml (one equivalent) of a 1.64 M solution of n-BuLi was added dropwise at that temperature (the addition of n-BuLi must be slow). The reaction solution immediately changed color to a dark purple red. The complex was only stable below -40°C. At higher temperature, it converted to Li$_2$[Fe(CO)$_3$(μ-PPh$_2$)$_2$]$_2$. The
complex was formulated as Li₂[(Cu)₃Fe(μ-PPh₂)(μ-Cu)-Fe(CO)₂(PPh₂)] by its P-31 NMR and C-13 NMR spectra. No attempts were made to obtain solid samples of the product.

\[ ^{13}C\{^1H\} \text{ NMR (THF, } -83^\circC \text{ carbonyl region)} \]
254.5, broad multiplet
225.1, broad singlet

\[ ^{31}P\{^1H\} \text{ NMR (THF, } -73^\circC \delta) \]
136.8, doublet
20.7 ppm, doublet
\[ J_{P-H} = 7 \text{ Hz} \]
No P-H coupling can be observed in \(^{31}P\) NMR spectrum

**k. Reaction with I₂**

A solution of Li[((Cu)₃Fe(μ-PPh₂)(μ-Cu)Fe(CO)₂(PPh₂H))] was prepared from 1.0 g (1.5 mmole) of [Fe(Cu)₃(μ-PPh₂)]₂ and 3.2 ml (two equivalents) of LiBEt₃H solution. To this solution was added 0.80 g (3.2 mmole) of solid I₂ under a blanket of nitrogen. The reaction solution was stirred at room temperature for 20 minutes. The solvent was removed by rotary evaporation, leaving a dark red oil. The oil was chromatographed on a Florisil column. Elution with petroleum ether resulted in a yellow band and a red band. The yellow band was eluted out with 3% ether/petroleum ether solution and was identified as [Fe(Cu)₃(μ-PPh₂)]₂ (0.45 g, 45%). The red band was eluted down with 10% ether/petroleum ether solution. The red band was collected and rotary evaporated to dryness. The resulting purple solid was identified as [((Cu)₃(I)Fe(μ-PPh₂)Fe(CO)₃(PPh₂H))]. The yield was 0.37 g (31%).
$^1$H NMR (CDCl$_3$)δ

<table>
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<tr>
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<td>7.4</td>
<td>doublet</td>
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</table>

IR (Cyclohexane)

$\nu$(C=O) 2029(s), 2003(s), 1987(s), 1972(s) cm$^{-1}$

$^{31}$P$^1$H NMR (THF, 25°C)δ

<table>
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<tr>
<th>Chemical Shift</th>
<th>Multiplicity</th>
<th>Jp-p</th>
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<td>34</td>
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<tr>
<td>36.1</td>
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$^{31}$P NMR (THF, 25°C)δ

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<th>Chemical Shift</th>
<th>Multiplicity</th>
<th>Jp-p</th>
<th>Jp-H</th>
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<tbody>
<tr>
<td>197.1</td>
<td>broad doublet</td>
<td>34</td>
<td>409</td>
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<tr>
<td>36.1</td>
<td>broad doublet</td>
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2. Reactions of \([\text{NO})_2\text{Fe(\mu-PPh}_2\text{)(\mu-NO)Fe(NO)(PPh}_2\text{H})\]$^-$

a. Reaction with Methyl Iodide

A solution of Li[(NO)$_2$Fe(\mu-NO)(\mu-PPh$_2$)Fe(NO)(PPh$_2$H)] was prepared from 0.60 g (1.0 mmole) of [Fe(NO)$_2$(\mu-PPh$_2$)]$_2$ and two equivalents (2.0 ml) of 1 M THF solution of LiEt$_3$H in 30 ml of THF at 0°C (ice water). The dark brown solution was then cooled to -78°C. To this solution was added 1.0 ml of MeI (tenfold excess) and the reaction mixture was stirred at -78°C for three hours. The solution was gradually warmed to room temperature while it was being stirred an additional three hours. The solvent was removed under reduced pressure, leaving a dark brown oil. The oil was treated with 30.0 ml of methanol. A red microcrystalline precipitate appeared and it was isolated by filtration to give 0.27 g of [Fe(NO)$_2$(\mu-PPh$_2$)]$_2$ (45%). The methanol solution was then concentrated by rotary evaporation to about 5 ml and dark red microcrystals fell out of solution. The crystals were collected on a fritted filter and washed with 10 ml portions.
of hexane three times. The compound was identified as Fe(NO)$_2$(PPh$_2$Me)$_2$. Yield = 0.24 g (38%).

Melting Point

Analytical Data

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$^1$H NMR (CDCl$_3$)$\delta$

IR(Cyclohexane)v(NO) 1724(s), 1680(s), cm$^{-1}$

$^{13}$C[$^1$H] NMR (d$_6$-Acetone)$\delta$

$^{31}$P[$^1$H] NMR(THF, 25°C)$\delta$

Mass Spectrum (EI)

Calc. 516 for M$^+$

m/e  Parent Ion, M$^+$

456  M$^+$-NO

b. Reaction with Ethyl Iodide

The procedure for this preparation was similar to that described above for the methyl iodide reaction. A solution of Li[(NO)$_2$Fe(μ-NO)(μ-PPh$_2$)Fe(NO)(PPh$_2$H)] was prepared from 0.60 g (1.0 mmole) of [Fe(NO)$_2$(μ-PPh$_2$)]$_2$ and two equivalents (2.0 ml) of 1 M THF solution of LiHET$_3$H in 30 ml of THF. To this reaction solution was added 1.0 ml (12 mmole) of EtI. Methanol was used to precipitate out starting material [Fe(NO)$_2$(μ-PPh$_2$)]$_2$ (0.5 g, 83%). The methanol solution was concentrated by rotary evaporation to about 5 ml and deep red brown crystals came out of the solution. The compound
was identified as \([(\text{NO})_2\text{Fe}(\text{PPh}_2\text{Et})_2]\). The yield was 0.08 g (13%).

\[\begin{align*}
\text{H} \text{NMR (CDCl}_3\delta \quad & 7.3, \text{multiplet, 20 H} \\
& 1.2, \text{multiplet, 10 H}
\end{align*}\]

\[\text{IR (THF) } \nu(\text{N=O}) = 1721(s), 1679(s) \text{ cm}^{-1}\]

\[3^1\text{P}[^1\text{H}] \text{ NMR(THF, 25°C)} \delta = 54.9, \text{singlet}\]

Mass Spectrum (tetraglyme, FAB)

<table>
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<th>m/e</th>
<th>Intensity</th>
<th>Ion</th>
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<tr>
<td>514</td>
<td>18.3</td>
<td>M^+-\text{N=O}</td>
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</table>

\section{c. Reaction with Diiodomethane}

A solution of Li\([(\text{NO})_2\text{Fe(\mu-\text{N=O})(\mu-\text{PPh}_2)}\text{Fe(\text{N=O})(\text{PPh}_2\text{H})}]\)

was prepared from 1.5 g (2.5 mmole) of \([\text{Fe(\text{NO})}_2(\text{\mu-\text{PPh}_2})]^2\)

with two equivalents (5.0 ml) of 1 M solution of LiEt\text{H}_3\text{H} in

30 ml of THF at 0°C. The dark brown solution was then cooled to -78°C and treated with 0.5 ml (6 mmole) of

\(\text{CH}_2\text{I}_2\). The reaction mixture was stirred at -78°C for three hours and warmed to room temperature while being stirred an additional three hours. The volume of the solution was reduced to around 10 ml under reduced pressure, which caused the precipitation of red \([\text{Fe(\text{Cu})}_3(\text{\mu-\text{PPh}_2})]^2\). The red solid was collected on a fritted filter (0.7 g, 47%). The filtrate was evaporated to dryness on a rotary evaporator, leaving a dark red oil. The oil was dissolved in a minimum amount of THF. Grade III alumina was added to the solution and the solvent was removed by rotary evaporation. The residue was added to the top of a grade III alumina-petroleum ether column. Initial elution with petroleum
ether produced a bright red purple band which was collected. Rotary evaporation of the solvent afforded a dark red oil. The oily residue was dissolved in CH$_2$Cl$_2$ and slow diffusion of hexane into this solution afforded deep red crystals. The yield was 0.071 g (5%). The compound was identified as [(N(u-PPh$_2$))$_2$Fe(NO)($\mu$-CH$_2$PPh$_2$)]$_2$.

Melting Point 138-139°C

Analytical Data

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<td>found</td>
<td>48.76</td>
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$^1$H NMR (CDCl$_3$)$\delta$

| 7.3, multiplet, 20 H |
| 1.5, triplet shape, 2 H (could be doublet of doublet) |

IR (Cyclohexane) $v$(N≡O)

| 1788(w), 1753(s) |
| 1731(s) cm$^{-1}$ |

$^{13}$C{$^1$H} NMR(CDCl$_3$)$\delta$

| 128.4-138.4, multiplet |
| -30.3, triplet |
| $J_{p-C} = 7$ Hz |

$^{13}$C NMR(CDCl$_3$)$\delta$

| 128.4-138.4, multiplet |
| -30.3, multiplet |

$^{31}$P{$^1$H} NMR(THF, 25°C)$\delta$

| 232.8, doublet |
| -1.6, doublet |
| $J_{p-p} = 56$ Hz |

Mass Spectrum (tetraglyme, FAB)

Calc. 616 for M$^+$

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<td>Parent ion, M$^+$</td>
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<tr>
<td>586</td>
<td>M$^+$-NO</td>
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<tr>
<td>556</td>
<td>M$^+$-2NO</td>
</tr>
<tr>
<td>526</td>
<td>M$^+$-3NO</td>
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</tbody>
</table>

When the solvent was switched to ether, a long red band was collected. Removal of the solvent afforded a red solid
which was identified as \([(\text{NO})_2\text{Fe}(\mu-\text{PPh}_2\text{PPh}_2)(\mu-\text{CH}_2)\text{Fe}(\text{NO})_2]\). The yield was 0.52 g (34%).

Melting Point

152-153°C

Analytical Data

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<th>% of hydrogen</th>
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<td>3.60</td>
</tr>
<tr>
<td>Found: 48.91</td>
<td>3.74</td>
</tr>
</tbody>
</table>

\( ^1H \text{ NMR (CDCl}_3) \delta \)

10.3, broad singlet, 2 H
7.1, broad singlet, 20 H

\( \text{IR(THF)} v(\text{N=O}) \)

1771(w), 1736(s), 1715(s) cm\(^{-1}\)

\( ^{13}C\{^1H\} \text{ NMR(d}_8\text{-THF)} \delta \)

177.7, triplet, \( J_{P-C}=13 \) Hz
127.9-134.6, multiplet

\( ^{31}P\{^1H\} \text{ NMR(THF, 25°C)} \delta \)

-24.6, singlet

Mass Spectrum

(tetraglyme, FAB)

Calc. 616 for \( M^+ \)

m/e Ion

616 Parent ion, \( M^+ \)

fragmentation pattern not clear

d. Reaction with n-Butyllithium

A solution of \( \text{Li[}(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)\text{Fe}(\text{NO})(\text{PPh}_2\text{H})] \)

was prepared from 0.12 g (0.20 mmole) of \( \text{[Fe(CO)}_3(\mu-\text{PPh}_2)]_2 \) with one equivalent (0.2 ml) of 1 M solution of \( \text{LiBEt}_3\text{H} \) in 1.0 ml of THF. The monoanion solution was cooled to -78°C. At that temperature, 0.12 ml of 1.64 M n-BuLi solution was added by syringe. The dark brown solution immediately turned deep purple red. The product dianion was formulated as \( [(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)\text{Fe}(\text{NO})(\text{PPh}_2\text{H})]^2^- \) based on its P-31 NMR spectrum at -78°C.
$^3$P$\{^1H\}$ NMR (THF, $-78^\circ$C)

- 159.6, doublet
- 20.5, doublet
- $J_{\text{P-H}} = 50 \text{ Hz}$

No P-H coupling can be observed in the $^3$P NMR spectrum.

H. Reactions of the Unsymmetrical Dianions

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

   a. Reaction with Methyl Iodide (one equivalent)

   A 10 mm NMR tube containing $[\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2$ (0.26 g, 0.40 mmole) was placed inside a Schlenk tube equipped with serum cap. The Schlenk tube was evacuated and filled with nitrogen. THF (1 ml) was added to the 10 mm NMR tube to dissolve the starting material, and 10 ml of THF was added to the Schlenk tube to provide a constant temperature bath. By syringe, 0.40 ml of 1 M LiBF$_4$H (0.40 mmole, one equivalent) was added into the 10 mm NMR tube to prepare the Li$[\text{Fe(CO)}_3(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(CO)}_2(\text{PPh}_2)]$ solution, and the solution was cooled to $-78^\circ$C (Dry Ice/isopropyl alcohol). To this deep orange red solution, 0.25 ml of n-BuLi was added (1.64 M in hexane, one equivalent). Upon addition of the n-BuLi the solution changed color from orange red to deep purple red immediately, which indicated the formation of Li$[\text{Fe(CO)}_3(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(CO)}_2(\text{PPh}_2)]$. To this dianion solution was added (at $-78^\circ$C) 26 yl (0.40 mmole, one equivalent) of methyl iodide, MeI. The color of the solution changed to red immediately. Variable temperature $^3$P-31 NMR spectra of the solution were measured from $-78^\circ$C to room temperature at every 20 degree interval. The compound was
identified primarily by comparisons of its P-31 NMR and infrared spectra with those of Li[(Cu)₃Fe(μ-PPh₂)(μ-CO)-Fe(CO)₂(PPh₂H)] and was formulated as Li[(Cu)₃Fe(μ-PPh₂)-(μ-CO)Fe(CO)₂(PPh₂Me)], with a methyldiphenylphosphine ligand. No attempts were made to isolate a solid sample of the product. Quantitative formation of the monoanion was estimated from the P-31 NMR spectrum.

IR(THF) ν (C=O) 1989 (m), 1938 (s),
       1895 (s, broad),
       1840 (sh) cm⁻¹
       1625 (m) cm⁻¹

¹³C{¹H} NMR (THF, -83°C)
(carbonyl region)δ 257.7, broad singlet
                  219.9, broad singlet

³¹P{¹H} NMR(THF, 25°C)δ 128.2, doublet
                  59.2, doublet
                  Jₚ₋ₚ = 37 Hz

Similar reactions were carried out in which other alkyl halides or dihalides were added to a THF solution of Li₂[(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(CO)₂(PPh₂)] prepared in this manner. Larger scale preparations were performed in a 100 ml Schlenk flask equipped with serum cap and a magnetic stirring bar.

b. Reaction with Excess Methyl Iodide and Deuteriated Methyl Iodide

The procedure for this preparation was similar to that described for the reaction with one equivalent methyl iodide. When 0.2 ml of MeI (3.0 mmole) was added to a solution of Li₂[(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(CO)₂(PPh₂)] at -78°C (from 0.26 g (0.4 mmole) of [Fe(CO)₃(μ-PPh₂)]₂, the deep purple red
color of the solution changed to red. The reaction mixture
was stirred at -78°C for three hours and then was allowed to
warm slowly to room temperature over a three hour period.
The solution was stirred at room temperature for an addi-
tional three hours. Column chromatography of the reaction
mixture on grade III alumina column-petroleum ether gave
0.24 g (90%) of the orange red product. The compound was
identified as the bridging acetyl complex, \[((\text{Cu})_3\text{Fe}(\text{μ-PPh}_2)\text{-}
(\text{μ-C(Me)U})\text{Fe(Cu)}_2(\text{PPh}_2\text{Me})]\), by its P-31 NMR spectrum.

A solution of \(\text{Li}_2[(\text{CO})_3\text{Fe}(\text{μ-PPh}_2)(\text{μ-Cu})\text{Fe(Cu)}_2(\text{PPh}_2)]\)
(prepared from 0.26 g (0.40 mmole) of \([\text{Fe(Cu)}_3(\text{μ-PPh}_2)]_2\)
was also treated with 0.20 ml (3.2 mmole) of C\(_\text{D}_3\)I and the
same procedure as that described above was used. The
deuterium-labeled product, \(((\text{Cu})_3\text{Fe}(\text{μ-PPh}_2)(\text{μ-C(CD}_3\text{O})-
\text{Fe(CO)}_2(\text{PPh}_2\text{CD}_3)\), was obtained in comparable yield.

Melting Point

| 142-143°C |

Analytical Data

| Calc. for Fe\(_2\)P\(_2\)O\(_6\)C\(_32\)H\(_20\)D\(_6\) |
|------------------|------------------|
| % of carbon      | 56.01            |
| % of hydrogen    | 4.69             |
| Found            | 55.94            |
|                  | 4.59             |

\(^2\text{H} \text{NMR (THF)} \delta 2.4, \text{ broad singlet} \)

\(13\text{C}[^1\text{H}] \text{NMR (CDCl}_3) \delta \)

<table>
<thead>
<tr>
<th>213.5, multiplet</th>
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<tr>
<td>126.7-134.7, multiplet</td>
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</table>

\(31\text{P}[^1\text{H}] \text{NMR (THF, 25°C)} \delta \)

<table>
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<tr>
<td>39.7 ppm, doublet</td>
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<td>(J_{p-p} = 53 \text{ Hz} )</td>
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Mass Spectrum

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<td>658 ( \text{Parent Ion, } M^+ )</td>
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<td>630 ( \text{M}^+-\text{CO} )</td>
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<td>618 ( \text{M}^+-2\text{CO} )</td>
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</table>
c. Reaction with Ethyl Iodide

The procedure for this preparation was similar to that described for the reaction of $\text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(}\text{CO})_2(\text{PPh}_2)]$ with methyl iodide. When 62 μl of EtI (one equivalent) was added to a solution of $\text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(}\text{CO})_2(\text{PPh}_2)]$ at -78°C (from 0.26 g of $[\text{Fe(}\text{CO})_3\text{(PPh}_2\text{)}]_2$), the deep red purple color of the solution changed to red. The P-31 NMR spectrum of the solution was measured at -78°C. The complex was identified as $\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(}\text{CO})_2(\text{PPh}_2\text{Et})]$ from its P-31 NMR and infrared spectra. No attempts were made to isolate solid sample of the product. Quantitative formation of the mono-anion product was estimated from the P-31 NMR spectrum.

$$\text{IR(THF})\nu(\text{C}=\text{O})$$  
$$\nu(\text{C}=\text{O})$$  
$$1991(\text{m}), 1938(\text{s}), 1926(\text{s}), 1893(\text{s}), 1878(\text{m}) \text{ cm}^{-1}$$  
$$1622(\text{w}) \text{ cm}^{-1}$$

$$31^p{[1_h]} \text{NMR(THF, -25°C})\delta$$  
$$128.2, \text{doublet}$$  
$$70.9, \text{doublet}$$  
$$J_\text{p-p} = 35 \text{ Hz}$$

To the foregoing solution of $\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(}\text{CO})_2(\text{PPh}_2\text{Et})]$, excess EtI (0.2 ml) was added at -78°C. The reaction solution was gradually warmed to room temperature and stirred at room temperature for 40 hours to complete the reaction. The reaction mixture was chromatographed on a grade III alumina-petroleum ether column to give 0.032 g of $[\text{Fe(}\text{CO})_3(\mu-\text{PPh}_2)]_2$ (12%) and 0.18 g (60%) of $[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C(}\text{Et})\text{O})\text{Fe(}\text{CO})_2(\text{PPh}_2\text{Et})]$. Both products were identified by their P-31 NMR spectra.
d. Reaction with 1-Iodopropane

The procedure for this preparation was similar to that described for the reaction of Li$_2$[(CO)$_3$Fe($\mu$-PPh$_2$)($\mu$-Cu)-Fe(CO)$_2$(PPh$_2$)] with methyl iodide. Reaction of n-PrI (40 $\mu$l, 0.40 mmole, one equivalent) with the solution of Li$_2$[(CO)$_3$Fe($\mu$-PPh$_2$)($\mu$-Cu)Fe(CO)$_2$(PPh$_2$)] prepared from 0.40 mmole of [Fe(CO)$_3$($\mu$-PPh$_2$)]$_2$ (0.26 g) and 0.40 mmole of LiBEt$_3$H (0.40 ml) and 0.40 mmole of n-BuLi (0.25 ml) at -78°C gave a reddish solution of Li[(CO)$_3$Fe($\mu$-PPh$_2$)-($\mu$-Cu)Fe(CO)$_2$(PPh$_2$n-Pr)], formulated from its P-31 NMR and infrared spectra. Quantitative formation of the above monoanion was estimated from the P-31 NMR spectrum.

IR(THF) $\nu$(C=O)  
1991(m), 1939(s), 1910(s),
1879(m) cm$^{-1}$  
1625(m) cm$^{-1}$

$^{31}$P{$^{1}$H} NMR(THF, -25°C) $\delta$
128.7, doublet  
67.5, doublet  
$J_{P-P} = 29$ Hz

The reaction of Li$_2$[(CO)$_3$Fe($\mu$-PPh$_2$)($\mu$-Cu)Fe(CO)$_2$(PPh$_2$)] (prepared from 0.40 mmole, 0.26 g of [Fe(CO)$_3$($\mu$-PPh$_2$)]$_2$) with excess 1-iodopropane (0.20 ml, 2.0 mmole) was also carried out at -78°C. The reaction solution was stirred at -78°C for three hours and then gradually warmed to room temperature. The red solution was heated at 50°C for a ten hour period. The solvent was removed by rotary evaporation. The residue was dissolved in the minimum amount of CH$_2$Cl$_2$ and covered with a minimum amount of grade III alumina. This mixture was rotary evaporated to dryness and then added to a grade III alumina-petroleum ether column.
Initial elution with petroleum ether produced a yellow band which was collected. After rotary evaporation of the solvent, the yellow material was identified by P-31 NMR spectroscopy as $\text{[Fe(CO)}_3(\mu-\text{PPh}_2)]_2$, 0.036 g (14%). Elution with 3% ether/petroleum ether mixed solvent produced an orange band which was collected. Rotary evaporation of the solvent from this fraction afforded 0.16 g (53%) of an orange red oil. Attempts to obtain solid samples by adding hexane or pentane to the CH$_2$Cl$_2$ solution of this orange red oil failed.

$^1$H NMR (CDCl$_3$)δ

7.4, multiplet, 20 H
2.5, multiplet, 4 H
1.4, multiplet, 2 H
0.9, multiplet, 5 H
0.4, multiplet, 3 H

IR(Cyclohexane) $\nu$(C=O)

2038(m), 1976(s), 1950(m), 1927(m) cm$^{-1}$
1481(w) cm$^{-1}$

$^{13}$C($^1$H) NMR (CDCl$_3$)δ

299.9, doublet, $J_{P-C}$= 19 Hz
214.0, multiplet
127.6-134.1, multiplet
63.8, singlet
33.4, doublet, $J_{P-C}$= 22 Hz
17.8, singlet
16.4, doublet, $J_{P-C}$= 10 Hz
15.5, singlet
13.3, singlet

$^{31}$P($^1$H) NMR (THF)δ

169.5, doublet
49.4, doublet
$J_{P-P} = 36$ Hz

Mass Spectrum
(tetraglyme, FAB)

Calc. 736 for M$^+$

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<td>680</td>
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e. Reaction with 2-Iodopropane

The procedure for this preparation was similar to that described for the reaction of \( \text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})-\text{Fe}(\text{CO})_2(\text{PPh}_2)] \) with methyl iodide. When 0.40 mmole (40 \( \mu l \)) of \( \text{i-PrI} \) was added to a solution of \( \text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)-(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PPh}_2)] \) (prepared from 0.40 mmole, 0.26 g of \( \text{[Fe(CO)}_3(\mu-\text{PPh}_2)]_2 \) at -78°C with 0.40 ml of \( \text{LiBEt}_3\text{H} \) and 0.25 ml of \( \text{n-BuLi} \) the color of the purple solution changed to red immediately. No attempts were made to isolate a solid product. The complex was formulated as \( \text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)-(\mu-\text{CO})\text{Fe}(\text{CO})_2\text{PPh}_2)(\text{PPh}_2\text{i-Pr}] \) based on its \( ^{31}\text{P} \{^1\text{H}\} \text{ NMR} \) spectrum and infrared spectrum.

\[
\begin{align*}
\text{IR(THF) } & \nu(\text{C=O}) \\
& 1995(\text{s}), 1942(\text{s}), 1908(\text{s}) , \\
& 1890(\text{sh}) \text{ cm}^{-1} \\
& 1648(\text{m}) \text{ cm}^{-1} \\
\nu(\text{C=O}) & 1995(\text{s}), 1942(\text{s}), 1908(\text{s}) , \\
& 1890(\text{sh}) \text{ cm}^{-1} \\
^{31}\text{P} \{^1\text{H}\} \text{ NMR(THF, -73°C)} & 128.4, \text{ doublet} \\
& 80.3, \text{ doublet} \\
& J_{p-p} = 36 \text{ Hz}
\end{align*}
\]

In a larger scale preparation, a solution of \( \text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PPh}_2)] \) was prepared from 1.56 g of \( \text{[Fe(CO)}_3(\mu-\text{PPh}_2)]_2 \) (2.4 mmole), one equivalent (2.4 ml) of 1 M \( \text{LiBEt}_3\text{H} \) solution, and one equivalent (1.5 ml) of 1.64 M \( \text{n-BuLi} \) solution. To the resulting solution was added 1.0 ml (tenfold excess) of \( \text{i-PrI} \) at -78°C. The reaction solution was stirred at -78°C for three hours and then gradually warmed to room temperature while being stirred an additional 48 hours. The solvent was removed by rotary evaporation and the residue was chromatographed on a grade III alumina-petroleum ether column. Initial elution with petroleum
ether moved a yellow band down the column. The band was collected and identified as $[\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2$ (0.16 g, 10%). When the eluting solvent was changed to 3% ether/petroleum ether an orange band eluted down the column. After this band was collected, removal of the solvent produced an orange red oil. Dissolution of the oil in 2 ml of $\text{CH}_2\text{Cl}_2$, followed by slow addition of 20 ml of hexane, afforded orange red crystals. The compound was identified as $[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C(i-Pr)}_0)\text{Fe(CO)}_2(\text{PPh}_2\text{i-Pr})]$. The yield was 1.15 g (65%).

**Melting Point** 110-111°C

**Analytical Data**

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**$^1H$ NMR** ($\text{CDCl}_3$)$\delta$

- 7.4, multiplet, 20 H
- 3.1, multiplet, 1 H
- 2.0, multiplet, 1 H
- 1.2, multiplet, 6 H
- 0.5, doublet, 3 H, $J$ = 7 Hz
- 0.1, doublet, 3 H, $J$ = 7 Hz

**IR** (Cyclohexane) $\nu(\text{C=O})$

- 2029(m), 2021(m), 1973(s), 1949(m), 1942(m), 1923(m) cm$^{-1}$
- 1480(w) cm$^{-1}$

**$^{13}C$[$^1H$] NMR** ($\text{CDCl}_3$)$\delta$

- 304.5, doublet, $J_{p-C} = 21$ Hz
- 214.0, multiplet
- 125.3-135.5, multiplet
- 58.1, singlet
- 30.2, doublet, $J_{p-C} = 23$ Hz
- 18.7, singlet
- 18.3, singlet
- 16.7, singlet
\[ ^{31}P\{^1H\} \text{NMR(THF, } 25^\circ C\} \delta \]

168.7, doublet
62.2, doublet
\(J_{P-P} = 38 \text{ Hz}\)

Mass Spectrum
(tetraglyme, FAB)

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\textbf{f. Reaction with Allyl Iodide}

The procedure for this preparation was similar to that described for the reaction of \(\text{Li}_2[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)\mu-\text{Cu}-\text{Fe}(\text{Cu})_2(\text{PPh}_2)]\) with methyl iodide. A solution of \(\text{Li}_2[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)\mu-\text{Cu})\text{Fe}(\text{Cu})_2(\text{PPh}_2)]\) was prepared from 0.26 g of \([\text{Fe}(\text{Cu})_3(\mu-\text{PPh}_2)]_2\) and 0.40 ml of 1 M \(\text{LiBEt}_3\text{H}\) solution and then 0.25 ml of 1.64 M \(\text{n-BuLi}\) solution at \(-78^\circ C\). To the resulting solution was added 36 \(\mu\)l (0.4 mmole) of \(\text{C}_3\text{H}_5\text{I}\) at \(-78^\circ C\) and the dark purple solution changed color to orange red immediately. No attempts were made to isolate a solid product. The complex was formulated as \(\text{Li}[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)-\mu\text{-Cu})\text{Fe}(\text{Cu})_2(\text{PPh}_2\text{C}_3\text{H}_5)]\) based on its \(P-31\) NMR and IR spectral measurements.

\(\text{IR(THF) } \nu(\text{C=O})\)

1995(m), 1940(s), 1899(s), 1885(sh) cm\(^{-1}\)
1630(m) cm\(^{-1}\)

\(^{31}P\{^1H\} \text{NMR(THF, } -25^\circ C\} \delta \)

128.5, doublet
66.6, doublet
\(J_{P-P} = 38 \text{ Hz}\)

To a solution of the above was added 0.20 ml of \(\text{C}_3\text{H}_5\text{I}\) (tenfold excess). The mixture was stirred at \(-78^\circ C\) for 30 minutes and then gradually warmed to room temperature. The solvent was removed by rotary evaporation leaving a dark red
oil. The oil was then chromatographed on a grade III alumina-petroleum ether column. Elution with petroleum ether resulted in a yellow band which was identified as \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2\) (0.04 g, 15%). Continued elution with 3%-5% ether/petroleum ether solution resulted in a long red band, which was collected. The compound was identified as \([(\text{Cu})_2(\text{n}^3-\text{C}_3\text{H}_5)\text{Fe(}\mu-\text{PPh}_2)\text{Fe(Cu)}_3(\text{PPh}_2\text{C}_3\text{H}_5)]\) by its P-31 NMR spectrum (0.21 g, 72%).

**g. Reaction with Diiodomethane**

A solution of \(\text{Li}_2[(\text{Cu})_3\text{Fe(}\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(Cu)}_2(\text{PPh}_2)]\) was prepared by the addition of 20 ml of a 1 M solution of \(\text{LiBEt}_3\text{H}\) to a solution of 2.0 mmole (1.3 g) of \([\text{Fe(Cu)}_3(\mu-\text{PPh}_2)]_2\) in 30 ml of THF and then 1.25 ml of \(\text{n-BuLi}\) (1.64 M) at -78°C. To the resulting dianion solution was added 10 ml (12.4 mmole) of \(\text{CH}_2\text{I}_2\). After the mixture had been stirred for three hours at -78°C, the solution was warmed to room temperature. Solvent was removed from the deep red solution on a rotary evaporator, leaving a black oil which was chromatographed on a Florisil column (the material decomposed on grade III alumina column). Elution with petroleum ether afforded a yellow band which was collected. Rotary evaporation of the solvent from this fraction recovered 0.54 g (42%) of \([\text{Fe(Cu)}_3(\mu-\text{PPh}_2)]_2\) which was identified by its P-31 NMR spectrum. Continuous elution with petroleum ether produced a brown band which was collected. After removal of the eluting solvent, 0.32 g (25%) of an olive green color product was obtained. The compound was formulated as \([(\text{CO})_3\text{Fe(}\mu-\text{PPh}_2)(\mu-\text{CH}_2\text{PPh}_2)\text{Fe(CO)}_3]\).
Melting Point

Analytical Data

% of carbon 56.06 56.26
% of hydrogen 3.34 3.50

$^1$H NMR (CDCl$_3$)$\delta$
7.2, multiplet, 20 H
1.6, doublet, 2 H
$J_{p-H} = 33$ Hz

IR(Cyclohexane)$\nu$(C=O)
2046(s), 2004(s), 1991(s),
1963(s), 1952(s) cm$^{-1}$

$^{13}$C{$^1$H} NMR(CDCl$_3$)$\delta$
213.3, multiplet
127.9-134.3, multiplet
-18.8, triplet, $J_{p-C} = 7$ Hz

$^{31}$P{$^1$H} NMR(THF)$\delta$
181.0, doublet
20.4, doublet
$J_{p-p} = 31$ Hz

Mass Spectrum
(tetraglyme, FAB)
Calc. 664 for M$^+$

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h. Reaction with One Equivalent and Excess Amount
of CF$_3$COOD

A solution of Li$_2[${(CO)}$_3$Fe($\mu$-PPh$_2$)($\mu$-CO)Fe(CO)$_2$(PPh$_2$)]
was prepared from 0.20 g (0.40 mmole) of [Fe(CO)$_3$($\mu$-PPh$_2$)]$_2$
and 0.4 ml of 1 M LiBEt$_3$H solution and 0.25 ml of 1.64 M
n-BuLi solution at -78°C. The resulting solution was
treated with 30 $\mu$l (one equivalent) of CF$_3$COOD.
Immediately, the deep purple red solution changed color to
dark red. The reaction was monitored by $P$-31 NMR spectroscopy. The $P$-31 NMR spectrum of the reaction solution
indicated that the monoanion [{(CO)}$_3$Fe($\mu$-PPh$_2$)($\mu$-CO)Fe(CO)$_2$-
(PPh₂D)⁻ was prepared in quantitative yield by this reaction.

In another reaction, a solution of Li₂[(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(CO)₂(PPh₂)] (prepared from 0.40 mmole, 0.26 g of [Fe(CO)₃(μ-PPh₂)]₂) was treated with 0.2 ml (2.6 mmole) of CF₃COOD at -78°C. The dark purple red solution immediately turned color to orange red. The reaction was monitored by P-31 NMR spectroscopy. The product of this reaction was identified as [[(CO)₃Fe(D)(μ-PPh₂)Fe(CO)₃(PPh₂D)] based on its P-31 NMR chemical shift values.

2. Reactions of [(NO)₂Fe(μ-PPh₂)(μ-NO)Fe(NO)(PPh₂)]²⁻
   a. Reaction with Methyl Iodide

A solution of Li₂[(NO)₂Fe(μ-NO)(μ-PPh₂)Fe(NO)(PPh₂)] was prepared from 0.12 g (0.20 mmole) of [Fe(NO)₂(μ-PPh₂)]₂ and 0.22 ml (one equivalent) of 1 M LiB(Et)₃H solution and then 0.10 ml of 1.64 M solution of n-BuLi at -78°C. The dark brown solution was treated with 12 μl (one equivalent) of MeI by syringe. No obvious color change of the solution could be observed. After the mixture had been stirred for 10 minutes at -78°C, P-31 NMR monitoring showed quantitative formation of a new species. This species was formulated as Li[(NO)₂Fe(μ-NO)(μ-PPh₂)Fe(NO)(PPh₂Me)]⁻. The monoanion was stable at room temperature. No attempts were made to obtain solid samples of the product.

IR(THF) ν(N=O)  1699(m), 1654(s) cm⁻¹
   ν(N=O)  1420(w) cm⁻¹
\[ ^{31}P\{^1H\} NMR(THF, -73^\circ C) \delta \]

160.1, doublet
42.1, doublet
\( J_{P-P} = 14 \text{ Hz} \)

No P-H coupling can be observed in the \( ^{31}P \) NMR spectrum.

In other experiments, excess MeI was added to a THF solution of \( \text{Li}_2[(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)\text{Fe}(\text{NO})(\text{PPh}_2)] \)
(prepared from 0.12 g, 0.20 mmole of \([\text{Fe}(\text{NO})_2(\mu-\text{PPh}_2)]_2 \)).
The reaction mixture was stirred at -78\(^\circ\)C for 10 minutes and
then gradually warmed to room temperature, with a lot of
\([\text{Fe}(\text{NO})_2(\mu-\text{PPh}_2)]_2 \) falling out of solution. Monitoring by
\( ^{31}P \) NMR spectroscopy showed only a weak signal of
\( \text{Fe}(\text{NO})_2(\text{PPh}_2\text{Me})_2 \).

b. Reaction with Diiodomethane

The procedure for this preparation was similar to that
described above. A solution of \( \text{Li}_2[(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)-\text{Fe}(\text{NO})(\text{PPh}_2)] \) was prepared from 0.12 g (0.2 mmole) of
\([\text{Fe}(\text{NO})_2(\mu-\text{PPh}_2)]_2 \) and \( \text{LiBET}_3\text{H} \) and \( n-\text{BuLi} \) solutions at
-78\(^\circ\)C. At -78\(^\circ\)C, 0.10 ml (1.4 mmole) of \( \text{CH}_2\text{I}_2 \) was added to
this dianion solution by syringe. The reaction mixture was
stirred at -78\(^\circ\)C for 30 minutes while \( ^{31}P \) NMR monitoring
showed no sign of reaction. The solution was gradually
warmed to room temperature while being stirred an additional
one hour. Red solid of \([\text{Fe}(\text{NO})_2(\mu-\text{PPh}_2)]_2 \) precipitated out
of the solution and no products could be detected by NMR
measurements.
I. Reactions of Alkyldiphenylphosphine-Substituted Monoanions, \([\text{CO})_3\text{Fe(}\mu\text{-PPh}_2\text{)}(\mu\text{-CO})\text{Fe(CO)}_2\text{(PPh}_2\text{)}\text{R}\]^- 

1. Alkylation Reactions of Li\([\text{CO})_3\text{Fe(}\mu\text{-PPh}_2\text{)}(\mu\text{-CO})\text{Fe(CO)}_2\text{(PPh}_2\text{)}\text{Me})\]

a. Reaction with Deuteriated Methyl Iodide

A THF solution of Li\([\text{CO})_3\text{Fe(}\mu\text{-PPh}_2\text{)}(\mu\text{-CO})\text{Fe(CO)}_2\text{(PPh}_2\text{)}\text{Me})\] was prepared from 0.52 g (0.80 mmole) of [Fe(CO)]_3-(\mu-PPh_2)_2, 0.80 ml of 1 M LiBEt_3H solution and 0.50 ml of 1.64 M n-BuLi solution at -78°C. To this dianion solution was added one equivalent of MeI (52 μl, 0.80 mmole) at -78°C (Dry Ice/isopropanol alcohol bath). The monoanion solution was stirred at -78°C for 30 minutes and then treated with 60 μl (0.90 mmole) of CD_3I. The solution was stirred at -78°C for three hours and then gradually warmed to room temperature. The solvent was removed by rotary evaporation and the residue was dissolved in a minimum amount of CH_2Cl_2. This solution was then absorbed by grade III alumina and was added to a grade III alumina-petroleum ether column. Initial elution with petroleum ether produced a trace yellow band which was identified by infrared spectroscopy as [Fe(CO)]_3(\mu-PPh_2)_2. Elution with 3% ether/petroleum ether mixed solution produced an orange band which was collected and evaporated to dryness. The orange product was then recrystallized by slow diffusion of hexane into ether solution at ~5°C. The complex was formulated as \([\text{CO})_3\text{Fe(}\mu\text{-PPh}_2\text{)}(\mu\text{-C(}\text{CD}_3\text{)})\text{O})\text{Fe(CO)}_2\text{(PPh}_2\text{Me})\]. The yield was 0.45 g (83%).
Melting Point
139-140°C

Analytical Data

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<td>% of hydrogen</td>
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$^1$H NMR (CDCl$_3$)δ
7.5, multiplet, 20 H
2.0, doublet, 3 H
$J_{p-H} = 9$ Hz

$^2$D NMR(THF)δ
2.4, broad singlet

IR (Cyclohexane) $\nu$(C=O)
- 2040(m), 2031(m), 1980(s),
- 1952(m), 1939(m)
- 1932(m) cm$^{-1}$
- 1485(w) cm$^{-1}$

$^{13}$C{$^1$H} NMR(CDC$_3$)δ
213.9, multiplet
128.6, multiplet
15.7, doublet, $J_{p-C} = 24$ Hz

$^{31}$P{$^1$H} NMR(THF, 25°C)δ
174.1, doublet
39.7, doublet
$J_{\mu-p} = 53$ Hz

Mass Spectrum
(tetraglyme, FAB)
Calc. 683 for $M^+$

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b. Reaction with 1-Iodopropane

A THF solution of Li$_2$[(CO)$_3$Fe($\mu$-PPh$_2$)($\mu$-Cu)Fe(CO)$_2$-(PPh$_2$)] was prepared from 0.26 g (0.40 mmole) of [Fe(CO)$_3$-(($\mu$-PPh$_2$)]$_2$ by using the LiBEt$_3$H and n-BuLi procedure. The dark purple solution was then treated with one equivalent of MeI (26 µl) at -78°C. The solution was stirred at -78°C for 20 minutes and then treated with 40 µl (0.40 mmole) of 1-iodopropane. The resulting solution was stirred at -78°C for one hour and then gradually warmed to room temperature. Solvent was removed on a rotary evaporator,
leaving a dark red oil which was dissolved in a minimum amount of CH$_2$Cl$_2$ and absorbed by grade III alumina. The alumina was then added to a column packed with grade III alumina. Elution with petroleum ether produced a yellow band which was collected and identified as [Fe(Cu)$_3$-(μ-PPP$_2$)$_2$] (0.036 g, 14%). When the solvent was switched to 3% ether/petroleum ether solvent mixture, an orange band passed down the column. After collection of the band and removal of solvent, the orange material was identified as [(Cu)$_3$Fe(μ-PPP$_2$)(μ-C(n-Pr)U)Fe(Cu)$_2$(PPP$_2$Me)].

Yield = 0.18 g, 65%.

**Melting Point**

118°C

**$^1$H NMR (CDCl$_3$)$\delta$**

7.3, multiplet 20 H  
2.0, multiplet 5 H  
1.5, multiplet, 5 H

**IR(Cyclohexane)$\nu$(C=O)**

1928 (sh), 1923 (s), 1979 (s),  
1949 (s), 1930 (m) cm$^{-1}$  
1482 (w) cm$^{-1}$

**$^{13}$C{$^1$H} NMR (CDCl$_3$)$\delta$**

214.0, multiplet  
127.6-134.2, multiplet  
63.9, singlet  
17.0, singlet  
16.1, doublet, $J_{p-C} =$ 23 Hz  
13.3, singlet

**$^{31}$P{$^1$H} NMR (THF, 25°C)$\delta$**

171.8, doublet  
40.0, doublet  
$J_{p-p} =$ 45 Hz
Mass Spectrum
(tetraglyme, FAB)  
Calc. 708 for M⁺

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**c. Reaction with Iodoacetonitrile**

A solution of Li₂[(Fe(CO)₃Cu-PPh₂)(μ-CU)Fe(CO)₂(PPh₂)] was prepared from 0.26 g (0.40 mmole) of [Fe(CO)₃(μ-PPh₂)]₂ and LiBEt₃H and n-HuLi at -78°C. The resulting dianion solution was treated with one equivalent (26 μl) of MeI at -78°C and the reaction mixture was stirred for 30 minutes. To this solution of Li[(Cu)₃Fe(μ-PPh₂)(μ-CU)Fe(CO)₂(PPh₂Me)] was added 30 μl (one equivalent) of CH₂CN. The reaction mixture was then gradually warmed to room temperature while being stirred an additional hour. The solvent was removed by rotary evaporation, leaving a dark red oil which was chromatographed on a grade III alumina-petroleum ether column. Initial elution with petroleum ether afforded a band which was collected and identified as [Fe(CO)₃-
(μ-PPh₂)]₂ (0.074 g, 28%). When the column was eluted with 10% ether/petroleum ether solution, a purple band developed and passed down the column. After collection of the band and removal of the solvent by rotary evaporation, 0.060 g (19%) of a purple solid identified as [(CO)₃(I)Fe(μ-PPh₂)-Fe(CO)₃(PPh₂Me)] was isolated.
Melting Point 146°C (decomposed)

Analytical Data

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$^1$H NMR (CDCl$_3$) $\delta$

- 7.4, multiplet 20 H
- 2.4, doublet, 3 H
- $J_{p-H} = 9$ Hz

IR(THF) $\nu$(C≡O)

- 2062(w), 2009(s), 1994(s),
- 1975(sh, broad) cm$^{-1}$

$^{13}$C($^1$H) NMR(CDC$_3$) $\delta$

- 212.3, multiplet
- 126.1-137.2, multiplet
- 19.1, doublet, $J_{p-C} = 31$ Hz

$^{31}$P($^1$H) NMR(THF, 25°C) $\delta$

- 195.1, doublet
- 54.9, doublet
- $J_{p-p} = 30$ Hz

Mass Spectrum

(tetraglyme, FAB)

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2. Alkylation Reaction of Li[[(CO)$_3$Fe($\mu$-PPh$_2$)($\mu$-CO)-Fe(CO)$_2$(PPh$_2$CD$_3$)] with MeI

A solution of Li$_2$[[(CO)$_3$Fe($\mu$-PPh$_2$)($\mu$-CO)Fe(CO)$_2$(PPh$_2$)]] was prepared from 0.26 g (0.40 mmole) of [Fe(CO)$_3$(P-PPh$_2$)$_2$]$_2$ by the reaction with LiB$\text{Et}_3$H and $n$-BuLi at -78°C. The resulting dianion solution was treated with one equivalent (26 μl) of CD$_3$I at -78°C to produce a solution of Li[[(CO)$_3$-Fe($\mu$-PPh$_2$)($\mu$-CO)Fe(CO)$_2$(PPh$_2$CD$_3$)].

$^2$H NMR(THF) $\delta$

- 1.9, broad singlet

$^{31}$P($^1$H) NMR(THF, 25°C) $\delta$

- 123.8, doublet
- 54.9, doublet
- $J_{p-p} = 31$ Hz
To the above solution of the monoanion was added 26 μl of MeI at room temperature and the reaction mixture was stirred overnight. The solvent was removed by rotary evaporation and the residue was chromatographed on grade III alumina column. Elution with 3% ether/petroleum ether solution resulted in an orange band, which was collected. The orange red solid obtained was formulated as [(Cu)$_3$-\(\text{Fe(μ-PPh}_2\)(μ-C(Me)O)Fe(CO)$_2$(PPh$_2$CD$_3$))]$. The yield was 0.17 g (63%).

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<td>% of carbon</td>
<td>calc.</td>
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<td>% of hydrogen</td>
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<td>1H NMR (CDCl$_3$)$\delta$</td>
<td>7.3, multiplet, 20 H</td>
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<td>2H NMR (THF)$\delta$</td>
<td>1.90, singlet, 3 H</td>
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<td>IR (Cyclohexane)$v$(C=O)</td>
<td>2040(s), 2031(s), 1982(s), 1953(s), 1938(w), 1930(w) cm$^{-1}$</td>
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<tr>
<td>(THF)$v$(C=O)</td>
<td>1435(w) cm$^{-1}$</td>
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<tr>
<td>13C{$^1$H} NMR (THF, 25°C)$\delta$</td>
<td>299.2, doublet, $J_{P-C}$ = 17 Hz</td>
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<td>31P{$^1$H} NMR (CDCl$_3$)$\delta$</td>
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<td>Mass Spectrum (tetraglyme, FAB)</td>
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3. Alkylation Reaction of Li[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)-Fe(CO)$_2$(PPh$_2$Et)] with MeI

The procedure for this preparation was similar to that described for the reactions above. A solution of Li$_2$[(CO)$_3$-Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$)] was prepared from 0.52 g (0.80 mmole) of [Fe(CO)$_3$(μ-PPh$_2$)]$_2$ and LiBEt$_3$H and n-BuLi at -78°C. The resulting dianion solution was first treated with 62 μl (one equivalent) of EtI at -78°C and this solution was gradually warmed to room temperature. To the resulting solution of Li[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$Et)] was added 52 μl of MeI (one equivalent). The reaction mixture was stirred at room temperature for ten hours, and the solvent was removed by rotary evaporation. The residue was then chromatographed on a grade III alumina-petroleum ether column. Elution with petroleum ether resulted in a yellow band which was collected and identified as [Fe(CO)$_3$-(μ-PPh$_2$)]$_2$ (0.12 g, 23%). Continued elution with 3% ether/petroleum ether resulted in an orange band, which was collected. Rotary evaporation of the solvent afforded an orange red compound which was identified as [(CO)$_3$-Fe(μ-PPh$_2$)(μ-C(Me)Bu)Fe(CO)$_2$(PPh$_2$Et)]. The yield was 0.38 g (68%).

Melting Point

133°C

IR(Cyclohexane)ν(C=O)  2035(sh), 2028(m), 1980(s), 1953(s), 1930(w) cm$^{-1}$ 1480(w) cm$^{-1}$

ν(C=O)

$^{13}$C[1$^H$] NMR(CDC$_3$)δ  298.5, doublet, J$_{P-C}$= 17 Hz 213.7, singlet 127.4-133.7, multiplet
$^{31}$P$^1$H NMR (THF, 25°C)

-100- 47.2, singlet
24.2, doublet, $J_{p-C} = 24$ Hz
8.3, singlet

174.3, doublet
52.7, doublet
$J_{p-p} = 55$ Hz

Mass Spectrum (tetraglyme, FAB)

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<td>638</td>
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<td>$M^+ - 2Cu$</td>
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J. X-ray Crystal Structure Determinations

The X-ray crystal diffraction intensity data collections for the three crystals described in the following sections (1), (2) and (3) were performed by Dr. J. Gallucci at The Ohio State University by using a Syntex PI diffractometer with graphite monochromated MoKα radiation. The structures were solved with the MULTAN 80 program or a combination of MULTAN 80 and Patterson methods.

The intensity data collections for the three crystals described in the following sections (4) and (5) were performed by Dr. M. Calligaris at the University of Trieste, Italy, using an Enraf-Nonius CAD-4 automatic diffractometer or an AED-Siemens automatic single-crystal diffractometer with MoKα radiation. The structures were solved mainly by the heavy atom method.
1. \[\text{[(CO)}_3\text{Fe(\mu-PPh}_2\text{)(\mu-C(Me)O)Fe(CO)}_2\text{(PPh}_2\text{Me)}]\]

Crystals suitable for an X-ray diffraction study of the complex were grown by the method of slow solvent diffusion. About 0.3 g of the complex was dissolved in 3 ml of ether at room temperature in a test tube, and about 15 ml of hexane was slowly added drop by drop without disturbing the ether layer. The test tube was sealed with a serum cap stopper and placed at about 5°C for two days. The crystals were collected and washed with 5 ml portions of hexane several times. The deep red crystals were then dried under a stream of nitrogen. Pertinent crystal and intensity data are listed in Table 2.

2. \[\text{[(CO)}_2(\text{3}_\text{n-C}_3\text{H}_5)\text{Fe(\mu-PPh}_2\text{)Fe(CO)}_3\text{(PPh}_2\text{C}_3\text{H}_5)}]\]

Crystals suitable for an X-ray diffraction study were grown by dissolving about 0.5 g of the complex in 5 ml of \text{CH}_2\text{Cl}_2 in a test tube. About 10 ml of hexane was slowly added drop by drop without disturbing the \text{CH}_2\text{Cl}_2 layer. The test tube was sealed with a serum cap stopper and placed in a refrigerator (ca. 5°C) for three days. The crystals were collected and washed with portions of hexane. The dark red crystals were then dried under a stream of nitrogen. Important crystal and intensity data are listed in Table 3.

3. \[\text{[(CO)}_3\text{Fe(\mu-PPh}_2\text{)}_2\text{Fe(CO)}_2\text{(PPh}_2\text{C}_3\text{H}_5)}]\]

Orange-red crystals of this complex, suitable for X-ray diffraction study, were grown by a procedure similar to that described in the above section. Slow diffusion of a \text{CH}_2\text{Cl}_2
Table 2. Data for the X-Ray Diffraction Study of

\[
[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C(Me)O})\text{Fe(CO)}_2(\text{PPh}_2\text{Me})] 
\]

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**Measurements of Intensity Data**

| Radiation | MoKα(λ-0.70926Å, graphite monochromator) |
| Temperature | -123°C |
| Scan Speed | Variable (2° to 24°/min in ω) |
| Scan Range | 1.8° in ω |
| Data Limits | 4° < 2θ < 44° |
| Data Collected | + h, ±k, ±l |
| Unique Data | 7364 |
| Unique Data with | pFo² > 3σ(pFo²) 4880 |
| R(F) | 0.049 |
| Rw(F) | 0.055 |
Table 3. Data for the X-ray Diffraction Study of
\[\text{[(CO)}_2(3\text{H}_3\text{C}_5\text{Fe}(\mu-\text{PPh}_2)\text{Fe(CO)}_3\text{PPh}_2\text{C}_3\text{H}_5)]\]

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**Measurements of Intensity Data**

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solution of the complex into liquid hexane afforded good quality crystals. Important crystal and intensity data are listed in Table 4.

4. \([(\text{NO})_2 \text{Fe}(\mu-\text{PPh}_2\text{PPh}_2)(\mu-\text{CH}_2)\text{Fe(NO)}_2]\)

This complex has very poor solubility in non-polar solvents and decomposes in chlorinated solvents. Crystals suitable for an X-ray diffraction study of the complex were grown by preparing a saturated solution of the complex in 5 ml of THF in a Schlenk tube and slowly adding, drop by drop, about 15 ml of ether. The slow addition process must be carried out extremely carefully to avoid any cloudiness in the THF layer. The Schlenk tube was then sealed with a serum cap and flushed with nitrogen. The solution was placed at about 5°C for two days. The deep red crystals were collected and stored under nitrogen in a sealed ampule. Important crystal and intensity data are listed in Table 5.

5. \([(\text{NO})_2 \text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CH}_2\text{PPh}_2)\text{Fe(NO)}_2]\)

Crystals suitable for an X-ray diffraction study of the complex were grown by a combination of slow diffusion and slow cooling methods. A saturated solution of the complex in ether was prepared at room temperature in a test tube. About 10 ml of hexane was slowly added, drop by drop. The test tube was then wrapped in a paper towel which served as insulating material and placed inside a freezer (ca. -10°C) for one day. The deep red crystals were collected and stored under nitrogen. Important crystal and intensity data are listed in Table 6.
Table 4. Data for the X-ray Diffraction Study of 

\[ \text{(Cu)}_3\text{Fe(μ-PPh}_2\text{)}\text{Fe(Cu)}_2\text{(PPh}_2\text{C}_3\text{H}_5) \]

Crystal Parameters

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<td>b</td>
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<td>c</td>
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Measurements of Intensity Data

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Table 5. Data for the X-ray Diffraction Study of 
\[ [(\text{NO})_2\text{Fe}(\mu-\text{PPh}_2\text{PPh}_2)(\mu-\text{CH}_2)\text{Fe(NU)_2}] \]

**Crystal Parameters**

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<th>Value</th>
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**Measurements of Intensity Data**

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Table 6. Data for the X-ray Diffraction Study of [(NO)$_2$Fe(μ-PPh$_2$)(μ-CH$_2$PPh$_2$)Fe(NO)$_2$]

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<td>R(F)</td>
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<td>R$_w$(F)</td>
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III. RESULTS AND DISCUSSION

A. Preparation and Characterization of \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2\) and \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\)

1. \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2\)

The carbonyl neutral dimer, \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2\), contains an iron-iron single bond between two equivalent iron atoms. Each iron atom is bound to three terminal carbonyl ligands and two bridging \(\mu-\text{PPh}_2\) ligands. The \(\text{Fe}_2\text{P}_2\) core adopts a symmetrical but nonplanar arrangement to give a bent structure as shown below.\(^{92}\)
The dimer was first prepared by Thompson by reaction of iron pentacarbonyl and tetraphenylbiphosphine at 200°C (eq. 20), a reaction which cannot be conveniently performed on a large scale. Large scale preparation was made possible by Collman and co-workers by using Fe(CO)$_5$, Na$_2$Fe(CO)$_4$ and PPh$_2$Cl (eq. 3). In order to avoid the use of extremely air-sensitive Na$_2$Fe(CO)$_4$ and large quantity of silica gel in the purification process, another preparative method for this dimeric compound was desired. The method developed is illustrated in equations (59) and (60).

$$
2\text{Na} + 2\text{Fe(CO)}_5 \xrightarrow{25^\circ\text{C}, \text{THF}} \text{Na}_2\text{Fe}_2(\text{CO})_8 + 2\text{CO} \tag{59}
$$

$$
\text{Na}_2\text{Fe}_2(\text{CO})_8 + 2\text{PPh}_2\text{Cl} \xrightarrow{25^\circ\text{C}, \text{THF}} \text{Fe}_2(\nu\text{-PPh}_2)_2(\text{CO})_6 + 2\text{CO} + 2\text{NaCl} \tag{60}
$$

It is noteworthy that the entire reaction sequence may be carried out on a scale of tens of grams with approximately 50% yield and only small amount of alumina is needed for the purification of the product. The infrared spectra (Figure 2) of the complex in cyclohexane and THF display strong carbonyl stretching absorptions but slightly different patterns. The complex has good solubility in common organic solvents.

The $^{31}\text{P}^{(1\text{H})}$ NMR spectrum of the dimer shows a singlet at 142.6 ppm which is attributed to the two equivalent phos-
Figure 2. The Infrared Spectra of \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2\) in (A) THF and (B) Cyclohexane in the Region of 2100-1600 cm\(^{-1}\)
phorus atoms of the \( \mu\text{-PPh}_2 \) ligand bridging across the Fe-Fe bond.\(^{62}\)

A previous X-ray\(^{88}\) diffraction study of the complex showed that there are two different types of carbonyl ligands in the complex. Four carbonyl ligands are positioned trans to a phosphido-bridged ligand while the remaining two carbonyls are positioned trans to the metal-metal bond. However, the room temperature \(^{13}\)C NMR spectrum (Figure 3) of the complex exhibits only a triplet at 212.6 ppm which is assigned to the equivalent carbonyl ligands coupled to two equivalent bridging phosphorus atoms of the \( \mu\text{-PPh}_2 \) ligands. The spectrum is temperature invariant through the range of 25°C to -73°C. In a similar complex, \([\text{Fe(CO)}_3(\mu\text{-PMe}_2)]_2\), Cotton and Adams have shown that in the temperature range of -130°C to 150°C the two types of carbonyl ligands are magnetically nonequivalent and the molecule is stereochemically nonrigid.\(^{93}\) Probably the barrier to axial-basal carbonyl ligand exchange is lowered by the substitution of a methyl group with a phenyl group to the point that only a small extent of broadening is observed at -73°C.

2. \([\text{Fe(NO)}_2(\mu\text{-PPh}_2)]_2\)

The nitrosyl neutral dimer, \([\text{Fe(NO)}_2(\mu\text{-PPh}_2)]_2\), also contains an iron-iron bond between two equivalent iron atoms. Each iron atom is bound to two terminal nitrosyl ligands and two bridging \( \mu\text{-PPh}_2 \) ligands. In contrast to its
Figure 3. The $^{13}$C NMR Spectra of $[\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2$ (Carbonyl Region) at Different Temperatures
isoelectronic carbonyl complex, the Fe$_2$P$_2$ core of the nitro-syl neutral dimer adopts a planar arrangement.$^{94}$

The complex was first prepared by Hayter by reaction of [Fe(CO)$_2$(NO)$_2$] with tetraphenylbiphosphine in toluene under reflux conditions with 25% product yield.$^9$ A higher yield (60-70%) synthesis of the complex was provided by Hieber$^{31}$ by the reaction of [Fe(NO)$_2$X]$_2$ (X=Cl,Br) with KPPh$_2$ in THF (eq. 6). Since the product yields by the known methods are low, another preparative method for this complex was desired. The method developed is shown in equation (61). By the reaction of [Fe(NO)$_2$X]$_2$ (X=I,Br) with lithium diphenylphosphide, the product yield is about 90% based on
\[
\text{Fe(NO)}_2 \text{X} \text{Fe(NO)}_2 + \text{LiPPh}_2 \xrightarrow{\text{THF}} \text{Fe(NO)}_2 \text{Fe(NO)}_2
\]

\[X = \text{Br, I}\]

\[(\text{NO})_2 \text{Fe} \text{Fe(NO)}_2\] and the reaction conditions are very mild. The compound is insoluble in common organic solvents, but does dissolve to a small extent in THF. The compound is easily identified by mass spectrometry, which shows a parent ion at m/e 602 and three consecutive dissociations of a nitrosyl ligand. The \[^{31}\text{P}\{^{1}\text{H}\}]\) NMR spectrum of the dimer shows a singlet at 261.5 ppm which is assigned to the two equivalent phosphorus atoms of the \(\mu\)-PPh\(_2\) ligands bridging across the Fe-Fe bond.

**B. Reduction of [Fe(CO)\(_3\)(\(\mu\)-PPh\(_2\))]\(_2\)**

1. **Symmetrical Dianion, [Fe(CO)\(_3\)(\(\mu\)-PPh\(_2\))]\(_2\)^{2-}\)**

The reductive electrochemical behavior of [Fe(CO)\(_3\)-(\(\mu\)-PPh\(_2\))]\(_2\) has been reported by Collman and co-workers.\(^{62}\) Reductive cyclic voltammetry of the neutral dimer at a hanging mercury-drop electrode exhibits a single, two-electron, reversible reduction wave at -1.26V vs. the standard calomel electrode.

The chemical reduction of the neutral dimer was accomplished by treatment of the complex with sodium dispersion in tetrahydrofuran after overnight stirring, and the sodium salt of the symmetrical dianion, Na\(_2\)[Fe(CO)\(_3\)(\(\mu\)-PPh\(_2\))]\(_2\), was isolated as red-orange crystals (eq. 62).\(^{62}\)
It was found in this study that the symmetrical dianion, \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]^2^-\), can be conveniently prepared by the reaction of the neutral dimer with other reducing agents (eq. 62). Among these reducing agents, both \(\text{LiAlH}_4\) (1 M in THF solution) and Vitride (70% in toluene) provide the best results. The use of these two reagents enables a rapid, room temperature, one flask synthesis of the symmetrical dianion \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]^2^-\) to be achieved in near quantitative yield under homogeneous conditions. The solution changes color from yellow to deep brown immediately. However, the employment of potassium hydride and 1% Na/Hg as reducing agents gives results similar to sodium dispersion reduction. The problems involved with these heterogeneous metal reducing agents are mainly those of manipulation and handling. The yield is generally low and the reaction proceeds much slower (overnight stirring required) than that with homogeneous reducing agents.

As expected, the carbonyl stretching vibrations of these symmetrical dianion salts, \(M_2[\text{Fe(CO)}_3(\mu-\text{PPh}_2)]^2^-\) (\(M =\)
Li, Na, K), appear at lower frequencies (Table 7) than those of the neutral dimer. The infrared spectrum of Li$_2$[Fe(CO)$_3$(μ-PPh$_2$)]$_2$ is shown in Figure 4.

The $^{31}$P{¹H} NMR spectrum of Li$_2$[Fe(CO)$_3$(μ-PPh$_2$)]$_2$ shows a sharp singlet at δ -62.4 which is assigned to the phosphorus atoms of the two equivalent bridging μ-PPh$_2$ ligands (Figure 7). The $^{31}$P{¹H} NMR spectral data of the M$_2$[Fe(CO)$_3$(μ-PPh$_2$)]$_2$ complexes are listed in Table 7 for comparison. All of these symmetrical dianions with different counterions exhibit a sharp singlet around -60 ppm which is assigned to the two equivalent phosphorus atoms of the bridging μ-PPh$_2$ ligands. Evidently, the different counterions have little effect on the $^{31}$P NMR chemical shift values of the bridging μ-PPh$_2$ ligands of the symmetrical dianion [Fe(CO)$_3$(μ-PPh$_2$)]$_2^2^-$. These signals remain as singlets in the proton-coupled spectrum and are temperature invariant (-78°C to 25°C). The $^{31}$P{¹H} NMR resonances for the μ-PPh$_2$ ligands of [Fe(CO)$_3$(μ-PPh$_2$)]$_2^2-$ have shifted about 200 ppm upfield from the resonance of μ-PPh$_2$ ligands of [Fe(CO)$_3$(μ-PPh$_2$)]$_2$. Such dramatic change of the $^{31}$P NMR chemical shift gives a strong indication that the μ-PPh$_2$ groups of [Fe(CO)$_3$(μ-PPh$_2$)]$_2^2-$ are bridging non-interacting metals. As pointed out elsewhere, for bisphosphido-bridged iron, ruthenium, and osmium compounds, the $^{31}$P NMR chemical shift of the phosphorus atom of the μ-PPh$_2$ group may indeed be a useful spectroscopic criterion for
Figure 4. The Infrared Spectrum of Li$_2$[Fe(CO)$_3$(μ-PPh$_2$)]$_2$

as THF Solution in the Region of 2000-1600 cm$^{-1}$
### Table 7. Selected IR and $^{31}$P NMR Spectral Data for $M_2[\text{Fe(CO)}_3(\mu-P\text{Ph}_2)]_2$

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<th>$\delta\mu$-PPh$_2$, ppm*</th>
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*in THF solution at 25°C
determining the presence or absence of metal-metal interactions provided that the comparison is made within structurally related compounds.

The X-ray structure determination of Na$_2$[Fe(CO)$_3$-(μ-PPh$_2$)]$_2$ provides a supporting evidence for the absence of an Fe-Fe bond and adds further support to the proposal that $^{31}$P NMR chemical shifts may be used to detect the presence or absence of metal-metal bonds in phosphido-bridged complexes.

The non-bonding Fe--Fe distance in the dianion (3.630 (3)Å) is 1.01Å greater than the bonding Fe-Fe distance (2.623(3)Å) in [Fe(CO)$_3$(μ-PPh$_2$)]$_2$. In contrast to the folded arrangement of the Fe$_2$P$_2$ core in [Fe(CO)$_3$(μ-PPh$_2$)]$_2$, the Fe$_2$P$_2$ core of the symmetrical dianion [Fe(CO)$_3$(μ-PPh$_2$)]$_2^-2$ adopts a
planar arrangement. As expected, the Fe-P-Fe angle increases from 72.0° in the neutral dimer to 105.5° in the symmetrical dianion which reflects the breakage of the metal-metal bond.

The room temperature $^{13}$C NMR spectrum of Li$_2$[Fe(CO)$_3$($\mu$-PPh$_2$)]$_2$ shows a triplet at 299.6 ppm ($J_{P-C} = 5$ Hz). It is assigned to the terminal carbonyl ligands, which are equivalent. The spectrum is temperature invariant in the temperature range of -73°C to 30°C (Figure 5).

2. Monoanion [(CO)$_3$Fe(\(\mu\)-PPh$_2$)(\(\mu\)-CO)Fe(CO)$_2$(PPh$_2$H)]$^-$

In contrast to Collman's finding, reaction of [Fe(CO)$_3$($\mu$-PPh$_2$)]$_2$ with one equivalent of MBR$_3$H (M = Li, Na, K; R = Et, sec-Bu) in THF at room temperature proceeds instantly with color change from yellow-orange to deep red to afford a different anion (equation 63). The rate of these reduction reactions is temperature dependent. The reactions only proceed slowly at -24°C, and no reaction can be observed at -78°C. The monoanion is formulated as [(Cu)$_3$Fe(\(\mu\)-PPh$_2$)(\(\mu\)-Cu)Fe(CO)$_2$(PPh$_2$H)]$^-$ on the basis of its spectroscopic properties and chemical behavior.
Figure 5. The $^{13}\text{C}$ NMR Spectra of $\text{Li}_2[\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2$ (Carbonyl Region) in THF at Different Temperatures
Quantitative formation of these product monoanions was estimated from $^{31}P$ NMR spectral measurements. These monoanions are very air sensitive and react rapidly with oxygen to form $[{\text{Fe(CO)}}_3(\mu-\text{PPh}_2)]_2$. Removal of solvent always gave a dark red oil. All attempts to obtain solid samples of the product by treating THF solutions 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 various organic solvents such as ether, hexane, benzene or cyclohexane failed. However, a solid sample of this monoanion was obtained by the metathesis reaction 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 $(\text{Ph}_3\text{P})_2\text{NCl (PPNC1)}$ as shown in the following equation.

$$M^+(\text{CO})_3\text{Fe} \quad \text{Fe(CO)}_2 \quad + \quad (\text{Ph}_3\text{P})_2\text{NCl} \quad \text{THF} \quad \rightarrow \quad (\text{Ph}_2\text{P})^+(\text{CO})_3\text{Fe} \quad \text{Fe(CO)}_2 \quad + \quad \text{HPPh}_2$$

The $^{31}P$ NMR spectral data of these $M[{(\text{CO})_3\text{Fe(\mu-\text{PPh}_2})-(\mu-\text{CO})\text{Fe(CO)}_2(\text{PPh}_2\text{H})}]$ ($M = \text{Li, Na, K, PPN}$) complexes are presented in Table 8. Regardless of the different cations $M^+$, the $^{31}P\{^1\text{H}\}$ NMR spectra of these compounds exhibit a similar pattern: they all display a downfield doublet at about 120 ppm and an upfield doublet at about 50 ppm. For
Table 8. $^{31}P$ NMR Spectral Data of $M[[\text{Cu}]_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(CO)}_2(\text{PPh}_2\text{H})]$$^a$

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<td>Na$\text{B}(s-\text{Bu})_3\text{H}$</td>
<td>Na</td>
<td>126.4</td>
<td>50.7</td>
<td>11</td>
<td>336</td>
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<tr>
<td>KB$\text{B}(s-\text{Bu})_3\text{H}$</td>
<td>K</td>
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<td>52.1</td>
<td>10</td>
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<tr>
<td>PPN</td>
<td></td>
<td>129.8</td>
<td>56.3</td>
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<td>316</td>
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</tbody>
</table>

$^a$ in THF solution at 25°C

$^b$ ppm, relative to (MeO)$_3$P=O external standard, $\delta = 58.09$ Hz
Figure 6. The $^{31}$P NMR Spectrum of Li[$(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PPh}_2\text{H})$] in THF at Room Temperature.
example, the $^{31}P\{^1H\}$ NMR spectrum of Li[(CO)$_3$Fe(μ-PPh$_2$)-(μ-CO)Fe(CO)$_2$(PPh$_2$H)] (Figure 6) shows a doublet at 122.5 ppm and another doublet at 51.3 ppm with the coupling constant of 11 Hz. The downfield resonance is assigned to the phosphorus atom of the bridging μ-PPh$_2$ ligand, and its position implies that the ligand is bridging across two metals joined by a metal-metal bond. The upfield resonance is assigned to the phosphorus atom of the terminally coordinated PPh$_2$H ligand. Upon $^1$H coupling (Figure 6), the resonance at 51.3 ppm splits into a broad doublet with $J_{P-H} = 334$ Hz. This observed phosphorus-hydrogen coupling provides evidence for the existence of P-H bonding, and the value is comparable to the $J_{P-H}$ coupling in a similar neutral complex [(CO)$_3$Fe(μ-PPh$_2$)$_2$Fe(CO)$_2$(PPh$_2$H)] ($J_{P-H} = 360$ Hz). Typically, in substituted metal carbonyl compounds of secondary phosphines, the $J_{P-H}$ values are around 300-320 Hz. In order to prove that the reducing agents, MBR$_3$H, are the source of hydrogen eventually bonded to the phosphorus atom of the diphenylphosphine ligand, a deuterium-labeled experiment was performed. The reduction of [Fe(CO)$_3$(μ-PPh$_2$)]$_2$ was repeated with one equivalent of Super Deuteride, LiB$(\mathrm{Et}_3\mathrm{D})$, under identical reaction conditions as with LiB$(\mathrm{Et}_3\mathrm{H})$ (equation 65). The $^{31}P\{^1H\}$ NMR spectrum of the complex Li[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$D)] is shown in Figure 7. The downfield doublet at 122.5 ppm is assigned to the phosphorus atom of the bridging μ-PPh$_2$ ligand.
Figure 7. The $^{31}$P NMR Spectrum of Li[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$D)] in THF at Room Temperature.
The doublet originally present in the spectrum of Li[(CO)₃-Fe(μ-PPh₂)(μ-CO)Fe(CO)₂(PPh₂H)] (Figure 6) at 51.3 ppm is now observed as a triplet of doublets. The triplet is due to the phosphorus-deuterium coupling since deuterium has a spin equal to 1. The value of $J_{P-D}$ is equal to 51 Hz, and the ratio $J_{P-H}/J_{P-D}$ is equal to 6.55, which is very close to the gyromagnetic ratio $γ_H/γ_D$ of 6.51. The isotopic chemical shift $Δδ_{PD}$ calculated from the spectrum is 1.0 ppm, approximately equal to isotopic NMR shifts determined for other four-coordinate phosphorus atoms.

The coupling of the phosphorus atom of the terminally coordinated PPh₂H ligand to the phosphorus of the phosphido-bridge in the room temperature $^3$P{¹H} NMR spectra of these M[(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(CO)₂(PPh₂H)] complexes is relatively small, around 10 Hz. These small phosphine phosphide phosphorus phosphorus coupling constants suggest that the PPh₂H ligand is cis to the μ-PPh₂ ligand rather than trans. In a similar complex, [(CO)₃Fe(μ-PPh₂)₂-Fe(CO)₃(PPh₂H)], such cis arrangement of the PPh₂H ligand to the μ-PPh₂ ligand was also suggested based on the small value of the $J_{P-P}$ coupling constant ($J_{P-P} = 3$ Hz).
One noteworthy feature of the $^{31}\text{P}$ NMR spectra of $\text{M}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(\text{CO})}_2(\text{PPH}_2\text{H})]$ is their dependence on temperature. The limiting spectra were obtained around $-73^\circ\text{C}$ and do not significantly change on further cooling to $-83^\circ\text{C}$ (Table 9). For example, the low temperature limiting spectrum ($-73^\circ\text{C}$) of $\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(\text{CO})}_2(\text{PPH}_2\text{H})]$ shows one set of doublets centered at 128.5 ppm and 65.3 ppm ($J_{\text{P-P}} = 39 \text{ Hz}$), with another set of doublets centered at 124.8 ppm and 45.0 ppm ($J_{\text{P-P}} = 38 \text{ Hz}$). Details of this fluxional behavior will be discussed in a later section.

The $^{31}\text{P}[\text{H}]$ NMR spectra of $[\text{Fe(\text{CO})}_3(\mu-\text{PPh}_2)]_2$, $\text{Li}_2[\text{Fe(\text{CO})}_3(\mu-\text{PPh}_2)]_2$, and $\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(\text{CO})}_2(\text{PPH}_2\text{H})]$ are shown in Figure 8. As can be seen from these spectra, $^{31}\text{P}$ NMR spectroscopy can be quite useful in structural characterization of metal-metal-bonded complexes.

Infrared spectral data for $\text{M}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(\text{CO})}_2(\text{PPH}_2\text{H})]$ are summarized in Table 10. The infrared spectrum of $\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(\text{CO})}_2(\text{PPH}_2\text{H})]$ is
Table 9. Low Temperature $^{31}$P NMR Spectral Data for $\text{M}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(CO)}_2(\text{PPh}_2\text{H})]$\textsuperscript{a}

<table>
<thead>
<tr>
<th>Reducing Agent</th>
<th>M</th>
<th>$\delta(\mu-\text{PPh}_2)$\textsuperscript{b}</th>
<th>$\delta(\text{PPh}_2\text{H})$</th>
<th>$J_{P-P}$, Hz</th>
<th>$\delta(\mu-\text{PPh}_2)$</th>
<th>$\delta(\text{PPh}_2\text{H})$</th>
<th>$J_{P-P}$, Hz</th>
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<tr>
<td>LiBe$_3$H</td>
<td>Li</td>
<td>128.5</td>
<td>65.3</td>
<td>39</td>
<td>124.8</td>
<td>45.0</td>
<td>38</td>
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<tr>
<td>NaBe$_3$H</td>
<td>Na</td>
<td>133.6</td>
<td>65.2</td>
<td>39</td>
<td>128.5</td>
<td>46.1</td>
<td>39</td>
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<tr>
<td>KBe$_3$H</td>
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<td>62.0</td>
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<td>123.5</td>
<td>41.7</td>
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<td>LiB(s-Bu)$_3$H</td>
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<td>65.2</td>
<td>39</td>
<td>124.7</td>
<td>44.9</td>
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<tr>
<td>NaB(s-Bu)$_3$H</td>
<td>Na</td>
<td>133.5</td>
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<td>128.4</td>
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<td>39</td>
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<tr>
<td>K(B(s-Bu)$_3$H</td>
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<td>132.1</td>
<td>66.0</td>
<td>38</td>
<td>127.4</td>
<td>45.8</td>
<td>38</td>
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</tbody>
</table>

\textsuperscript{a}in THF at -78°C
\textsuperscript{b}ppm, relative to (MeO)$_3$P=O external standard, $\delta = 58.09$ Hz
Figure 8. The $^{31}$P NMR Spectra of Structurally Related Binuclear Iron Carbonyl Complexes
Figure 9. The Infrared Spectrum of Li[\((\text{Cu})_2\text{Fe}(\mu-\text{Cu})-(\mu-\text{PPh}_2)\text{Fe}(\text{CO})_2(\text{PPh}_2\text{H})]\) in THF in the 2000-1600 cm\(^{-1}\) Region.
Table 10. Infrared Carbonyl Stretching Frequencies of M\[\((\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{Cu})\text{Fe}(\text{Cu})_2(\text{PPh}_2\text{H})]\)^a

<table>
<thead>
<tr>
<th>Reducing Agent</th>
<th>Terminal Carbonyl, cm(^{-1})</th>
<th>Bridging Carbonyl cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li BET(_3)H</td>
<td>1992(s), 1941(s) 1905(s), 1887(s)</td>
<td>1645(m)</td>
</tr>
<tr>
<td>Li BET(_3)D</td>
<td>1994(s), 1940(s) 1905(s), 1890(s)</td>
<td>1648(m)</td>
</tr>
<tr>
<td>Li B(s-Bu(_3)H</td>
<td>1992(s), 1939(s) 1901(s), 1888(sh)</td>
<td>1645(m)</td>
</tr>
<tr>
<td>Na BET(_3)H</td>
<td>1986(s), 1933(s) 1890(s)</td>
<td>1669(m)</td>
</tr>
<tr>
<td>Na B(s-Bu(_3)H</td>
<td>1992(s), 1933(s) 1890(s)</td>
<td>1665(m)</td>
</tr>
<tr>
<td>K BET(_3)H</td>
<td>1983(s), 1932(s) 1900(s)</td>
<td>1672(m)</td>
</tr>
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</tr>
<tr>
<td>PPN</td>
<td>1990(s), 1940(s) 1900(s)</td>
<td>171U(m)</td>
</tr>
</tbody>
</table>

^a in THF solution at 25°C
illustrated in Figure 9. As expected, all of these infrared spectra exhibit absorption bands at nearly identical positions and with similar relative intensities in the region of 2000-1850 cm\(^{-1}\), a region characteristic of terminal metal carbonyl stretching vibrations. The values are shifted to lower energy when compared to those for \([\text{Fe} (\text{Cu})_3^- (\mu-\text{PPh}_2)]_2\). In addition, absorptions of medium intensity are observed in the region of 1750-1600 cm\(^{-1}\), a region characteristic of bridging metal carbonyl stretching vibrations.

The infrared spectra of the bridging carbonyl region of the lithium, sodium, potassium and PPN salts of \([(\text{Cu})_3^- \text{Fe}(\mu-\text{PPh}_2)(\mu-\text{Cu})\text{Fe}(\text{Cu})_2(\text{PPh}_2\text{H})]\)^- are illustrated in Figure 10. The position of these absorption bands in the bridging carbonyl region changes as a function of the cation \(M^+\). One of the possible interpretations of this behavior is that the oxygen atom of the bridging carbonyl ligand forms an ion pair with the cation \(M^+\) (eq. 66).

\[
\text{O} \quad \text{M}^+ \\
\text{Fe} \quad \text{Fe} + M^+ \quad \text{Fe} \quad \text{Fe}
\]

Therefore, the bridging carbonyl stretching frequencies decrease with reduction in the size of the cation \(M^+\). The smallest \(\text{Li}^+\) will form the strongest ion pair among the other cations \(M^+\) and indeed the \(v(\mu-\text{Cu})\) appears at the
Figure 10. The Infrared Spectra of $M[(CO)_3Fe(\mu-PPh_2)_2(\mu-CO)Fe(CO)_2(PPh_2H)]$ Complexes in THF in the 1600-1800 cm$^{-1}$ Region.
lowest frequency. In the case of the large PPN\(^+\) cation, ion pairing is expected to be absent. A band is seen at 1710 cm\(^{-1}\), which is the highest frequency among these cations.

Similar ion-pairing interaction is observed for anionic metal-acyl complexes,\(^6\)\(^2\),\(^9\)\(^9\) \(M[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)\text{Fe}(\text{CO})_2(\text{C(O)R})] \)

\((M = \text{Li}, \text{Na}, \text{PPN}; R = \text{Me, Ph}). Among these complexes, the lithium salt exhibits the lowest acetyl carbonyl stretching frequency (1545 cm\(^{-1}\)) compared to that for the sodium salt (1570 cm\(^{-1}\)) and the PPN\(^+\) salt (1587 cm\(^{-1}\)). In this case, experimental support of ion-pairing is provided by the X-ray structures of the sodium and PPN\(^+\) salts of the acetyl anions. The structure of sodium salt shows that the acetyl oxygen is strongly coordinated to the sodium ion, while no indications were found for the close contact of PPN\(^+\) ion with the acetyl oxygen. Another example of this ion-pairing trend was previously noted by Fischer and Kiener\(^1\)\(^0\)\(^0\) in the complexes \(M[\text{Fe(CO)}_4(\text{C(O)R})] \)

\((M = \text{Li, NMe}_4; R = \text{Me, Ph}). A lower acetyl carbonyl stretching frequency is reported for the lithium-containing complex than for the NMe\(^4\)+- containing complex.

Attempts at the preparation of solid samples of these \(M[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PPh}_2\text{H})] \)

complexes failed. Removal of THF solvent from the reaction mixture leaves a dark red oil, whereas addition of nonpolar organic solvents to the oil failed to initiate crystallization of the complexes. Thus, a clean \(^1\)H NMR spectra of these complexes
in the region of 0 to 6 ppm is not available at this moment due to the presence of the THF solvent residue peaks. The phenyl protons exhibit resonances at around 7.2 ppm, and no resonances can be observed downfield from 10 ppm to 20 ppm, which is the region characteristic for metal formyl resonances, or upfield from 0 ppm to -20 ppm, which is the region characteristic for metal hydride resonances.

Because of a difficulty in obtaining \(^1\text{H}\) NMR spectra, a D-NMR study was undertaken. The reaction of [Fe(CO)\textsubscript{3}-(\mu-PPh\textsubscript{2})]\textsubscript{2} with one equivalent of LiBEt\textsubscript{3}D in THF provides an unequivocal evidence for the formation of a terminally coordinated PPh\textsubscript{2}D ligand. The D-NMR spectrum of Li[(CO)\textsubscript{3}-Fe(\mu-PPh\textsubscript{2})(\mu-CO)Fe(CO)\textsubscript{2}(PPh\textsubscript{2}D)] is shown in Figure 11. The doublet centered at 6.3 ppm (\(J_{P-D} = 51\) Hz) is assigned to the D atom of the PPh\textsubscript{2}D ligand. The chemical shifts value falls in the normal range of coordinated secondary phosphines, and the phosphorus-deuterium coupling constant, \(J_{P-D}\), is identical with that obtained from the \(^{31}\text{P}\) NMR spectral measurement (Table 8).

The 47°C \(^{13}\text{C}\) NMR spectrum of \(^{13}\text{C}\)-enriched Li[(CO)\textsubscript{3}-Fe(\mu-PPh\textsubscript{2})(\mu-CO)Fe(CO)\textsubscript{2}(PPh\textsubscript{2}H)] exhibits a broad resonance at 234.4 ppm with no discernible coupling. The spectrum implies that at 47°C all the carbonyl sites exchange very rapidly and are equivalent on the NMR time scale. However, the -83°C \(^{13}\text{C}\) NMR spectrum of the complex displays a totally different pattern (Figure 12). It shows resonances at 295.3
Figure 11. The D-NMR spectrum of Li[(CU)₃Pe(μ-CU)(μ-PPh₂)Pe(CU)₂(PPh₂D)] in THF at Room Temperature.
Figure 12. The $^{13}$C NMR Spectrum of the CO Ligands of Li[(CO)$_3$Fe(μ-CO)(μ-PPh$_2$)Fe(CO)$_2$(PPh$_2$H)] in THF at $-83^\circ$C.
139-ppm (two doublets, $J_{C-P}(1) = 15$ Hz, $J_{C-P}(2) = 56$ Hz), 257.8 ppm (multiplet) and 222.3 ppm (multiplet). The resonances at 295.3 ppm are tentatively assigned to some type of bridging carbonyl ligand.

Since MBR₃H reducing agents are known to react with bimetallic complexes to give metal formyl complexes,¹⁰¹ special efforts were made to rule out the formation of metal formyl complexes in these reactions. The first evidence of the absence of C(U)H (formyl) group is derived from the proton and deuterium NMR spectra of the reduced species. Formyl complexes generally display $^1$H NMR resonance in the 12-17 ppm range,¹⁰¹ but no resonances can be observed in that range for the reduced species. The second evidence comes from the proton-coupled $^{13}$C NMR spectrum of Li[(CO)$_3$-Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$H)] at -83°C. No further splitting of the resonance at 295.7 ppm is observed that can be ascribed to proton coupling. Generally, a large one-bond coupling constant $J_{13C-H}$ (around 150 Hz) is observed for metal formyl complexes.¹⁰¹ The position of bridging carbonyl stretching frequencies of the reduced species provided the third evidence. Anionic and neutral metal-formyl complexes display $ν_{C=O}$ bands between 1530 and 1630 cm$^{-1}$, which are considerably lower than the observed $ν_{C=O}$ bands of M[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$H)] (1640-1710 cm$^{-1}$).¹⁰¹

A possible structure of the M[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)-Fe(CO)$_2$(PPh$_2$H)] complexes derived on the basis of the above
spectroscopic data and fulfilling the eighteen electrons requirement is tentatively assigned as follows.

One can count electrons around each iron atom in the following way: Fe(1) has eight electrons of its own, acquires six more from the three terminal CO groups, one from the bridging CO group, one from the metal-metal bond, one from the \( \mu^-\text{PPh}_2 \) ligand, and one from the negative charge; this gives it eighteen. Fe(2) has eight electrons of its own, plus four electrons from the two terminal CO groups, two from the \( \text{PPh}_2\text{H} \) ligand, one from the bridging CO ligand, one from the metal-metal bond, and two from the \( \mu^-\text{PPh}_2 \) ligand (neutral three-electron donor); this gives it a valence shell of eighteen electrons.

The proposed structure is somewhat speculative at present. Unambiguous characterization of the complex will require an X-ray crystal structure determination.
3. Mechanism of the Reduction of \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2\)

a. Metal-Metal Bond Cleavage

Dahl and co-workers have provided a systematic investigation of representative \([\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)_2]^{n-}\) \((n = 0, 1, 2)\) species via the nonparametrized Fenske-Hall molecular orbital model. These calculations indicated that (1) the HOMO in each neutral species corresponds to the "bent" Fe-Fe bond, and (2) the LUMO is of predominantly anti-bonding diiron character. Therefore, cleavage of the Fe-Fe bond upon addition of two electrons to \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2\) as described in equation 67 is understandable.

\[
\begin{align*}
\text{(CO)}_3\text{Fe} & \quad \quad \text{Fe(CO)}_3 + 2e^- \quad \longrightarrow \quad \text{(CO)}_3\text{Fe} \\
\text{Ph}_2\text{P}_2 & \quad \quad \quad \text{Ph}_2\text{P}_2
\end{align*}
\]

Upon cleavage of Fe-Fe bond, the folded arrangement of the \(\text{Fe}_2\text{P}_2\) core in \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2\) changes to the planar arrangement in \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2^{2-}\). As pointed out by Burdett in his extended Hückel MO calculations, this geometrical change is necessary to reduce the electron repulsion between the iron atoms.

b. Metal-Phosphorus Bond Cleavage

In contrast to the 2e- reduction of the Fe-Fe bond, reactions of \([\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2\) with one equivalent of a \(\text{MBR}_3\text{H}\) reducing agent lead to the cleavage of an iron-phosphorus bond of one phosphido-bridge.

The reduction may proceed by attack of \(\text{H}^-\) at an Fe-bonded carbonyl ligand with \(\text{BH}_3\) group becoming coordinated.
to the oxygen of the carbonyl ligand. The H\textsuperscript{-} will then migrate from the so formed formyl ligand of the resultant complex to another iron atom with elimination of the BR\textsubscript{3} ligand. Reductive elimination of μ-PPh\textsubscript{2} and H from Fe as PPh\textsubscript{2}H followed by rearrangement gives the M[(CO)\textsubscript{3}Fe(μ-PPh\textsubscript{2})(μ-CO)Fe(CO)\textsubscript{2}(PPh\textsubscript{2}H)] product. The reduction mechanism is summarized in Scheme I. It is speculative at the present time.

Since MBR\textsubscript{3}H reducing agents are known to react with bimetallic complexes to give metal formyl complexes\textsuperscript{101} the first step of the reduction is proposed to be the formation of a metal-formyl species. The role that the trialkyl borane plays in this reaction is not clear. However, since these compounds are good Lewis acids, BR\textsubscript{3} might be expected to coordinate to the oxygen of the carbonyl ligand to stabilize the formyl group.

Reagents such as LiAlH\textsubscript{4} and KH are not effective for the synthesis of formyl complexes\textsuperscript{103} Reactions of these types of reducing agent with some metal carbonyls are not very rapid and any formyl intermediates are likely to decompose faster than they form. This may explain why reduction of [Fe(CO)\textsubscript{3}(μ-PPh\textsubscript{2})\textsubscript{2}] with LiAlH\textsubscript{4}, KH, or Vitride only leads to the cleavage of the metal-metal bond\textsuperscript{103}

The second step of the mechanism is suggested to involve the decomposition of the formyl complex to form the metal hydride with the cleavage of the metal-metal bond. This kind of decomposition pattern is generally observed for formyl complexes\textsuperscript{104,105} For example, it has been reported
Scheme 1

\[
\begin{align*}
&(\text{CO})_3\text{Fe} \quad \text{Fe(\text{CO})_3} \\
\xrightarrow{\text{BR}_3\text{H}^-} \quad &\text{Fe(\text{CO})}_2
\end{align*}
\]

\[
\begin{align*}
&(\text{CO})_3\text{Fe} \quad \text{Fe(\text{CO})}_2
\xrightarrow{-\text{BR}_3} \quad &\text{Fe(\text{CO})}_3
\end{align*}
\]

\[
\begin{align*}
&(\text{CO})_3\text{Fe} \quad \text{Fe(\text{CO})}_3
\xrightarrow{\text{ph}_2\text{P}} \quad &\text{Fe(\text{CO})}_3
\end{align*}
\]

\[
\begin{align*}
&(\text{CO})_3\text{Fe} \quad \text{Fe(\text{CO})}_2
\xrightarrow{\text{Br}_3\text{H}^-} \quad &\text{Fe(\text{CO})}_2
\end{align*}
\]

\[
\begin{align*}
&(\text{CO})_3\text{Fe} \quad \text{Fe(\text{CO})}_2
\xrightarrow{-\text{BR}_3} \quad &\text{Fe(\text{CO})}_3
\end{align*}
\]

\[
\begin{align*}
&(\text{CO})_3\text{Fe} \quad \text{Fe(\text{CO})}_3
\xrightarrow{\text{ph}_2\text{P}} \quad &\text{Fe(\text{CO})}_3
\end{align*}
\]

\[
\begin{align*}
&(\text{CO})_3\text{Fe} \quad \text{Fe(\text{CO})}_2
\xrightarrow{\text{Br}_3\text{H}^-} \quad &\text{Fe(\text{CO})}_2
\end{align*}
\]
that \([\text{Fe(CO)}_3\text{(P(OPh)_3)}\text{CO}H]\text{N(Et)_4}\) underwent ligand dissociation followed by rapid hydride migration to the metal (equation 68).

\[
\begin{align*}
\text{(CO)}_3\text{(PhO)}_3\text{PF}_{\text{C}}&\rightarrow \text{Fe(CO)}_4H^+ + \text{P(OPh)}_3
\end{align*}
\]

(68)

The cleavage of the metal-metal bond here probably has the same effect as ligand dissociation in the above case.

Reductive elimination of \(\mu\text{-PPh}_2\) and hydride from \(\text{Fe(2)}\) as \(\text{PPh}_2\text{H}\) ligand bound to \(\text{Fe(1)}\) lead to the formation of a \(16e^-\) coordinatively unsaturated \(\text{Fe(2)}\). Rearrangement of this unstable intermediate to form a metal-metal bond and a bridging carbonyl ligand will provide both iron atoms with an \(18e^-\) valence shell. The \(\mu\text{-CO}\) and \(\mu\text{-PPh}_2\) ligands in \(\text{M}[(\text{Cu})_3\text{Fe(\mu-PPh}_2)\text{(\mu-CO)Fe(CO)}_2\text{(PPh}_2\text{H})]\) probably assume a bent arrangement, since a planar arrangement would most likely lead to cleavage of the metal-metal bond.

C. Unsymmetrical Dianion, \([(\text{Cu})_3\text{Fe(\mu-PPh}_2)\text{-} \\
(\mu-\text{Cu})\text{Fe(Cu)}_2\text{(PPh}_2)]^{2-}\), and its Conversion to

\([\text{Fe(Cu)}_3\text{(\mu-PPh}_2)]^{2-}\)

1. Preparation of \([(\text{Cu})_3\text{Fe(\mu-PPh}_2)(\mu-\text{CO})\text{Fe(CO)}_2\text{-} \\
(\text{PPh}_2)]^{2-}\)

At \(-78^\circ\text{C}\), the addition of one equivalent of \(\text{n-BuLi}\) to a \(\text{THF}\) solution of \(\text{Li}[(\text{Cu})_3\text{Fe(\mu-PPh}_2)(\mu-\text{Cu})\text{Fe(CO)}_2\text{(PPh}_2\text{H})]\)
leads to the formation of \(\text{Li}_2[(\text{Cu})_3\text{Fe(\mu-PPh}_2)(\mu-\text{Cu})\text{Fe(CO)}_2\text{-} \\
(\text{PPh}_2)]\) in nearly quantitative yield (equation 69).
The deep orange red solution of the monoanion changed color immediately to dark purple. The $-73^\circ C$ $^{31}P\{^1H\}$ NMR spectrum of $\text{Li}_2[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PPh}_2)]$ is shown in the bottom of Figure 13. The spectrum consists of a doublet at 136.8 ppm and another doublet at 20.7 ppm with $J_{p-p} = 4$ Hz. Upon proton coupling, the $^{31}P$ NMR spectrum remains the same and no phosphorus-hydrogen coupling can be observed. The resonance at 136.8 ppm is assigned to the phosphorus atom of the bridging $\mu$-PPh$_2$ ligand and is in the region observed for $\mu$-PPh$_2$ ligand bridging across a metal-metal bond. The resonance at 20.7 ppm is assigned to the phosphorus atom of the PPh$_2$ ligand terminally attached to Fe. As expected, the chemical shift value of the $\mu$-PPh$_2$ ligand is ~20 ppm upfield compared with its precursor. A similar upfield shift of the $^{31}P$ NMR resonance has been observed in the preparation of Li[Fe(CO)$_4$(PPh$_2$)] from [Fe(CO)$_4$(PPh$_2$)$_2$] and n-BuLi (Table 11).

The $-73^\circ C$ $^{13}C$ NMR spectrum of $\text{Li}_2[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)-(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PPh}_2)]$ is shown in the bottom of Figure 14. The resonance at 225.1 ppm (broad doublet, $J_{p-C} = 4$ Hz) is assigned to the carbonyl ligands. Since the limiting $^{13}C$ NMR spectrum of this species is unavailable at the present time, unambiguous assignment to the resonance at 254 ppm.
Figure 13. Variable Temperature $^{31}$P $^{1}$H NMR Spectra for the Conversion of $\text{Li}_2[(\text{Cu})_3\text{Fe}(\mu-\text{CO})(\mu-\text{PPh}_2)\text{Fe}(\text{CO})_2(\text{PPh}_2)]$ to $\text{Li}_2[\text{Fe}(\text{CO})_3(\mu-\text{PPh}_2)]_2$. Peaks Labeled "U" and "S" belong to $\text{Li}_2[(\text{Cu})_3\text{Fe}(\mu-\text{CO})(\mu-\text{PPh}_2)\text{Fe}(\text{CO})_2(\text{PPh}_2)]$ and $\text{Li}_2[\text{Fe}(\text{CO})_3(\mu-\text{PPh}_2)]_2$, Respectively.
Figure 13.
Figure 14. Variable Temperature $^{13}$C NMR Spectra of the CO Ligands for the Conversion of $\text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{CO})(\mu-\text{PPh}_2\text{Fe}(\text{CO})_2(\text{PPh}_2))]$ to $\text{Li}_2[\text{Fe}(\text{CO})_3(\mu-\text{PPh}_2)_2]$. Peaks Labeled "U" and "S" belong to $\text{Li}_2[(\text{CO})_3\text{Fe}(\mu-\text{CO})(\mu-\text{PPh}_2)\text{Fe}(\text{CO})_2(\text{PPh}_2)]$ and $\text{Li}_2[\text{Fe}(\text{CO})_3(\mu-\text{PPh}_2)]_2$, Respectively.
Figure 14.
(broad multiplet) is not possible. However, the assignment of this broad resonance to the terminal carbonyl ligand is probably correct. At present, infrared spectrum of the complex is not available and efforts will be made to obtain the spectrum at low temperature.

The proposed structure is based on the above spectral data and is speculative at present. Full characterization of the complex would require X-ray crystal structure determination, if possible, since the spectroscopic data are insufficient.

\[
\text{Secondary phosphines are known to be readily metalated by alkali metals or by n-BuLi to form alkali metal phosphides.}^{106} \text{ However, only a few transition metal complexes containing terminal organophosphide ligand (PR}_2^-) \text{ have been thoroughly investigated. Some examples are illustrated as follows.}^{8,37}
\]

\[
\text{Fe(CO)}_4\text{PPh}_2\text{H} + \text{n-BuLi} + \text{Li[Fe(CO)}_4\text{PPh}_2]\]

(70)
These anions are generally very reactive, and a wide range of metal phosphine complexes can be prepared by using them as starting materials.\textsuperscript{8,107}

While this dissertation was in preparation, it was learned that a bimetallic iron carbonyl complex with linked phosphido-bridge ligand was used to generate a dianionic species analogous to the unsymmetrical dianion prepared in this study.\textsuperscript{108}

The linking of the two phosphido groups by a phenylene bridge provides a geometric constraint which prevents the \( \text{Fe}_2\text{P}_2 \) core from becoming planar, and therefore no \( \text{Fe}-\text{Fe} \) bond cleavage occurs. The other noteworthy feature is the formation of a bridging carbonyl ligand upon reduction. The \( ^{31}\text{P} \) NMR chemical shift data of these anionic complexes with
Table 11. $^{31}$P NMR Spectral Data for \( \mu\text{-PPh}_2 \) and \( \text{PPh}_2 \) Ligands\(^a\) in Some Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \delta_{\mu\text{-PPh}_2} )</th>
<th>( \delta_{(\text{PPh}_2\text{H})} )</th>
<th>( \delta_{(\text{PPh}_2)} )</th>
<th>( J_{\mu-\mu, \text{Hz}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe(CO)}_4\text{PPh}_2\text{H} )</td>
<td></td>
<td></td>
<td>39.1</td>
<td></td>
</tr>
<tr>
<td>( \text{Li}[\text{Fe(CO)}_4\text{PPh}_2\text{H}] )</td>
<td></td>
<td></td>
<td>-3.8</td>
<td></td>
</tr>
<tr>
<td>( \text{Li}[(\text{CO})_3\text{Fe(\mu-PPh}_2)\text{Fe(CO)}_2(\text{PPh}_2\text{H})] )</td>
<td>122.5</td>
<td>52.3</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>( \text{Li}_2[(\text{CO})_3\text{Fe(\mu-PPh}_2)\text{Fe(CO)}_2(\text{PPh}_2)] )</td>
<td>136.8</td>
<td>20.7</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>( \text{Li(NO)}_2\text{Fe(\mu-NO)(\mu-PPh}_2)\text{Fe(NO)(PPh}_2\text{H})] )</td>
<td>164.6</td>
<td>43.4</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>( \text{Li}_2[(\text{NO})_2\text{Fe(\mu-NO)(\mu-PPh}_2)\text{Fe(NO)(PPh}_2)] )</td>
<td>159.6</td>
<td>20.5</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

\[\text{Na} \quad \begin{array}{c}
\begin{array}{c}
\text{Ph}
\end{array}
\end{array} \quad \begin{array}{c}
\begin{array}{c}
\text{Fe(CO)}_3
\end{array}
\end{array} \quad \begin{array}{c}
\begin{array}{c}
\text{Ph}
\end{array}
\end{array} \quad \begin{array}{c}
\begin{array}{c}
\text{Ph}
\end{array}
\end{array}
\] \[202.4 \quad 57.0 \quad 31 \quad \text{major}\]

\[\text{Na}_2 \quad \begin{array}{c}
\begin{array}{c}
\text{Ph}
\end{array} \quad \begin{array}{c}
\begin{array}{c}
\text{Fe(CO)}_3
\end{array}
\end{array} \quad \begin{array}{c}
\begin{array}{c}
\text{Ph}
\end{array}
\end{array} \quad \begin{array}{c}
\begin{array}{c}
\text{Ph}
\end{array}
\end{array}
\] \[193.5 \quad 32.1 \quad 4 \quad \text{minor}\]

\(^a\)ppm.
terminal phosphido ligands and their neutral precursors are listed in Table 11 for comparison.

2. Conversion of \([(CO)_{3}\text{Fe}(\mu-\text{PPh}_2)-(\mu-\text{Cu}\text{)}\text{Fe}(\text{CO})_2(\text{PPh}_2)]\) and \([(CO)_{3}\text{Fe}(\mu-\text{PPh}_2)-(\mu-\text{Cu}\text{)}\text{Fe}(\text{CO})_2(\text{PPh}_2)]\) to \([\text{Fe}(\text{Cu})_3(\mu-\text{PPh}_2)]_2\)

As discussed earlier, the complex \(\text{Li}_2[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)-(\mu-\text{Cu}\text{)}\text{Fe}(\text{CO})_2(\text{PPh}_2)]\) is thermally unstable. The complex was prepared at \(-78^\circ\text{C}\), and when the temperature is raised to \(-33^\circ\text{C}\) the complex quantitatively converts to \(\text{Li}_2[\text{Fe}(\text{Cu})_3(\mu-\text{PPh}_2)]_2\) as shown in the following equation.

\[
\begin{align*}
(CO)_3Fe & \quad \frac{2-}{(CO)FeCO} \quad \text{at } T>30^\circ\text{C} \quad \frac{2-}{(CO)FeCO} \\
\text{Ph}_2 & \quad \text{Ph}_2 & \quad \text{Ph}_2 & \quad \text{Ph}_2
\end{align*}
\]

This conversion was monitored by \(^{31}\text{P}[^{1}\text{H}]\) and \(^{13}\text{C}\) NMR measurements and the spectra are shown in Figures 13 and 14, respectively.

The addition of excess \(\text{MBR}_3\text{H}\) (second equivalent) to a THF solution of \(\text{M}[(CO)_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{Cu}\text{)}\text{Fe}(\text{CO})_2(\text{PPh}_2\text{H})]\) also results in its conversion to \(\text{M}_2[\text{Fe}(\text{Cu})_3(\mu-\text{PPh}_2)]_2\). However, the extent of this conversion depends largely on the cation \(\text{M}^+\) and temperature. The percentage of \(\text{M}_2[\text{Fe}(\text{Cu})_3(\mu-\text{PPh}_2)]_2\) in the reaction mixtures is estimated from \(^{31}\text{P}\) NMR spectral measurements and the results are listed in Table 12. Evidently, at room temperature, only a small amount of \(\text{M}[(CO)_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{Cu}\text{)}\text{Fe}(\text{CO})_2(\text{PPh}_2\text{H})]\) has been converted. However, when the solution was heated in THF at reflux for two
Table 12. Conversion of $M[(CO)_3Fe(\mu-PPh_2)(\mu-CO)Fe(CO)_2(PPh_2H)]$ to $M_2[Fe(CO)_3(\mu-PPh_2)]_2$

<table>
<thead>
<tr>
<th>Reducing Agent</th>
<th>$% \text{ of } M_2[Fe(CO)_3(\mu-PPh_2)]_2^a$</th>
<th>$25^\circ C$</th>
<th>$65^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBEt$_3$H</td>
<td>0</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>NaBEt$_3$H</td>
<td>8.3</td>
<td>60.7</td>
<td></td>
</tr>
<tr>
<td>KBEt$_3$H</td>
<td>6.3</td>
<td>65.3</td>
<td></td>
</tr>
<tr>
<td>LiB(s-Bu)$_3$H</td>
<td>0</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>NaB(s-Bu)$_3$H</td>
<td>5.4</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>KB(s-Bu)$_3$H</td>
<td>19.7</td>
<td>99</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Estimated from $^{31}$P NMR Spectrum of the Reaction Mixture
minutes, the amount of conversion increased dramatically in
the case of the Na\(^+\) and K\(^+\) salts. This result indicates
that ion-pairing plays an important role in the stability of
\(M[(\text{Cu}_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{Cu})\text{Fe}(\text{Cu})_2(\text{PPh}_2H))]\). However, addition
of a third equivalent of a MBK\(_3\)H reagent and overnight stir­
ring resulted in total conversion to \(M_2[\text{Fe}(\text{Cu})_3(\mu-\text{PPh}_2)]\)_2
with evolution of dihydrogen gas (\(M = \text{Li}, R = \text{Et}\)).

D. Reduction of \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\)

1. Symmetrical Dianion, \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\)\(^2^-\)

The reductive electrochemical behavior of \([\text{Fe(NO)}_2-
(\mu-\text{PPh}_2)]_2\) has been reported by Dessy and co-workers.\(^{109}\)
The reduction involves two successive one electron steps to
give a radical anion and dianion, respectively.

\[
\begin{align*}
\text{(NO)}_2\text{Fe} & \rightarrow \text{Fe(NO)}_2^- \rightarrow \text{Fe(NO)}_2(\mu-\text{PPh}_2)^2^- \rightarrow \text{Fe(NO)}_2(\mu-\text{PPh}_2)^2^- \\
\end{align*}
\]

(74)

The chemical reduction of \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\) was con­
ducted in a similar way as that of its isoelectronic complex
\([\text{Fe}(\text{Cu})_3(\mu-\text{PPh}_2)]_2\). Treatment of the complex with LiAlH\(_4\)
(THF solution) enables a rapid, room temperature, one flask
preparation of \(\text{Li}_2[\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\) to be achieved in near
quantitative yield (equation 75). The employment of sodium
dispersion and sodium amalgam gives similar results as
LiAlH\(_4\), but long reaction time is required for these two
heterogeneous metal reducing agents.
The $^{31}$P{$^1$H} NMR spectrum of Li$_2$(Fe(NO)$_2$(μ-PPh$_2$))$_2$ shows a sharp singlet at -34.6 ppm which is assigned to the phosphorus atoms of the two equivalent bridging μ-PPh$_2$ ligands. The $^{31}$P{$^1$H} NMR spectral data of M$_2$(Fe(NO)$_2$(μ-PPh$_2$))$_2$ (M = Li, Na) are listed in Table 13. All of these M$_2$(Fe(NO)$_2$(μ-PPh$_2$))$_2$ complexes exhibit a sharp singlet around -35 ppm. The highfield chemical shift values imply that the two equivalent μ-PPh$_2$ ligands are now bridging across two iron atoms with no metal-metal interaction. The $^{31}$P NMR spectra of these complexes remain unchanged after the broadband $^1$H decoupling is eliminated and are temperature invariant in the range of -73°C to 30°C.

The IR spectra of these M$_2$(Fe(NO)$_2$(μ-PPh$_2$))$_2$ complexes show a strong broad nitrosyl stretching absorption around 1670 cm$^{-1}$ with unsymmetrical shape. These compounds have a D$_{2h}$ symmetry. They are predicted to show two infrared active fundamentals in the NO stretching region corresponding to the modes B$_{2u}$ and B$_{3u}$. Contrary to the prediction of two bands in the NO stretching region, only one broad band is observed in this work. This may be due to an overlap of the two peaks.
Table 13. $^{31}P$ NMR Spectral Data of Anionic Binuclear Iron Nitrosyl Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta$(PPh$_2$H)$_b$</th>
<th>$\delta$(PPh$_2$H)</th>
<th>$J_{P-P}$, Hz</th>
<th>$J_{P-H}$, Hz</th>
<th>$(D)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Li}_2[\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2$</td>
<td>-34.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Na}_2[\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2$</td>
<td>-32.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Li}[(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)-\text{Fe(NO)}(\text{PPh}_2H)]$</td>
<td>164.6</td>
<td>43.4</td>
<td>20</td>
<td>338</td>
<td></td>
</tr>
<tr>
<td>$\text{Li}[(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)-\text{Fe(NO)}(\text{PPh}_2D)]$</td>
<td>164.0</td>
<td>42.2</td>
<td>20</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>$\text{Na}[(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)-\text{Fe(NO)}(\text{PPh}_2H)]$</td>
<td>161.4</td>
<td>44.0</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{K}[(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)-\text{Fe(NO)}(\text{PPh}_2H)]$</td>
<td>161.5</td>
<td>43.3</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Li}_2[(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)-\text{Fe(NO)}(\text{PPh}_2)]$</td>
<td>159.6</td>
<td>20.5</td>
<td>50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ in THF solution at 25°C  
$^b$ ppm
2. Monoanion, [(NO)₂Fe(µ-PPH₂)(µ-NO)Fe(NO)(PPh₂H)]⁻

The complex [Fe(NO)₂(µ-PPH₂)]₂ reacts with MB₃H to give products that are similar to the products obtained from the reaction of [Fe(CO)₃(µ-PPH₂)]₂ with MBR₃H. Treatment of [Fe(NO)₂(µ-PPH₂)]₂ in THF with one equivalent of MB₃H (M = Li, Na, K) causes a change from red suspension to dark brown solution over a ten minute period. The resulting product is formulated as M[(NO)₂Fe(µ-PPH₂)(µ-NO)Fe(NO)(PPh₂H)] on the basis of its spectroscopic data and similarity to the isoelectronic complex M[(CO)₃Fe(µ-PPH₂)(µ-CO)Fe(CO)]₂-

\[
\begin{align*}
\text{Li} & \quad \begin{array}{c}
\text{Ph}_2 \\
\text{P}
\end{array} \\
\text{Fe(NO)}_2 + \text{MBE}_3\text{H} & \rightarrow \text{THF} \\
\text{Li} & \quad \begin{array}{c}
\text{Ph}_2 \\
\text{P}
\end{array} \\
\text{Fe(NO)(PPh}_2\text{H}) & \quad \text{Li} \\
\text{NO} & \quad \text{N}
\end{align*}
\]

M = Li, Na, K

These complexes, M[(NO)₂Fe(µ-PPH₂)(µ-NO)Fe(NO)(PPh₂H)], are very air sensitive and convert to [Fe(NO)₂(µ-PPH₂)]₂ upon exposure to air. Attempts to obtain solid samples by the metathesis reaction of Li[(NO)₂Fe(µ-PPH₂)(µ-NO)Fe(NO)-(PPh₂H)] with (Ph₃P)₂NCl failed. No resonances besides that due to PPh₃ were found in the \(^{31}\text{P}\{^1\text{H}\} \) NMR spectrum of the solid product.

Quantitative formation of these product monoanions was estimated from \(^{31}\text{P}\{^1\text{H}\} \) NMR spectral measurements. The \(^{31}\text{P}\{^1\text{H}\} \) NMR spectral data are summarized in Table 13. The \(^{31}\text{P}\{^1\text{H}\} \) and \(^{31}\text{P} \) NMR spectra of Li[(NO)₂Fe(µ-PPH₂)⁻
(μ-NO)Fe(NO)(PPh₂H)} in THF at room temperature are shown in Figure 15. However, in contrast to the close resemblance of this $^{31}\text{P}[^1\text{H}]$ NMR spectrum to that of Li[((CO)$_3$Fe(μ-PPh$_2$)-(μ-CO)Fe(CO)$_2$(PPh$_2$H)], the former spectrum is temperature invariant. Basically, these spectra consist of a doublet at about 160 ppm and another doublet around 40 ppm with a phosphorus-phosphorus coupling constant of 20 Hz (similar to that in M[((CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$H)]). The downfield resonance is assigned to the phosphorus atom of the bridging μ-PPh$_2$ ligand, and its position implies that the μ-PPh$_2$ ligand is bridging across two iron atoms joined by a metal-metal bond. The upfield resonance is assigned to the phosphorus atom of the terminally coordinated PPh$_2$H ligand, and the chemical shift values are in the normal range for metal-coordinated phosphine. When the broad band proton decoupling is eliminated, the doublet at high field is further split by over 340 Hz; this indicates that the high field resonance centered at 40 ppm is that of the PPh$_2$H ligand. The large increase in $^1J_{P-H}$ on coordination of the PPh$_2$H ligand (204 Hz in free ligand) to metal has also been observed in the case of M[((CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$H)] ($^1J_{P-H} \approx 330$ Hz).

The reduction of [Fe(NO)$_2$(μ-PPh$_2$)]$_2$ with LiBH$_3$ has also been executed (equation 77). The $^{31}\text{P}[^1\text{H}]$ NMR spectrum
Figure 15. The $^{31}$P NMR Spectrum of Li[$\text{NO}_2\text{Fe(μ-PPh}_2\text{)(μ-NO)Fe(NO)(PPh}_2\text{H)}$] in THF at Room Temperature
of the deuterium labeled complex, Li[(NO)$_2$Fe($\mu$-PPh$_2$)($\mu$-NO)-Fe(NO)PPh$_2$D], is shown in Figure 16. The highfield resonance at 42.2 ppm is now split into three doublets of 1:1:1 intensity by deuterium ($I=1$). The phosphorus-deuterium coupling constant is 50 Hz, which is very close to the $\nu$-D coupling constant in Li[(CO)$_3$Fe($\mu$-PPh$_2$)($\mu$-CO)Fe(CO)$_2$PPh$_2$D], $\nu_{P-D} = 51$ Hz. The ratio $\nu_{P-H}/\nu_{P-D}$ is equal to 6.76, which is very close to the gyromagnetic ratio $\nu_H/\nu_D$ of 6.51.$^95$

Infrared spectral data for M[(NO)$_2$Fe($\mu$-PPh$_2$)($\mu$-NO)-Fe(NO)(PPh$_2$H)] are summarized in Table 14. The infrared spectrum of Li[(NO)$_2$Fe($\mu$-PPh$_2$)($\mu$-NO)Fe(NO)(PPh$_2$H)] is displayed in Figure 17. These IR spectra all exhibit two absorption bands in the region of 1650-1700 cm$^{-1}$ and are nearly identical with respect to position and relative intensity. In addition, absorptions with weak intensity are observed in the region around 1420 cm$^{-1}$, which can probably be assigned to the bridging nitrosyl stretching vibrations. The positions of these absorptions are also affected by the cation of the complex. The smallest Li$^+$ cation forms the strongest ion pair with the oxygen of the bridging nitrosyl ligand and exhibits the lowest $\nu$(NO) frequency. A D-NMR study of the reaction of [Fe(NO)$_2$($\mu$-PPh$_2$)$_2$] with one equivalent of LiBEt$_3$D in THF solution provides supporting evidence for the formation of the PPh$_2$D ligand. The D-NMR spectrum of Li[(NO)$_2$Fe($\mu$-PPh$_2$)-
Figure 16. The $^{31}$P NMR Spectrum of Li[(NO)$_2$Fe($\mu$-NO)(\(\mu\)-PPh$_2$)Fe(NO)-(PPh$_2$D)] in THF at Room Temperature.
Table 14. Infrared Spectral Data of

\[ \text{M}[(\text{NO})_2 \text{Fe(\mu-NU)(\mu-PPh}_2)\text{Fe(NU)(PPh}_2\text{H})] \]

and \( \text{M}_2[\text{Fe(NU)}_2(\mu-PPh_2)]_2 \)\(^a\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \nu(\text{NU}), \text{ cm}^{-1} )</th>
<th>( \nu(\mu-\text{NU}), \text{ cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Li}_2[\text{Fe(NU)}_2(\mu-PPh}_2)]_2 )</td>
<td>1673(s,broad)</td>
<td></td>
</tr>
<tr>
<td>( \text{Na}_2[\text{Fe(NU)}_2(\mu-PPh}_2)]_2 )</td>
<td>1672(s,broad)</td>
<td></td>
</tr>
<tr>
<td>( \text{Li}[(\text{NO})_2 \text{Fe(\mu-NU)(\mu-PPh}_2)-\text{Fe(NU)(PPh}_2\text{H})] )</td>
<td>1704(m), 1660(s)</td>
<td>1420(w)</td>
</tr>
<tr>
<td>( \text{Na}[(\text{NO})_2 \text{Fe(\mu-NU)(\mu-PPh}_2)-\text{Fe(NU)(PPh}_2\text{H})] )</td>
<td>1696(s), 1656(s)</td>
<td>1435(w)</td>
</tr>
<tr>
<td>( \text{K}[(\text{NO})_2 \text{Fe(\mu-NU)(\mu-PPh}_2)-\text{Fe(NU)(PPh}_2\text{H})] )</td>
<td>1696(m), 1660(s)</td>
<td>1435(w)</td>
</tr>
</tbody>
</table>

\(^a\)in THF solution at 25°C
Figure 17. The Infrared Spectrum of Li[(NO)$_2$Fe(μ-PPh$_2$)$_2$-
(μ-NO)Fe(NO)(PPh$_2$H)] in THF in the Region of
1800-1400 cm$^{-1}$.
(μ-NO)Fe(NO)PPh₂D] is shown in Figure 18. The doublet centered at 6.0 ppm is assigned to the deuterium bonded to phosphorus (Jp-D = 50 Hz). This coupling constant is comparable with the one obtained for Li[Co₃μ-PPh₂Fe(μ-PPh₂)¬(μ-CO)Fe(CO)₂PPh₂]₂.

Based on the spectral data discussed above, the structure of the complex is tentatively proposed as follows.

A metal-metal bond is proposed on account of the downfield μ-PPh₂ ³¹P{¹H} NMR resonance. However, there is no experimental evidence to support a folded or planar arrangement of the two bridging donor atoms and the two iron atoms.

The reduction of [Fe(NO)₂(μ-PPh₂)]₂ with L-Selectride and K-Selectride does not proceed in the same manner as that with the MBEt₃H reagents. Treatment of [Fe(NO)₂(μ-PPh₂)]₂ with L-Selectride resulted in a dark brown solution which oxidized back to the neutral dimer immediately upon contact with air. The fact that no ³¹P{¹H} NMR resonance could be observed after a long data collection time suggests that the reaction may yield free radical products. The reaction of
Figure 18. The D-NMR Spectrum of Li[(NO)$_2$Fe($\mu$-PPh$_2$)($\mu$-NO)Fe(NO)(PPh$_2$D)] in THF.
[Fe(NO)$_2$(μ-PPP)$_2$]$_2$ with K-Selectride gives a similar result as that with L-Selectride, and the dark brown product solution does not exhibit any $^3$P NMR resonance.

3. Mechanism for the Reduction of [Fe(NO)$_2$(μ-PPP)$_2$]$_2$

a. Cleavage of Fe-Fe Bond

Although there is no theoretical calculation of the species [Fe$_2$(NO)$_4$(μ-PPP)$_2$]$^{n-}$ (n = 0,1,2) as in the case of [Fe(CO)$_3$(μ-PPP)$_2$]$_2$, the HOMO of the neutral species is expected to be mainly the Fe-Fe bond and the LUMO to be of predominately antibonding diiron character. Therefore, cleavage of the Fe-Fe bond upon addition of two electrons to [Fe(NO)$_2$(μ-PPP)$_2$]$_2$ as depicted in the following equation is understandable.

$$\begin{align*}
(\text{NO})_2\text{Fe} &+ 2\text{e}^- 
\rightarrow (\text{NO})_2\text{Fe}(\text{NO})_2
\end{align*}$$

b. Cleavage of Fe-P Bond

Treatment of [Fe(NO)$_2$(μ-PPP)$_2$]$_2$ with one equivalent of the MBE$_3$H reducing agents resulted in the cleavage of one iron-phosphorus bond of the phosphido bridges.

A mechanism similar to that illustrated in Scheme I for the reaction of [Fe(CO)$_3$(μ-PPP)$_2$]$_2$ with MBR$_3$H is summarized in Scheme II. The reduction may proceed by attack of H$^-$ at an Fe bonded nitrosyl ligand, with the MBE$_3$ ligand coordinating to the oxygen of the nitrosyl ligand to
Scheme 11

\[
\begin{align*}
\text{(NO)}_2\text{Fe} & \xrightarrow{\text{BR}_3^+} \text{Fe(NO)}_2 \\
\text{H Ph}_2 & \quad \text{P Ph}_2 \\
\text{(NO)}_2\text{Fe} & \xrightarrow{-\text{BR}_3} \text{Fe(NO)}_2 \\
\text{P Ph}_2 & \quad \text{H Ph}_2 \\
\text{(NO)}_2\text{Fe} & \quad \text{Fe(NO)}_2 \\
\text{P Ph}_2 & \quad \text{HP Ph}_2 \\
\text{(NO)}_2\text{Fe} & \quad \text{Fe(NO)}(\text{Ph}_2\text{H})
\end{align*}
\]
stabilize this intermediate. The H" will then migrate from
the HNO group to iron with elimination of the BEt
ligand. Reductive elimination of μ-PPh₂ and H forms a PPh₂H ligand
bonded to an iron atom, while the other iron atom will be
 coordinatively unsaturated (16e⁻). Rearrangement of this
species with the formation of a bridging nitrosyl ligand
will then have both iron atoms fulfilling the 18-electron
requirement.

The formation of amido products by the reaction of
complex hydride reducing agents with binuclear metal
nitrosyl complexes provides an experimental support for the
nucleophilic attack of H" at the nitrosyl ligand.¹⁰,¹¹¹
Treatment of [C₅H₅Cr(NO)₂]₂ with Vitride in benzene at room
temperature affords a mixture of (C₅H₅)₂Cr₂(NO)₃(NH₂),
(C₅H₅)₂Cr₂(NO)₂(NH₂)₂, and (C₅H₅)₂Cr₂(NO)₂(NH₂)(OH).¹¹² The
formation of these amido products has been rationalized as
arising from the nucleophilic attack of H" on the nitrogen
atom of the nitrosyl ligand in the organometallic reac-
tant. The reaction of LiBEt₃H with [C₅H₅Cr(NO)₂]₂ at
ambient temperature gives similar results of formation of
bimetallic amido compounds (equation 79).¹¹³
In contrast to the above reaction, the second step of the proposed mechanism illustrated in Scheme II involves the formation of a metal hydride instead of scavenging of $\text{U}^{2-}$ by the Lewis acid present in the reaction mixture. It is possible that the metal hydride is simply the more kinetically stable species resulting from rearrangement of the precursor. Although there is no evidence to prove that metal hydride is actually formed during the reaction, the preparation of metal nitrosyl hydride complexes by reaction of $[\text{C}_5\text{H}_5\text{W(NO)}\text{I}_2]_2$ with Vitride has been reported.\(^{112}\)
E. Unsymmetrical Nitrosyl Dianion, \([(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)\text{Fe}(\text{NO})(\text{PPh}_2)]^{2-}\), and its Conversion to \([\text{Fe}(\text{NO})_2(\mu-\text{PPh}_2)]^{2-}\)

Treatment of the THF solution of \(\text{Li}[(\text{NO})_2\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{NO})\text{Fe}(\text{NO})(\text{PPh}_2)]\) with one equivalent of \(n\)-BuLi in hexane solution at \(-78^\circ\text{C}\) resulted in the formation of \(\text{Li}_2[(\text{NO})_2\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{NO})\text{Fe}(\text{NO})(\text{PPh}_2)]\) immediately in nearly quantitative yield (equation 81)

\[
\begin{align*}
\text{(NO)}_2\text{Fe} & \quad \text{Fe(NO)(PPh}_2\text{H)} \\
\text{Ph}_2 & \quad \text{NO} \\
\text{Li}_2 & \quad \text{Fe(NO)(PPh}_2\text{)} \\
\text{Fe} & \quad \text{Fe(NO)} \\
\text{Fe} & \quad \text{Fe(NO)(PPh}_2\text{H)} \\
\text{Ph}_2 & \quad \text{NO} \\
\text{n-BuLi} & \quad \text{78°C} \\
\text{Li}_2 & \quad \text{Fe(NO)(PPh}_2\text{)} \\
\text{Fe} & \quad \text{Fe(NO)} \\
\text{Fe} & \quad \text{Fe(NO)(PPh}_2\text{H)} \\
\text{Ph}_2 & \quad \text{NO} \\
\end{align*}
\]

The \(^{31}\text{P}{^1\text{H}}\) NMR spectrum of \(\text{Li}_2[(\text{NO})_2\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{NO})\text{Fe}(\text{NO})(\text{PPh}_2)]\) at \(73^\circ\text{C}\) is shown in Figure 19. The spectrum consists of a doublet at 159.6 ppm and another doublet at 20.5 ppm with \(J_{\text{P-P}} = 50\ \text{Hz}\). When the broadband \(^1\text{H}\) decoupling is eliminated, the \(^{31}\text{P}\) NMR spectrum remains the same and no further phosphorus-hydrogen coupling can be observed. The downfield resonance is assigned to the phosphorus atom of the bridging \(\mu-\text{PPh}_2\), ligand and its position implies that the \(\text{PPh}_2\) ligand is bridging across an iron-iron
Figure 19. The $^{31}P$ NMR Spectrum of Li$_2$[(NO)$_2$Fe(μ-PPPh$_2$)(μ-NO)Fe(μ-NO)Ph$_2$] in THF at -73°C. Peaks Labeled "UN" and "SN" are those for Li$_2$[(NO)$_2$Fe(μ-NO)Fe(μ-NO)Ph$_2$] and Li$_2$[Fe(NO)$_2$(μ-PPPh$_2$)], Respectively.
bond. The upfield resonance is assigned to the phosphorus atom of the terminal PPh$_2$ ligand. Similarly to Li$_2$[(Cu)$_3$-Fe(μ-PPh$_2$)(μ-Cu)Fe(Cu)$_2$(PPh$_2$)], the chemical shift value of the terminal PPh$_2$ ligand moves about 20 ppm upfield compared with its precursor. This upfield shift effected by the negative charge on phosphorus is clearly illustrated in Table 11.

A low temperature infrared spectrum of Li$_2$[(NU)$_2$-Fe(μ-PPh$_2$)(μ-NO)Fe(NO)(PPh$_2$)] is unavailable at this moment. At a temperature slightly higher than -78°C (around -70°C), Li$_2$[(NU)$_2$Fe(μ-PPh$_2$)(μ-NO)Fe(NO)(PPh$_2$)] rapidly converts to Li$_2$[Fe(NO)$_2$(μ-PPh$_2$)]$_2$, and this arrangement is irreversible.

\[
\begin{align*}
\text{(NO)$_2$Fe} & \quad 2^- \\
\text{Fe(PO)(PPh$_2$)} & \quad T > -70^\circ C \\
\text{Fe(NO)$_2$} & \quad 2^- \\
\end{align*}
\] (82)

The proposed structure of the complex is based solely on the $^{31}P$/$^1$H NMR spectrum, and is speculative at present. There is no experimental evidence to support the existence of a bridging nitrosyl ligand. However, the close resemblance of the reaction chemistry of the carbonyl and nitrosyl dianionic complexes suggests that the two complexes exhibit similar structures.

The addition of a second equivalent of the MBEt$_3$H reducing agent to a THF solution of M[(NO)$_2$Fe(μ-PPh$_2$)(μ-NO)Fe(NO)(PPh$_2$)] resulted in the conversion of the
latter to $M_2[Fe(NO)_2(\mu-PPh_2)]_2$. The extent of this conversion depends on the cation $M^+$ and temperature, and the results are summarized in Table 15. At room temperature, the amount of $M_2[Fe(NO)_2(\mu-PPh_2)]_2$ in the reaction solution increases as a function of $M^+$ in the order $K^+ > Na^+ > Li^+$. In the similar conversion study of $M[(Cu)_3Fe(\mu-PPh_2)-(\mu-Cu)Fe(Cu)_2(PPh_2H)]$, there is no noticeable amount of $M_2[Fe(Cu)_3(\mu-PPh_2)]_2$ in the solution at room temperature when the reducing agent is LiBEt$_3$H. However, under identical experimental conditions, 20% of Li[(NO)$_2$-Fe(\mu-PPh$_2$)(\mu-NO)Fe(NO)(PPh$_2$H)] converts to Li$_2$[Fe(NO)$_2$-(\mu-PPh$_2$)]$_2$.

When a THF solution of $M[(NO)_2Fe(\mu-PPh$_2$)(\mu-NO)Fe(NO)-(PPh$_2$H)]$ was heated in THF at reflux temperature for two minutes, the only resonances in the $^{31}P^{1}H$ NMR spectra were those of $M_2[Fe(NO)_2(\mu-PPh_2)]_2$.

The conversion reactions discussed herein illustrate that the PPh$_2$H ligand in $M[(NO)_2Fe(\mu-PPh$_2$)(\mu-NO)Fe(NO)-(PPh$_2$H)]$ can be deprotonated as easily as that in $M[(Cu)_3Fe-$
Table 15. Conversion of $M[(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)]\text{Fe(\text{NO})(PPh}_2\text{H})]_2$ to $M_2[\text{Fe(\text{NO})}_2(\mu-\text{PPh}_2)]_2$

<table>
<thead>
<tr>
<th>$M^+$</th>
<th>$%$ of $M_2[\text{Fe(\text{NO})}_2(\mu-\text{PPh}_2)]_2$ in solution&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$25^\circ \text{C}&lt;sup&gt;b&lt;/sup&gt;$</th>
<th>$65^\circ \text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>20</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>30</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>60</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Estimated from $^{31}P$ NMR spectra of the solutions
<sup>b</sup>At $25^\circ \text{C}$ after 20 minutes
(μ-PPh₂)(μ-CU)Fe(CO)₂(PPh₂H)] to form the corresponding unsymmetrical dianionic complexes. As the temperature is raised, the deprotonation reaction by a second equivalent of MBEt₃H is more favorable and more M₂[(NO)₂Fe(μ-PPh₂)(μ-NO)-Fe(NO)(PPh₂)] complex will form, which then converts immediately to M₂[Fe(NO)₂(μ-PPh₂)]₂.

F. Reactions of [(CO)₃Fe(μ-PPh₂)(μ-CU)Fe(CO)₂(PPh₂)]²⁻ with Alkylating Agents and Protonating Agents

Addition of two equivalents of various alkyl iodides to the dianion [(CO)₃Fe(μ-PPh₂)(μ-CU)Fe(CU)₂(PPh₂)]²⁻ results in the formation of some new binuclear neutral carbonyl complexes.

The complex Li₂[(CO)₃Fe(μ-PPh₂)(μ-CU)Fe(CU)₂(PPh₂)] also reacts with one equivalent of various alkylating agents to give PPh₂R-containing monoanionic complexes. These deri-
vatives have been characterized, and each of the reactions will be discussed in turn.

1. Reaction of Li$_2$[(CO)$_3$Fe(µ-PPh$_2$)(µ-CO)Fe(CO)$_2$-(PPh$_2$)]$^{2-}$ with One Equivalent of Alkylating Agents

Treatment of Li$_2$[(CO)$_3$Fe(µ-PPh$_2$)(µ-CO)Fe(CO)$_2$(PPh$_2$)] with 1.0 equivalent of alkyl iodide in THF solution at -78°C produces an immediate color change from dark purple to orange red. The reaction yields new complexes, Li[(CO)$_3$Fe(µ-PPh$_2$)(µ-CO)Fe(CO)$_2$(PPh$_2$R)]$_2$, as shown in equation 84. The alkylating agents used in this study included MeI, EtI, n-PrI, i-PrI, allyl iodide and CD$_3$I.

\[
\begin{array}{c}
\text{(CO)$_3$Fe(PPh$_2$)} \\
\end{array} + \text{RI} \xrightarrow{\text{THF}} \begin{array}{c}
\text{(CO)$_3$Fe(PPh$_2$R)} \\
\end{array} (84)
\]

R = Me, Et, n-Pr, i-Pr, allyl, CD$_3$

These new complexes have been characterized by their $^{31}$P NMR and IR spectra. The $^{31}$P[1$^\text{H}$] NMR spectral data of these complexes are summarized in Table 16. The $^{31}$P[1$^\text{H}$] NMR spectrum of the PPh$_2$Me-containing product is presented in Figure 20. The IR spectrum of the carbonyl stretching frequency region of the PPh$_2$Me-containing product is displayed in Figure 21. From Table 16, the $^{31}$P[1$^\text{H}$] NMR spectra of these complexes Li[(CO)$_3$Fe(µ-PPh$_2$)(µ-CO)Fe(CO)$_2$(PPh$_2$R)]$_2$ display a general pattern of a downfield doublet, which is assigned to the phosphorus atom of the bridging µ-PPh$_2$. 


Table 16. $^{31}\text{P}$ NMR and IR Spectral Data of 
Li[(CO)$_3$Fe(µ-PPh$_2$)(µ-CO)Fe(CO)$_2$(PPh$_2$R)]

<table>
<thead>
<tr>
<th>Complex</th>
<th>δ(µ-PPh$_2$)$^a$</th>
<th>δ(PPh$_2$R)</th>
<th>J$_{P-P}$, Hz</th>
<th>ν(µ-CO)$^b$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = Me</td>
<td>128.2</td>
<td>59.2</td>
<td>37</td>
<td>1625(m)</td>
</tr>
<tr>
<td>R = Et</td>
<td>128.2</td>
<td>70.9</td>
<td>35</td>
<td>1622(m)</td>
</tr>
<tr>
<td>R = n-Pr</td>
<td>128.7</td>
<td>67.5</td>
<td>29</td>
<td>1625(m)</td>
</tr>
<tr>
<td>R = i-Pr</td>
<td>128.4</td>
<td>80.3</td>
<td>36</td>
<td>1648(m)</td>
</tr>
<tr>
<td>R = allyl</td>
<td>128.5</td>
<td>66.6</td>
<td>38</td>
<td>1630(m)</td>
</tr>
</tbody>
</table>

$^a$ppm, in THF solution at 25°C

$^b$in THF solution at 25°C
Figure 20. The $^{31}P \{^1H\}$ NMR Spectrum of Li[(Cu)$_3$Fe(μ-PPPh$_2$)(μ-Cu)Fe(CO)$_2$-(PPPh$_2$Me)] in THF at Room Temperature.
ligand, and a highfield doublet, which is assigned to the phosphorus atom of the PPh₂R ligand. A few aspects of the \(^{31}P\{^1H\}\) NMR spectra of these derivatives are noteworthy. The phosphorus-31 NMR chemical shift values for the bridging \(\mu\)-PPh₂ ligands are all within the range of 120-130 ppm. These values are all very close to the chemical shift values of \(\mu\)-PPh₂ ligand in Li[(C₅H₅)Fe(\(\mu\)-PPh₂)(\(\mu\)-C₅H₅)Fe(C₅H₅)₂(PPh₂H)]. These bridging phosphido ligands exhibit resonances which are well downfield from the standard; thus the complexes in Table 16 do contain Fe-Fe bonds in their structure. The phosphorus-31 chemical shift values for the various phosphine ligands are well within normal limits for metal-coordinated phosphine ligands. It is notable that the \(^{31}P\) NMR resonance positions of these alkyl-substituted diphenylphosphine ligands increase in the series Me < Et < 1-propyl < 2-propyl, where PPh₂(2-propyl) displays the most downfield resonance at 80.3 ppm. This observed trend is in contrast to that predicted from the inductive effect of the R group.\(^{114-116}\) The phosphine-phosphide phosphorus-phosphorus coupling constants of these derivatives are relatively small and are in the range of 35-45 Hz. These small phosphorus-phosphorus coupling constants imply that the \(\mu\)-PPh₂ ligand and the PPh₂R ligand probably adopt a cis arrangement.\(^{60}\) In contrast to the \(^{31}P\{^1H\}\) NMR spectra of the PPh₂H-containing monoanionic complexes, the \(^{31}P\{^1H\}\) NMR spectra of these PPh₂R containing complexes are temperature invariant in the temperature range of -83°C to 30°C.
Selected IR spectral data of these monoanionic complexes $\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PPh}_2\text{R})]$ are summarized in Table 16. The IR spectrum of the PPh$_2$Me-containing product in the carbonyl stretching frequency region is displayed in Figure 21. All of these complexes exhibit absorption bands of nearly identical pattern but slightly different in positions and relative intensity in the region of 2000-1800 cm$^{-1}$, a region characteristic of terminal metal carbonyl stretching vibrations. In addition, absorptions are observed around 1630 cm$^{-1}$, a region characteristic of bridging carbonyl stretching vibrations. In general, these IR spectra are very similar to the IR spectra of the $\text{M}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PPh}_2\text{H})]$ complexes. However, the positions and relative intensities of the absorption bands in the bridging carbonyl stretching region are quite insensitive to alkyl substituents in the PPh$_2$R ligands.

The $^{13}$C NMR spectrum of the PPh$_2$Me-containing complex provides supporting evidence for the existence of a bridging carbonyl ligand. The $^{13}$C NMR spectrum of a $^{13}$C-enriched sample of $\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PPh}_2\text{Me})]$ at -83°C is shown in Figure 22. The resonances at 220 ppm are assigned to the terminally coordinated carbonyl ligands. At this moment, it is not possible to offer an unequivocal assignment to the resonance at 258.1 ppm. However, it does imply that some type of bridging carbonyl ligand does exist in the PPh$_2$Me-containing
Figure 21. The Infrared Spectrum of Li[(CO)$_3$Fe(μ-PPh$_2$) - (μ-CO)Fe(CO)$_2$(PPh$_2$Me)] in THF in the Region of 2000-1600 cm$^{-1}$. 
Figure 22. The $^{13}\text{C}$ NMR Spectrum of Cu Ligands of 
Li[(Cu)$_3$Fe($\mu$-PPh$_2$)(($\mu$-Cu)Fe(Cu)$_2$(PPh$_2$Me))] 
in THF at $-83^\circ\text{C}$.
complex. Details of the variable temperature $^{13}$C NMR study will be presented in a later section.

Based on the above spectral data, the structure of the Li[($\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2\text{(PPh}_2\text{R})]\] complexes is expected to be similar to that proposed for Li[($\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)-(\mu-\text{CO})\text{Fe}(\text{CO})_2\text{(PPh}_2\text{H})].$

As discussed earlier, the exact nature of the bridging carbonyl ligand is uncertain. Only an X-ray structure determination will reveal detailed geometry of these monoanionic complexes.

2. Reaction of Li$_2$[($\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2\text{(PPh}_2\text{)}] with Two Equivalents of Alkylating Agents

As seen from the above discussion, when Li$_2$[($\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2\text{(PPh}_2\text{)}]$ is reacted with one equivalent of an alkylating agent, the product obtained is a PPh$_2$R-containing monoanionic complex, Li[($\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2\text{(PPh}_2\text{R})].$ The $^{31}$P NMR spectra of all these compounds fall into a common pattern. However, when Li$_2$[($\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2\text{(PPh}_2\text{)}]$ was treated with two equivalents of an alkylating agent, the
structure of the product falls into two different categories. The nature of the product is similar when methyl iodide, ethyl iodide, 1-propyl iodide or 2-propyl iodide is used as an alkylating agent. The reaction of \( \text{Li}_2\[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)-(\mu-\text{CO})\text{Fe}(\text{Cu})_2(\text{PPh}_2)] \) with two equivalents of allyl iodide gives product of a totally different nature. Each reaction will be discussed in turn.

a. Reaction of \( \text{Li}_2\[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)-(\mu-\text{CO})\text{Fe}(\text{Cu})_2(\text{PPh}_2)] \) with MeI, EtI, n-PrI and i-PrI

The reaction of \( \text{Li}_2\[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)-(\mu-\text{CO})\text{Fe}(\text{Cu})_2(\text{PPh}_2)] \) with two equivalents of each of the above alkylating agents resulted in the formation of orange red complexes \([(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C}(R)\text{O})\text{Fe}(\text{Cu})_2(\text{PPh}_2)] \) (equation 85).

\[
\begin{align*}
\text{(CO)}_3\text{Fe} & \quad \text{Fe(CO)}_2 \\
P\text{Ph}_2 & \quad \text{2 RI}
\end{align*}
\]

\[
\Rightarrow \quad \begin{array}{c}
\text{(CO)}_3\text{Fe} \\
\text{Fe(CO)}_2 \\
P\text{Ph}_2 R
\end{array}
\]

Mechanistic aspects of the methylation reaction of \( \text{Li}_2\[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{Cu})_2(\text{PPh}_2)] \) with two equivalents of MeI will be described in detail in Section III-F-2-e.

Two equivalents of an alkylating agent was added at \(-78^\circ\text{C}\) to a THF solution of \( \text{Li}_2\[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{Cu})_2(\text{PPh}_2)] \). The dark purple solution immediately changed color to orange red, which indicates the formation of \( \text{Li}[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{Cu})_2(\text{PPh}_2)] \). The solution was then gradually warmed to room temperature while being stirred an
additional period of time. The stirring time required to complete the reaction at room temperature varied for each alkylating agent. For methyl iodide, two hours is enough; however, for the other three reagents, longer stirring time (around 10 hours) is necessary. Column chromatography on grade III alumina column by 3%-5% ether-petroleum ether affords these complexes in good yield (>70%). The $^{31}$P[$^1$H] NMR spectral data of these complexes are presented in Table 17. The $^{31}$P[$^1$H] NMR spectrum of [(Cu)$_3$Fe($\mu$-PPh$_2$)(μ-C(Me)U)Fe(CO)$_2$(PPh$_2$Me)] is displayed in Figure 23. These spectra exhibit a downfield doublet around 170 ppm and an upfield doublet around 50 ppm. The downfield resonance is assigned to the phosphorus atom of the $\mu$-PPh$_2$ ligand bridging across two Fe atoms with a metal-metal interaction. The upfield resonance is assigned to phosphorus atom of the Fe-coordinated PPh$_2$R ligand, and the position of this resonance depends on the alkyl-substituted group. An important point to note here is the temperature dependence of these $^{31}$P[$^1$H] NMR spectra. Details of the fluxional mechanism will be described in Section III-J.

These complexes with a bridging $\eta^2$-acyl ligand exhibit IR terminal carbonyl stretching bands in the region of 1900-2050 cm$^{-1}$ with similar patterns. In addition to these strong absorption bands of the terminal carbonyl groups, weak absorptions at around 1480 cm$^{-1}$ are observed. These weak absorptions are assigned to the νCu of the acyl group bonded to metal through oxygen. The νCu bands of the acyl group of these complexes are summarized in Table 17. The IR spectrum of
Table 17 Selected $^{31}$P NMR and IR Spectral Data of 
$[(Cu)_3Fe(\mu-PPh_2)(\mu-C(R)O)Fe(CO)_2(PPh_2R)]$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta^{31}$P NMR ((\mu-PPh_2))$^a$</th>
<th>$\delta^{31}$P NMR (PPh$_2R$)</th>
<th>$J_{p-p}$, Hz</th>
<th>IR((\mu-C(R)O))(v(C=O))$^b$, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = Me</td>
<td>174.1</td>
<td>39.7</td>
<td>55</td>
<td>1483(w)</td>
</tr>
<tr>
<td>R = Et</td>
<td>171.6</td>
<td>53.1</td>
<td>49</td>
<td>1482(w)</td>
</tr>
<tr>
<td>R = n-Pr</td>
<td>169.5</td>
<td>49.4</td>
<td>36</td>
<td>1481(w)</td>
</tr>
<tr>
<td>R = i-Pr</td>
<td>168.7</td>
<td>62.2</td>
<td>38</td>
<td>1480(w)</td>
</tr>
</tbody>
</table>

$^a$ in THF at 25°C, ppm  
$^b$ in cyclohexane at 25°C
Figure 23. The $^{31}$P NMR Spectrum of \[ \text{[(CO)$_3$Fe(μ-PPh$_2$)(μ-C(Me)O)Fe(CO)$_2$(PPh$_2$Me)]} \]
in THF at Room Temperature.
[(CO)₃Fe(μ-PPh₂)(μ-C(Me)O)Fe(CO)₂(PPh₂Me)] is shown in Figure 24.

The $^{13}$C NMR spectra of the complexes [(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(C(R)O)₂(PPh₂R)] are summarized in Table 18. For the purpose of discussion, the $^{13}$C NMR spectrum of the complex containing a bridging acetyl ligand, [(CO)₃Fe(μ-C(Me)O)Fe(CO)₂(PPh₂Me)], is illustrated in Figure 25 and will be described in detail. The spectrum clearly shows two different methyl groups. The singlet at 47.8 ppm is assigned to the methyl group of the bridging acetyl ligand. The doublet at 15.3 ppm ($J_{P-C} = 54.7$ Hz) is assigned to the methyl group bonded to phosphorus. The resonance at 215 ppm is assigned to three terminal carbonyl ligands bonded to the iron atoms with no phosphine ligand. The doublet of doublets at 218.4 ppm ($J_{P-C} = 15$ Hz, $J_{P-C} = 10$ Hz) and another doublet of doublets at 215.5 ppm ($J_{P-C} = 14$ Hz, $J_{P-C} = 5$ Hz) are assigned to the two terminal carbonyl ligands of the Fe(CO)₂PPh₂Me moiety. Figure 26 shows the $^{13}$C NMR spectrum in the terminal carbonyl region.

The $^{13}$C NMR spectrum of the complex is temperature dependent. Details of the fluxional mechanism will be discussed in Section III-J.

The proton NMR chemical shifts and relative peak intensities of these complexes are tabulated in Table 19. The proton NMR spectrum of the complex with the bridging acetyl ligand is shown in Figure 27. For the complex with a bridging acetyl ligand, three principal features are observed: a broad multiplet centered at 7.3 ppm followed by a sharp singlet at
Figure 24. The Infrared Spectrum of \( [(CO)_3Fe(\mu-PPh_2)(\mu-C(Me)O)Fe(CO)_2(PPh_2Me)] \)
in Cyclohexane in the Region of 3500-1400 cm\(^{-1}\).
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<tr>
<th>Complex</th>
<th>Chemical Shift (ppm)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=CH₃</td>
<td>299.6, d(Jₚ₋C = 21 Hz)</td>
<td>μ-C(CH₃)O</td>
</tr>
<tr>
<td></td>
<td>219.5-214.8, m</td>
<td>CO</td>
</tr>
<tr>
<td></td>
<td>140.9-128.3, m</td>
<td>C₆H₅</td>
</tr>
<tr>
<td></td>
<td>47.8, s</td>
<td>μ-C(CH₃)O</td>
</tr>
<tr>
<td>R=CH₂CH₃</td>
<td>304.9, d(Jₚ₋C = 17 Hz)</td>
<td>μ-C(CH₂CH₃)O</td>
</tr>
<tr>
<td></td>
<td>214.1, m</td>
<td>CO</td>
</tr>
<tr>
<td></td>
<td>127.5-133.9, m</td>
<td>C₆H₅</td>
</tr>
<tr>
<td></td>
<td>73.7, s</td>
<td>μ-C(CH₂CH₃)O</td>
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<td></td>
<td>54.7, s</td>
<td>μ-C(CH₂CH₃)O</td>
</tr>
<tr>
<td></td>
<td>24.6, d(Jₚ₋C = 23 Hz)</td>
<td>P-CH₂CH₃</td>
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<tr>
<td></td>
<td>8.1, d(Jₚ₋C = 13 Hz)</td>
<td>P-CH₂CH₃</td>
</tr>
<tr>
<td>R=CH₂CH₂CH₃</td>
<td>299.9, d(Jₚ₋C = 19 Hz)</td>
<td>μ-C(CH₂CH₂CH₃)O</td>
</tr>
<tr>
<td></td>
<td>214.0, m</td>
<td>CO</td>
</tr>
<tr>
<td></td>
<td>127.6-134.1, m</td>
<td>C₆H₅</td>
</tr>
<tr>
<td></td>
<td>63.8, s</td>
<td>μ-C(CH₂CH₂CH₃)O</td>
</tr>
<tr>
<td></td>
<td>33.4, d(Jₚ₋C = 22 Hz)</td>
<td>P-CH₂CH₂CH₃</td>
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Table 18 (continued)

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<th>Multiplicity</th>
<th>Assignment</th>
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<td>17.8, s</td>
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<td>μ-C(CH₂CH₂CH₃)O</td>
</tr>
<tr>
<td>16.4, d(Jp-C = 10 Hz)</td>
<td></td>
<td>ν-CH₂CH₂CH₃</td>
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<tr>
<td>15.5, s</td>
<td></td>
<td>μ-C(CH₂CH₂CH₃)O</td>
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<tr>
<td>13.3, s</td>
<td></td>
<td>P-CH₂CH₂CH₃</td>
</tr>
<tr>
<td>R=CH(CH₃)₂</td>
<td>304.5, d(Jp-C = 21 Hz)</td>
<td>μ-C(CH(CH₃)₂)O</td>
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<tr>
<td></td>
<td>214.0, m</td>
<td>CO</td>
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<td></td>
<td>125.3-135.5, m</td>
<td>C₆H₅</td>
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<tr>
<td></td>
<td>58.1, s</td>
<td>μ-C(CH(CH₃)₂)O</td>
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<td></td>
<td>30.2, d(Jp-C = 23 Hz)</td>
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<td>18.7, s</td>
<td>μ-C(CH(CH₃)₂)O</td>
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<td></td>
<td>18.3, s</td>
<td>P-CH(CH₃)₂</td>
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<tr>
<td></td>
<td>16.7, s</td>
<td>P-CH(CH₃)₂</td>
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</table>
Figure 25. The $^{13}$C NMR of $\left[ (\text{CO})_3 \text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C(Me)O})-\text{Fe}(\text{CO})_2(\text{PPh}_2\text{Me}) \right]$ in Acetone-$d_6$. 
Figure 26. The $^{13}$C NMR of CO Ligands of [(CO)$_3$Fe(μ-PPh$_2$)-(μ-C(Me)O)Fe(CO)$_2$(PPh$_2$Me)] in Acetone-$d_6$ in the Region of 220-215 ppm.
Table 19. $^1$H NMR Spectral Data of
$[(Co)_3Fe(\mu-PPh_2)(\mu-C(R)O)Fe(CO)_2(PPh_2R)]$

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<th>Chemical Shift (ppm)$^a$</th>
<th>Intensity</th>
<th>Assignment</th>
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<tr>
<td>$R=CH_3$</td>
<td>7.3, m</td>
<td>20</td>
<td>$P-C_6H_5$</td>
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<tr>
<td></td>
<td>1.90, d ($J_{P-H}$)=7.5 Hz</td>
<td>3</td>
<td>$P-CH_3$</td>
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<tr>
<td></td>
<td>1.89, s</td>
<td>3</td>
<td>$\mu-C(CH_3)_2$</td>
</tr>
<tr>
<td>$R=CH_2CH_3$</td>
<td>7.3, m</td>
<td>20</td>
<td>$P-C_6H_5$</td>
</tr>
<tr>
<td></td>
<td>2.3, m</td>
<td>4</td>
<td>$\mu-C(CH_2CH_3)_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>and $P-CH_2CH_3$</td>
</tr>
<tr>
<td></td>
<td>1.1, m</td>
<td>3</td>
<td>$P-CH_2CH_3$</td>
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<tr>
<td></td>
<td>0.1, t ($J=7.0$ Hz)</td>
<td>3</td>
<td>$\mu-C(CH_2CH_3)_2$</td>
</tr>
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<td>$R=CH_2CH_2CH_3$</td>
<td>7.4, m</td>
<td>20</td>
<td>$P-C_6H_5$</td>
</tr>
<tr>
<td></td>
<td>2.5, m</td>
<td>4</td>
<td>$\mu-C(CH_2CH_2CH_3)_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>and $P-CH_2CH_2CH_3$</td>
</tr>
<tr>
<td></td>
<td>1.4, m</td>
<td>2</td>
<td>$P-CH_2CH_2CH_3$</td>
</tr>
<tr>
<td></td>
<td>0.9, m</td>
<td>5</td>
<td>$\mu-C(CH_2CH_2CH_3)_2$</td>
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<td></td>
<td></td>
<td></td>
<td>and $P-CH_2OHCH_3$</td>
</tr>
<tr>
<td></td>
<td>0.4, m</td>
<td>3</td>
<td>$\mu-C(CH_2CH_2CH_3)_2$</td>
</tr>
<tr>
<td>$R=CH(CH_3)_2$</td>
<td>7.4, m</td>
<td>20</td>
<td>$P-C_6H_5$</td>
</tr>
<tr>
<td></td>
<td>3.1, m</td>
<td>1</td>
<td>$P-CH(CH_3)_2$</td>
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<td></td>
<td>2.0, m</td>
<td>1</td>
<td>$\mu-C(CH(CH_3)_2)_2$</td>
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<tr>
<td></td>
<td>1.2, m</td>
<td>6</td>
<td>$P-CH(CH_3)_2$</td>
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<tr>
<td></td>
<td>0.5, d ($J=7$ Hz)</td>
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<tr>
<td></td>
<td>-0.1, d ($J=7$ Hz)</td>
<td>3</td>
<td>$\mu-C(CH(CH_3)_2)_2$</td>
</tr>
</tbody>
</table>

$^a$ in CDCl$_3$ solution at 25°C. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet or complex pattern.
Figure 27. The $^1$H NMR Spectrum of $[(CO)_3Fe(\mu-PPh_2)(\mu-C(Me)O)Fe(Cu)_2(PPh_2Me)]$ in CDCl$_3$ at 25°C with TMS as Internal Standard.
1.89 ppm and a doublet at 1.9 ppm \((J_{P-H} = 7.5 \text{ Hz})\). The total relative intensity under the broad multiplet, which falls in the phenyl region, is 20, while that of the two resonances in the methyl region is 6. The other complexes exhibit more complicated spectra in the alkyl proton region, and the assignments are summarized in Table 19.

An X-ray diffraction study of \([\text{Fe}(\text{CO})_3(\mu-\text{PPh}_2)(\mu-\text{C(Me)Me})\text{Fe}(\text{CO})_2(\text{PPh}_2\text{Me})]\) has been carried out, and the structure of this complex will be described in detail in Section III-F-2-b.

Only a few binuclear acyl complexes have been reported to have a structure with an \(\eta^2\)-acyl bridge arrangement. Fischer has reported that the reaction of anionic carbenes with alkylation agents yields bimetallic \(\eta^2\)-acyl complexes (equation 86).$^{100}$

$$\text{MeN}c=O\xrightarrow{\text{Me}_3}\text{OBF}_4\text{Fe-C}\text{Me} + \text{Fe(CO)}_3\text{Fe(CO)}_3(86)$$

In refluxing benzene, \(\text{MeMn(CO)}_5\) reacts with \(\text{C}_5\text{H}_5\text{M(CO)(PPh}_3)\) to form binuclear \(\eta^2\)-acyl mixed metal complexes also containing a \(\mu-\text{PPh}_2\) ligand.$^{118}$
Methylation of the linked phosphido-bridged dianionic complex (equation 72) with MeI also produces a similar \( \eta^2 \)-acetyl bridged compound (equation 88).

One noteworthy feature in the infrared spectra of these compounds is the absorption position of the bridging acyl group which is around 1500 cm\(^{-1} \). This position is relat- dentate C(O)R group.

A valence bond representation of the \([[(\text{CO})_2\text{Fe}(\mu-\text{PPH}_2)]-(\mu-C(R)O)\text{Fe}(\text{CO})_2(\text{PPH}_2R)]\) complexes may be written as follows, which conforms to the noble gas formalism (EAN rule) with the need for a metal-metal bond.
b. Crystal Structure of \([\text{CO}_3\text{Fe}(\mu-\text{PPh}_2)\text{Fe}(\mu-\text{C(Me})_0)\text{Fe(OCO)}_2(\text{PPh}_2\text{Me})]\)

The complex \([\text{CO}_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C(Me})_0)\text{Fe(OCO)}_2(\text{PPh}_2\text{Me})]\) crystallizes with two independent molecules in the asymmetric unit. ORTEP drawings of molecules A and B with hydrogen atoms included are shown in Figures 28 and 29, respectively. The atom numbering schemes for the two molecules are similar. Comparisons of bond angles and bond lengths are given in Tables 20 and 21. The stereodrawing of the unit cell is shown in Figure 30.

The binuclear framework consists of an \(\text{Fe(CO)}_3\) and an \(\text{Fe(OCO)}_2(\text{PPh}_2\text{Me})\) moieties joined by an Fe-Fe bond, a symmetrical bridging \(\text{PPh}_2\), and a bridging acetyl group bonded to \(\text{Fe(2)}\) atom through oxygen. The \(\text{Fe(1)Fe(2)P(2)(C(6)O(6))}\) core is folded, and the bridging and terminal phosphorus atoms are trans to each other. The major difference between molecules A and B is in the orientation of the \(\text{PPh}_2\text{Me}\)
Figure 28. An ORTEP Representation of Molecule A of 
$$[(CO)_3Fe(\mu-PPh_2)(\mu-C(\text{Me})O)Fe(CO)_2(PPh_2\text{Me})]$$
Including Hydrogen Atoms and Showing the Atom Numbering Scheme.
Figure 29. An ORTEP Representation of Molecule B of 
\[((\text{Cu})_3\text{Fe}(\mu-\text{C(Me)O})\text{Fe}(\text{CO})_2\text{PPh}_2\text{Me})\] 
Including Hydrogen Atoms.
Table 20. Selected Bond Lengths for [(CO)$_3$Fe($\mu$-PPh$_2$)(\(\mu\)-C(Me)O)Fe(CO)$_2$PPh$_2$Me)]

<table>
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<tr>
<th>Bond</th>
<th>Molecule A</th>
<th>Molecule B</th>
<th>Average</th>
</tr>
</thead>
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<td>2.663(1)</td>
<td>2.659</td>
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<td>Fe(1)-P(1)</td>
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<td>2.276(2)</td>
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<td>Fe(1)-P(2)</td>
<td>2.201(2)</td>
<td>2.198(2)</td>
<td>2.200</td>
</tr>
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<td>Fe(1)-C(1)</td>
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<td>1.767(7)</td>
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<td>Fe(1)-C(2)</td>
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<td>1.757(8)</td>
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<tr>
<td>Fe(1)-O(6)</td>
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<td>1.998(4)</td>
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<td>Fe(2)-P(2)</td>
<td>2.204(4)</td>
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<td>Fe(2)-C(3)</td>
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<td>1.821(7)</td>
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Table 21. Selected Bond Angles for 

\[((\text{Cu})_3\text{Fe(}\mu-\text{PPh}_2\text{)(}\mu-\text{C(Me)}\text{O})\text{Fe(CO)}_2(\text{PPh}_2\text{Me}))\]

<table>
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<th>Molecule B (degree)</th>
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</thead>
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<td>98.6(2)</td>
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<td>66.8(2)</td>
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<td>95.6(3)</td>
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Figure 30. Stereodrawing of the Unit Cell of
\[ [(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C(Me)}\text{U})\text{Fe(Cu)}_2(\text{PPh}_2\text{Me})]. \]
ligand, with the two phenyl groups being twisted in different directions.

The average Fe-Fe bond length is 2.659(6) Å, consistent with the presence of a single metal-metal bond. Among related "bent" Fe₂ complexes, it is slightly longer than that found in [Fe(CO)₃(μ-PPh₂)]₂ (2.623(3) Å),¹² Fe₂(CO)₆-[μ-0=CCHC(Ph)NEt₂](μ-PPh₂) (2.60 Å),¹¹⁹ and Fe₂(CO)₆-[μ-0=CPh₂]₂ (2.568(2) Å).¹²⁰ However, it is shorter than the Fe-Fe bond distance in [Na(THF)₂][Fe₂(CO)₅(C(OMe))(μ-PPh₂)]₂ (2.718(5) Å).¹⁹⁹ Evidence for Fe-Fe bonding also comes from a downfield position of the ³¹P NMR resonance of the phosphide phosphorus, which has already been discussed in relation to metal-metal bonding.

For the purpose of discussion, only the structure parameters of molecule A will be discussed. The Fe(1) - P(2) bond distance (2.201(2) Å) and Fe(2) - P(2) bond distance (2.204(2) Å) are in the normal range of Fe-P bond lengths and are similar to that found in [Na(THF)]⁺[Fe₂(CO)₅(C(OMe))(μ-PPh₂)]₂ (2.226(0) Å).¹⁹⁹ No distortion of the phosphide phosphorous is observed.

The Fe(1) - P(2) - Fe(2) bond angle of molecule A is 74.1(1)°, which is larger than that found in [Fe(CO)₃(μ-PPh₂)]₂ (72.0(1)°)¹² and Fe₂(CO)₆(Cl)(PPh₂) (69.8(0)°).¹⁷ However, it is comparable to that found in [Na(THF)][Fe₂(CO)₅(C(OMe))(μ-PPh₂)]₂ (74.4(3)°, 73.0(3)°) and is substantially smaller than the Fe-P-Fe bond angle in [Fe(CO)₃(μ-PPh₂)]₂⁻ (105.5(1)°).¹² It has been proposed...
that the size of M-P-M angle is an indicator of the extent of M-M bonding.\textsuperscript{17} This is reasonable since the M-P-M angle is dependent on the M-M distance. Thus, M-P-M angles greater than 92° are found in complexes without metal-metal bonds, and M-P-M angles in the range of 68° - 80° are found in complexes with metal-metal bonds.\textsuperscript{11} The M-P-M bond angles discussed here support this generalization.

The Fe(21)-C(6) bond length is 1.962(7)Å in molecule A, which is comparable to that found in Fe\textsubscript{2}(CO)\textsubscript{6}(\mu\textsuperscript{-}OCPH)\textsubscript{2} (1.95Å).\textsuperscript{120} The bridging acyl C(6)-O(6) bond length is 1.244Å. This value is smaller than that in Fe\textsubscript{2}(CO)\textsubscript{6}(\mu\textsuperscript{-}OCPH)\textsubscript{2} (1.257Å)\textsuperscript{120} and [(CO)\textsubscript{3}Mn(\mu\textsuperscript{-}C(Me)O)(\mu\textsuperscript{-}C(Ph)O)-(\mu\textsuperscript{-}PPh\textsubscript{2})Ir(C\textsubscript{5}H\textsubscript{5})] (1.258Å).\textsuperscript{118} A double-bonded CO, as in acetophenone, has a bond distance of 1.216Å.\textsuperscript{121} A single CO bond length is on the order of 1.43Å.\textsuperscript{122} It would thus appear that the C(6)-O(6) bond order lies between 1 and 2.

The Fe(1)-O(6) bond distance is 2.006Å, which is less than the value found in ionic FeO (2.15Å).\textsuperscript{123} The Fe-O bond in [(CO)\textsubscript{3}Fe(\mu\textsuperscript{-}PPh\textsubscript{2})(\mu\textsuperscript{-}C(Me)O)Fe(CO)\textsubscript{2}(PPh\textsubscript{2}Me)] is stable toward reactions with carbon monoxide or Lewis acids (BF\textsubscript{3}, AlCl\textsubscript{3}).

d. **Reaction of Li\textsubscript{2}[(CO)\textsubscript{3}Fe(\mu\textsuperscript{-}CO)(\mu\textsuperscript{-}PPh\textsubscript{2})Fe(CO)\textsubscript{2}(PPh\textsubscript{2})] with Allyl Iodide**

In contrast to the alkylation reaction described in equation 85, Li\textsubscript{2}[(CO)\textsubscript{3}Fe(\mu\textsuperscript{-}PPh\textsubscript{2})(\mu\textsuperscript{-}CO)Fe(CO)\textsubscript{2}(PPh\textsubscript{2})] reacts with two equivalents of allyl iodide to form a red binuclear η\textsubscript{3}-allyl complex as shown in the following equation.
Two equivalents of allyl iodide were added at -78°C to a THF solution of Li$_2$[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$)]. The solution was then gradually warmed to room temperature and chromatographed on grade III alumina.

The $^{31}$P-$^1$H NMR spectrum of the complex shows two doublets at 180.5 ppm and 53.9 ppm ($J_{P-P} = 16$ Hz). The downfield resonance is assigned to the phosphorus atom of the bridging μ-PPh$_2$ ligand and the upfield resonance to the phosphorus atom of the terminal PPh$_2$CH$_2$ ligand. The downfield position of the μ-PPh$_2$ resonance implies the presence of a Fe-Fe bond in the complex. In contrast to that of the bridging acetyl complex, the $^{31}$P-$^1$H NMR spectrum of this n$_3$-allyl complex is temperature invarient.

The proton NMR spectrum of the complex is shown in Figure 3l. The spectrum shows a broad multiplet centered at...
Figure 31. The $^1$H NMR Spectrum of $[(\text{CO})_2(\eta^3-C_3H_5)\text{Fe}(\mu-\text{PPh}_2\text{Fe})\text{Cu}_3(\text{PPh}_2C_3H_5)]$ in CDCl$_3$ at 25°C with TMS as Internal Standard.
7.4 ppm which is assigned to the phenyl group. In the region of the allylic protons, two sets of signals are observed, which are identified by selective decoupling experiments. For the \( \eta^3 \)-allyl group, the resonances exhibit an \( A_2M_2X \) pattern, which consists of two doublets and a multiplet. The multiplet at 4.3 ppm is assigned to \( H(1) \) (relative intensity 1). The broad doublet at 2.4 ppm is assigned to the \( H(2) \) protons (relative intensity 2, syn protons). Another doublet centered at 2.0 ppm is assigned to the \( H(3) \) protons (relative intensity 2, anti protons). This pattern is very similar to that reported for \( (C_5H_5)Fe(CO)_3X \) (\( X = Cl, Br, I \)).\(^{124}\) For the \( \sigma \)-allyl group bonded to phosphorus, the resonances exhibit a more complicated pattern due to phosphorus-proton coupling. The multiplet at 5.5 ppm is assigned to the \( H_b \) proton, the broad multiplet at 5.0 ppm is assigned to the \( H_c \) protons, and the triplet at 3.3 ppm is assigned to the \( H_a \) protons.

The \( ^{13}C \) NMR spectrum of this \( \eta^3 \)-allyl complex (Figure 32) also shows a complicated pattern for the allylic carbons. There are two sets of signals in the spectrum which can be assigned to the \( \sigma \)-allyl carbons and \( \eta^3 \)-allyl carbons. The singlet at 92.8 ppm is assigned to \( C(1) \) and the singlet at 49.9 ppm is assigned to the equivalent \( C(2) \) and \( C(3) \). The \( \sigma \)-allyl carbon atoms all display carbon-phosphorus coupling which can be used to distinguish them from the \( \eta^3 \)-allylic carbons. The doublet at 38.6 ppm (\( J_{p-C} = 27 \text{ Hz} \)) is assigned to \( C(a) \) and the doublet at 143.7
Figure 32. The $^{13}$C NMR Spectrum of [(CO)$_2$(n$^3$-C$_3$H$_5$)]

In Acetone-$d_6$ at 25°C.
ppm ($J_{p-C} = 29$ Hz) is assigned to C(b). The doublet at 121.0 ppm ($J_{p-C} = 11$ Hz) is assigned to the C(c).

The carbon-13 NMR spectrum of $(n^3-C_3H_5)Fe(CO)_3X$ ($X = \text{Cl, Br, I}$) also shows similar patterns for the allylic carbon atoms. In these complexes, the C(l) atom displays a downfield singlet at about 102 ppm, and the other two equivalent carbon atoms show a singlet at around 65 ppm.

The infrared spectrum of the $n^3$-allyl complex displays absorptions in the region of 1900 to 2050 cm$^{-1}$, which is the region characteristic of terminal carbonyl stretching vibrations. No absorptions can be observed in the region of bridging carbonyl stretching vibrations.

d. Crystal Structure of $[(\text{Cu})_2(n^3-C_3H_5)-Fe(\mu-\text{PPh}_2)Fe(CO)_3(\text{PPh}_2C_3H_5)]$

The molecular structure of $[(\text{Cu})_2(n^3-C_3H_5)Fe(\mu-\text{PPh}_2)-Fe(CO)_3(\text{PPh}_2C_3H_5)]$, together with important bond distances and bond angles is shown in Figure 33. An ORTEP drawing of the molecule is shown in Figure 34. Hydrogen atoms are omitted for clarity. A stereodrawing of the unit cell is shown in Figure 35. Selected bond lengths and bond angles are listed in Tables 22 and 23, respectively.

The binuclear framework basically consist of an $\text{Fe(CO)}_2(n^3-C_3H_5)$ and an $\text{Fe(CO)}_3(\text{PPh}_2C_3H_5)$ moieties joined by an iron-iron bond and a symmetrical bridging $\text{PPh}_2$ ligand. The terminal $\text{PPh}_2C_3H_5$ ligand and the diphenylphosphido bridge ligand are considered to be cis to each other in the solid state. This cis arrangement explains the small
Fe — Fe 2.802(2)  Fe(1) - P(1) - Fe(2) 79.0(1)
Fe(1) - C(1) 2.153(10)  Fe(2) - Fe(1) - P(1) 51.2(1)
Fe(1) - C(3) 2.175(12)
Fe(1) - C(2) 2.097(10)
Fe(1) - P(1) 2.180(3)
Fe(2) - P(1) 2.225(2)

Figure 33. The Molecular Structure of $[(\text{CO})_2(\eta^3-\text{C}_3\text{H}_5)\text{Fe(\mu-PPh}_2)\text{Fe(CO)}_3$-
$(\text{PPh}_2\text{C}_3\text{H}_5)]$ with Selected Bond Lengths and Bond Angles. Bond
lengths are given in angstroms and bond angles are given in
degrees.
Figure 34. An ORTEP Drawing of $[(\text{CO})_2(\eta^3-\text{C}_3\text{H}_5)]\text{Fe}-(\mu-\text{PPh}_2)\text{Fe(CO)}_3(\text{PPh}_2\text{C}_3\text{H}_5)]$ Showing the Atom Numbering Scheme Including All Non-Hydrogen Atoms.
Table 22. Selected Bond Lengths for 
\([((CO)_2(n^3-C_3H_5)Fe(\mu-PPh_2)Fe(CO)_3(PPh_2C_3H_5))]\)

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Table 23. Selected Bond Angles for
\[ (\text{CO})_2(n-C_3H_5)\text{Fe}(\mu-\text{PPh}_2)\text{Fe(CO)}_3(\text{PPh}_2C_3H_5) \]

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</tr>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>Fe(2)-C(4)-O(4)</td>
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</tr>
<tr>
<td>Fe(2)-C(5)-U(5)</td>
<td>175.1(8)</td>
</tr>
<tr>
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<tr>
<td>Fe(1)-P(1)-C(18)</td>
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</tr>
<tr>
<td>C(12)-P(1)-C(18)</td>
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</tr>
<tr>
<td>C(12)-P(1)-Fe(2)</td>
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</tr>
<tr>
<td>C(18)-P(1)-Fe(2)</td>
<td>121.0(2)</td>
</tr>
<tr>
<td>Fe(1)-P(2)-C(9)</td>
<td>112.8(6)</td>
</tr>
<tr>
<td>Fe(1)-P(2)-C(24)</td>
<td>117.2(2)</td>
</tr>
<tr>
<td>Fe(1)-P(2)-C(30)</td>
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<tr>
<td>C(9)-P(2)-C(30)</td>
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</tr>
<tr>
<td>C(24)-P(2)-C(30)</td>
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<tr>
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<td>117.5(2)</td>
</tr>
<tr>
<td>P(1)-C(18)-C(19)</td>
<td>120.1(2)</td>
</tr>
<tr>
<td>P(1)-C(18)-C(23)</td>
<td>119.9(2)</td>
</tr>
<tr>
<td>P(2)-C(24)-C(25)</td>
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<td>P(2)-C(24)-C(29)</td>
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<td>P(2)-C(30)-C(31)</td>
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<td>P(2)-C(30)-C(35)</td>
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<td>P(2)-C(10)-C(11)</td>
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<td>Fe(1)-Fe(2)-P(2)</td>
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<tr>
<td>Fe(1)-Fe(2)-P(3)</td>
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<tr>
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<td>Fe(1)-Fe(2)-C(2)</td>
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<tr>
<td>Fe(1)-Fe(2)-C(3)</td>
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<tr>
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<td>P(2)-Fe(2)-C(1)</td>
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<tr>
<td>P(2)-Fe(2)-C(2)</td>
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</tr>
<tr>
<td>P(2)-Fe(2)-C(3)</td>
<td>108.7(2)</td>
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<tr>
<td>P(3)-Fe(2)-C(1)</td>
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<tr>
<td>P(3)-Fe(2)-C(2)</td>
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<td>C(1)-Fe(2)-C(2)</td>
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<tr>
<td>C(1)-Fe(2)-C(3)</td>
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<tr>
<td>C(2)-Fe(2)-C(3)</td>
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</tr>
<tr>
<td>Bond</td>
<td>Angle (°)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Fe(2)-C(1)-U(1)</td>
<td>176.3(5)</td>
</tr>
<tr>
<td>Fe(2)-C(2)-O(2)</td>
<td>178.2(5)</td>
</tr>
<tr>
<td>Fe(2)-C(3)-U(3)</td>
<td>178.7(5)</td>
</tr>
<tr>
<td>C(6)-P(1)-C(9)</td>
<td>99.7(3)</td>
</tr>
<tr>
<td>C(6)-P(1)-C(15)</td>
<td>104.9(3)</td>
</tr>
<tr>
<td>C(9)-P(1)-C(15)</td>
<td>103.9(2)</td>
</tr>
</tbody>
</table>
Figure 35. Stereodrawing of the Unit Cell of
\[
[(\text{CO})_2 (\eta^3-\text{C}_3\text{H}_5)\text{Fe}(\mu-\text{PPh}_2)\text{Fe}(\text{CO})_3 (\text{PPh}_2\text{C}_3\text{H}_5)].
\]
phosphine-phosphide phosphorus-phosphorus coupling constant 
\( J_{\text{P-P}} = 16 \text{ Hz} \) obtained from \(^{31}\text{P} \) NMR.

The Fe-Fe bond distance is 2.801Å which is 0.142Å 
longer than the Fe-Fe bond distance in the bridging-acetyl 
complex \(((\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\text{C(Me)R})\text{Fe}(\text{CO})_2(\text{PPh}_2\text{Me})\rangle\) and 0.18Å 
longer than that in \([\text{Fe}(\text{CO})_3(\mu-\text{PPh}_2)]_2\).\(^{92}\) However, this 
long Fe-Fe bond distance is still well within the limit of 
the Fe-Fe single bond, since it is only 0.09Å longer than 
that in the \(\text{PPN}[\text{Fe}_2(\text{PPh}_2)_2(\text{CO})_5(\text{C(U)CH}_3)]\) (2.718(5)Å).\(^{99}\) It 
is very close to the Fe-Fe bond distance found in \([\text{Fe}(\text{Cu})_3(\mu-\text{P(CF}_3)_2)]_2\) (2.819(1)Å), although in this complex the 
phenyl groups bonded to phosphorus are replaced by the 
strong electron-withdrawing CF\(_3\) groups. The Fe-P-Fe bond 
angle (78°) falls within the range found in the other iron 
phosphido-bridged compounds.\(^{92,99,126}\) This large bond angle 
also reflects the fact that there is a long iron-iron bond.

The C(6)-C(7) and C(7)-C(8) bond lengths are 1.386(15)Å 
and 1.385(16)Å, respectively. These two almost identical 
bond lengths show that in the \(\eta^3\)-allyl group C(6) and C(8) 
carbon atoms are equivalent.\(^{127}\) The three \(\eta^3\)-allyl carbons 
show comparable bond distances to Fe(2), with the Fe(2)-C(7) 
bond length about 0.07Å shorter than the other two.

The phosphido bridge is basically symmetrical with a 
small distortion toward the Fe(2), the Fe(2)-P(1) bond being 
shorter than that of Fe(1) to P(1).
e. Mechanism of Alkylation Reaction

On the basis of the X-ray crystal structure of
\[ [(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C(Me)}\text{O})\text{Fe(CO)}_2(\text{PPh}_2\text{Me})] \] and
\[ [(\text{CO})_2(\text{n}^3\text{-C}_3\text{H}_5)\text{Fe}(\mu-\text{PPh}_2)\text{Fe(CO)}_3(\text{PPh}_2\text{C}_3\text{H}_5)] \] it is obvious that two of the possible alkylation centers of
\[ [(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{Cu})\text{Fe(CO)}_2(\text{PPh}_2)]^{2-} \] are the Fe atoms with three carbonyl ligands and the phosphorus atom of the terminal diphenylphosphide ligand. It is necessary to determine which of these two possible reaction sites undergoes alkylation first. Therefore, the following isotope labeling cross-over experiments were run to provide detailed information with regard to this issue, and these reactions are summarized in Scheme III.

In one experiment, the dianion \[ [(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{Cu})-\text{Fe(CO)}_2(\text{PPh}_2)]^{2-} \] was treated first with one equivalent of MeI and then treated with one equivalent of CD\textsubscript{3}I. In the other experiment, the dianion was first treated with one equivalent of CD\textsubscript{3}I and then treated with one equivalent of MeI. Details of these two preparations are given in the Experimental Section.

The resultant products, \[ [(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C(Me)}\text{O})-\text{Fe(CO)}_2(\text{PPh}_2\text{CD}_3)] \] and \[ [(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C(CD}_3\text{)}\text{O})\text{Fe(CO)}_2- (\text{PPh}_2\text{Me})] \] can be easily distinguished by their proton NMR and \(^{13}\text{C} \) NMR spectra. The proton NMR spectrum of the complex with the \( \mu-\text{C(CD}_3\text{)}\text{O} \) ligand shows a doublet at 1.90 ppm \( (J_{\text{p-H}} = 7.5 \text{ Hz}) \) for the methyl group bonded to phosphorus. The proton NMR spectrum of the complex with the \( \mu-\text{C(Me)}\text{O} \)
Scheme III

\[
\begin{align*}
\text{(CO)}_3\text{Fe} & \hspace{1cm} \text{Fe(CO)}_2 \\
\text{PPh}_2 & \\
\text{MeI} & \leftarrow \\
\text{CD}_3\text{I} & \\
\text{(CO)}_3\text{Fe} & \hspace{1cm} \text{Fe(CO)}_2 \\
\text{PPh}_2\text{Me} & \\
\text{CD}_3\text{I} & \leftarrow \\
\text{MeI} & \\
\text{(CO)}_3\text{Fe} & \hspace{1cm} \text{Fe(CO)}_2 \\
\text{C}=\text{O} & \hspace{1cm} \text{PPh}_2\text{Me} \\
\text{CD}_3 & \\
\end{align*}
\]
ligand shows a singlet at 1.89 ppm which is assigned to the methyl group bonded to the carbon of the bridging acetyl ligand. The deuteriated methyl iodide used in this work shows no resonance in its proton NMR spectrum. The deuterium NMR spectra of both complexes show broad signals around 2 ppm.

The carbon-13 NMR spectrum of the complex with the \( \mu\-C(CD_3)\=U \) ligand also indicates that a methyl group bonded to phosphorus is present. A doublet at 15.6 ppm with \( J_{P-C} = 23.5 \) Hz is observed. The carbon-13 NMR spectrum of the complex with the \( \mu\-C(Me)\=U \) ligand shows a singlet at 47.5 ppm which is assigned to the methyl group bonded to the carbon of the bridging acetyl ligand. The deuteriated methyl groups of both complexes do not exhibit resonances in their \( ^{13}\text{C} \) NMR spectra. This is probably due to the deuterium-carbon coupling which splits the carbon signal into triplets and dramatically decreases their intensity.

The \( {^{31}\text{P}}[{^1\text{H}}] \) NMR spectra of both isotope-labeled bridging acetyl complexes are presented in Table 24. They show patterns identical with those of the \( {^{31}\text{P}}[{^1\text{H}}] \) NMR spectra of unlabeled \( [(CO)_3\Fe(\mu-\text{PPh}_2)(\mu-C(Me)U)\Fe(CO)_2-(\text{PPh}_2\text{Me})] \).

From the isotope labeling experiments, it is concluded that the first equivalent of methyl iodide reacts with the \( \text{PPh}_2 \) ligand of the \( [(CO)_3\Fe(\mu-\text{PPh}_2)(\mu-\text{CU})\Fe(CO)_2(\text{PPh}_2)]^{2-} \) dianion. In order to further prove the generality of this alkylation reaction with one equivalent of RI, various alkyl
Table 24. $^{31}P$ NMR Spectral Data for
\[(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)(\mu\text{-C}(R^2)\text{U})\text{Fe}(\text{CO})_2(\text{PPh}_2R^1)\]^a

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta(\mu\text{-PPh}_2)^b$</th>
<th>$\delta(\text{PPh}_2R^1)$</th>
<th>$J_{\text{P-P}}$, Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^1 = \text{Me}, R^2 = \text{CD}_3$</td>
<td>174.1</td>
<td>39.7</td>
<td>53</td>
</tr>
<tr>
<td>$R^1 = \text{CD}_3, R_2 = \text{Me}$</td>
<td>174.3</td>
<td>39.2</td>
<td>54</td>
</tr>
<tr>
<td>$R^1 = \text{Me}, R^2 = \text{i-Pr}$</td>
<td>171.8</td>
<td>40.0</td>
<td>45</td>
</tr>
<tr>
<td>$R^1 = \text{Et}, R^2 = \text{Me}$</td>
<td>174.3</td>
<td>52.7</td>
<td>55</td>
</tr>
</tbody>
</table>

^a in THF solution at 25°C

^b ppm
-iodides were allowed to react with the dianion. Details of the preparation of these alkyldiphenylphosphine substituted monoanions were presented in Section III-F-1 (equation 84). Various monoanions \( [(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{Cu})\text{Fe(CO)}_2^-(\text{PPh}_2\text{R})]^- \) were treated with \( \text{R'I} \) where \( \text{R}' \) is different from \( \text{R} \). The \( ^{31}\text{P}[^1\text{H}] \) NMR spectral data of the resultant complexes with different alkyl groups bonded to phosphorus and carbon of the bridging acyl ligand are presented in Table 24. These spectra consist of a downfield doublet which is assigned to the phosphorus atom of the bridging phosphido ligand and a highfield doublet which is assigned to the phosphorus atom of the terminal phosphine ligand with various alkyl groups.

At this point, the mechanism of the reaction of the monoanion \( [(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{Cu})\text{Fe(CO)}_2(\text{PPh}_2\text{Me})]^- \) with a second equivalent of \( \text{MeI} \) to form the final bridging-acetyl complex is still not clear. Therefore this alkylation reaction with a second equivalent of \( \text{MeI} \) was followed very carefully by \( ^{31}\text{P}[^1\text{H}] \) NMR spectroscopy. The \( ^{31}\text{P}[^1\text{H}] \) NMR spectra over the temperature range \(-78^\circ\text{C}\) to \(+30^\circ\text{C}\) are illustrated in Figure 36. At \(-78^\circ\text{C}\), the spectrum shows only resonances of the monoanion (M). Reaction with a second equivalent of \( \text{MeI} \) began at around \(-15^\circ\text{C}\) with the formation of an intermediate A. The monoanion M was still observed in the spectrum. As the temperature increased to \(7^\circ\text{C}\), the intensity of the resonances due to the monoanion decreased and a second reaction intermediate B was observed. At \(17^\circ\text{C}\), the reaction mixture
Figure 36. Variable Temperature $^{31}$P NMR Spectra

For the Reaction of Li[((CO)$_3$Fe($\mu$-Cu)-(\footnotesize{$\mu$-PPh$_2$})Fe(CO)$_2$(PPh$_2$Me)) with MeI.

Peaks Labeled "M" and "P" belong to Li[((CO)$_3$Fe($\mu$-Cu)(\footnotesize{$\mu$-PPh$_2$})Fe(CO)$_2$(PPh$_2$Me))]

and [(CO)$_3$Fe($\mu$-PPh$_2$)(\footnotesize{$\mu$-C(Me)O})Fe(CO)$_2$

(PPh$_2$Me)], Respectively. Peaks Labeled "A" and "B" belong to the Reaction Intermediates.
Figure 36.
consisted of three components: intermediate A, intermediate B, and final product P. The monoanion was totally consumed at 17°C. At room temperature, the resonances of the final product increased at the expense of the second intermediate B. The reaction mixture was then stirred at room temperature for 10 hours; the spectrum showed only the resonances of final product.

The $^{31}$P$[^{1}H]$ NMR spectrum of the reaction mixture at 17°C shows that the predominant species in the reaction mixture is intermediate B. Therefore efforts were made to observe a $^{13}$C NMR spectrum of the reaction mixture at 17°C. The same reaction was therefore repeated using $^{13}$Cu enriched Li[($\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{Cu})\text{Fe(CO)}_2\text{PPh}_2\text{Me})]$ and MeI and monitored by $^{13}$C NMR measurements. The $^{13}$C NMR spectrum of the reaction mixture at 17°C is presented in Figure 37. In order to freeze the reaction and eliminate complications due to stereochemically nonrigid behavior of the reacting species, the spectrum was taken at -73°C. The spectrum consists of a broad multiplet at 310 ppm, a hump at 299 ppm, and a complicated terminal carbonyl resonance pattern at around 220 ppm. The weak intensity hump at 299 ppm is assigned to the bridging acyl C=O resonance of the final product. Therefore, it is reasonable to assign the 310 ppm peak to the intermediate B. The peak is in the region characteristic of metal acyl C=O resonances.$^{101}$

A possible mechanism for the methylation of the dianion [$($Cu$)_3$Fe(μ-PPh$_2$)(μ-Cu)Fe(CO)$_2$PPh$_2$)]$^{2-}$ is summarized in
Scheme IV

$\text{(CO)}_3\text{Fe} \xrightarrow{\text{MeI}} \text{THF} \xrightarrow{-78^\circ C} \text{Fe(CO) }_2 \xrightarrow{\text{MeI}} \text{M}$

$\text{(P)} \xrightarrow{\text{MeI}} \text{PPh}_2\text{Me}$

$\text{(B)} \xrightarrow{\text{MeI}} \text{PPh}_2\text{Me}$
Figure 37. The $^{13}$C NMR Spectrum of the Reaction Mixture of Li[((CO)$_3$-Fe($\mu$-PPh$_2$)(\(\mu\)-CO)Fe(CO)$_2$(PPh$_2$Me)] with MeI at 17°C.
Scheme IV. The dianion reacts immediately with the first equivalent of MeI at -78°C to form \{[(Cu)\textsubscript{3}Fe(µ-PPPh\textsubscript{2})(µ-CO)\textsubscript{-}Fe(CO)\textsubscript{2}(PPPh\textsubscript{2}Me)]\textsuperscript{-}\}. At higher temperature, this PPPh\textsubscript{2}Me substituted monoanion reacts with a second equivalent of MeI to form the bridging acetyl complex through two reaction intermediates A and B. Exact nature of these intermediates is not clear at present. The second equivalent of MeI might attack the Fe atom of the Fe(Cu)\textsubscript{3} moiety first to form the intermediate A with a metal-Me bond. The methyl group may then migrate to one of the carbonyl ligands to form a monodentate acetyl ligand leaving the Fe atom of the Fe(CO)\textsubscript{3}(µ-PPPh\textsubscript{2}Me) moiety with only 16e-. Coordination of the oxygen of the acyl ligand to the coordinatively unsaturated Fe atom will lead to the formation of the final product with a bridging acetyl ligand in which both Fe atoms will satisfy the effective atomic number rule.

An entirely analogous alkylation reaction sequence was expected for ethyl iodide, 1-propyl iodide, and 2-propyl iodide. Indeed the dianion reacts immediately with the first equivalent of the alkylating agent at -78°C. However, the conditions required for the reaction of Li[(Cu)\textsubscript{3}Fe(µ-PPPh\textsubscript{2})(µ-CO)Fe(Cu)\textsubscript{2}(PPPh\textsubscript{2}K)] with a second equivalent of RI vary. The alkylation of the dianion proceeds by a somewhat different pathway than the methylation reaction. The dianion reacts with a first equivalent of allyl iodide at -78°C immediately to form \{[(Cu)\textsubscript{3}Fe(µ-PPPh\textsubscript{2})(µ-CO)Fe(Cu)\textsubscript{2}-(PPPh\textsubscript{2}C\textsubscript{3}H\textsubscript{5})]\textsuperscript{-}\}. Reaction of this monoanion with a second
equivalent of allyl iodide was monitored by $^{31}$P NMR measurements. The $^{31}$P{$^1$H} NMR spectra of the reaction mixture over the range $-78^\circ$C to $+30^\circ$C are presented in Figure 38. At $-73^\circ$C, the spectrum shows resonances of the monoanion (M). Reaction then began at around $-35^\circ$C with conversion of the monoanion to the intermediate (A). At $-13^\circ$C, the spectrum consists of the resonances of the intermediate (A) and the final product (P). No resonances of the monoanion can be observed. At around $0^\circ$C, the conversion of the intermediate (A) to the final product (P) is complete. The $^{31}$P{$^1$H} NMR of the intermediate A exhibits a doublet at 81.9 ppm and another doublet at 76.5 ppm ($J_{P-P} = 27$ Hz). At this moment, the nature of the intermediate (A) is not clear. A possible mechanism based on the reaction of $[C_5H_5Mo(CO)_3]^-$ with allyl chloride is summarized in Scheme V.\textsuperscript{105} In the proposed mechanism, the monoanion reacts with a second equivalent of allyl iodide to form the intermediate (A) with a $\sigma$-allyl group. The intermediate $\sigma$-allyl derivative then rearranges to the $\pi^3$-allyl form with the expulsion of a carbonyl ligand.\textsuperscript{128} However, an interpretation of the $^{31}$P{$^1$H} NMR highfield position of the phosphorus of the bridging phosphido ligand of the intermediate (A) is unavailable at present.
Figure 38. Variable Temperature $^{31}P\{^1H\}$ NMR Spectra for the Reaction of $\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{CO})(\mu-\text{PPh}_2)\text{Fe}(\text{CO})_2(\text{PPh}_2\text{C}_3\text{H}_5)]$ with $\text{C}_3\text{H}_5\text{I}$.

Peaks Labeled "M" and "P" Belong to $\text{Li}[(\text{CO})_3\text{Fe}(\mu-\text{CO})(\mu-\text{PPh}_2)\text{Fe}(\text{CO})_2(\text{PPh}_2\text{C}_3\text{H}_5)]$ and $[(\text{CO})_2(\eta^3-\text{C}_3\text{H}_5)\text{Fe}(\mu-\text{PPh}_2)\text{Fe}(\text{CO})_3(\text{PPh}_2\text{C}_3\text{H}_5)]$. Peaks Labeled "A" Belong to the Reaction Intermediate.
Figure 38.
3. Reaction of \[ [(CO)_3Fe(\mu-PPh_2)(\mu-CO)Fe(CO)_2(PPh_2)]^{2-} \]

with \( \text{CH}_2\text{I}_2 \)

The reaction of the dianion \[ [(CO)_3Fe(\mu-PPh_2)(\mu-CO)-Fe(CO)_2(PPh_2)]^{2-} \] with \( \text{CH}_2\text{I}_2 \) at \(-78^\circ\text{C}\) yields a new complex \[ [(CO)_3Fe(\mu-PPh_2)(\mu-\text{CH}_2PPh_2)Fe(CO)_3] \] in good yield (equation 90). The new methylenediphenylphosphine-bridge complex has been characterized spectroscopically.

This reaction process was monitored by \( ^{31}\text{P}[^1\text{H}] \) NMR measurements. In contrast to the methylation of the dianion, \( \text{CH}_2\text{I}_2 \) reaction with the dianion at \(-78^\circ\text{C}\) immediately leads to the formation of the final product with no observable intermediates.

The \( ^{31}\text{P}[^1\text{H}] \) NMR spectrum of the complex shows resonances at 181.0 ppm (doublet) and 20.4 ppm (doublet, \( J_{\mu\mu} = 31 \text{ Hz} \)). The resonance at 181.0 ppm is assigned to the phosphorus atom of the bridging \( \mu-PPh_2 \) ligand and is in the region normally observed for a diphenylphosphido ligand bridging across an Fe-Fe bond. The doublet at 21.4 ppm is assigned to the phosphorus atom of the \( \text{CH}_2PPh_2 \) ligand attached to two Fe atoms.

The \( ^{13}\text{C}[^1\text{H}] \) NMR spectrum of the complex is shown in Figure 39. The spectrum shows terminal carbonyl resonances.
Figure 39. The $^{13}$C NMR Spectrum of $[(\text{Cu})_3 \text{Fe} (\mu-\text{PPh}_2)(\mu-\text{CH}_2\text{PPh}_2)\text{Fe}(\text{CO})_3]$ in CDCl$_3$ at 25°C.
at around 213.3 ppm. One interesting feature of the spectrum is a highfield resonance of the CH$_2$ carbon atom of the bridging CH$_2$PPh$_2$ group. The triplet at -18.8 ppm is assigned to the carbon of the CH$_2$ group. It is coupled to the phosphorus atoms of the two different PPh$_2$ groups and a doublet of doublets splitting pattern is expected. However, the two coupling constants are probably very similar, and the observed triplet results from overlapping of the two doublets. The methylene protons show a doublet at 1.6 ppm ($J_{P-H} = 33$ Hz, relative intensity 2) in the proton NMR spectrum. The multiplet at 7.2 ppm (relative intensity 20) is assigned to the phenyl protons. The infrared spectrum of the complex shows only absorptions in the region of 1950 to 2050 cm$^{-1}$, which are assigned to terminal carbonyl stretching vibrations. The mass spectrum of the complex shows a parent ion at m/e 664, with the fragment ions corresponding to stepwise loss of the five carbonyl ligands.

G. Reaction of [(CO)$_3$Fe($\mu$-PPh$_2$)($\mu$-CO)Fe(CO)$_2$PPh$_2$H] with Alkylation Agents

1. Reaction of Li[(CO)$_3$Fe($\mu$-PPh$_2$)($\mu$-CO)Fe(CO)$_2$(PPh$_2$H)] with Excess MeI, EtI, n-PrI, i-PrI and Allyl Iodide

Treatment of a THF solution of Li[(CO)$_3$Fe($\mu$-PPh$_2$)-($\mu$-CO)Fe(CO)$_2$(PPh$_2$H)] at -78°C with excess MeI followed by warming to room temperature and chromatography on alumina eluting with petroleum ether-ether mixed solution (0-10%) affords [Fe(CO)$_3$(PPh$_2$)$_2$]$_2$ (35%),
[(CO)$_3$Fe($\mu$-PPh$_2$)(\(\mu\)-C(Me)O)Fe(CO)$_2$(PPh$_2$Me)] (25%), and Fe$_2$(CO)$_5$(PPh$_2$Me)($\mu$-PPh$_2$)$_2$ (<10%) (equation 91).

\[
\begin{align*}
\text{(CO)$_3$Fe} & \quad \text{Excess} \quad \text{MeI} & \quad \text{(CO)$_3$Fe} \\
\text{HPPh$_2$} & & \quad \text{Fe(CO)$_2$} \\
\end{align*}
\]

The bridging acetyl complex [(CO)$_3$Fe($\mu$-PPh$_2$)(\(\mu\)-C(Me)O)-Fe(CO)$_2$(PPh$_2$Me)] was first prepared by this method in low yield. A much higher yield (>70%) synthetic route to this complex is provided by methylation of the [(CO)$_3$Fe($\mu$-PPh$_2$)-(\(\mu\)-CO)Fe(CO)$_2$(PPh$_2$)]$^2$- dianion. Characterization of this complex was fully discussed in Section III-F-2-a.

An analogous reaction sequence was apparent for the bridging propionyl complex, [(CO)$_3$Fe($\mu$-PPh$_2$)(\(\mu\)-C(Et)O)-Fe(CO)$_2$(PPh$_2$Et)]. However, the yield of this product was very poor (<5%) (equation 92). No reaction appears to occur when Li[(CO)$_3$Fe($\mu$-PPh$_2$)(\(\mu\)-CO)Fe(CO)$_2$(PPh$_2$H)] is treated with excess 1-propyl iodide or 2-propyl iodide even at the temperature of THF at reflux.

For these alkylation reactions, the PPh$_2$H substituted monoanion was prepared by using two equivalents of the reducing agent LiBEt$_3$H. When the monoanion was obtained by
using only one equivalent of LiBEt₃H, the methylation reaction gives a lower yield of the bridging acetyl complex (<15%).

The monoanion also reacts with allyl iodide to form the \( \eta^3 \)-allyl complex, \([\text{Fe}(\eta^3-C_3H_5)\text{Ph}(\mu-\text{PPh}_2)\text{Fe}(\text{CO})_3]^{-}\). Characterization of this complex was fully discussed in Section III-F-2-d.
b. Reaction of \([(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PPh}_2\text{H})]^-)\]

with Benzyl Chloride

Treatment of \(\text{Li}[\text{Fe}(\text{CO})_3(\mu-\text{PPh}_2)]_2\) and two equivalents of \(\text{LiBET}_3\text{H}\) in THF, with excess benzyl chloride affords no reaction at room temperature. The solution was then heated in THF at reflux for three days. Chromatography on alumina afforded three complexes (equation 94).

\[
\begin{align*}
\text{(CO)}_3\text{Fe} & \quad \text{Ph}_2\text{O} \\
\text{Ph}_2\text{CH}_2\text{Cl} & \quad \text{THF, } \Delta \\
\text{HPPH}_2 & \quad \text{Fe(CO)}_3
\end{align*}
\]

(94)

It was found that the monoanion \([(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe}(\text{CO})_2(\text{PPh}_2\text{H})]^-)\) reacts with alkylation agents to give phosphine-substituted products of \([\text{Fe}(\text{CO})_3(\mu-\text{PPh}_2)]_2\). \(^{62}\) Collman has reported that the complex \([\text{Fe}(\text{CO})_3(\mu-\text{PPh}_2)]_2\) undergoes phosphine substitution reactions under photolytic conditions, \(^{62}\) and Ellgen\(^{129}\) has also reported related thermal substitutions. However, no detailed \(^{31}\)P NMR spectra of these complexes have been reported.

The \(^{31}\)P\(^{1}H\) NMR spectra of these derivatives are presented in Table 25. These spectra exhibit a general pattern of a downfield doublet around 140 ppm and a triplet at
Table 25. $^{31}$p NMR Spectral Data for

$$[(\text{CO})_3 \text{Fe}(\mu-\text{PPh}_2)_2 \text{Fe(\text{CO})}_2 \text{(PPh}_2 \text{R})]\text{a}$$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta(\mu-\text{PPh}_2)$</th>
<th>$\delta(\text{PPh}_2 \text{R})$</th>
<th>$J_{p-p}$, Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R = H$</td>
<td>143.3, d</td>
<td>49.8, t</td>
<td>4</td>
</tr>
<tr>
<td>$R = \text{Me}$</td>
<td>138.7, d</td>
<td>46.3, t</td>
<td>10</td>
</tr>
<tr>
<td>$R = \text{Et}$</td>
<td>138.2, d</td>
<td>58.9, t</td>
<td>10</td>
</tr>
<tr>
<td>$R = \text{allyl}$</td>
<td>138.3, d</td>
<td>54.9, t</td>
<td>9</td>
</tr>
<tr>
<td>$R = \text{CH}_2\text{Ph}$</td>
<td>138.3, d</td>
<td>63.9, t</td>
<td>9</td>
</tr>
</tbody>
</table>

$^a$in THF solution at 25°C

$^b$ppm. Abbreviations: d, doublet; t, triplet.
around 50 ppm. The downfield doublet is assigned to the phosphorus of the two equivalent \( \mu-\text{PPh}_2 \) ligands, and its position implies the presence of an Fe-Fe bond. The upfield triplet is assigned to the phosphorus of the terminal \( \text{PPh}_2\text{R} \) ligand. The small phosphine-phosphide phosphorus phosphorus coupling constants (<10 Hz) suggest that the phosphine ligand \( \text{PPh}_2\text{R} \) is positioned trans to the metal-metal bond (cis to the two bridging \( \mu-\text{PPh}_2 \) ligand) in all of these derivatives.\(^{62}\)

Proton NMR and \(^{13}\text{C}\) NMR spectral data of these complexes indicate that the proton or the alkyl group is bonded to the phosphorus to form an iron-coordinated phosphine. The chemical shift values and coupling patterns of these alkyl groups (see Experimental section) provide useful information for assignment of the proton and \(^{13}\text{C}\) NMR spectra of the \( [(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)\text{(\text{Cu})_2\text{(PPh}_2\text{R})]} \) complexes.

The infrared spectra of these complexes exhibit terminal carbonyl stretching absorptions and are similar to those reported previously by Collman and by Geoffroy.\(^{62,8}\)

The X-ray crystal structure of \( \text{Fe}_2(\text{Cu})_5(\mu-\text{PPh}_2)_2(\text{PPh}_2\text{C}_3\text{H}_5) \) has been determined. An ORTEP drawing of the molecule is shown in Figure 40. The structure consists of an \( \text{Fe(CO)}_3 \) moiety and an \( \text{Fe(CO)}_2(\text{PPh}_2\text{C}_3\text{H}_5) \) moiety joined by a metal-metal bond and two diphenylphosphido bridging ligands. Selected bond lengths and bond angles of the complex are listed in Appendix A.
Figure 40. An ORTEP drawing of the [(CO)$_3$Fe(μ-PPh$_2$)-Fe(CO)$_2$(PPh$_2$C$_3$H$_5$)] molecule showing the atom numbering scheme.
The presence of an Fe-Fe bond is confirmed by the short Fe-Fe distance (2.644 Å). As expected, the two diphenylphosphido bridging ligands are symmetrical and adopt a folded arrangement with the two Fe atoms. The small Fe-P-Fe bond angles (73.11° and 72.20°) also reflect that there is a strong Fe-Fe interaction. The terminal PPh₂C₃H₅ ligand adopts a cis arrangement (on the same side of the Fe-Fe bond) with the phosphido ligands, which confirms the prediction of a cis arrangement from the ³¹P[¹H] NMR spectrum.

H. Reactions of [(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(CO)₂(PPh₂)]²⁻ and [(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(CO)₂(PPh₂H)]⁻ with Trifluoroacetic Acid

1. Reaction of [(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(CO)₂(PPh₂H)]⁻ with CF₃COOH

Treatment of Li[(CO)₃Fe(μ-PPh₂)(μ-CO)Fe(CO)₂(PPh₂H)] with excess CF₃COOH at 25°C leads to the formation of a binuclear iron hydride complex as shown in equation 95. The yellow-orange solid is air sensitive and decomposes to form [Fe(CO)₃(μ-PPh₂)]₂.
The $^1$H NMR spectrum of \([\text{Fe}(\nu-\text{PPh}_2)\text{Fe}(\text{CO})_2(\text{PPh}_2\text{H})]\) exhibits the expected doublet of doublets at $\delta=9.45$ ppm ($^2J_{P(1)-H} = 51$ Hz, $^3J_{P(2)-H} = 4$ Hz). This highfield resonance is assigned to the hydrogen bonded to Fe(1).\footnote{102}

The $^{31}P[1H]$ NMR spectrum of the reaction mixture shows resonances which can be assigned to [Fe(CO)$_3$(\nu-PPh$_2$)$_2$] and the metal hydride complex. The doublet at 172.3 ppm is assigned to the phosphorus atom of the bridging \nu-PPh$_2$ ligand. The downfield position implies that the \nu-PPh$_2$ ligand bridges two Fe atoms joined by a metal-metal bond. The doublet at 37.4 ppm ($J_{P-P} = 17$ Hz) is assigned to the phosphorus atom of the PPh$_2$H ligand attached to Fe(2). The $^{31}P[1H]$ NMR spectrum is temperature invariant in the range of $-73^\circ\text{C}$ to $52^\circ\text{C}$.

When the broadband $^1$H decoupling is eliminated, the upfield doublet at 37.4 ppm is observed as a broad doublet with $J_{P(2)-H} = 380$ Hz. The downfield doublet at 172.3 ppm appears as a doublet of doublets ($J_{P-P} = 17$ Hz, $^2J_{P(1)-H} = 50$ Hz). The $^{31}P[1H]$ coupling obtained in the $^{31}P$ NMR spectrum is comparable to that obtained from the proton NMR spectrum. The small coupling of 17 Hz observed between the phosphorus atom of the terminal phosphine and that of the bridging phosphide suggests a cis arrangement for these two ligands.

The IR spectrum shows only stretching absorptions of the terminal carbonyls at 2057, 2014, 1995, and 1995 cm$^{-1}$. No bridging carbonyl absorptions can be observed. The
corresponding deuteriated complex can be prepared by reaction of Li[(Cu)_3Fe(μ-PPh_2)(μ-Cu)Fe(Cu)_2(PPh_2D)], prepared from [Fe(Cu)_3(μ-PPh_2)]_2 and LiHEt_3D, with excess CF_3COOD. The 3^1P[1H] NMR spectrum of the metal deuteride shows a quintet at 172.9 ppm (J_P-P = 18 Hz, J_P(1)-D = 8 Hz), which is possibly a doublet of triplets with two peaks overlapping each other. As expected, the PPh_2D ligand shows a doublet of triplets at 38.5 ppm (J_P-P = 18 Hz, J_P(2)-D = 58.5 Hz). The values of 2J_P(1)-H/2J_P(1)-D = 6.25 and 1J_P(2)-H/1J_P(2)-D = 6.5 are close to the gyromagnetic ratio γ_H/γ_D of 6.51. The isotopic chemical shift difference of the PPh_2H ligand is 1.1 ppm, which is comparable to that observed for [(Cu)_3Fe(μ-PPh_2)-(μ-Cu)Fe(Cu)_2(PPh_2H)]^− (1.0 ppm).

Generally, hydride ligand in metal hydride complexes has not been observed to migrate to the carbonyl group to form corresponding metal formyl complexes, although the reverse reaction is well known. Therefore, complex [(Cu)_3(H)Fe(μ-PPh_2)Fe(Cu)_3(PPh_2H)] may be the hydrogen analogue of the proposed intermediate A (Scheme III) in the methylation of [(Cu)_3Fe(μ-PPh_2)(μ-Cu)Fe(Cu)_2(PPh_2)]^2−.

2. Reaction of [(Cu)_3Fe(μ-PPh_2)(μ-Cu)Fe(Cu)_2(PPh_2)]^2− with CF_3COOD.

As expected, treatment of the dianion Li_2[(Cu)_3Fe(μ-PPh_2)(μ-Cu)Fe(Cu)_2(PPh_2)] with one equivalent of CF_3COOD at -70°C yields the PPh_2D-substituted complex Li[(Cu)_3Fe(μ-PPh_2)(μ-Cu)Fe(Cu)_2(PPh_2D)]^− (equation 96)
The product monoanion is identified by its $^{31}\text{P}[^{1}\text{H}]$ NMR spectrum.

The dianion reacts immediately with two equivalents of CF$_3$COOD at -78°C to give [(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$-PPh$_2$D)] as its dark purple solution changes color to orange red. The $^{31}\text{P}[^{1}\text{H}]$ NMR spectrum of the reaction solution exhibits identical chemical shift values and coupling patterns as that obtained for the products of the reaction of Li[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$D)] with CF$_3$COOD.

I. Reactions of \( [(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)\text{Fe}(\text{NO})(\text{PPh}_2\text{H})]^- \) and \( [(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)\text{Fe}(\text{NO})(\text{PPh}_2)]^{2-} \) with Alkylating Agents

1. Reaction of \( [(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)\text{Fe}(\text{NO})(\text{PPh}_2\text{H})]^- \) with RI (R = Me, Et)

Treatment of Li\( [(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)\text{Fe}(\text{NO})(\text{PPh}_2\text{H})] \), from \( \text{[Fe(NO)$_2$(μ-PPh$_2$)]_2} \) and two equivalents of LiB$\text{Et}_2$H in THF, with excess RI (R = Me, Et) at -78°C followed by
warming to room temperature affords \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\) and \(\text{Fe(NO)}_2(\text{PPh}_2\text{Me})_2\) (equation 97).

\[\begin{array}{c}
\text{Fe(NO)}_2(\text{PPh}_2\text{Me})_2 \\
\text{THF} \quad \text{RI} \\
\text{Fe(NO)}_2(\text{PPh}_2\text{Me})_2
\end{array}\]

The \(^{31}\text{P}[^1\text{H}]\) NMR spectra of the mononuclear products show a singlet for the two equivalent phosphine ligands in the normal range for metal phosphine complexes \((R = \text{Me}, 41.8 \text{ ppm}; R = \text{Et}, 54.9 \text{ ppm})\).\(^9\) Proton and \(^{13}\text{C}[^1\text{H}]\) NMR spectra of the complexes indicate that there is one type of alkyl group bonded to phosphorus. The mass spectra of the complexes show parent ion at m/e 516 for the diphenylmethyl phosphine complex and at m/e 544 for the diphenylethyl phosphine complex with fragment ions corresponding to stepwise loss of the two nitrosyl ligands. These mass spectra provide conclusive evidence that the products formed in these alkylation reactions are actually monomeric iron complexes containing two phosphine ligands and two nitrosyl ligands.

The complex \([\text{Fe(NO)}_2(\mu-\text{PPh}_2\text{Me})]_2\) has been previously prepared by the reaction of \([\text{Fe(NO)}_2(\text{CO})_2]\) and \(\text{PPh}_2\text{Me}\) in hexane, and the infrared spectrum reported is comparable to that obtained in this study. The IR spectra of the complexes show two stretching absorptions of the terminal nitrosyls in the region of 1680-1725 cm\(^{-1}\).
The formation of the monomeric complexes may proceed by methylation of the monoanion \([\text{NO}]_2\text{Fe}(\mu-\text{NO})-(\mu-\text{PPh}_2)\text{Fe(NO)}(\text{PPh}_2\text{H})\)\(^-\) at the deprotonated P(1) and at Fe(2) (equation 97), followed by reductive elimination of the bridging PPh\(_2\) ligand and the methyl group to form diphenylmethylphosphine ligand bonded to Fe(1) with cleavage of the metal-metal bond.

2. Reaction of \([\text{NO}]_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)\text{Fe(NO)}(\text{PPh}_2\text{H})\)\(^-\) with \(\text{CH}_2\text{I}_2\)

The reaction of \(\text{CH}_2\text{I}_2\) with \(\text{Li}[\text{NO}]_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)-\text{Fe(NO)}(\text{PPh}_2\text{H})\) affords \(\text{[Fe(NO)\(_2\)(\mu-\text{PPh}\(_2\))]}_2\) and two new complexes formulated as \([\text{NO}]_2\text{Fe}(\mu-\text{CH}_2\text{PPPh}_2)\text{Fe(NO)}\)\(_2\) and \([\text{NO}]_2\text{Fe}(\mu-\text{CH}_2)(\mu-\text{PPh}_2\text{PPPh}_2)\text{Fe(NO)}\)\(_2\).

The complex \(\text{Li}[\text{NO}]_2\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{NU})\text{Fe(NO)}(\text{PPh}_2\text{H})\) was prepared from \([\text{Fe(NO)}\(_2\)(\mu-\text{PPh}_2)]_2\) and two equivalents of \(\text{LiBET}_3\) in THF. Excess \(\text{CH}_2\text{I}_2\) was added to the monoanion at room temperature. These new complexes were first characterized.
spectroscopically and then by complete single-crystal X-ray diffraction studies which will be discussed in turn.

a. Characterization and X-ray Structure of

\[(\text{NO})_2\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CH}_2\text{PPh}_2)\text{Fe(NO)}_2\]

The X-ray diffraction study of complex (XI) showed the structure sketched below.

![Diagram of complex (XI)](image)

The \(^{31}P\{^1H\} \text{ NMR spectrum of complex (XI) shows resonances at } -1.59 \text{ ppm (doublet) and } 232.9 \text{ ppm (doublet) with the phosphine-phosphide phosphorus-phosphorus coupling equal to } 56 \text{ Hz. The resonance at } 232.9 \text{ is assigned to the phosphorus atom of the bridging PPh}_2 \text{ ligand and the resonance at } -1.6 \text{ ppm is assigned to the phosphorus atom of the methylenediphenyl phosphine ligand.}

The proton NMR spectrum of complex (XI) shows resonances at 7.3 ppm (relative intensity 20) and 1.5 ppm (relative intensity 2). The broad multiplet at 7.3 ppm is assigned to the phenyl protons, and the triplet-shaped resonance at 1.5 ppm is assigned to the CH\(_2\) protons. The
triplet-shaped peak is probably due to two overlapping doublets.

The IR spectrum of complex (XI) shows bands at 1771, 1736, and 1715 cm$^{-1}$ which are attributed to stretching modes of the terminal nitrosyl ligands. The $^{13}$C NMR spectrum of complex (XI) consists of resonances at 128.5 - 138.4 ppm and -30.3 ppm (triplet) which can be assigned respectively to phenyl and CH$_2$ group carbons. As in its isoelectronic carbonyl complex [(CO)$_3$Fe($\mu$-PPh$_2$)($\mu$-CH$_2$PPh$_2$)Fe(CO)$_3$], the CH$_2$ group exhibits a highfield triplet. In the off-resonance spectrum, the triplet further splits into unresolvable multiplets due to proton coupling. The mass spectrum of complex (XI) shows a parent ion at m/e 616, with the expected fragment ions corresponding to stepwise loss of three nitrosyl ligands.

Some monomeric metal complexes containing a bidentate $\mu$-CH$_2$PPh$_2$ ligand have been prepared.$^{131}$ One of the interesting spectral features of these complexes is the resonance position of the CH$_2$ carbon in the $^{13}$C NMR spectrum. Seemingly, the carbon atom of the three-membered ring in [M-CH$_2$-P] exhibits its resonance at a lower frequency than TMS. Some examples are illustrated in Table 26.

Relatively, only a few binuclear metal complexes containing a $\mu$-CH$_2$PPh$_2$ ligand have been reported.$^{134,135}$ A dicobalt complex with $\mu$-PPh$_2$ and $\mu$-CH$_2$PPh$_2$ ligands has been recently described by Klein and co-workers.$^{135}$ The complex
was prepared by the reaction shown in equation 99.

\[
\text{PM}_{3}CoN_{2}K + \text{PM}_{3}CoCl \rightarrow \text{PM}_{3}Co(Co(\text{PM}_{3})_{2})
\]

The molecular structure of complex (XI) with important bond lengths and bond angles is shown in Figure 41. Figure 42 shows the molecular structure with a numbering scheme of atoms. Selected bond lengths and bond angles of complexes (XI) are listed in Tables 27 and 28. Complex (XI) crystallizes with two independent molecules A and B in the asymmetric unit. Structural differences between molecules A and B occur in some torsion and bond angles as well as in the iron-iron bond distance.

In each molecule the two iron atoms bond to two nitrosyl ligands and are bridged by the \(\mu\)-PPh\(_2\) and \(\mu\)-CH\(_2\)PPh\(_2\) ligands. The two bridging ligands are roughly positioned in a plane perpendicular to the plane defined by the two Fe(NO\(_2\))\(_2\) groups. The two phosphorus atoms and the two Fe atoms comprise a plane with the carbon atom of the methylene group twisted out of this plane.

The Fe-Fe distances of 2.836(4) and 2.812(5)\(\text{Å}\) in molecules A and B, respectively, are in the range of longer known iron-iron bond distances. They are shorter than the Fe-Fe bond distance in [Fe(NO)\(_2\)I]\(_2\) (3.05(5)\(\text{Å}\)),\(^{136}\) [\(\eta^3\)-C\(_3\)H\(_5\)]Fe(CO)\(_3\)]\(_2\) (3.138\(\text{Å}\)),\(^{137}\) and [Fe\(_2\)(CO)\(_8\)]\(^{2-}\) (2.88\(\text{Å}\));
Table 26. $^{13}$C NMR Spectral Data of the CH$_2$ Group in μ-CH$_2$PR$_2$ Ligands in Some Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>δ(μ-CH$_2$PR$_2$), ppm</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[((Cu)$_3$Fe(μ-PPh$_2$)-) (μ-CH$_2$PPh$_2$)Fe(Cu)$_3$]</td>
<td>-18.8</td>
<td>This study</td>
</tr>
<tr>
<td>[((Nu)$_2$Fe(μ-PPh$_2$)-) (μ-CH$_2$PPh$_2$)Fe(Nu)$_2$]</td>
<td>-30.3</td>
<td>This study</td>
</tr>
<tr>
<td>Ir(PMe$_2$Ph)$_2$Cl$_2$(CH$_2$PMe$_2$)</td>
<td>-9.3</td>
<td>132</td>
</tr>
<tr>
<td>Mn(CO)$_4$(CH$_2$PPh$_2$)</td>
<td>-16.6</td>
<td>131</td>
</tr>
<tr>
<td>[((Cu)$_3$Fe(μ-PPh$_2$PCHPPh$_2$)-) FeH(Cu)$_3$]</td>
<td>-15.9</td>
<td>133</td>
</tr>
</tbody>
</table>
**BOND DISTANCES AND ANGLES**

\[
\begin{align*}
\text{A} & : & \text{NO}_2\text{Fe} & - 2.698 & \text{Fe(NO)}_2 & - 2.230 & \text{PPh}_2 & - 74.5 \cr
\text{B} & : & \text{NO}_2\text{Fe} & - 2.08 & \text{Fe(NO)}_2 & - 2.824 & \text{PPh}_2 & - 95.8 \cr
\text{C} & : & \text{NO}_2\text{Fe} & - 2.288 & \text{Fe(NO)}_2 & - 2.730 & \text{PPh}_2 & - 93.3 \cr
\end{align*}
\]

**Figure 41.** The Molecular Structure of (A) \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\),
(B) \([\text{NO}_2\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CH}_2\text{PPh}_2)\text{Fe(NO)}_2]\) and
(C) \([\text{NO}_2\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CH}_2)\text{Fe(NO)}_2]\) with Selected
Bond Distances and Angles.
Table 27. Selected Bond Lengths for
\[[\text{NO}_2\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CH}_2\text{PPh}_2)\text{Fe(NU)}_2]\]

<table>
<thead>
<tr>
<th>Bond Length, Å</th>
<th>Molecule A</th>
<th>Molecule B</th>
</tr>
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<tbody>
<tr>
<td>Fe(1)-Fe(2)</td>
<td>2.836(4)</td>
<td>2.812(5)</td>
</tr>
<tr>
<td>Fe(1)-P(1)</td>
<td>2.234(4)</td>
<td>2.249(5)</td>
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<td>Fe(1)-N(1)</td>
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<td>1.64(2)</td>
</tr>
<tr>
<td>Fe(1)-N(2)</td>
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<td>1.59(1)</td>
</tr>
<tr>
<td>Fe(1)-C(1)</td>
<td>2.06(2)</td>
<td>2.10(2)</td>
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<tr>
<td>Fe(2)-P(1)</td>
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<td>2.226(8)</td>
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<td>1.20(2)</td>
</tr>
<tr>
<td>N(4)-O(4)</td>
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<td>1.21(2)</td>
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</table>
Table 28. Selected Bond Angles for [(NO)$_2$Fe($\mu$-PPh$_2$)(\(\mu\)-CH$_2$PPh$_2$)Fe(NU)$_2$]

<table>
<thead>
<tr>
<th>Angle</th>
<th>Bond Angle, degree</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Molecule A</td>
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<tr>
<td>Fe(2)-Fe(1)-N(1)</td>
<td>119.9(5)</td>
</tr>
<tr>
<td>Fe(2)-Fe(1)-N(2)</td>
<td>117.6(7)</td>
</tr>
<tr>
<td>P(1)-Fe(1)-C(1)</td>
<td>132.0(6)</td>
</tr>
<tr>
<td>P(1)-Fe(1)-N(1)</td>
<td>105.9(5)</td>
</tr>
<tr>
<td>P(1)-Fe(1)-N(2)</td>
<td>100.9(4)</td>
</tr>
<tr>
<td>N(1)-Fe(1)-N(2)</td>
<td>121.2(9)</td>
</tr>
<tr>
<td>N(1)-Fe(1)-C(1)</td>
<td>98.4(8)</td>
</tr>
<tr>
<td>N(2)-Fe(1)-C(1)</td>
<td>100.7(7)</td>
</tr>
<tr>
<td>Fe(1)-Fe(2)-P(1)</td>
<td>50.6(1)</td>
</tr>
<tr>
<td>Fe(1)-Fe(2)-P(2)</td>
<td>68.2(2)</td>
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<tr>
<td>Fe(1)-Fe(2)-N(3)</td>
<td>123.4(8)</td>
</tr>
<tr>
<td>Fe(1)-Fe(2)-N(4)</td>
<td>114.1(6)</td>
</tr>
<tr>
<td>P(1)-Fe(2)-P(2)</td>
<td>118.1(2)</td>
</tr>
<tr>
<td>P(1)-Fe(2)-N(3)</td>
<td>103.5(8)</td>
</tr>
<tr>
<td>P(1)-Fe(2)-N(4)</td>
<td>107.3(7)</td>
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<tr>
<td>P(2)-Fe(2)-N(3)</td>
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<td>P(2)-Fe(2)-N(4)</td>
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<tr>
<td>N(3)-Fe(2)-N(4)</td>
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<td>Fe(1)-P(1)-C(2)</td>
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<td>Fe(1)-P(1)-C(8)</td>
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<td>Fe(2)-P(1)-C(2)</td>
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<tr>
<td>Fe(2)-P(1)-C(8)</td>
<td>118.4(4)</td>
</tr>
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<td>C(2)-P(1)-C(8)</td>
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</tr>
<tr>
<td>Fe(2)-P(2)-C(1)</td>
<td>107.5(6)</td>
</tr>
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<td>Fe(2)-P(2)-C(14)</td>
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<td>Fe(2)-P(2)-C(20)</td>
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<td>C(1)-P(2)-C(14)</td>
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<tr>
<td>C(1)-P(2)-C(20)</td>
<td>108.0(8)</td>
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<tr>
<td>C(14)-P(2)-C(20)</td>
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<td>Fe(1)-N(1)-O(1)</td>
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<td>Fe(1)-N(2)-O(2)</td>
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</tr>
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<td>Fe(2)-N(4)-O(4)</td>
<td>176.1</td>
</tr>
<tr>
<td>Fe(1)-C(1)-P(2)</td>
<td>98.6(7)</td>
</tr>
</tbody>
</table>
Figure 42. The Molecular Structure of
\[ ((\text{NU})_2\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CH}_2\text{PPh}_2)\text{Fe}(\text{NU})_2) \]
Showing the Atom Numbering Scheme
but longer than that in \([\text{Fe(NO)}_2(\mu-\text{PPh}_2)]_2\) (2.698Å)\(^{63}\) and \([\text{Fe(NO)}_2(\mu-\text{P} (\text{CF}_3)_2)]_2\) (2.747(1)Å).\(^{126}\) The large \(\text{Fe}(1)-\text{P}(1)-\text{Fe}(2)\) bond angle (79.0° in A, 77.8° in B) also reflects the fact that the \(\text{Fe}-\text{Fe}\) bond is long. The \(\text{Fe}-\text{N}-\text{O}\) angles are essentially linear, ranging from 171° to 178°. The \(\text{Fe}-\text{N}\) and \(\text{N}-\text{O}\) bond distances are comparable with the values found in other \(\text{Fe}-\text{NO}\) systems.\(^{136,63}\)

The \(\text{P}(2)-\text{C}(1)-\text{Fe}(1)\) bond angle (98.6° in A and 92.9° in B) is distorted from the tetrahedral value of the \(\text{sp}^3\) carbon. This distortion was also observed in the \(\text{P}-\text{C}-\text{Co}\) bond angle (88°) of the complex \(\{(\text{PMe}_3)_2\text{Co}(\mu-\text{PPh}_2)(\mu-\text{CH}_2\text{PPh}_2)\text{Co}-\text{(PMe}_3)_2\}\) where it was attributed to an \(\text{sp}^2\) type \(\text{CH}_2\) group.\(^{134,138,139}\)

b. Characterization and X-ray Structure of
\([\text{Fe(NO)}_2\text{Fe}(\mu-\text{CH}_2)(\mu-\text{PPh}_2\text{PPh}_2)]\)

The X-ray diffraction study of complex (XII) showed the structure sketched below.

The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of complex (XII) shows a resonance at -24.6 ppm (singlet) which is assigned to the two
equivalent phosphorus atoms of the tetraphenylbiphosphine ligand. Proton and $^{13}C$ NMR spectra of the complex indicate that there is a CH$_2$ bridge ligand. The proton NMR spectrum of complex (XII) shows resonances at 7.1 ppm (relative intensity 20), which is assigned to the phenyl protons, and at 10.3 ppm (relative intensity 2), which is assigned to the bridging methylene ligand. The chemical shift values of the methylene protons have been used to establish a criterion to determine whether the ligand is bridging across a metal-metal bond.$^{140}$ With a metal-metal interaction, the methylene protons generally show a resonance in the region of 5-11 ppm,$^{191}$ while significant upfield shifts to the region of 1-3 ppm will be experienced by the methylene protons bridging two metals with no metal-metal interaction. Therefore, the chemical shift value of the μ-CH$_2$ protons in complex (II) supports the existence of an Fe-Fe bond.

The carbon-13 NMR spectrum of complex (XII) in THF-d$_8$ is shown in Figure 43. This spectrum shows a triplet at 177.7 ppm ($J_{p-C} = 13$ Hz) and multiplets at around 130 ppm. The triplet at 177.7 ppm is assigned to the carbon atom of the bridging μ-CH$_2$ group. As does proton NMR spectroscopy, $^{13}C$ NMR spectroscopy enables one to establish whether a metal-metal bond is present.$^{140}$ Methylene ligand bridging across a metal-metal bond generally displays a resonance in the region of 100-210 ppm. On the other hand, a CH$_2$ group bridging across two metals with no metal-metal bonding will generally show a resonance in the region of 0-10 ppm. The
Figure 43. The $^{13}$C NMR spectrum of [(NO)$_2$Fe(μ-Ph$_2$PPh$_2$)(μ-CH$_2$)Fe(NO)$_2$] in THF-$_d_8$ at 25°C.
downfield position of the resonance of the \( \mu-\text{CH}_2 \) ligand provides further evidence for the existence of a metal-metal bond. The methylene carbon couples with the two equivalent phosphorus atoms of the \( \text{Ph}_2\text{PPh}_2 \) group and hence shows a triplet signal.

The molecular structure of complex (XII) with important bond angles and bond lengths is shown in Figure 41. An ORTEP drawing with the atom numbering scheme is shown in Figure 44. Selected bond angles and bond lengths are presented in Table 28 and 29, respectively.

The binuclear framework consists of two \( \text{Fe(NO)}_2 \) moieties joined by an Fe-Fe bond, a symmetrical bridging \( \text{PPh}_2\text{PPh}_2 \) ligand and a bridging methylene group. The average Fe-N and N-O distances are 1.65(1) and 1.17(2)\( \text{Å} \), respectively, which are comparable with the values found in complex (XII). The Fe-N-O angles are essentially linear, ranging from 173.0° to 178.1°, with the exception of the Fe-N(2)-O(2) angle which is 167.6°.

The Fe-Fe bond distance of 2.730(1)\( \text{Å} \) is longer than the Fe-Fe distance in \( [\text{Fe(CO)}_3(\mu-\text{PPh}_2)]_2 \) (2.698\( \text{Å} \)) but is somewhat shorter than the average Fe-Fe distance in complex (XII) (2.824\( \text{Å} \)). Both bridging ligands are slightly distorted toward the Fe(2) atom. The Fe-C bond distances found in complex (XII) are shorter than those found in iron-(alkylidene) compounds, which average to 2.063\( \text{Å} \). The P-P bond length of 2.179(1)\( \text{Å} \) is slightly shorter than 2.215(3)\( \text{Å} \) found in the
Figure 44. An ORTEP Drawing of the \([(\text{NO})_2\text{Fe}(\mu-\text{PPh}_2\text{PPh}_2)(\mu-\text{CH}_2)\text{Fe}(\text{NO})_2]\)
Molecule Showing Atom Numbering Scheme.
Table 29. Selected Bond Lengths for [(NO)$_2$Fe($\mu$-PPh$_2$PPh$_2$)($\mu$-CH$_2$)Fe(NO)$_2$]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length, Å</th>
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<td>1.665(4)</td>
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<tr>
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<td>1.644(4)</td>
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<td>1.953(5)</td>
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<td>2.179(1)</td>
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<tr>
<td>N(3)-O(3)</td>
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<tr>
<td>N(4)-O(4)</td>
<td>1.191(5)</td>
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<td>P(1)-C(6)</td>
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<td>P(2)-C(14)</td>
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<td>P(2)-C(20)</td>
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Table 30. Selected Bond Angles for [(NO)$_2$Fe($\mu$-PPh$_2$PPh$_2$)($\mu$-CH$_2$)Fe(NO)$_2$] 

<table>
<thead>
<tr>
<th>Angle</th>
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<td>112.7(2)</td>
</tr>
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<td>Fe(2)-Fe(1)-C(1)</td>
<td>45.6(2)</td>
</tr>
<tr>
<td>P(1)-Fe(1)-N(1)</td>
<td>104.4(2)</td>
</tr>
<tr>
<td>P(1)-Fe(1)-N(2)</td>
<td>107.3(1)</td>
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<td>P(1)-Fe(1)-C(1)</td>
<td>122.9(2)</td>
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<td>N(1)-Fe(1)-N(2)</td>
<td>119.4(2)</td>
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<tr>
<td>N(1)-Fe(1)-C(1)</td>
<td>98.6(2)</td>
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<td>N(2)-Fe(1)-C(1)</td>
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<td>Fe(1)-Fe(2)-P(2)</td>
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<td>Fe(1)-Fe(2)-N(3)</td>
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<td>Fe(1)-Fe(2)-N(4)</td>
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<td>Fe(1)-Fe(2)-C(1)</td>
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</tr>
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<td>P(2)-Fe(2)-N(4)</td>
<td>102.7(2)</td>
</tr>
<tr>
<td>P(2)-Fe(2)-C(1)</td>
<td>125.5(2)</td>
</tr>
<tr>
<td>N(3)-Fe(2)-N(4)</td>
<td>121.5(3)</td>
</tr>
<tr>
<td>N(3)-Fe(2)-C(1)</td>
<td>103.3(2)</td>
</tr>
<tr>
<td>N(4)-Fe(2)-C(1)</td>
<td>100.6(2)</td>
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<td>Fe(2)-N(3)-O(3)</td>
<td>173.0(6)</td>
</tr>
<tr>
<td>Fe(2)-N(4)-O(4)</td>
<td>178.1(5)</td>
</tr>
<tr>
<td>Bond</td>
<td>Angle (°)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>Fe(1)-P(1)-C(8)</td>
<td>114.9(1)</td>
</tr>
<tr>
<td>P(2)-P(1)-C(2)</td>
<td>113.2(1)</td>
</tr>
<tr>
<td>P(2)-P(10)-C(8)</td>
<td>106.5(2)</td>
</tr>
<tr>
<td>C(2)-P(1)-C(8)</td>
<td>106.0(2)</td>
</tr>
<tr>
<td>Fe(2)-P(2)-P(1)</td>
<td>91.89(6)</td>
</tr>
<tr>
<td>Fe(2)-P(2)-C(14)</td>
<td>120.6(1)</td>
</tr>
<tr>
<td>Fe(2)-P(2)-C(20)</td>
<td>116.4(1)</td>
</tr>
<tr>
<td>P(1)-P(2)-C(14)</td>
<td>115.5(1)</td>
</tr>
<tr>
<td>P(1)-P(2)-C(20)</td>
<td>105.1(1)</td>
</tr>
<tr>
<td>C(14)-P(2)-C(20)</td>
<td>106.1(2)</td>
</tr>
<tr>
<td>Fe(1)-C(1)-Fe(2)</td>
<td>87.9(1)</td>
</tr>
</tbody>
</table>
free ligand, but in the range found for compounds containing P-P bonds, 2.17-2.24Å.

The Fe-Fe-P-P cycle in complex (XII) is puckered, with a torsion angle around the P-P bond of 34.0°, owing to intramolecular steric interactions. These seem to be responsible also for the nonequivalence of the Fe-C and Fe-P bond lengths.

3. Reaction of $[(\text{NO})_2\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{NO})\text{Fe(NO)}_2(\text{PPh}_2)]^{2-}$ with MeI

Treatment of Li$_2[(\text{NO})_2\text{Fe}(\mu-\text{NO})(\mu-\text{PPh}_2)\text{Fe(NO)}(\text{PPh}_2)]$ at -78°C with one equivalent of MeI at -78°C leads to the alkylation at the phosphorus atom of the terminal phosphide ligand (equation 100).

$$
\begin{align*}
\text{(NO)}_2\text{Fe} & \text{N} \text{O} \text{P} \text{P} \text{Ph}_2 \quad 2^- \\
\text{MeI} & \quad -78°C \\
\text{MeI} & \quad \text{(NO)}_2\text{Fe} \text{N} \text{O} \text{P} \text{P} \text{Ph}_2 \text{Me}
\end{align*}
$$

The new monoanion was characterized by its $^{31}P[^{1}H]$ NMR and IR spectra. The $^{31}P[^{1}H]$ NMR spectrum of the monoanion shows a doublet at 160.0 ppm ($J_{P-P} = 14$ Hz) which is assigned to the bridging $\mu$-$\text{PPh}_2$ ligand and a doublet at 42.1 ppm which is assigned to the phosphorus atom of the terminal
PPh₂Me ligand bonded to Fe. The downfield position of the μ-PPh₂ phosphorus resonance implies the presence of a metal-metal bond in the monoanion. The infrared spectrum of the monoanion shows stretching absorptions of terminal nitrosyls at 1699 and 1654 cm⁻¹. In addition, a weak peak at 1420 cm⁻¹ is assigned to the stretching absorption of a bridging nitrosyl group. Both the ³¹P NMR and the IR spectra of Li[(NO)₂Fe(μ-NO)(μ-PPh₂)Fe(NO)(PPh₂Me)] are similar to those exhibited by Li[(NO)₂Fe(μ-PPh₂)(μ-NO)-Fe(NO)(PPh₂H)].

At -78°C, the monoanion thus prepared was treated with excess MeI followed by gradual warming to room temperature. The ³¹P{¹H} NMR spectrum of the reaction mixture showed only the resonance attributable to Fe(NO)₂(PPh₂Me)₂, with [Fe(NO)₂(μ-PPh₂)]₂ precipitationg out of the solution.

J. Fluxional Behavior of Some Binuclear Iron Carbonyl Complexes

During the course of this dissertation research it was discovered that the ³¹P and ¹³C NMR spectra of some binuclear iron carbonyl complexes showed temperature dependent behavior. The results are summarized in Table 31 with respect to whether or not newly prepared complexes are stereochemically nonrigid. The ³¹P{¹H} NMR spectra of the binuclear iron nitrosyl complexes are all temperature invarient.

As can be seen from Table 31, two types of complex show ³¹P NMR fluxional behavior. One is the monoanion [(CU)₃-
Table 31. Stereochemically Nonrigid Behavior of Some Binuclear Iron Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{31}$P NMR Fluxionality</th>
<th>$^{13}$C NMR Fluxionality (carbonyl region)</th>
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</thead>
<tbody>
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<td>yes</td>
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<tr>
<td>(CO)$_3$Fe—Fe(CO)$_2$</td>
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<td>yes</td>
</tr>
<tr>
<td>(CO)$_3$Fe—Fe(CO)$_2$</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>(CO)$_3$Fe—Fe(CO)$_3$</td>
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<td>--</td>
</tr>
<tr>
<td>(CO)$_2$Fe—Fe(CO)$_3$</td>
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<td>--</td>
</tr>
<tr>
<td>(CO)$_3$Fe—Fe(CO)$_3$</td>
<td>no</td>
<td>--</td>
</tr>
</tbody>
</table>

*R*= Me, Et, n-Pr, i-Pr
$\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{Cu})\text{Fe}(\text{Cu})_2(\text{PPh}_2\text{H})$ with different counterions (Li$^+$, Na$^+$, K$^+$) and the other is the bridging acyl complex $[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C}(\text{R})\text{U})\text{Fe}(\text{Cu})_2(\text{PPh}_2\text{R})]$ ($\text{R} = \text{Me}, \text{Et}, \text{n-Pr}, \text{i-Pr}$). Only the bridging acetyl complex $[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)-$(\mu-\text{C}(\text{Me})\text{U})\text{Fe}(\text{Cu})_2(\text{PPh}_2\text{Me})]$ was studied in detail and will be discussed here.

A THF solution of $[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C}(\text{Me})\text{U})\text{Fe}(\text{Cu})_2(\text{PPh}_2\text{Me})]$ gave the $\text{^31P[^1H]}$ NMR spectra shown in Figure 45 over the temperature range of $-73^\circ \text{C}$ to $+30^\circ \text{C}$. At $-73^\circ \text{C}$ the spectrum indicates the existence of two isomers. The assignments are as follows:

\[\text{TRANS}\quad \text{CIS}\]

The isomer with the trans arrangement of phosphine and bridging phosphide shows a downfield doublet at 187.8 ppm and a highfield doublet at 43.5 ppm ($J_{\text{P-P}} = 112 \text{ Hz}$). The isomer with a cis arrangement of phosphine and bridging phosphide shows a downfield doublet at 166.7 ppm and a highfield doublet at 39.8 ppm ($J_{\text{P-P}} = 15.1 \text{ Hz}$). As the temperature is raised, the cis and trans isomers start to exchange as evidenced by the resonances associated with both isomers beginning to coalesce. They eventually give rise to one set of doublets at 172.4 ppm and 53.5 ppm ($J_{\text{P-P}} = 51.4 \text{ Hz}$).
Figure 45. Temperature Dependent $^{31}P\{^1H\}$ NMR Spectra of 
$\left[(\text{Cu})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C(Me)}O\text{Fe(Cu)}_2\text{PPh}_2\text{Me})\right]$. 
Figure 46. Temperature Dependent $^{13}$C NMR Spectra of the CO Ligands of $[(CO)_{3}Fe(\mu-PPh_{2})(\mu-C(Me)O)\mu-C(Me)O]Fe(CO)_{2}(PPh_{2}Me)$.
The $^{13}$C NMR spectra of a $^{13}$CO-enriched sample of the acetyl complex supports this interpretation. The spectra in the temperature range of $-73^\circ$C to $30^\circ$C are shown in Figure 46. At low temperatures the $^{13}$C NMR spectrum is consistent with the presence of two isomers in solution.

The low temperature $^{31}$P{$^1$H} NMR spectral data of these [[(Co)$_3$Fe($\mu$-PPh$_2$)($\mu$-C(R)U)Fe(CO)$_2$(PPh$_2$R)] complexes (R = Me, Et, n-Pr, i-Pr) are summarized in Table 32. For the purpose of comparison, the $^{31}$P{$^1$H} NMR spectra of [[(Co)$_3$Fe($\mu$-PPh$_2$)($\mu$-C(Et)U)Fe(CO)$_2$(PPh$_2$Et)]] in the temperature range of $-73^\circ$C to $30^\circ$C are listed in Appendix B.

A line-shape analysis of the $^{31}$P{$^1$H} NMR spectra of [[(Co)$_3$Fe($\mu$-PPh$_2$)($\mu$-C(Me)U)Fe(CO)$_2$(PPh$_2$Me)]] was performed by using the DNMR III Program. Some of the representative spectra obtained are presented in Figure 47. The computer simulation was performed in terms of one exchange process with two possible exchanging isomers. An Arrhenius plot of the data is illustrated in Figure 48. Analysis of the straight-line graph yields $\Delta G^\ddagger_{298} = 11.0$ Kcal/mole, $\Delta S^\ddagger_{298} = 1.6$ eu, $\Delta H^\ddagger_{298} = 11.5$ Kcal/mole, and $E_a = 12.0$ Kcal/mole.

One of possible mechanisms that account for this stereochemically nonrigid behavior is a propeller-like or pseudo-C$_3$ rotation of the three terminally coordinated ligands about the metal. In analogous complexes, [[(Co)$_3$Fe($\mu$-PPh(CH$_2$)$_3$PPh)Fe(CO)$_2$(PPh$_2$R)]], similar pseudo-C$_3$ rotation has also been proposed to explain the stereo
Table 32. Low Temperature $^{31}\text{P}$ NMR Spectral Data of 
$[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-C(R^2)O)\text{Fe(CO)}_2(\text{PPh}_2R^1)]$

<table>
<thead>
<tr>
<th>Complex</th>
<th>Trans Isomer</th>
<th>Cis Isomer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta(\mu-\text{PPh}_2)^b$</td>
<td>$\delta(\text{PPh}_2R^1)$</td>
</tr>
<tr>
<td>$R^1=R^2=$Me</td>
<td>187.8</td>
<td>43.5</td>
</tr>
<tr>
<td>$R^1=R^2=$Et</td>
<td>185.8</td>
<td>57.8</td>
</tr>
<tr>
<td>$R^1=R^2=n$-Pr</td>
<td>186.7</td>
<td>53.9</td>
</tr>
<tr>
<td>$R^1=R^2=i$-Pr$^c$</td>
<td>183.2</td>
<td>66.9</td>
</tr>
<tr>
<td>$R^1=$Me,$R^2=n$-Pr</td>
<td>186.4</td>
<td>44.0</td>
</tr>
<tr>
<td>$R^1=$Et,$R^2=$Me</td>
<td>188.5</td>
<td>56.6</td>
</tr>
</tbody>
</table>

$^a$ in THF at $-73^\circ$C

$^b_{ppm}$

$^c$ in THF at $-83^\circ$C
Figure 47. The Computer Simulated Temperature Dependent $^{31}P$ NMR Spectra of $[(CO)_3Fe(\mu-PhH_2)(\mu-C(Me)O)Fe(CO)_2(PH_2Me)]$. 
Figure 48. The Arrhenius Plot for \[ \text{[(CO)}_3\text{Fe(μ-PPh}_2\text{)(μ-C(Me)O)Fe(CO)}_2\text{(PPh}_2\text{Me)}\text{]} \]

Exchange Data.
chemical nonrigidity on the $\text{Fe}(\text{CO})_2PR_3$ ($R_3 = \text{PPh}_2\text{Me}$, $\text{PPh}_2\text{CH}_2\text{Ph}$) terminus. There are some other possible mechanisms$^{145,146}$ which can explain this fluxional behavior as well. However, at this point, further discussion of the mechanism would be speculative.

The $^{31}\text{P}[^1\text{H}]$ NMR and $^{13}\text{C}$ NMR spectra of the complex $\text{Li}[\text{(CO)}_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C}=\text{O})\text{Fe}(\text{CO})_2(\text{PPh}_2\text{H})]$ in the temperature range of $-83^\circ\text{C}$ to $30^\circ\text{C}$ are presented in Appendix C. At this time, not enough information has been accumulated to offer a plausible mechanism for the stereochemically nonrigid behavior. The $^{13}\text{C}$ NMR spectra of the $^{13}\text{Cu}$ enriched sample of $\text{Li}[\text{(CO)}_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C}=\text{O})\text{Fe}(\text{CO})_2(\text{PPh}_2\text{Me})]$ in the temperature range of $-83^\circ\text{C}$ to $30^\circ\text{C}$ are presented in Appendix D.
IV. CONCLUDING REMARKS

Although the chemistry of \([\mathrm{Fe(CO)}_3(\mu\text{-}\text{PPh}_2)]_2\) was studied more thoroughly than that of the \([\mathrm{Fe(NO)}_2(\mu\text{-}\text{PPh}_2)]_2\), a few conclusions can be made about the reactions of these two complexes and their derivatives in terms of their similarity and difference.

Both \([\mathrm{Fe(CO)}_3(\mu\text{-}\text{PPh}_2)]_2\) and \([\mathrm{Fe(NO)}_2(\mu\text{-}\text{PPh}_2)]_2\) react with alkali-metal trialkylborohydride reducing agents to form \([(\text{CO})_3\text{Fe}(\mu\text{-}\text{PPh}_2)(\mu\text{-}\text{Cu})\text{Fe(CO)}_2(\text{PPh}_2H)]^-\) and \([(\text{NO})_2\text{Fe}(\mu\text{-}\text{PPh}_2)(\mu\text{-}\text{NO})\text{Fe(NO)}(\text{PPh}_2H)]^-\), respectively. At \(-78^\circ\text{C}\), both of these monoanions react with \text{n-BuLi} to form the unsymmetrical dianions \([(\text{CO})_3\text{Fe}(\mu\text{-}\text{PPh}_2)(\mu\text{-}\text{Cu})\text{Fe(CO)}_2(\text{PPh}_2)]^{2-}\) and \([(\text{NO})_2\text{Fe}(\mu\text{-}\text{PPh}_2)(\mu\text{-}\text{NO})\text{Fe(NO)}(\text{PPh}_2)]^{2-}\), respectively. Both \([\mathrm{Fe(CO)}_3(\mu\text{-}\text{PPh}_2)]_2\) and \([\mathrm{Fe(NO)}_2(\mu\text{-}\text{PPh}_2)]_2\) react with \text{LiAlH}_4 and sodium to form the symmetrical dianions \([\mathrm{Fe(CO)}_3(\mu\text{-}\text{PPh}_2)]^{2-}\) and \([\mathrm{Fe(NO)}_2(\mu\text{-}\text{PPh}_2)]^{2-}\), respectively.

Thermal stabilities of \([(\text{CO})_3\text{Fe}(\mu\text{-}\text{PPh}_2)(\mu\text{-}\text{Cu})\text{Fe(CO)}_2(\text{PPh}_2)]^{2-}\) and \([(\text{NO})_2\text{Fe}(\mu\text{-}\text{PPh}_2)(\mu\text{-}\text{NO})\text{Fe(NO)}(\text{PPh}_2)]^{2-}\) are different. The conversion of \([(\text{CO})_3\text{Fe}(\mu\text{-}\text{PPh}_2)(\mu\text{-}\text{Cu})\text{Fe(CO)}_2(\text{PPh}_2)]^{2-}\) to \([\mathrm{Fe(CO)}_3(\mu\text{-}\text{PPh}_2)]^{2-}\) starts at about \(-40^\circ\text{C}\), whereas, \([(\text{NO})_2\text{Fe}(\mu\text{-}\text{PPh}_2)]^{2-}\)
NU)Fe(NU)(PPh₂)]₂²⁻ totally converts to [Fe(NU)_2(μ-PPh₂)]₂²⁻ at about -70°C.

Treatment of the respective unsymmetrical dianions with one equivalent of MeI leads to the formation of [(CO)₃Fe-(μ-PPh₂)(μ-CO)Fe(CO)₂(PPh₂Me)]⁻ and [(NU)₂Fe(μ-PPh₂)(μ-NU)Fe(NU)(PPh₂Me)]⁻. Alkylation of [(CO)₃Fe(μ-PPh₂)-(μ-CO)Fe(CO)₂(PPh₂)]₂²⁻ with excess MeI affords the bridging-acetyl complex [(CO)₃Fe(μ-PPh₂)(μ-C(Me)U)Fe(CO)₂(PPh₂Me)]; however, alkylation of [(NU)₂Fe(μ-PPh₂)(μ-NU)Fe(NU)(PPh₂)]₂²⁻ with excess MeI leads to the formation of [Fe(NU)_2(μ-PPh₂)]₂ and Fe(NU)_2(PPh₂Me)_2, with no methylated binuclear iron nitrosyl complex being observed.
Appendix A

Selected Bond Angles and Bond Lengths of

\[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe}(\text{PPh}_2\text{C}_3\text{H}_5)(\text{CO})_2]\]
Table 33. Selected Bond Lengths for \([(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)_2\text{Fe(\text{CO})_2(PPH}_2\text{C}_3\text{H}_5})]\)

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<tr>
<th>Bond</th>
<th>Bond Length, Å</th>
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<td>Fe(1)-Fe(2)</td>
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<tr>
<td>Fe(1)-P(1)</td>
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<tr>
<td>Fe(1)-P(2)</td>
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</tr>
<tr>
<td>Fe(1)-P(3)</td>
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</tr>
<tr>
<td>Fe(1)-C(4)</td>
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<tr>
<td>Fe(1)-C(5)</td>
<td>1.752(6)</td>
</tr>
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<td>Fe(2)-C(2)</td>
<td>1.794(6)</td>
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<td>Fe(2)-C(3)</td>
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<tr>
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Table 34. Selected Bond Angles for 
\[ ((CO)_3Fe(\mu-PPh_2)_2Fe(CO)_2(PPh_2C_3H_5) ]

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<th>Angle</th>
<th>Bond Angle, Degrees</th>
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<td>Fe(2)-Fe(1)-P(3)</td>
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(continued)
Table 34 continued

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Appendix B

Variable Temperature $^{31}P\{^{1}H\}$ NMR Spectra of

$$[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-C(\text{Et})O)\text{Fe}(\text{CO})_2(\text{PPh}_2\text{Et})]$$
Figure 49. Variable Temperature $^{31}_P \{^1_H\}$ NMR Spectra of
$[(\text{CO})_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{C(Et)}\text{O})\text{Fe(\text{CO})}_2(\text{PPh}_2\text{Et})]$.
Figure 49.
Appendix C

Variable Temperature $^{31}P$ $\{^1H\}$ and $^{13}C$

(CO Only) NMR Spectra of

$[\text{(CO)}_3\text{Fe}(\mu-\text{PPh}_2)(\mu-\text{CO})\text{Fe(CO)}_2\{\text{PPh}_2\text{H}\}]^-$
Figure 50. Variable Temperature $^{31}P\ H$ NMR Spectra 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})] $
Figure 51. Variable Temperature $^{13}\text{C}$ NMR of the CO Ligands of Li[(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$H)].
Appendix D

Variable Temperature $^{13}$C NMR Spectra of the CO Ligands of

$[(CO)_3Fe(\mu-PPh_2)(\mu-CO)Fe(CO)_2(PPh_2Me)]^-$
Figure 52. Variable Temperature $^{13}$C NMR Spectra of the CO Ligands of Li[(CO)$_3$Fe(µ-PPh$_2$)(µ-CO)Fe(CO)$_2$-$
(FPh$_2$Me)$]$. 


