1985

Reactivity of bridging thiocarbyne complexes of iron

Norman Clark Schroeder

Iowa State University

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REACTIVITY OF BRIDGING THIOCARBYNE COMPLEXES OF IRON

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Reactivity of bridging thiocarbyne complexes of iron

by

Norman Clark Schroeder

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemistry

Approved:

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Iowa State University
Ames, Iowa
1985
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DEDICATION

To my wife and children
SYMBOLS AND ABBREVIATIONS

acac  acetylacetonato ligand
All  CH₂CH=CH₂
Bu  n-butyl
b  broad
Bz  benzyl
Cp  η⁵-cyclopentadienyl
Cy  cyclohexyl
d  doublet
4-DMAP  4-dimethylaminopyridine
dp  decomposition point
dppe  1,2 bis(diphenylphosphino) ethane
DPPH  diphenylpicrylhydrazide
dppm  1,2 bis(diphenylphosphino) methane
ε  molar extinction coefficient

E_p  peak potential
E_{p}^{a}  anodic peak current
E_{p}^{c}  cathodic peak potential
Eqn  equation or reaction
Et  ethyl
Fe*  Cp₂Fe₂(CO)₂
Fe'  Cp₂Fe₂
<table>
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<td>Fp</td>
<td>CpFe(CO)₂</td>
</tr>
<tr>
<td>h</td>
<td>Plank's constant</td>
</tr>
<tr>
<td>iₐP</td>
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<td>i₈P</td>
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<tr>
<td>L</td>
<td>donor ligand</td>
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<tr>
<td>M</td>
<td>metal atom</td>
</tr>
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<td>t</td>
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<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
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<tr>
<td>TMS</td>
<td>tetramethylsilane</td>
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\( \mu \) designates a bridging ligand

\( \nu \) infrared stretching mode

\( \nu \) scan rate

\( V \) volts

\( w \) weak
I. INTRODUCTION

A. Bridging Carbynes: Potential Intermediates in CO Hydrogenation Reactions

The reactivity of organic species bonded to two or more metal centers is a topic of considerable contemporary interest especially in the area of carbon monoxide hydrogenation chemistry.¹⁻³ Three common CO hydrogenation reactions are shown in equations 1-3.

a) methanol synthesis

\[ \text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} \]  

(1)

b) methanation reaction

\[ \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \]  

(2)

c) Fischer-Tropsch synthesis

\[ \text{CO} + \text{H}_2 \rightarrow \text{alkanes, alkenes, aromatics, alcohols, aldehydes, etc.} \]  

(3)

In general, catalysts for these reactions have been heterogeneous systems consisting of transition metals (Co, Fe, Rh, Ru, Zn, Cu, Cr, Ni) immobilized in or on solid matrices (alkaline melts, SiO₂, zeolites). The economic
necessity of developing alternative sources of chemical raw materials from synthesis gas will require a new generation of highly selective catalysts. To this end, research and development of homogeneous catalysts will become of greater importance due to their potential for selective product control.\textsuperscript{4-7}

Many mechanisms have been proposed for CO hydrogenation reactions.\textsuperscript{3} In these discussions, various transient precursor species, including carbide,\textsuperscript{8} formyl,\textsuperscript{9} hydroxycarbonyne\textsuperscript{10} and oxygen bonded formaldehyde moieties\textsuperscript{11} (Figure 1a), have been proposed to be formed on the metal surface. Thermochemical and extended Hückel calculations suggest that a hydroxycarbonyne intermediate may be more favorable than a formyl species.\textsuperscript{10} However, the formation of both these surface bonded precursors are thermodynamically unfavorable. No suitable model system exists to support the speculative oxygen bonded formaldehyde mechanism. Recent work on the Fischer-Tropsch reaction catalyzed by nickel, cobalt and ruthenium, indicate that surface carbides are formed from the dissociation of chemisorbed carbon monoxide.\textsuperscript{12} Treatment of these catalysts with \textsuperscript{13}CO gave labeled carbide surfaces which when exposed to CO/H\textsubscript{2} mixtures under Fischer-Tropsch reaction conditions produced significant quantities of \textsuperscript{13}CH\textsubscript{4} and hydrocarbons containing
Figure 1. Idealized Fischer-Tropsch reaction on a metal surface
more than one $^{13}$C atom. That surface carbides are reactive intermediates was supported by a prior experiment showing that they do not exchange with adsorbed CO. Formation of methane and hydrocarbon products was proposed to result from hydrogenation of the initially formed carbide to give surface bound carbynes, carbenes and alkyl moieties. This process is depicted in Figure 1b. These intermediates could then undergo further hydrogenation or carbon-carbon coupling to give the observed products (Figure 1c). If surface carbynes, especially those that bridge two metal centers, are intermediates leading to hydrocarbon products, then research on the reactivity of bridging dinuclear carbyne complexes may elucidate some of the chemistry occurring on Fischer-Tropsch catalysts.

B. Carbyne Complexes: Historical Perspective

The first carbyne complex $\text{Co}_3(\text{CO})_9(\mu_3-\text{CCH}_3)$, synthesized by Markby et al.,$^{13}$ in 1958, (Eqn 4) contained a

$$\begin{align*}
\text{(CO)}_3\text{Co} & \quad \text{H} \\
\text{C} & \quad \text{H} \\
\text{C} & \quad \text{H} \\
\text{Co(CO)}_3 & \quad \text{H}_2\text{SO}_4
\end{align*} \quad \text{H}_2\text{O/EtOH} \quad \begin{align*}
\text{(CO)}_3\text{Co} & \quad \text{CH}_3 \\
\text{C} & \quad \text{C} \\
\text{Co(CO)}_3 & \quad \text{Co(CO)}_3 \\
\text{Co(CO)}_3 & \quad \text{Co(CO)}_3
\end{align*}$$

triply-bridged ethylidyne ligand. Since then the chemis-
try of other triply bridging alkylidyne tricobalt complexes has been thoroughly studied by Seyferth. The first bridging dinuclear complexes were pentavalent niobium and tantalum complexes, which contained two bridging trimethylsilylmethylidyne ligands (Eqn 5). These

\[
MCl_5 + RMgCl \xrightarrow{\text{Et}_2\text{O/pet ether}} R_2M \begin{array}{c}
\text{C} \\
\text{SiMe}_3
\end{array} \text{MR}_2
\]

\[\text{SiMe}_3
\]

M = Nb, Ta

R = Me_3SiCH_2
diamagnetic complexes which do not contain a metal-metal bond, are apparently stabilized by the presence of the beta-silicon atom, as the corresponding neopentyl complexes cannot be prepared. A tungsten analogue, which is diamagnetic indicating the presence of a W-W bond, has also been prepared.

Herrmann prepared the first low-valent dinuclear bridging carbyne complex by reacting bis(ethoxycarbonyl-diazo)methylmercury with Mn(CO)_5Br (Eqn 6). The diamagnetic nature of the complex corresponds to an eighteen electron configuration about the Mn atom if each of the bridging carbyne ligands is a three electron donor.
The first mononuclear complexes containing a metal-carbon triple bond were prepared by E. O. Fischer et al.\textsuperscript{19} in 1973, (Eqn 7). Lewis acid (M'X\textsubscript{3}) attack at the O-alkyl group yields a cationic carbyne complex, which then undergoes CO substitution by halide at the trans position to give the neutral product. Since this discovery, many other neutral and cationic terminally bonded carbyne complexes have been synthesized using transition metals from groups 5, 6, 7 and 8.\textsuperscript{20-25} The R substituent for these complexes have included alkyl, aryl, amino, silyl, vinyl, alkynyl, mercapto, hydrido, and halide groups.\textsuperscript{23,25}
C. Dinuclear Bridging Carbyne Complexes

1. Syntheses

Three general classes of dinuclear bridging carbyne complexes have been prepared: 1) methylidyne complexes which contain a bridging CH ligand; 2) alkylidyne complexes which have bridging C-alkyl or C-aryl ligands, and 3) heteroatom-stablized, carbyne complexes, containing a C-XR\textsubscript{n} (n = 1-3) bridging-ligand where X = O, S, Si and R = alkyl or aryl.

a. Methylidyne complexes

The first known complex with methylidyne bridging between two transition metals is Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{2}(\mu-CO)(\mu-CH)\textsuperscript{+}. Casey et al.\textsuperscript{26} prepared this air sensitive complex by abstracting a hydride from the bridging methylene ligand in Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{2}(\mu-CO)(\mu-CH\textsubscript{2}) (Eqn 8). Alternatively, Kao et al.\textsuperscript{27} has synthesized this complex by using HBF\textsubscript{4}-Et\textsubscript{2}O or Ph\textsubscript{3}C\textsuperscript{+} to remove the methoxide group from the carbene complex, Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{2}(\mu-CO)(\mu-C(H)-OMe). Recently, Davies et al.\textsuperscript{28} obtained a small amount of

b. **Alkylidyne complexes** The iron methylidyne complex above, reacts with alkenes to add the methylidyne carbon-hydrogen bond across carbon-carbon double bonds (Eqn 9). Iron$^{30}$ and ruthenium$^{31}$ µ-ethylidyne complexes are prepared by protonation reactions of the corresponding µ-vinylidene compounds (Eqn 10). A similar reaction occurs

\[
\text{Cp}_2M_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{C}=\text{CH}_2) \overset{\text{HBF}_4}{\longrightarrow} \text{Cp}(\text{CO})M_2(\text{CO})\text{Cp}
\]

with Cp$_2$Mn$_2$(CO)$_4$(µ-C=CH$_2$)$_3$, and the heterodinuclear µ-vinylidene, (CO)$_4$W(dppm)(µ-C=CH$_2$)Pt(CO)$_3$ to give Cp$_2$Mn$_2$-(CO)$_4$(µ-C=CH$_3$)$_+^+$ and (CO)$_4$W(dppm)(µ-C=CH$_3$)Pt(CO)$_3^+$. The higher µ-vinylidene analogues, µ-alkenylidene complexes, such as Cp$_2$Fe$_2$(CO)$_2$(µ-CO)(µ-C=CH$_3$), also undergo protonation reactions to give alkylidyne complexes, Cp$_2$Fe$_2$(CO)$_2$(µ-CO)-
The reaction of excess Li[CpFe(CO)$_2$], LiFp, with cyclic epoxides gives an eighteen electron, alkyl complex which may undergo alkyl migration to a carbonyl ligand (Eqn 11). Attack by LiFp at this unsaturated iron center leads to a bridged, lithiated intermediate which is protonated to yield a μ-alkylidyne complex. Ion pairing by lithium ions is essential for promoting the formation of the dinuclear complex. No reaction of this type is observed using Na[CpFe(CO)$_2$]. This reaction is unique in that the thermodynamically unfavorable trans isomer is obtained.

\[
\text{Eqn 11:}\quad \text{O}_\text{Li} \quad \text{25°C} \quad \text{LiFp} \quad \text{5 hrs.} \quad \text{CpFe(CO)$_2$}
\]
The proposed lithiated intermediate in equation 11 was instrumental in developing the synthesis of μ-alkylidyynes from \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})_2 \)\(^{27,35} \) and \( \text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu-\text{CO})_2 \). Treatment of these dimers with alkyl or aryl lithium reagents followed by excess \( \text{HBF}_4\cdot\text{Et}_2\text{O} \), gives a convenient synthesis of μ-alkylidyne complexes from readily available starting materials (Eqn 12). In the ruthenium case the intermediate species, \( \text{Cp}_2\text{Ru}_2(\text{CO})_3[\text{C}(\text{R})\text{OLi}] \), which was not isolated, was observed to have only terminal carbonyl bands at 2029 and 1966 cm\(^{-1} \).

Reaction of [Me\(_3\)O]BF\(_4\) with heteronuclear bridging carbene complexes (Eqn 13 and 14) yields the corresponding bridging alkylidyne cations.\(^{36} \) The Mn and Re containing
cations are produced in high yield (> 80%). Low yields (< 20%) of bridging alkylidyynes are obtained from Cr and W bridging carbene complexes when L = CO. This is apparently due to rupture of the M-Pt bond when reactions at the μ-carbene ligand are attempted. The PMe^- substituted Cr and W carbene complexes have a shorter M-Pt bond. Since the metal-metal bond is now less likely to fragment, the reaction in equation 14 gives a higher yield (ca. 35%). Because the bridging phosphine ligand, Ph₂PCH₂PPh₂, further stabilizes the M-Pt bond, the reaction in equation 15 gives a 60% yield of the bridging alkylidyne complex.
The mononuclear carbyne, Cp(CO)$_2$W=CC$_6$H$_4$Me-4, reacts with Pt(C$_2$H$_4$)(PMe$_2$Ph)$_2$, displacing ethylene, to give a neutral heteronuclear bridging carbyne compound (Eqn 16). \(^\text{39}\)

\[
\text{Pt(C$_2$H$_4$)L$_2$} \quad \frac{\text{Cp(CO)$_2$W=CC$_6$H$_4$Me-4}}{\text{HBF$_4$-Et$_2$O}} \quad \frac{\text{Cp(CO)$_2$W=PtL$_2$}}{\text{C}_{6}H_{4}Me-4}
\]

Other complexes containing easily displaced ligands react similarly. Thus, (C$_6$H$_6$)(CO)$_2$Cr(THF), Cp(CO)$_2$Re(THF), (C$_5$H$_4$Me)(CO)$_2$Mn(THF) and Fe(CO)$_4$(THF) give (C$_6$H$_6$)(CO)$_2$Cr(\(\mu\)-CC$_6$H$_4$Me-4)W(CO)$_2$Cp, Cp(CO)$_2$Re(\(\mu\)-CC$_6$H$_4$Me-4)W(CO)$_2$Cp, (C$_5$H$_4$Me)(CO)$_2$Mn(\(\mu\)-CC$_6$H$_4$Me-4)W(CO)$_2$Cp and (CO)$_4$Fe(\(\mu\)-C$_6$H$_4$Me-4)W(CO)$_2$Cp, respectively. \(^\text{40,41}\) Likewise, complexes containing Rh, Ir, Co, Zr and Ti were obtained by the reactions shown in equations 17 and 18. \(^\text{40,42}\) The crystal structure of the titanium complex shows that one of the tungsten carbonyl ligands is \(\eta^2\)-coordinated to titanium. Because of the isolobal relationship between the CC$_6$H$_4$Me-4 and CpW(CO)$_2$ fragments, the alkylidyne complex, Cp(CO)$_2$W=CC
The reaction of $\text{M(CO)}_2\eta^5-\text{R'}$ with $\text{W=CR}$ results in the formation of $\eta^5-\text{R'(CO)}\text{M=W(CO)}_2\text{Cp}$ (17)

\[ M = \text{Co, Rh, Ir} \]

\[ \text{R'} = \text{C}_5\text{H}_5, \text{C}_9\text{H}_7 \]

\[ \text{R} = \text{C}_6\text{H}_4\text{Me}-4, \text{Me} \]

The reaction of $\text{Cp}_2\text{M(CO)}_2\text{W=CC}_6\text{H}_4\text{Me}-4$ with $\text{C}_6\text{H}_4\text{Me}-4$, may be considered an organometallic analogue of an alkyne. As such, the products of equations 16-18 are analogous to metal-alkyne complexes and therefore their structures may be viewed as dimetallocyclopropenes. This is supported by structural data which show relatively short $\text{W}-(\mu-\text{C})$ bond lengths (ca. 1.96 Å) reflecting considerable $\text{W=C}$ character. Clark et al. has also described the products obtained from the reaction (Eqn 19) of $\text{Cl(CO)(PPh}_3)_2\text{Os=CC}_6\text{H}_4\text{Me}-4$ with group 1B halides (AgCl, CuI, AuCl) as dimetallocyclopropenes. Due to the electrophilic silver atom, backbonding is minimal and therefore the Os-(\mu-C) bond length increased by only 0.07 Å on coordination.
of AgCl. In comparison, the greater pi-backbonding afforded by Pt in the product of equation 16 increases the W-(μ-C) bond length by 0.14 Å.

$$\text{Cl(CO)(PPh}_3)_2\text{Os}_2\text{CR} \rightarrow \text{Cl(CO)(PPh}_3)_2\text{Os} \rightarrow \text{AgCl}$$  \hspace{1cm} (19)

$R = C_6H_4Me-4$

Photolysis of Br(CO)$_4$W=CR with F$_2$PN(CH$_3$)PF$_2$ gives, in 14% yield, the unusual bridging carbyne complex shown in equation 20.$^{46}$ The crystal structure of this complex shows a W-W distance of 2.623(5) Å, significantly shorter than the W-W single bond (2.937(1) Å) in $[W_2(CO)_5Br(μ-Br)(μ-Ph_2AsCH_2AsPh_2)(μ-CH_3C≡CH_3)]^+$. Thus, the complex contains a W-W double bond which is in agreement with
the diamagnetism of the compound.

c. Heteroatom-stabilized carbyne complexes The syntheses of silicon-stabilized, μ-alkylidyne complexes were shown in equation 5. Oxygen-stabilized complexes are limited to the reaction shown in equation 21.48

\[
\begin{array}{c}
\text{Cp}_2\text{Fe}_2\text{(CO)}_2(\mu-\text{CS}) \quad \text{(21)} \\
\text{Cp}_2\text{Fe}_2\text{C}^+ \text{FeC}^- \text{Cp} \\
\end{array}
\]

R = Me, Et

Dunker et al.49 synthesized the first bridging thiocarbonye, \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CS})(\mu-\text{CSMe})^+\), by treating \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CS})_2\) with MeOSO_3F. The most extensive series of bridging thiocarbonye complexes have been prepared by Quick and Angelici.50 They showed that the bridging thiocarbonyl ligand in \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CS})\) is easily alkylated by alkyl fluorosulfonates or trialkyloxonium salts (Eqn 22). Alkylation of this thiocarbonyl is also achieved by stirring it in neat primary alkyl iodides (Eqn 23) or with reactive primary alkyl bromides (allyl and benzyl bromides). The halide salts are converted by ion exchange chromatography to the PF_6 salts. This step is necessary to improve the solubility, spectroscopic properties and sta-
bility (some alkylation reactions are reversible, e.g. benzyl and allyl) of these complexes.

\[
\begin{align*}
\text{CO} & \quad \text{Fe} \quad \text{Fe} \quad \text{CO} \\
\text{Cp} & \quad \text{Cp} & \quad \text{ROSO}_3\text{F} \\
& \quad \text{or } [\text{R}_3\text{O}]\text{BF}_4 \\
& \quad \text{25°C, 1 hr} \\
\Rightarrow \\
\text{CO} & \quad \text{Fe} \quad \text{Fe} \quad \text{CO} \\
\text{Cp} & \quad \text{Cp} & \quad \text{SR} \\
& \quad \text{C}^+ \\
& \quad \text{C} \quad \text{O}
\end{align*}
\]

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

\[
\begin{align*}
\text{RX} & \quad \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CS}) \quad \text{---} \\
& \quad \text{[Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSR})]X \\
& \quad \text{25°C, 24 hrs.} \\
& \quad \text{exchange} \\
& \quad \text{[Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSR})]PF_6 \\
R = \text{Me, Et, Pr, Bu, Bz, All} \\
X = \text{I, Br}
\end{align*}
\]

A complex containing both a bridging thiocarbyne and a bridging alkylated isocyanide ligand was prepared by Quick and Angelici$^{50}$ by alkylation of \text{Cp}_2\text{Fe}_2(\text{CNCH}_3)(\text{CO})(\mu-\text{CNCH}_3)(\mu-\text{CS}) (Eqn 24).
Heteronuclear bridging thiocarbyne complexes were prepared using the methylation reaction shown in equations 25 and 26.51,52
2. Chemical reactivity

The crystal structures of heteronuclear bridging carbyne complexes, MM'(μ-CR), show that the carbyne ligand is displaced toward one of the metal centers (M) such that the M-(μ-C) bond has significant double bond character, M=(μ-C).\(^{39,40,44,45}\) For this reason, these complexes are often viewed as dimetallocyclopropenes and, as such, the M=(μ-C) bond should be subject to electrophilic attack. This idea has been exploited extensively by Stone and co-workers by the preparation of triply bridged carbyne complexes, MM'-M"'(μ-CR).\(^{44,53-55}\) Electrophilic metal fragments (e.g. Fe(CO)\(_4\), Rh(η\(^5\)-C\(_9\)H\(_7\)), generated in situ, were used to attack the W=(μ-CR) bond of Cp(CO)\(_2\)W(μ-CR)ML complexes. Examples of these reactions are shown in equation 27\(^{53}\) and 28.\(^{54}\)

\[
\begin{align*}
\text{Cp(CO)}_2\text{W} & \xrightarrow{\text{Fe}_2(\text{CO})_2} \text{Cp(CO)}_2\text{W} \\
\text{PtL}_2 & \text{THF, 25°C} & \text{PtL}_2
\end{align*}
\]

\(R = \text{C}_6\text{H}_4\text{Me}-4\)
\(L = \text{PMe}_2\text{Ph}\)
The electrophilic reagents, HBF$_4$ and CF$_3$SO$_3$Me, add H$^+$ or CH$_3^+$ to the carbyne carbon in Cp(CO)$_2$W(μ-CR)Pt(PMe$_3$)$_2$ (R = C$_6$H$_4$Me-4, Me) to give the bridging carbene cations (Eqn 29 and 30). However, products formed from the μ-CMe carbyne complex are unstable and rearrange to olefin (A) and μ-alkenyl (B) complexes.
Although diazomethane does not react, Tebbe's reagent adds CH$_2$ across the $W=(\mu-$C$)$ bond in Cp(CO)$_2$$W(\mu-$CC$_6$H$_4$Me-4)-Pt(PMe$_3$)$_2$ (Eqn 31).$^{57}$

Heteronuclear bridging carbyne cations, MM'$(\mu-$CR)$^+$, react with nucleophiles (Nuc$^-$ = H, Me, MeO, EtO, t-BuC$=C$, C$_6$H$_4$Me-4, SC$_6$H$_4$Me-4, and Cp) to give variable yields (4-90%) of bridging carbene products, MM'[$\mu-$CR(Nuc)].$^{36,37}$ Quantitative yields are obtained for the Mn and Re complexes, [Cp(CO)$_2$$M(\mu-$CC$_6$H$_4$Me-4)Pt(PMe$_3$)$_2$]$^+$, in their reactions with MeO$^-$ (Eqn 32). However, the Cr and W complexes, [(CO)$_5$$M(\mu-$CPh)Pt(PMe$_3$)$_2$]$^+$, give less than 10% yields with the same nucleophile, apparently due to the instability of
the metal-metal bond in these cations. Using the bridging

\[
\text{Cp(CO)}_2 M \text{C}^+ \text{PtL}_2 \xrightarrow{-\text{MeO}^-} \text{Cp(CO)}_2 M \text{C}^+ \text{PtL}_2
\]

\( R = \text{C}_6\text{H}_4\text{Me}-4 \)
\( M = \text{Mn, Re} \)
\( L = \text{PMe}_3 \)

phosphine ligand, dppm, to hold the metal atoms together, the complex, \([(\text{CO})_4 \text{W(μ-C}_{6}\text{H}_4\text{Me-4})(\mu-\text{dppm})\text{Pt(CO)}]\), gives a 70% yield of the carbene product on reaction with \(\text{MeO}^-\). Curiously, the monodentate phosphine substituted cation, \([(\text{CO})_4 \text{PMe}_3 \text{W(μ-C}_{6}\text{H}_4\text{Me-4})\text{Pt(PMe}_3)_2]\), gives a bridging acyl carbene product (19% yield) with \(\text{MeO}^-\) (Eqn 33). This

\[
\text{(CO)}_4 \text{LW} \text{C}^+ \text{PtL}_2 \xrightarrow{-\text{MeO}^-} \text{(CO)}_4 \text{LW} \text{C}^+ \text{PtL}_2
\]

\( R = \text{C}_6\text{H}_4\text{Me}-4 \)
\( L = \text{PMe}_3 \)

reaction is presumed to occur by nucleophilic attack on an intermediate bridging ketene species, C. The low yields suggest that the ketene CO is obtained by intermolecular transfer.
A difference in reactivity is observed for MM'('\mu\text{-}C\text{Me})^+ complexes. Bases, such as H^- or MeO^-, deprotonate the Me group to give a \mu\text{-}vinylidene product, MM'(\mu\text{-}C=CH_2).^{33}

Homonuclear bridging carbyne cations, M_2('\mu\text{-}CR)^+, show variable reactivity which depends largely on the R substituent. Thus, the methyldiyne complex, Cp_2Fe_2(CO)_2('\mu\text{-}CO)-('\mu\text{-}CH)^+, reacts with CO, NMe_3, PPh_3, H^- and t-BuO^- to form the corresponding adducts and \mu\text{-}carbenes (Eqn 34).^{27,58}

The reaction of this methyldiyne complex with olefins to give alkylidyynes was shown in equation 9.

\[
\begin{align*}
\text{Cp(CO)Fe} & \quad \text{Fe(CO)Cp} \quad \text{----} \quad \text{R} \\
\text{C} & \quad \text{C} \quad \text{R}
\end{align*}
\]

R = CO, NMe_3, PPh_3, H^-, t-BuO^-

Alkylidyne complexes, M_2('\mu\text{-}CR)^+, react with hydride to give bridging hydridoalkyl carbenes, M_2[\mu\text{-}C(H)R].^{27,31} However, bases such as HCO_3^-, NEt_3, MeLi, deprotonate the alpha-carbon of alkylidyynes to give \mu\text{-}vinylidene, M_2('\mu\text{-}C=CH_2), or \mu\text{-}alkenylidene, M_2(\mu\text{-}C=C(H)R), complexes.^{30,34}
Alkylidyne complexes will also rearrange on heating to give \( \mu \)-alkenyl complexes (Eqn 35).\textsuperscript{34} The rate of this \( 1,2- \)

\[
\text{Cp(CO)Fe} \overset{\text{H}}{\longrightarrow} \text{Fe(CO)Cp} \quad \overset{88^\circ\text{C}}{\rightarrow} \quad \text{Cp(CO)Fe} \overset{\text{+}}{\longrightarrow} \text{Fe(CO)Cp} \quad (35)
\]

hydride shift is highly dependent on the substituents attached to the carbon alpha to the carbyne carbon. Thus, the ethylidyne complex, \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-C\text{CH}_3)]^+\), does not rearrange while the cyclohexyl derivative rearranges at \(-13^\circ\text{C}\) (Eqn 36).

\[
\text{Cp(CO)Fe} \overset{\text{H}}{\longrightarrow} \text{Fe(CO)Cp} \quad \overset{-13^\circ\text{C}}{\rightarrow} \quad \text{Cp(CO)Fe} \overset{\text{+}}{\longrightarrow} \text{Fe(CO)Cp} \quad (36)
\]

Quick and Angelici\textsuperscript{50} have examined the CO substitution reactions of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSR})]^+\) by phosphines, phosphites, isocyanides and halides. However, reactivity at the \( \mu \)-carbyne carbon has not been explored.
3. **Structure and bonding**

As mentioned previously, neutral heteronuclear bridging carbynes, \( MM'(\mu-\text{CR}) \), may be described as dimetallocyclopropenes. Structural data on these complexes show a \( M=(\mu-\text{C}) \) double bond and a \( M'-(\mu-\text{C}) \) single bond. For example, the \( W-(\mu-C) \) bond length in \( \text{Cp(CO)}_2W(\mu-\text{CC}_6H_4\text{Me-4})-\text{Pt(PMe}_2\text{Ph)}_2 \) is \( 1.967(6) \, \text{Å} \). This lies between the distances observed for the \( W=C \) bond in \( \text{Cp(CO)}_2=\text{CC}_6H_4\text{Me-4} \), \( 1.82(2) \, \text{Å} \), and values observed for \( W-C \) single bonds, \( 2.14-2.20 \, \text{Å} \). Based on the known \( W=W \) \((2.623(5) \, \text{Å}) \) and \( C=C \) \((1.337 \, \text{Å}) \) bond distances, \( 1.98 \, \text{Å} \) is a reasonable estimate of a \( W=C \) bond length which is very close to the observed value in \( \text{Cp(CO)}_2W(\mu-\text{CC}_6H_4\text{Me-4})\text{Pt(PMe}_2\text{Ph)}_2 \). The \( \text{Pt-(\mu-C)} \) bond distance, \( 1.997 \, \text{Å} \), in this complex is in the range observed for \( \text{Pt-C} \) sigma bonds, \( 1.99-2.15 \, \text{Å} \).

Only one x-ray structure determination has been reported for a heteronuclear carbyne cation, \( \text{Cp(CO)}_2\text{Mn}(\mu-\text{CC}_6H_4\text{Me-4})\text{Pt(PMe}_3\text{)}_2^+ \). In comparison, the \( \text{Mn-(\mu-C)} \) bond length is slightly shorter than the \( \text{Mn=C} \) bond length in the terminal carbene complex, \( \text{Cp(CO)}_2\text{Mn}[\text{C(COPh)}\text{Ph}] \), \( 1.83 \, \text{Å} \) versus \( 1.88 \, \text{Å} \); the \( \text{Pt-(\mu-C)} \) bond length is slightly shorter than the \( \text{Pt-(\mu-C)} \) single bond length in \( [\text{Cp(CO)}_2W(\mu-\text{CC}_6H_4-\text{Me-4})\text{Pt(Me}_2\text{Ph)}_2] \), \( 1.967(8) \, \text{Å} \) versus \( 1.997(9) \, \text{Å} \). Thus,
even in these cationic complexes, there is one $\text{M-}($µ-$\text{C})$
double bond and one $\text{M-}($µ-$\text{C})$ single bond, and therefore, the
molecule can still be described as a dimetallocyclopropene.

Colborn et al.\(^1\) have discussed the bonding of the
carbyne ligand in cis-$\text{Cp}_2\text{Ru}_2(\text{CO})_2($µ-$\text{CO})($µ-$\text{CCH}_3)^+$. The
carbyne carbon is described as an 'sp' hybridized carbon
possessing two equivalent vacant 'p' orbitals which act as
in-plane and out-of-plane acceptor orbitals (Figure 2).
The carbyne ligand, CCH\(_3\), donates two electrons from the
carbyne carbon 'sp' orbital to the $\text{Cp}_2\text{Ru}_2(\text{CO})_2($µ-$\text{CO})$ frag­
ment. Backbonding from the metal fragment is mainly into
the in-plane 'p' orbital. Because of spatial limitations,
backbonding into the out-of-plane 'p' orbital is probably
less effective. In agreement with this bonding picture,
the crystal structure of cis-$\text{Cp}_2\text{Ru}_2(\text{CO})_2($µ-$\text{CO})($µ-$\text{CCH}_3)^+$,
shows a $C_{\text{carbyne}}$-$\text{CH}_3$ bond distance of 1.462(6) Å which is a
standard distance for $C_{\text{sp}-C_{\text{sp}}}$ bonds (1.460(3) Å).\(^{62}\) The
average Ru-$C_{\text{carbyne}}$ bond distance is 1.937(3) Å. This is
substantially shorter than Ru-$C_{\text{carbene}}$ bond lengths in
$\text{Cp}_2\text{Ru}_2(\text{CO})_2($µ-$\text{CO})($µ-$\text{CMe}_2)$, 2.113(4) Å,\(^{67}\) where the carbene
carbon is considered to be 'sp\(^2\)' hybridized.

Similar results have been observed for heteroatom-
stablized µ-carbyne complexes. The crystal structure of
$\text{Cp}_2\text{Fe}_2(\text{CO})_2($µ-$\text{CO})($µ-$\text{CSEt})^+$ (Figure 3) shows a $C_{\text{carbyne}}$-$S$
'sp' hybridized carbon which donates two electrons into the LUMO of the metal fragment.

The carbyne carbon possesses two equivalent vacant 'p' orbitals which act as in-plane and out-of-plane $\pi$ acceptor orbitals.

Figure 2. Bonding description of bridging carbyne cations
Figure 3. Structure of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSEt})^*$
bond distance of 1.666(11) Å, which compares with the calculated value of 1.64 Å for a Csp–S bond.\(^{62}\) The average Fe–C carbyne bond distance in this cation is shorter than the average Fe–C carbene bond distance in Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)Me),\(^{69}\) 1.834 Å versus 1.987 Å. This can be attributed to the interaction of the iron centers with the Csp hybridized carbon in Cp₂Fe₂(CO)₂(μ-CO)(μ-CSEt)\(^+\) and with a Csp² carbon in Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)Me)\(^-\).

Extended Hückel molecular orbital calculations on cis-Cp₂Ru₂(CO)₂(μ-CO)(μ-CCH₃)\(^+\) cation, show that its lowest unoccupied molecular orbital is composed mainly of the out-of-plane 'p' orbital.\(^{31,70}\) Since this orbital is isolated in energy from higher-lying virtual orbitals, the expected reactivity of this and analogous complexes would be nucleophilic attack at the carbyne carbon. The reaction of Cp₂Fe₂(CO)₂(μ-CO)(μ-CH)\(^+\) and the other homonuclear bridging alkylidyynes discussed previously substantiate this theory.

D. The Present Research

Sulfur-containing organometallic complexes have been studied extensively in this laboratory. Included in this work has been the synthesis of sulfur-stabilized carbene and carbyne complexes, including the first μ-thiocarbyne
Since then, other cationic \( \mu \)-thiocarbynes have been synthesized; the most prolific work being that of Quick and Angelici.\(^5\) Aside from CO substitution,\(^5\) the reactivity of \( \mu \)-thiocarbyne complexes has been limited to a few preliminary reactions involving nucleophiles with \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CS})(\mu-\text{CSMe})]\) PF\(_6\).\(^7\) This work, therefore, examines the reactivity of this complex and its analogues with organic nucleophiles and metal carbonyl anions.
II. EXPERIMENTAL

A. Techniques

Unless stated otherwise, all manipulations were carried out under an inert atmosphere in Schlenk type glassware or similar apparatus\(^72\) at room temperature. Solvents, solutions and suspensions were transferred using syringes or stainless steel transfer (cannula) tubes. The inert atmosphere consisted of nitrogen or argon gas. Argon was used as received. Nitrogen was deoxygenated by passage through a 5.0 x 45 cm column of BASF catalyst at 100°C and then dried by passage through a 5.0 x 45 cm column of 4A molecular sieves. The generation of an inert atmosphere in a reaction vessel was accomplished by evacuating the apparatus to 0.02 torr, back-flushing with inert gas and repeating at least twice. Glassware was dried by baking at 100°C or by heating the evacuated apparatus with a heat gun.

Compounds were crystallized from mixed solvent systems by one of three methods. 1) Neutral or easily crystallizable cationic organometallic compounds were crystallized using a layering technique. For example, the compound was dissolved in a solubilizing solvent (e.g. CH\(_2\)Cl\(_2\)), filtered
and concentrated. Then, three to five volumes of a less polar solvent (e.g. hexane) were slowly added via syringe down the side of the crystallization vessel such that two separate layers were formed. The mixture was allowed to stand at the indicated temperature until the solution was homogeneous. The resulting crystals were separated by cannulating the supernatant from the crystallization vessel. Crystals were washed three times with 5 mL aliquots of the less polar solvent and then vacuum dried. 2) Cationic complexes, which were difficult to crystallize by the layering technique, were crystallized by a slow diffusion technique, whereby a concentrated and filtered solution of the compound (generally in acetone) was placed in vapor contact with a more volatile precipitating solvent (diethyl ether). Diffusion of the precipitating solvent into the solution of the compound at room temperature over several days effected crystallization. This method was conveniently executed by putting a solution of the compound, contained in a beaker, into a vacuum desiccator containing a pool of ether. A bubbler was attached to the desiccator to vent excess pressure. 3) Alternatively, crystallization by the slow evaporation technique was sometimes used. In this method the compound to be crystallized was dissolved in a suitable solvent, and a higher-boiling solvent in which the
compound is less soluble was added; the solution was evaporated to a small volume (10-15 mL) under reduced pressure (50-60 torr) at room temperature with a rotary evaporator. Crystals obtained from diffusion or evaporative techniques were filtered, washed with hexane and ether, then vacuum dried.

Exchange of PF$_6^-$ for halide ions in cationic complexes was accomplished with a 2.5 x 17 cm column of Amberlite IRA-400 resin in acetone. Conversion of the resin from Cl$^-$ to PF$_6^-$ was achieved by slowly passing a saturated aqueous solution of KPF$_6$ through the column. Excess KPF$_6$ was removed by washing the column with deionized water. Water was removed by passing acetone through the column.

B. Instrumental Techniques

1. **Routine infrared spectra**

Routine infrared (IR) spectra in the range 4000-6000 cm$^{-1}$ were determined with a Perkin Elmer 681 infrared spectrophotometer. Calibration of the instrument was checked periodically by comparing observed and actual values for the frequencies of lines in the spectrum of CO gas (300 torr, path length = 4 cm) in the region 2242-2013 cm$^{-1}$. Below 2000 cm$^{-1}$, calibrations were checked a-
against the 1944.0 or 1603.0 cm\(^{-1}\) line of polystyrene film. Frequencies reported are accurate to ±2 cm\(^{-1}\).

Cells used for solution spectra consisted of two, 3 cm diameter, NaCl plates separated by a 1 mm Teflon spacer. Solution IR spectra were obtained in the double beam mode with pure solvent in a matched cell as reference.

Solid state IR spectra were measured as Nujol mulls sandwiched between two, 2.5 cm diameter, NaCl plates. These spectra were taken in the double beam mode with air as the reference.

2. Nuclear magnetic resonance (NMR) spectra

Proton NMR (\(^1\)H NMR) spectra were measured on either a Varian A-60, JOEL FX-90Q or Nicolet NT-300 spectrometer. The JOEL FX-90Q, Nicolet NR-300 and Bruker WM-300 spectrometers were used for obtaining carbon-13 (\(^{13}\)C NMR) spectra, with the latter used for obtaining phosphorus-31 (\(^{31}\)P [H] NMR) spectra. All spectra were taken in deuterated (>99.5%) solvents. Proton chemical shifts are reported in ppm downfield from the internal reference tetramethylsilane (TMS). Chemical shifts in \(^{13}\)C NMR spectra are referenced to the chemical shift of the solvent signal: CDCl\(_3\), 77.06 ppm; CD\(_2\)Cl\(_2\), 53.80 ppm; (CD\(_3\))\(_2\)CO, 29.80 ppm; CD\(_3\)CN, 1.30 ppm. Phosphorus NMR are referenced to the external standard, 85% H\(_3\)PO\(_4\), and reported as positive ppm values for
chemical shift downfield from this standard. Solutions of compounds for $^{13}$C analysis contained Cr(acac)$_3$ as a shiftless relaxation reagent$^{73}$ to enhance the signal of quaternary carbons.

3. **Mass spectra**

Mass spectra were determined on solid samples using a Finnegan 4000 mass spectrometer at ionization potentials of 22 ev.

4. **Ultra-violet spectra**

Perkin Elmer Model 320 or Beckman DU-8 spectrophotometers were used for the measurement of electronic spectra. Rectangular quartz cells with 1.00 cm path length were employed. Positions of absorption maxima are given in nanometers (nm).

5. **Cyclic voltammetry measurements**

The apparatus used for cyclic voltammetry studies was a Bioanalytical Systems CV-1B Cyclic Voltammograph. A three-electrode configuration (Figure 4) was employed, consisting of a stationary, Pt disc, working electrode of area 3.1 mm$^2$, platinum wire counter electrode and a Ag/AgCl (NaCl, 3.0 M) reference electrode. The reference electrode was separated from the analyte solution by an electrolyte bridge consisting of the 2 mL syringe, 3-way valve, teflon tube and porous Vycor plug. Dry acetonitrile (see Section
Figure 4. Electrochemical cell for cyclic voltammetry
II.C) was used as solvent and contained 0.1 M Bu$_4$NPF$_6$ as supporting electrolyte. The Bu$_4$NPF$_6$ was prepared from a literature method. Analyte concentration was about 1.0-3.0 x 10$^{-3}$ M in a solution volume of about 20 ml. Analyte solutions were deoxygenated with argon and measurements were taken under an atmosphere of argon at 0°C.

6. **Bulk electrochemical experiments**

The apparatus used for conducting controlled potential or controlled current electrolysis experiments was a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat. For coulometric measurements the Model 173 was interfaced with a PAR Model 179 digital coulometer which was kindly provided by Dr. Robert E. McCarley. To minimize the length of the connection to the reference electrode for low noise pickup, a PAR Model 178 high impedance, voltage follower, amplifier was mounted externally to the potentiostat/galvanostat. Experiments were conducted in a three compartment cell, Figure 5, the compartments separated by medium porosity glass frits. The solution in the sample compartment was stirred with a magnetic stirrer. A copper coil (5-8 coils, 0.7 cm in diameter of 20 gauge wire) served as the auxiliary electrode. A Pt gauze (42 mesh, 2.0 x 5.0 cm) cylinder was used as the working electrode while the reference was a Ag/AgCl (NaCl, 3.0 M)
Figure 5. Electrolysis cell
electrode. The reference electrode was separated from the analyte solution by the electrolyte bridge shown in Figure 5. The electrolyte solution was CH$_3$CN (dry)/0.1 M NBu$_4$PF$_6$ which was deoxygenated with argon. All experiments were performed at 0°C, with stirring, under an argon atmosphere. Background current or blanks were measured under the same conditions.

7. **Elemental analysis**
   Carbon, hydrogen and sulfur analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

8. **Melting points**
   Melting (mp) or decomposition points (dp) of compounds were observed on a Thomas hot stage apparatus and are uncorrected.

9. **Electron paramagnetic resonance (EPR) spectra**
   Electron paramagnetic resonance spectra were measured on a Bruker Model ER 2000-SRC spectrometer. Temperature control was provided by either a Bruker Model ER 4111 variable temperature controller for measurements above 77 K, or an Oxford Model ESR-900 continuous flow cryostat for measurements at 4 K. Samples dissolved in CH$_3$CN (dry)/0.1 M NBu$_4$PF$_6$ or THF (dry, see Section II.C) were contained in quartz tubes (3.0 mm ID) or a 60.0 x 17.0 x 0.25 mm flat quartz cell. Spectra are referenced to diphenylpicrylhy-
drazide, DPPH, which has a g-value of $2.0037 \pm 0.0002$. ^75

10. **Ultra-violet photolysis reactions**

Large scale (> 0.2 mmol) ultra-violet (254 nm) photolysis reactions were conducted using a water jacketed, quartz immersion reactor with a solution volume of 125 mL. A 100 watt, medium pressure, mercury arc lamp was the photon source. Small scale (<0.2 mmol) reactions were carried out at 254 nm in a Bradford Scientific photolysis apparatus which holds a 28 x 2.0 cm quartz Schlenk tube fitted with an internal cooling probe. Nitrogen was bubbled through the reaction solution to remove any CO released during photolysis.

C. Solvents

Many of the solvents were purified prior to use. All distillations were carried out under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Anhydrous diethyl ether ($\text{Et}_2\text{O}$) was obtained similarly. Acetonitrile ($\text{CH}_3\text{CN}$), dichloromethane ($\text{CH}_2\text{Cl}_2$) and hexane were stirred overnight with CaH$_2$, then distilled. Acetone used for crystallization was dried and distilled from P$_2$O$_5$. All other solvents were AR grade and were stored over activated molecular sieves 4A and purged.
with nitrogen before use.

D. Reagents

The thiocarbonyl complex, \( \text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS}) \), 1, was prepared according to the method of Quick and Angelici.\(^{76}\) However, purification of 1 required an alternative chromatographic procedure which is described here. The \( \text{CS}_2 \) filtrate obtained as in in reference 76 was taken to dryness, redissolved in a minimum of \( \text{CS}_2 \), filtered, and loaded onto a 4.0 x 25 cm column of Florisil; the ratio of Florisil to sample was approximately 30:1 (w/w). Elution with \( \text{CS}_2 \) separated a yellowish-orange fraction; this was followed by the greenish-black band of 1. Elution with \( \text{CS}_2 \) continued until the reddish-brown band of \( \text{Cp}_2\text{Fe}_2(\text{CO})_4 \) started to contaminate the trailing edge of the 1 band. Remaining 1, contaminated with \( \text{Cp}_2\text{Fe}_2(\text{CO})_4 \), was collected as a separate fraction by elution with a 5/1 mixture of \( \text{CS}_2/\text{CH}_2\text{Cl}_2 \). Purified 1 was crystallized, according to the procedure in reference 76, to give a 26% yield.

The metal dimers, \( \text{Co}_2(\text{CO})_8 \), \( \text{Re}_2(\text{CO})_{10} \), \( \text{Mn}_2(\text{CO})_{10} \) and \( \text{Cp}_2\text{Fe}_2(\text{CO})_4 \), were obtained from commercial sources. Dicobaltoctacarbonyl was sublimed (25°C, 0.02 torr) prior to use. The molybdenum dimer, \( \text{Cp}_2\text{Mo}_2(\text{CO})_6 \), was prepared from
the method of Hayter.\textsuperscript{77} The metal carbonyl salts, $\text{PPN}[\text{Fe(CO)}_3\text{NO}]$,\textsuperscript{78} $\text{PPN}[\text{Co(CO)}_4]$,\textsuperscript{79} $\text{PPN}[\text{HFe(CO)}_4]$\textsuperscript{80} and $\text{PPN}[\text{Mn(CO)}_5]$,\textsuperscript{81} and solutions of $\text{Na}[\text{Mn(CO)}_5]$,\textsuperscript{82} $\text{Na}[\text{Re(CO)}_5]$,\textsuperscript{83} $\text{Na}[\text{CpFe(CO)}_2]$,\textsuperscript{83} $\text{Na}[\text{CpMo(CO)}_3]$\textsuperscript{77} and $\text{Na}[\text{Co(CO)}_4]$\textsuperscript{79} were prepared according to published procedures. Alternatively, $\text{Na}[\text{Co(CO)}_4]$ was prepared from the method of Edgell and Lyford,\textsuperscript{84} described in Section II.E.3.a. The complexes $\text{NBu}_4[\text{Cr(CO)}_5]\text{I}$\textsuperscript{85} and $\text{NBu}_4[\text{W(CO)}_4(\text{CS})\text{I}]$\textsuperscript{86} were prepared by M. Quick and W. Greaves, respectively, from literature procedures.

Trimethylamine oxide was prepared by sublimation (70°C, 0.02 torr) of Me$_3$NO-2H$_2$O. The phosphorus ligands, PEt$_3$, PMe$_2$Ph, PMe$_2$Ph and P(OMe)$_3$, were fractionally distilled and stored under nitrogen. The Grignard reagent, PhCH$_2$MgCl, was kindly provided by N. Sauer who prepared it using the method of Gilman and Robinson.\textsuperscript{87} Sodium phenoxide was prepared by adapting the procedure used for the preparation of $\text{Na}[\beta\text{-naphthol}]$.\textsuperscript{88} Sodium naphthalide was prepared by stirring naphthalene with sodium in THF.\textsuperscript{89} All other reagents were commercial products of the highest purity available and were used as received.
E. Procedures

1. Preparation of bridging thiocarbyne complexes
   a. Preparation of \([\text{Cp}_2\text{Fe}_2\text{(CO)}_2(\mu-\text{CO})(\mu-\text{CSMe})]\)PF\(_6\), 2.

Preparation of 2 by alkylation of \(\text{Cp}_2\text{Fe}_2\text{(CO)}_3\text{CS}\), 1, with methyl iodide has been previously reported.\(^{50}\) The preparation described here is a modification of this procedure which allows the synthesis of 2 from impure 1. Synthesis of 1 from \(\text{Cp}_2\text{Fe}_2\text{(CO)}_4\) (11.5 g, 32.5 mmol) follows the published procedure\(^{76}\) through the CS\(_2\) extraction step. This extract contains approximately equal amounts of 1 (ca. 8 mmol) and \(\text{Cp}_2\text{Fe}_2\text{(CO)}_4\), plus (PhO)\(_2\text{CS}\) and Hg[\(\text{CpFe(CO)}_2\)]\(_2\). The dried extract, hereafter referred to as "impure 1", was stirred overnight with methyl iodide (30.0 mL, 475 mmol). Addition of 100 mL of Et\(_2\)O precipitated the red product, \([\text{Cp}_2\text{Fe}_2\text{(CO)}_2(\mu-\text{CO})(\mu-\text{CSMe})]\)I, which was filtered and washed with Et\(_2\)O to remove unreacted \(\text{Cp}_2\text{Fe}_2\text{(CO)}_4\). The iodide salt was dissolved in acetone (ca. 1 L), filtered and passed through a PF\(_6^-\) ion exchange column. The solution of 2 was taken to dryness, then crystallized from acetone/Et\(_2\)O using the diffusion technique, or from acetone/heptane using the evaporation technique. The product was dried under vacuum and stored over P\(_2\)O\(_5\). The overall yield was 3.6 g (22%) starting from \(\text{Cp}_2\text{Fe}_2\text{(CO)}_4\). Synthesis of 2 from purified 1
gave 2.6 g (16% yield) of product.

IR(CH$_3$CN): 2044(s), 2013(w), 1853(m)
$^1$H($d^6$-acetone): 5.72 and 5.63(Cp, 10H),
3.80(CH$_3$, 3H)

$^{13}$C(CD$_3$CN): 408.3($\mu$-C), 252.3($\mu$-CO), 207.4(CO),
92.8 and 92.1(Cp), 38.2(CH$_3$)

b. Preparation of [Cp$_2$Fe$_2$(CO)$_2$(CO)(p-CSCH$_2$Ph)]PF$_6$, 3

Using the procedure for 2, [Cp$_2$Fe$_2$(CO)$_2$(CO)(p-CSCH$_2$Ph)]PF$_6$, 3, was prepared from the reaction of PhCH$_2$Br (30.0 mL, 244 mmol) with "impure 1" (ca. 8 mmol), in 13% (4.3 g) yield.

IR(CH$_3$CN): 2040(s), 2015(w), 1853(m)
$^1$H($d^6$-acetone): 7.5(m, Ph, 5H), 5.75 and
5.62(Cp, 10H), 5.43(CH$_2$, 2H)

c. Preparation of [Cp$_2$Fe$_2$(CO)$_2$(CO)(p-CSCH$_2$CH=CH$_2$)]PF$_6$, 4

The reaction of allyl bromide (30.0 mL, 347 mmol) with "impure 1" (ca. 8 mmol) according to the procedure used for 2 above, gave, after ion exchange and crystallization from CH$_2$Cl$_2$/hexane, the red product 4 in 28% (1.2 g) yield.

IR(CH$_3$CN): 2040(s), 2015(w), 1853(m)
$^1$H($d^6$-acetone): 6.18(m, b, vinyl), 5.70 and
5.65(Cp), 4.96(t, CH$_2$)
d. Attempted preparation of [Cp₂Fe₂(CO)₂(μ-CO)(μ-CSCH₂C(CH₃)₃)]SO₃CF₃, 5 The following reaction was carried out in the dark. Silver triflate (0.13 g, 0.50 mmol) was stirred with neopentyl bromide (0.50 mL, 4.0 mmol) in 20 mL of CH₂Cl₂ for 30 minutes to give a solution of neopentyl triflate and a yellow AgBr precipitate. The neopentyl triflate solution was filtered through a medium glass frit into a flask containing 1 (0.18 g, 0.48 mmol) and stirred for 60 minutes to give a brown reaction mixture which had a strong mercaptan odor and exhibited carbonyl bands in the IR spectrum at 2043 and 1850 cm⁻¹ characteristic of a Cp₂Fe₂(CO)₂(μ-CO)(μ-CSR)+ complex. The brown residue remaining after solvent removal was washed with benzene, dissolved in a 50:50 mixture of CH₂Cl₂:CH₃CN, layered with ether and stored at -20°C. A red oil formed which was washed with hexane and dried under vacuum. The oil was tentively identified as 5.

IR(CH₃CN): 2043(s), 2020(sh), 1850(m)

e. Preparation of [Cp₂Fe₂(CH₃CN)(CO)(μ-CO)(μ-CSMe)]PF₆, 6, and [Cp₂Fe₂(CH₃CN)₂(μ-CO)(μ-CSMe)]PF₆, 7 An CH₃CN solution of 2 (0.25 g, 0.47 mmol) was photolyzed at 254 nm. After 5 hours approximately 50% of 2 had reacted to give, as the major product (66%), Cp₂Fe₂(CH₃CN)(CO)⁻(μ-CO)(μ-CSMe)+, 6.

IR(CH₃CN): 2000(s), 1830(s)
The disubstituted product, 7, was also formed (33%).

\[ \text{IR}(\text{CH}_3\text{CN}): 1805(\text{s}) \]

Continued photolysis for 24 hours gave a 2:1 mixture of 7:6. Removing the solvent in vacuo and redissolving in CH\(_2\)Cl\(_2\) caused 7 to decompose. The CH\(_2\)Cl\(_2\) solution was loaded onto a 2.0 x 11 cm column of silica gel (60-200 mesh). Elution with acetone gave 6 contaminated with a decomposition product of 7. Crystallization of 6 from this impurity was unsuccessful.

An alternative preparation of 6, which was not contaminated by 7 or its decomposition products, was achieved by slowly titrating an CH\(_3\)CN solution (10 mL) of 2 (0.25 g, 0.38 mmol) with an CH\(_3\)CN solution of Me\(_3\)NO (0.038 M; required 10 mL) under a strong nitrogen purge. The titration caused a color change to brownish-green with vigorous evolution of CO. The residue after evaporation of the solvent was extracted with CH\(_2\)Cl\(_2\), filtered through anhydrous MgSO\(_4\), concentrated to 5 mL and layered with hexane. Attempted crystallization at room temperature gave a brownish oil of 6.

\[ \text{IR}(\text{CH}_3\text{CN}): 1998(\text{s}), 1827(\text{s}) \]

\[ ^1\text{H}(\text{CD}_3\text{NO}_2): 5.19 \text{ and } 5.03(\text{Cp}), 3.72(\text{SMe}), 1.91(\text{CH}_3\text{CN}) \]
f. Preparation of $[\text{Cp}_2\text{Fe}_2(\text{PET}_3)(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})]\text{PF}_6$,

8 Quick and Angelici$^{50}$ originally prepared this complex by stirring an CH$_3$CN solution of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})]\text{FSO}_3$ (0.50 mmol) with PET$_3$ (0.75 mmol) for 30 minutes at room temperature; ion exchange then gave the PF$_6^-$ form. Utilization of 2 (0.30 g, 0.54 mmol) required 20 hours of stirring with PET$_3$ (0.34 mL, 2.3 mmol) in CH$_3$CN at room temperature. After evaporation of the solvent, the residue was washed with ether, redissolved in a minimum of acetone and layered with ether. Crystallization at -20$^\circ$C gave 0.19 g (51%) of 8. The product was identified by comparing its IR absorption bands to published values.$^{50}$

IR(CH$_2$Cl$_2$): 1988(s), 1820(s), 1008(m) ($\nu$-CS)

9 g. Preparation of $[\text{Cp}_2\text{Fe}_2(\text{PMe}_2\text{Ph})(\text{CO})(\mu-\text{CO})(\mu-\text{SMe})]\text{PF}_6$,

This complex was originally prepared by stirring an CH$_3$CN solution of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})]\text{FSO}_3$ (0.50 mmol) with PMe$_2$Ph (0.70 mmol) for 30 minutes; ion exchange gave the PF$_6^-$ form.$^{50}$ Utilization of 2 (0.20 g, 0.38 mmol), required 30 minutes of refluxing in CH$_3$CN (30 mL) with PMe$_2$Ph (0.12 mL, 0.70 mmol) to give 9. The residue, after evaporation of CH$_3$CN, was washed with hexane, dissolved in acetone (5 mL) and layered with ether (20 mL). Crystallization at -20$^\circ$C gave 0.19 g (79%) of the green product, 9. The product was identified by comparing its IR absorption bands to published values.$^{50}$
h. Preparation of Cp₂Fe₂(CO)₂(I)(μ-CO)(μ-CSMe), 10

A solution of 6 was prepared by titrating an CH₃CN solution (10 mL) of 2 (0.50 g, 0.94 mmol) with a 0.1 M CH₃CN solution of Me₃NO (required 9.4 mL). The solution of 6 was refluxed for 6 hours with NaI (0.60 g, 4.0 mmol). The black residue, remaining after evaporation of the solvent, was dissolved in CH₂Cl₂ and passed through a silica gel column (1.0 x 10 cm). Heptane was added to the eluent and crystallization was promoted by the slow evaporation technique. The black crystalline product, 10, was obtained in 76% yield (0.35 g).

IR(CH₂Cl₂): 1995(s), 1810(s)

¹H(d₆-acetone): 4.86 and 4.84(Cp), 3.74(SMe)

This product, previously prepared by Quick and Angelici⁵⁰ by another method, gave a 91% yield.

2. Reactions of bridging thiocarbyne complexes with nucleophiles

a. Reactions of 2 with NaSMe

Excess methanethiol (MeSH) was condensed onto NaH (0.059 g of a 57% oil dispersion, 1.4 mmole) at -80°C. Addition of 5 mL of CH₃CN to the stirred suspension and slowly warming to 0°C formed a solution of NaSMe. Addition of 2 (0.40 g, 0.76 mmol) in 25
mL of CH$_3$CN gave an immediate reaction to form a purple solution. The reaction was stirred for 5 minutes at 0°C, brought to room temperature, and the solvent removed under vacuum. The residue was extracted with benzene; the resulting solution was filtered through anhydrous MgSO$_4$ and dried under vacuum. Crystallization from CH$_2$Cl$_2$ (4 mL)/hexane (20 mL) at -20°C, using the layering technique, gave 0.26 mg (80% yield) of purple needles of Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-C(SMe)$_2$], 11. Crystals of 11 are stable indefinitely under nitrogen at -20°C, and have a dp of 101.5°C. Solutions of 11, which are mixtures of the cis and trans isomers, decomposed to insoluble products when exposed to small amounts of water under a nitrogen atmosphere.

Anal calcd for C$_{16}$H$_{16}$O$_3$S$_2$Fe$_2$: C: 44.48, H: 3.73, S: 14.84

Found: C: 44.16, H: 3.75, S: 15.11

IR(CH$_2$Cl$_2$): 1985(s), 1952(m), 1785(m)

$^1$H(CD$_2$Cl$_2$): 4.90 and 4.89*(Cp, 10H), 2.77, 2.71* and 2.55*(Me, 6H) * = cis isomer

$^{13}$C(CD$_2$Cl$_2$): 271.7 and 270.9*(μ-CO), 210.9* and 210.4(CO), 189.2 and 186.9*(μ-C), 91.1 and 90.2*(Cp), 26.2, 25.6* and 24.1*(CH$_3$) * = cis isomer
b. Reaction of 2 with NaSPh

A solution of NaSPh was prepared by mixing benzenethiol (PhSH) (0.40 mL, 3.9 mmol) with NaH (0.16 g of a 57% oil dispersion, 3.8 mmol) in THF at room temperature. Removal of the solvent left a sticky white precipitate of NaSPh. Addition of CH₃CN (20 mL) to a mixture of 2 (0.53 g, 1.0 mmol) and NaSPh (0.26 g, 2.0 mmol) resulted in an immediate reaction to give a purple solution. After stirring for 30 minutes the solvent was removed under vacuum, and the resulting purple residue was extracted with benzene. The extract was filtered through anhydrous MgSO₄ and dried under vacuum. Crystallization from CH₂Cl₂ (4 mL)/hexane (25 mL) at 20°C gave 0.37 g (75% yield) of purple crystals of Cp₂Fe₂(CO)₂(μ-CO)[μ-C(SMe)SPh], 12, having a dp of 70°C. Complex 12 was stable in the solid state under nitrogen at -20°C. Crystals of 12, when exposed to air, decomposed slowly (3 months) at room temperature. Solutions of 12, which existed as mixtures of cis and trans isomers, decomposed thermally and photolytically under nitrogen to give a bridging carbyne product (see Section II.E.4. f and g).

Anal calcd for C₂₁H₁₆O₃S₂Fe₂: C: 51.53, H: 3.89, S: 13.76

Found: C: 51.12, H: 4.08, S: 13.87

IR(CH₂Cl₂): 1988(s), 1957(m), 1788(m)

¹H(CDCl₃): 7.58(m, Ph, 5H), 4.95 and 4.93(C₅p,
c. **Reaction of 2 with NaSCH₂Ph**  
A clear THF (5 mL) solution of dibenzyldisulfide (0.020 g, 0.080 mmol) was titrated with a THF solution of sodium naphthalide (ca. 0.04 mmol/mL) to a light green end point. The solvent was evaporated to give a white residue of naphthalene and NaSCH₂Ph. Addition of 2 (0.040 g, 0.080 mmol) followed by 5 mL of CH₃CN gave a purple colored solution. This color and the similarity of the IR spectrum to those of 11 and 12 identified the product as Cp₂Fe₂(CO)₂(μ-CO)[μ-C(SMe)- (SCH₂Ph)], 13. Since 51 (see Section II.E.5.i) did not react with PhCH₂S-SCH₂Ph to give 13, this synthesis was performed for diagnostic purposes to see if 13 was stable. For this reason, and the micro-scale of the reaction, the product was not isolated.

IR(CH₃CN): 1980(s), 1949(m), 1785(m)

**d. Reaction of 2 with NaBH₄**  
Sodium borohydride (0.019 g, 0.50 mmol) was stirred with 5 mL of CH₃CN at 0°C. Addition of 2 (0.27 g, 0.50 mmol) gave a red solution. The reaction was stirred at 0°C for 30 minutes, the solvent removed in vacuo and the red residue extracted with benzene; the extract was filtered through Celite and taken to dryness. Crystallization from CH₂Cl₂ (4 mL)/hexane (19 mL) at room temperature for 18 hours and then at -20°C for 2
days gave 0.12 g (64% yield) of light red crystals of predominantly trans-Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)(SMe)), 14. Microscopic examination of the product showed the majority of the crystals were light red, indicative of trans-Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)(SMe)). A small amount of the dark red crystals of cis-Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)(SMe)), 15, were also present. The dp was 80°C for the light red crystals and 100°C for the dark red crystals.

IR(CH₂Cl₂): 1997(s), 1962(sh), 1803(m)

¹H(CDCl₃): 11.51 and 10.03*(methine), 4.94*, 4.83* and 4.76(Cp), 2.84 and 2.72*(Me); * = trans isomer

¹H(d₆-acetone): 11.64(methine, 1H), 4.84(Cp, 10 H), 2.80(Me, 3 H)

The light red crystals decomposed at room temperature under nitrogen; after several months the spectroscopic properties changed to:

IR(CH₂Cl₂): 1987(s), 1948(sh), 1784(m)

¹H(CDCl₃): 11.47(methine), 4.76(Cp), 2.82(Me)

The supernatant from the CH₂Cl₂/hexane crystallization was evaporated under reduced pressure and the residue crystallized from CH₂Cl₂/hexane at -20°C. This gave a small amount of dark red crystals of cis-Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)(SMe)), 15.
An alternative crystallization procedure for the residue remaining from the benzene extraction utilized acetone (4 mL)/hexane (16 mL), and yielded 0.12 g (60%) of dark red 15 having a dp of 100°C.

Anal calcd C₁₅H₁₄O₃F₉2:  C: 46.67, H: 3.66,  
S: 8.31

Found:  C: 46.41, H: 3.73, S: 8.49

Crystals of 15 were stable at room temperature under nitrogen for at least 2 weeks. Under nitrogen at -20°C they are stable indefinitely.

e. Reaction of 3 with NaBH₄  

An CH₃CN (5 mL) solution of NaBH₄ (0.019 g, 0.50 mmol) and 3 (0.30 g, 0.50 mmol) was stirred for 30 minutes. The solvent was removed in vacuo, leaving a red residue which was extracted with CH₂Cl₂ (20 mL). The extract was filtered through Celite, concentrated to 5 mL and layered with 20 mL of hexane.
Crystals formed at room temperature; complete crystallization was achieved at \(-20^\circ\text{C}\) overnight, giving 0.17 g (72% yield) of red-violet needles of cis-Cp\(_2\)Fe\(_2\)(CO)\(_2\)(\(\mu\)-CO)[\(\mu\)-C(H)(SCH\(_2\)Ph)], 16, which has a dp of 102°C. The product is stable at \(-20^\circ\text{C}\) under nitrogen indefinitely.

Anal calcd for C\(_{21}\)H\(_{18}\)O\(_3\)SFe\(_2\): C; 54.50, H; 3.93, S; 6.94

Found: C; 54.20, H; 3.93, S; 6.96

IR(CH\(_2\)Cl\(_2\)): 1985(s), 1947(w), 1780(m)

\(^1\text{H}(\text{CDCl}_3): 11.43\text{(methine)}, 7.43\text{(m, Ph)}, 4.53\text{(Cp)}, 4.34\text{(CH}_2\text{)}

\(^1\text{H}(\text{d}^6\text{-aceton}): 11.68\text{(methine)}, 7.44\text{(m, Ph)}, 4.72\text{(Cp)}, 4.39\text{(CH}_2\text{)}

\(^{13}\text{C}(\text{CD}_2\text{Cl}_2): 272.5(\mu\text{-CO}), 210.9(\text{CO}), 163.7(\mu\text{-C}) 138.6, 128.8, 128.3 \text{ and } 126.6(\text{Ph}) 86.9(\text{Cp}), 46.8(\text{CH}_2\text{)}

f. Reactions of 4 with NaBH\(_4\) Stirring NaBH\(_4\) (0.014 g, 0.38 mmol) with 4 (0.21 g, 0.38 mmol) in 5 mL of CH\(_3\)CN at 25°C for 5 minutes gave a red reaction mixture. After evaporation of the solvent, the red residue was extracted with benzene; the resulting solution was filtered through Celite and the benzene removed under vacuum. Crystallization at \(-20^\circ\text{C}\) from CH\(_2\)Cl\(_2\) (4 mL)/hexane (20 mL) gave 0.112 g (76% yield) of a dark red powder, Cp\(_2\)Fe\(_2\)(CO)\(_2\)(\(\mu\)-...
which has a dp 44°C. The spectral data (NMR) indicated that 17 existed as three different isomers.

\[
\text{IR}(\text{CH}_2\text{Cl}_2): \quad 1993(s), 1957(sh), 1793(m)
\]

\[
^1\text{H}(\text{CDCl}_3): \quad 11.61, 11.37 \text{ and } 11.21(\text{methine}), \quad 4.78, 4.77, 4.74 \text{ and } 4.72(\text{Cp}), \quad 3.24(b, m, \text{vinyl}), \quad 2.11(m, b, \text{CH}_2)
\]

Reactions of 6 with NaBH\textsubscript{4}

Stirring 6 (0.21 g, 0.38 mmol) and NaBH\textsubscript{4} (0.014 g, 0.38 mmol) in CH\textsubscript{3}CN (5 mL) for 5 minutes gave a brown solution, tentatively identified from its IR spectrum as \(\text{Cp}_2\text{Fe}_2(\text{CH}_3\text{CN})(\text{CO})[\mu-\text{CO}](\mu-\text{C}(\text{H})\text{SMe})\), 18.

\[
\text{IR}(\text{CH}_3\text{CN}): \quad 1930(s), 1759(m)
\]

The solution of 18 was taken to dryness and the residue extracted with benzene; the extract was filtered through anhydrous MgSO\textsubscript{4} and evaporated. The resulting brown residue was reacted with PMe\textsubscript{2}Ph (0.048 mL, 0.38 mmol) in CH\textsubscript{3}CN (5 mL) for 5 minutes, solvent removed and the residue extracted with benzene. The extract was filtered through anhydrous MgSO\textsubscript{4}; the brown residue resulting upon evaporation of benzene was washed with 2 mL of hexane, dried and crystallized from CH\textsubscript{2}Cl\textsubscript{2} (3 mL)/hexane (15 mL) at -20°C overnight to give 0.072 g (38% yield) of green crystals of \(\text{Cp}_2\text{Fe}_2(\text{PMe}_2\text{Ph})(\text{CO})(\mu-\text{CO})(\mu-\text{C}(\text{H})(\text{SMe}))\), 19, having a dp of...
74°C. Because the product was contaminated with free PMe2Ph, no chemical analysis was obtained.

\[ \text{IR(\text{CH}_3\text{CN})}: \ 1917(\text{s}), \ 1735(\text{s}) \]
\[ \text{^1H(CDCl}_3\text{)}: \ 10.91(\text{methine}), \ 4.54 \text{ and } 4.37(\text{Cp}), \ 2.70(\text{d, SMe, } J_{\text{P,H}} = 9.3 \text{ Hz}); \]
\[ \text{Ph(ca. 7.4 ppm) and Me(ca. 1.6 ppm)} \]
resonances of the PMe2Ph ligand are masked by residual PMe2Ph in the product.

h. Reaction of 2 with 4-dimethylaminopyridine (4-DMAP)

An CH3CN (5 mL) solution of 4-DMAP (0.33 g, 3.0 mmol) and 2 (0.27 g, 0.50 mmol) was stirred for 6 hours. The solvent was removed in vacuo and the dark residue was washed with three, 5 mL aliquots of ether. The residue was dissolved in acetone (5 mL), and the resulting solution layered with ether (20 mL). Crystallization at -20°C gave 0.25 g (81% yield) of the black, crystalline product, \([\text{Cp}_2\text{Fe}_2(4-\text{DMAP})-\text{(CO})\mu-\text{CO})(\mu-\text{CSMe})]\text{PF}_6\), 20. The product is an air-stable solid with a dp of 108°C.

Anal calcd for C21H23O2SN2Fe2:  C: 40.67, H: 3.74, N: 4.52, S: 5.17

Found:  C: 40.12, H: 3.72, N: 4.41, S: 5.25

IR(CH3CN):  2000(s), 1815(s)

\[ \text{^1H(d6-acetone)}: \ 7.76(\text{d, py, } J_{\text{H,H}} = 7.5, \ 2\text{H}), \]
6.36(d, py, J_H,H = 7.5, 2H),
5.34 and 5.07(Cp, 10H),
3.85(SMe, 3H), 2.95(NCH_3, 6H).

^{13}C(CD_3CN): 407.1(\mu-C), 267.0(\mu-CO), 210.5 (CO),
155.1, 153.5 and 108.9(py),
90.7(Cp), 39.3(NCH_3), 36.0(SMe)

i. **Reaction of 3 with 4-DMAP**

An CH_3CN (5 mL) solution of 4-DMAP (0.33 g, 3.0 mmol) and 3 (0.30 g, 0.50 mmol) was stirred for 24 hours. The solution was evaporated in vacuo to give a dark residue. A benzene washing of the residue contained a significant amount of Cp_2Fe_2(CO)_3CS. The remaining residue was crystallized from CH_2Cl_2 (5 mL)/ether (20 mL) at room temperature for one week. A reddish-brown crystalline product, immersed in a dark oil, along with a small amount of yellow crystals was obtained. Washing with three, 5 mL aliquots of ether and drying under vacuum gave 0.13 g (36% yield) of brown [Cp_2Fe_2(4-DMAP)(CO)(\mu-CO)(\mu-CSCH_2Ph)]PF_6, 21, which was contaminated with a small amount of the yellow crystalline material.

IR(CH_2Cl_2): 2007(s), 1817(s)

^{1}H(d^6-acetone): 7.79(d, py, J_H,H = 7.5 Hz),
7.45(m, Ph), 6.39(d, py, J_H,H = 7.5 Hz),
5.60(CH_2),
5.39 and 5.10(Cp), 2.94(CH_3)
j. Reaction of 2 with NaSePh

A THF solution (20 mL) of PhSeSePh (0.16 g, 0.50 mmol) was stirred for 30 minutes with 5 mL of a 1% w/w Na(Hg), filtered through Celite and cooled to 0°C. Addition of 2 (0.27 g, 0.50 mmol) gave a purple solution having carbonyl bands at 2005 (sh), 1985 (s), 1958 (m), 1805 (sh) and 1792 (s) cm\(^{-1}\). The solvent was removed in vacuo at 0°C leaving a brown residue which was extracted with hexane to remove PhSeSePh and 1. The residue was dissolved in CH\(_2\)Cl\(_2\) and the resulting solution was filtered through Celite and concentrated to 4 mL. Layering with hexane (20 mL) and crystallization at -20°C gave 0.083 g (32% yield) of brownish-black crystals of the neutral \(\mu\)-carbyne complex, \(\text{Cp}_2\text{Fe}_2(\text{SePh})(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})\), 22, which have a dp of 95°C. Product 22 is stable indefinitely at -20°C under nitrogen. Bubbling CO through a solution of 22 does not produce the purple, \(\mu\)-carbene complex, \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-C(\text{SMe})(\text{SePh}))\), 23 (see Section II.E.5.j).

Anal calcd for \(\text{C}_{20}\text{H}_{18}\text{O}_2\text{SSeFe}_2\): C: 46.82, H: 3.54, S: 6.25

Found: C: 46.94, H: 3.58, S: 6.25

IR(CH\(_3\)CN): 1978 (s), 1800 (s)

\(^1\text{H}(\text{CDCl}_3): 7.32\text{(m, Ph, 5H)}, 4.84\text{ and } 4.75\text{(Cp, 10H)}, 3.39\text{(Me, 3H)}\)
$^{13}\text{C}(\text{CD}_2\text{Cl}_2)$: 403.3(μ-C), 261.3(μ-CO),
212.9(CO), 135.3, 134.3, 127.1
and 124.2(Ph), 88.9 and 87.0(Cp),
32.8(Me)

k. Reaction of 2 with PhCH$_2$MgCl

Addition of 1.2 mL of a 0.40 M diethyl ether solution of PhCH$_2$MgCl (0.48 mmol) to a suspension of 2 (0.25 g, 0.47 mmol) in THF (20 mL) gave an exothermic reaction which produced a brown solution and evolved a mercaptan odor. The residue, after solvent evaporation, was extracted with 15 mL of benzene. The extract was filtered through anhydrous MgSO$_4$ and evaporated to dryness under vacuum; the resulting residue was dissolved in a minimum of CH$_2$Cl$_2$ and loaded onto a 1.0 x 25 cm silica gel column (250-400 mesh). Elution with benzene caused two red fractions to develop. Initially, the first fraction was a discrete band, but, during the elution, it tailed, becoming incorporated with the second red fraction. The combined fractions were eluted from the column with CH$_2$Cl$_2$; the red solution was taken to dryness, redissolved in CH$_2$Cl$_2$ (4 mL), layered with hexane (20 mL) and crystallized for 3 days at -20°C to give 0.060 g (27% yield) of red needles of cis-Cp$_2$Fe$_2$(CO)$_2$($\mu$-CO)[($\mu$-(CSMe)(CH$_2$Ph))], 24, which have a dp of 90°C.

Anal calcd for C$_{22}$H$_{20}$O$_3$SFe$_2$: C: 55.46,
59

H: 4.24: , S: 6.74

Found:  C: 54.64, H: 4.43, S: 6.71

IR(Hexane)*:  1976(s), 1992(sh), 1964(sh), 1952(s), 1801(s), 1796(sh).

* limited solubility

IR(CD$_3$CN):  1977(s), 1940(m), 1782(m).

$^1$H(CD$_3$CN):  7.29(Ph), 4.84(Cp), 3.79(CH$_2$), 2.81(CH$_3$)

1. Reaction of 2 with NHMe$_2$ A stream of NHMe$_2$ was bubbled through a stirred CH$_3$CN (5 mL) solution of 2 (0.050 g, 0.094 mmol) at 0°C. After 5 minutes the reaction mixture turned greenish-brown. The IR spectrum of the reaction mixture, at this point, showed bands at 1972(s), 1938(s), and 1770-1780(m, br) cm$^{-1}$. The flow of NHMe$_2$ was stopped and the reaction mixture evaporated to dryness under vacuum. The IR spectrum (in CH$_3$CN) of the resulting brown residue had bands for 2 and another product (1938(s), and 1768(s) cm$^{-1}$). Repeating the experiment, but letting NHMe$_2$ bubble through the reaction mixture for 30 minutes at 0°C, gave a brown solution which has IR bands at 1972(sh), 1938(s) and 1770(m) cm$^{-1}$. The flow of NHMe$_2$ was stopped and the reaction mixture was evaporated to dryness under vacuum. The IR spectrum (in CH$_3$CN) of the brown residue again showed bands for 2 and another product (1938(s) and
1768(s) cm\(^{-1}\)). This product was extracted with CDCl\(_3\) and tentatively identified as \(\text{Cp}_2\text{Fe}_2(\text{SMe})(\text{CO})(\mu-\text{CO})(\mu-\text{CNMe}_2)\), 25.

\[
\text{IR(CDCl}_3\text{): } 1944(s), 1770(s)
\]
\[
\text{\(^1\text{H(CDCl}_3\): major isomer: } 4.72 \text{ and } 4.54(\text{Cp}), 3.45 \text{ and } 3.37(\mu-\text{CNMe}_2), 1.53(\text{SMe})
\]
\[
\text{minor isomer: } 4.69 \text{ and } 4.58(\text{Cp}), 3.24 \text{ and } 3.19(\mu-\text{CNMe}_2), 1.53(\text{SMe})^*
\]
* masked by major isomer

Attempted crystallization of the product from CDCl\(_3\)/hexane at -20\(^\circ\)C resulted in decomposition. The product, 25, was unstable in the solid state; the IR spectrum of the reaction mixture residue, after being stored under nitrogen at 25\(^\circ\)C for 3 days, showed only carbonyl bands for 2.

m. **Reaction of 2 with pyrrolidine** Stirring an CH\(_3\)CN solution (10 mL) of 2 (0.053 g, 0.10 mmol) with pyrrolidine (0.005 mL, 0.05 mmol) for 30 minutes showed no observable reaction by IR spectral analysis. Addition of another 0.05 mmol of pyrrolidine and stirring for 5 hours gave only a limited reaction (< 10% of 2 converted). Addition of a second, third, fourth and fifth equivalent of pyrrolidine at 20 minute intervals, gave incrementally greater reaction to form products with carbonyl bands at 2025(s), 1981(s), 1940(s) and 1775(m) cm\(^{-1}\). A significant
amount (ca. 60%) of 2 remained unreacted. Addition of a large excess of pyrrolidine (total of 15 equivalents, 1.5 mmol) and stirring for 1 hour gave a brown solution which did not contain 2. The reaction mixture was taken to dryness under vacuum giving a brown residue: IR(CH₃CN) 2025(s), 1981(s), 1938(s) and 1770(m) cm⁻¹. The band at 2025 cm⁻¹ is an unidentified by-product of the reaction. The other three bands are similar to those observed during the dimethylamine reaction. The bands at 1938 and 1770 cm⁻¹ are due to the final pyrrolidine product. A CDCl₃ extract of the residue has a ¹H NMR spectrum which shows resonances for a product similar to 25, and was tentatively identified as Cp₂Fe₂(SMe)(CO)(μ-CO)(μ-CNCH₂CH₂CH₂CH₂), 26.

¹H(CDCl₃): 4.73 and 4.53(Cp), 3.06(b, NCH₂), 1.87(b, CH₂), 1.53(SMe)

Other products in this reaction plus residual pyrrolidine make it difficult to assign resonances for the u-C pyrrolidine ligand. However, the resonances at 3.06 and 1.87 ppm are likely chemical shifts for the alpha and beta protons, respectively, of dialkyl aminocarbyne ligands. Attempted crystallization of the product from CDCl₃/hexane at -20°C, resulted in decomposition.

n. Reaction of 2 with other amines

An CH₃CN (3 mL) solution of 2 (0.010 g, 0.020 mmol) was stirred with a
ten to twenty fold excess of n-butylamine for 10 minutes giving a brown solution. In a similar manner, \( \text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2 \) \((n = 2, 3)\), \( \text{CH}_3\text{NH}(\text{CH}_2)_3\text{HNCH}_3 \) and \( \text{NH}_2(\text{CH}_2)_2\text{OH} \) reacted within 10 minutes giving brown solutions. Likewise, bubbling \( \text{NHMe}_2 \) through an \( \text{CH}_3\text{CN} \) (10 mL) solution of 2 (0.050 g, 0.10 mmol) at 0°C for 10 minutes gave a brown solution. The IR spectra (in CH₃CN) of these reaction products are given below.

BuNH₂, 27: 1970(sh), 1940(s), 1768(s)
HNEt₂, 28: 1971(sh), 1940(s), 1765(s)
H₂N(CH₂)₂NH₂, 29: 1948(s), 1770(s)
H₂N(CH₂)₃NH₂, 30: 1945(s), 1770(s)
CH₃(H)N(CH₂)₃N(H)CH₃, 31: 1945(s), 1770(s),
NH₂(CH₂)₂OH, 32: 1945(s), 1770(s),

The carbonyl bands at 1940-1948 cm⁻¹ and approximately 1770 cm⁻¹ are similar to those of 25 and 26, indicating that the final products of these amine reactions, 27-32, may be tentatively identified as the analogous \( \mu\text{-CNR}_2 \) complexes, \( \text{Cp}_2\text{Fe}_2(\text{SMe})(\text{CO})(\mu\text{-CO})(\mu\text{-CNR}_2) \). Under the same conditions an acetonitrile solution of \( \text{Me}_2\text{N(CH}_2)_3\text{NMe}_2 \) reacted with 2 slowly and incompletely giving very weak product bands at 1945 and 1770 cm⁻¹.
3. Reaction of bridging thiocarbyne complexes with metal carbonyl anions

a. Reaction of 2 with Na[Co(CO)₄] under photolytic conditions

A solution of Na[Co(CO)₄] was prepared in situ by combining Co₂(CO)₈ (0.45 g, 1.3 mmol) with finely ground NaOH (4.50 g, 113 mmol) in THF (25 mL). After shaking for 30 minutes the brown color of Co₂(CO)₈ disappeared. The resulting suspension was filtered through Celite into the photolysis tube containing 2 (1.0 g, 1.9 mmol) and 100 mL of THF. The resulting reddish-brown solution was photolyzed with stirring until the IR spectral bands of the carbyne starting material, 2, disappeared (ca. 6 hours). The residue, after solvent removal under vacuum, was extracted with benzene, the extract filtered through anhydrous MgSO₄ and evaporated to dryness, giving a brownish-purple residue. Crystallization from CH₂Cl₂ (10 mL) and hexane (50 mL) at -20°C gave brownish-purple crystals of Cp₂Fe₂Co(CO)₃(μ-CO)₂(μ-CSMe), 33. The yield of 33 was 0.76 g (80% yield). An analytical sample was recrystallized from the same solvents. Crystalline 33 decomposed at 60°C but is stable indefinitely under nitrogen at -20°C. Solutions of 33 decomposed slowly when exposed to air or moisture.

Anal calcd for C₁₇H₁₃O₅SCoFe₂: C: 40.84,
H: 2.62, S: 6.41

Found: C: 40.76, H: 2.50, S: 6.32

IR(CH2Cl2): 2023(s), 1981(s), 1951(w), 1818(s), 1781(w)

1H(CDCl3): 4.83 and 4.42(Cp), 2.75(Me)

13C(CD2Cl2, -60°C): 322.0(μ3-C), 262.1(μ-CO), 252.1(b, μ-CO), 211.3(CO), 207.7(b, CO), 201.7(b, CO), 86.6 and 86.3(Cp), 36.6(Me)

b. Reaction of 2 with PPN[Co(CO)4] Stirring PPN-[Co(CO)4] (0.18 g, 0.25 mmol) with 2 (0.13 g, 0.25 mmol) in 10 mL of CH3CN for 60 minutes showed no reaction. Re-fluxing for 30 minutes formed 33 and insoluble, decomposition products. The residue obtained after solvent evaporation was extracted with benzene, the extract filtered through Celite and taken to dryness under vacuum, giving a brownish-purple residue. Workup of the reaction mixture as in the previous section, gave approximately 0.01 g (8% yield) of a brownish-purple product, 33.

IR(CH2Cl2): 2023(s), 1981(s), 1951(w), 1818(s), 1781(w)

c. Reaction of 2 with Na[Co(CO)4] at 25°C and 45°C A Na[Co(CO)4] solution was prepared by stirring CO2(CO)8 (0.085 g, 0.24 mmol) in THF (30 mL) with 5 mL of 1% w/w
Na(Hg) until the solution was a very light yellow. Filtering the Na[Co(CO)₄] solution through Celite into a flask containing 2 (0.27 g, 0.50 mmol), gave a purple-brown reaction mixture. Stirring overnight at 25°C gave residual 2 and approximately equal amount (by IR spectral analysis) of 33 and 1. The solvent was removed under vacuum and the resulting residue extracted first with hexane to remove most of 1, and then with benzene. The concentrated benzene extract was chromatographed on a 2.0 x 16 cm silica gel column (230-400 mesh). Elution with benzene gave a dark colored fraction containing a number of products, the majority of which was 1. The second fraction, after crystallization from CH₂Cl₂ (2 mL)/hexane (12 mL) at -20°C, gave approximately 0.01 g (4% yield) of 33.

IR(CH₂Cl₂): 2022(s), 1981(s), 1953(w), 1820(s), 1780(w)

¹H(CDCl₃): 4.85 and 4.44(Cp, 10H), 2.79(Me, 3H)

Repeating this reaction, but stirring the THF reaction mixture for 21 hours at 45°C, again gave residual 2 and the products 33 and 1. Work-up of the reaction as described above gave 0.026 g (11% yield) of 33.

d. Reaction of 3 with Na[Co(CO)₄] Following the procedure in Section II.E.3.a, the reaction between 3 (0.30
g, 0.50 mmol) and Na[Co(CO)₄] [Co₂(CO)₈: 0.12 g, 0.35 mmol; NaOH: 1.2 g, 30 mmol] required 12 hours of photolysis at 12°C. After evaporating the solution to dryness, the residue was dissolved in a minimum of benzene and chromatographed on a 2.0 x 16 cm silica gel (230-500 mesh) column. Elution with benzene removed 1 and other side products. The product, Cp₂Fe₂Co(CO)₃(μ-CH₂Ph)₂, 34, eluted as a brown band with 1:1 CH₂Cl₂/benzene. Evaporation and crystallization from CH₂Cl₂ (4 mL)/hexane (20 mL) at -20°C gave 0.8 g (28% yield) of brownish-purple crystals. The crystalline product, 34, had a dp of 65°C and was stable for less than one month under nitrogen at room temperature.

Anal Calcd for C₂₃H₁₇O₅SCoFe₂: C: 47.96, H: 2.97
Found:  C: 47.59, H: 3.37
IR(CH₂Cl₂): 2024(s), 1982(s), 1950(w), 1820(s), 1752(w)
¹H(CDCl₃): 7.54(m, Ph, 5H), 4.92 and 4.50(Cp, 12H*);
* CH₂ resonances lies under Cp resonances

e. Reaction of 4 with Na[Co(CO)₄] A THF solution of Na[Co(CO)₄] (0.12 mmol) was prepared as in Section II.E.3.a and filtered into a THF solution of 4 (0.050 g, 0.090 mmol). Stirring for 45 minutes gave a light green
solution with carbonyl bands in the IR spectrum at 2000(s), 1970(sh) and 1808(s) cm$^{-1}$, indicative of 1. There was no IR spectral evidence for Cp$_2$Fe$_2$Co(CO)$_3$(μ-CO)$_2$(μ-CSCH$_2$CH=CH$_2$).

f. Reaction of 2 with Na[Mn(CO)$_5$]  Filtering 15 mL of a light yellow solution (THF) of Na[Mn(CO)$_5$] (0.50 mmol) through Celite into a flask containing 2 (0.27 g, 0.50 mmol), gave a deep emerald green solution. The IR spectrum of this mixture showed carbonyl bands for Mn$_2$(CO)$_{10}$ and other product bands at 1805 and 1770 cm$^{-1}$. After 5 minutes the reaction mixture turned brown and the IR spectrum exhibited carbonyl bands for Mn$_2$(CO)$_{10}$ and a band at 1805 cm$^{-1}$. The reaction mixture residue, after evaporation of the solvent, was dissolved in benzene and chromatographed on a 1.5 x 30 cm column of silica gel (230-400 mesh). Elution with benzene gave a yellow fraction containing Mn$_2$(CO)$_{10}$ as the dominant product. A second greenish-brown fraction was Cp$_2$Fe$_2$(CO)$_3$CS, 1.

The same products were obtained from the slow reaction (21 hours) of PPN[Mn(CO)$_5$] (0.37 g, 0.50 mmol) and 2 (0.27 g, 0.50 mmol) in THF (20 mL) at 25°C. Repeating the PPN-[Mn(CO)$_5$] reaction under photolytic conditions (254 nm, 0-10°C, 20 hours) gave Mn$_2$(CO)$_{10}$ and 1.
g. Reaction of 2 with Na[Re(CO)\(_5\)] Filtering 20 mL of a THF solution of Na[Re(CO)\(_5\)] (0.47 mmol) through Celite into a flask containing 10 mL of THF and 2 (0.25 g, 0.47 mmol) at -70°C, gave a green reaction mixture which turned brown on warming to 10°C. The solvent was removed in vacuo and the residue chromatographed on a 2.0 x 20 cm column of silica gel (230-400 mesh). Elution with hexane gave a yellow fraction which, when concentrated and cooled to -20°C, gave orange crystals. Spectroscopic analysis indicated a mixture of Re\(_2\)(CO)\(_{10}\) (M\(^+\) = 652) and CpFe(CO)\(_2\)Re(CO)\(_5\) (M\(^+\) = 503).\(^{93,94}\) Separation of these products was not possible by column chromatography, differential crystallization or sublimation.

IR(hexane): 2110(s), 2075(m), 2020(w), 1998(s), 1976(s), 1965(w), 1933(w)

\(^1\)H(CD\(_2\)Cl\(_2\)): 4.82(Cp)

\(^{13}\)C(CD\(_2\)Cl\(_2\)): 191.1(CO), 82.5(Cp)

MS: 652(M\(^+\), Re\(_2\)(CO)\(_{10}\)), 504(M\(^+\), CpFe(CO)\(_2\)Re(CO)\(_5\))

A second fraction obtained from the chromatographic separation had carbonyl bands characteristic of 1.

h. Reaction of 2 with PPN[HFe(CO)\(_4\)] An CH\(_3\)CN solution (10 mL) of PPN[HFe(CO)\(_4\)] (0.38 g, 0.54 mmol) and 2 (0.25 g, 0.48 mmol) was stirred at room temperature for five hours. The reddish-purple reaction mixture was taken
to dryness, the resulting residue extracted with benzene
and the extract filtered through silica gel, yielding a
reddish-brown filtrate which was then concentrated and
chromatographed on silica gel (230-400 mesh; 2.0 x 18 cm
column). Elution with CH$_2$Cl$_2$ gave two red fractions which
were crystallized from CH$_2$Cl$_2$ (2 mL)/hexane (10 mL) at -
20$^\circ$C. The first fraction gave (ca. 0.010 g) dark red
crystals which were not identified.

IR(CH$_2$Cl$_2$): 2050(s), 1996(vs), 1961(s), 1935(vs),
1925(sh), 1804(m)

$^1$H(CH$_3$CN): 10.47(methine), 5.00(Cp), 2.96(Me),
no H$^-$ to -15 ppm

The second fraction gave red needles (ca. 0.020 g) of 15.

IR(CH$_2$Cl$_2$): 1983(s), 1946(m), 1780(s)

$^1$H(CH$_3$CN): 11.60(methine), 4.82(Cp), 2.78(MeS)

i. **Reaction of 2 with Na[CpFe(CO)$_2$]** A THF solu-
tion (20 mL) of Na[CpFe(CO)$_2$] (0.50 mmol) was filtered
through Celite into an CH$_3$CN (5 mL) solution of 2 (0.27 g,
0.50 mmol). The reaction mixture immediately turned em-
erald green in color, then faded to brown after 2-3
minutes. The solution was evaporated in vacuo, and the
residue extracted with benzene. The extract contained a
dark brown product identified as Cp$_2$Fe$_2$(CO)$_4$ from its IR$^{95}$
and $^1$H NMR spectra.$^{96}$
IR(CH₂Cl₂): 2000(s), 1956(m), 1778(m)
H(CD₃CN): 4.75(Cp)

The residue left from the benzene extraction was residual 2 and an unidentified brown complex having carbonyl bands at 1998(s) and 1815(s) cm⁻¹.

j. Reaction of 2 with Na[CpMo(CO)₃]  A light yellow THF (20 mL) solution of Na[CpMo(CO)₃] (0.48 mmol) was filtered through Celite into a flask containing 2 (0.25 g, 0.47 mmol), giving a brown solution. After three hours the solvent was removed in vacuo; the residue was loaded on a silica gel column (230-400 mesh, 2.0 x 18 cm) and eluted with hexane giving a yellow fraction identified by its IR spectrum as CpMo(CO)₃CH₃. ⁹⁷

IR(CH₂Cl₂): 2030(w), 1930(s)

This was followed by a red fraction which was identified as Cp₂Mo₂(CO)₆. ⁹⁸

IR(CH₂Cl₂): 2020(w), 1960(s), 1917(s)

A green band eluted with 50:50, benzene:hexane. This compound proved to be Cp₂Fe₂(CO)₃CS, 1. This reaction, when performed under photolytic conditions (254 nm, 2 hours), gave the same products.

k. Reaction of 8 with Na[Co(CO)₄]  A THF solution of Na[Co(CO)₄] (0.38 mmol), prepared as in Section II.E.3.a, was filtered through Celite into a photolysis
tube containing 8 (0.19 g, 0.32 mmol). Photolysis for 10 hours gave products having carbonyl bands in the IR spectrum for 33 and Cp₂Fe₂Co(PEt₃)(CO)₂(μ-CO)₂(μ-CSMe), 35: 1976(s), 1930(w), 1810(s), 1773(w). The residue, after solvent evaporation, was dissolved in a minimum of benzene and loaded onto a 2.0 x 18 cm column of silica gel (230-400 mesh). Elution with 10% CH₂Cl₂ in benzene removed several minor, unidentified fractions. The major fraction, which eluted with 50:50, CH₂Cl₂:benezene, was 33. Product 35 was not obtained, apparently, due to decomposition on the column.

IR(CH₂Cl₂): 2025(s), 1982(s), 1954(w), 1820(s), 1780(w)

¹H(CDCl₃): 4.82 and 4.45(Cp), 2.78(Me)

1. Reaction of 2 with other metal carbonyl anions
No reaction between 2 and Cr(CO)₅I⁻, W(CO)₄(CS)I⁻ and Fe(CO)₃NO⁻ occurred in CH₃CN under thermal conditions (25°C). Under photolytic conditions 2 (in CH₃CN) also failed to react with Fe(CO)₃NO⁻. No reaction was observed between Cp₂Fe₂(I)(CO)(μ-CO)(μ-CSMe), 10, and CpMo(CO)₃⁻ at 25°C in THF. Refluxing this reaction mixture gave Cp₂Mo₂(CO)₂ and CpMo(CO)₂CH₃. No reaction occurred between 10 and Fe(CO)₄ in THF at 25°C.
4. Reactivity of u-carbene complexes and of \( \text{Cp}_2\text{Fe}_2\text{Co-(CO)}_3(\mu-\text{CO})_2(\mu-\text{CSMe}) \)

a. **Reaction of 11 with HBF\(_4\)-Et\(_2\)O**

Addition of excess HBF\(_4\)-Et\(_2\)O (0.025 mL, 0.19 mmol) to a CH\(_2\)Cl\(_2\) (5 mL) solution of 11 (0.020 g, 0.046 mmol), gave an immediate color change from purple to red and evolution of a mercaptan odor (MeSH). The solvent was removed and the residue dried under vacuum. Spectroscopic analysis of the residue showed it to be the BF\(_4^-\) salt of 2.

IR(\(\text{CH}_3\text{CN}\)): 2044(s), 2015(sh), 1852(m)

\(^1\text{H}(\text{d}^6\text{-acetone})\): 5.72 and 5.63(Cp), 3.80(Me)

b. **Reaction of 11 with oxidants**

The reactions of 11 with the oxidants I\(_2\), [C\(_7\)H\(_7\)]BF\(_4\), [(Ph)\(_3\)C]BF\(_4\), NOPF\(_6\), and [Cp\(_2\)Fe]FeCl\(_4\), were all conducted in a similar manner. For example, addition of an excess of I\(_2\) (ca. 0.01 g, 0.04 mmol) to an CH\(_3\)CN (2 mL) solution of 11 (ca. 0.010 g, 0.023 mmol), gave an immediate reaction to form a red solution and evolution of an odor indicative of CH\(_3\)SSCH\(_3\). IR analysis showed a clean conversion to the iodide salt of 2.

IR(\(\text{CH}_3\text{CN}\)): 2048(s), 2018(sh), 1854(m)

The oxidants, (C\(_7\)H\(_7\))BF\(_4\), [(Ph)\(_3\)C]BF\(_4\) and [Cp\(_2\)Fe]FeCl\(_4\), gave results similar to the I\(_2\) case. Complete oxidation to products containing no CO bands occurred with NOPF\(_6\).
c. Reaction of 12 with oxidants  A CH₂Cl₂ (3 mL) solution of 12 (0.020 g, 0.04 mmol) was stirred with I₂ (0.005 g, 0.02 mmol) for 5 minutes. The solvent was removed and the residue dried under vacuum for 5 hours. The ¹H NMR spectrum of the residue indicated that the thiocarbyne formed was 2. The aromatic multiplet at 7.1 to 7.6 ppm could be attributed to the compound PhSSPh. IR(CH₃CN): 2045(s), 2015(sh), 1853(m) ¹H(d⁶-acetone): 7.1-7.6(m, PhSSPh), 5.75 and 5.67(Cp), 3.83(SMe)

The oxidants, [Ph₃C]BF₄ and [C₇H₇]BF₄, reacted in a similar fashion to give the BF₄⁻ salt of 2.

d. Reaction of 12 with HBF₄  A CH₂Cl₂ (5 mL) solution of 12 (0.020 g, 0.040 mmol) was stirred at 0°C with HBF₄-Et₂O (0.006 mL, 0.04 mmol) for 5 minutes. The red solution gave off an odor characteristic of MeSH. The solvent was removed, and the residue was washed with hexane, benzene and ether, then dried for 2 hours. A ¹H NMR spectrum of the residue (in d⁶-acetone) shows that both [Cp₂Fe₂(CO)₂(μ-CO)(μ-CSPh)]BF₄, 36, and the BF₄⁻ salt of 2 were produced in approximately a 7:1 ratio, respectively. This same reaction performed in CH₃CN solvent produced approximately a 1:1 mixture of these products. The residue, after dissolving in acetone (0.5 mL) and layering with Et₂O (3 mL), was crystallized at 25°C for 10 hours, then at
-20°C overnight, giving (ca. 0.010 g) red-brown crystals of 36.

IR(CH$_3$CN): 2049(s), 2017(sh), 1856(m)

$^1$H(d$_6$-acetone): 7.80(m, Ph, 5H), 5.72 and 5.14 (Cp, 10H)

e. Reaction of 36 with NaBH$_4$

Addition of NaBH$_4$ (ca. 0.005 g, 0.1 mmol) to 36 (0.003 g, 0.005 mmol) in CH$_3$CN (2 mL) gave a red solution. The red color and IR spectrum were similar to those of compounds 15 and 16; the product was identified as Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-C(H)(SPh)], 37.

IR(CH$_3$CN): 1978(s), 1942(w), 1784(m)

f. Preparation of Cp$_2$Fe$_2$(SPh)(CO)(μ-CO)(μ-CSMe), 38,

by refluxing 12 in CH$_2$Cl$_2$

A CH$_2$Cl$_2$ (20 mL) solution of 12 (0.080 g, 0.16 mmol) was refluxed for 5 hours giving a brown solution. The residue, after solvent evaporation, was extracted with benzene; the extract was filtered through anhydrous MgSO$_4$ and evaporated. Crystallization of the brown-black residue from CH$_2$Cl$_2$ (3 mL)/hexane (20 mL) at -20°C gave 0.040 g (54%) of brownish-black crystals of 38, which have a dp of 95°C.

Anal Calcd for C$_{20}$H$_{18}$O$_2$S$_2$Fe$_2$: C: 51.53, H: 3.89, S: 13.76

Found: C: 51.12 H: 4.08 S: 13.87
IR(\text{CH}_2\text{Cl}_2): 1988(s), 1807(s)

$^1\text{H}(\text{CDCl}_3): 6.9-7.6(\text{m, Ph, } 5\text{H}), 4.84 \text{ and } 4.80$

(Cp, 10H), 3.39(Me, 3H)

g. **Photolysis of 12 in THF**  
A THF (30 mL) solution of 12 (0.12 g, 0.24 mmol) was photolyzed at 254 nm for 2 hours. The solvent was removed in vacuo and the residue extracted with benzene; the benzene extract was filtered through Celite, and the solvent was evaporated. Crystallization of the residue from CH$_2$Cl$_2$ (4 mL)/hexane (20 mL) at -20°C gave 0.023 g (20%) of 38.

IR(\text{CH}_2\text{Cl}_2): 1988(s), 1806(s)

h. **Reaction of 12 with PEt$_3$**  
Refluxing 12 (0.050 g, 0.10 mmol) in CH$_2$Cl$_2$ (20 mL) with PEt$_3$ (0.03 mL, 0.3 mmol) for 1 hour resulted in a greenish-brown solution having carbonyl IR spectral bands at 1990(s) and 1815(s) cm$^{-1}$. The residue, obtained after solvent evaporation, was washed with hexane and dried. A sample of the residue taken for $^1\text{H}$ NMR (CDCl$_3$) showed that the residue contained mostly (80%) 8, and some 38. The residue was washed with a 50:50 mixture of benzene:CH$_2$Cl$_2$ and dried, giving a green residue of 8.

IR(\text{CH}_2\text{Cl}_2): 1984(s), 1815(s)

i. **Reaction of 16 with oxidants and HBF$_4$**  
Stirring a CH$_2$Cl$_2$ (3 mL) solution of 16 (ca. 0.010 g, 0.020 mmol)
with excess (ca. 0.04 mmol) I₂, [Ph₃C]BF₄ or HBF₄-Et₂O gave an immediate reaction yielding unstable and non-identifiable products. Reaction of 16 (ca. 0.010 g, 0.020 mmol) in CH₂Cl₂ (3 mL) with excess HBF₄-Et₂O (ca. 0.04 mmol) in the presence of PPh₃ (ca. 0.010 g, 0.040 mmol) gave a red solution of [Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)PPh₃)]BF₄, 39, which was identified from its IR spectrum.²⁷

IR(CH₂Cl₂): 1995(s), 1960(sh), 1817(m)

j. Reaction of 33 with PPh₃  A solution of 33 (0.25 g, 0.50 mmol) and PPh₃ (0.92 g, 3.5 mmol) in CH₂Cl₂ (10 mL) was stirred for 9 hours, filtered through anhydrous MgSO₄ and concentrated under vacuum to 5 mL. Layering with hexane (25 mL) and allowing the solution to stand at room temperature for 24 hours, gave 0.34 g (93% yield) of black, rhombohedral crystals of Cp₂Fe₂Co(PPh₃)(CO)₂(μ-CO)₂(μ₃-C₃H₅-CSMe), 40. Crystalline 40 has a dp of 108°C and is stable indefinitely under nitrogen at -20°C. A solution of 40 in CH₂Cl₂ decomposed over 20 hours giving a mixture of 33 and 40.

Anal Calcd for C₃₄H₂₈O₄PSCoFe₂: C: 55.61, H: 3.84
S: 4.37

Found: C: 55.85, H: 3.86 S: 4.60

IR(CH₂Cl₂): 1980(s), 1930(w), 1798(s), 1760(w)

¹H(CDCl₃): 7.56(m, Ph), 4.87 and 3.97(Cp),
2.80(Me)

$^{13}$C(CD$_2$Cl$_2$)*: 317.7(d, $\mu_3$-C, $J_{PC} = 15.9$ Hz),
262.2(\mu-CO), 253.7(b, \mu-CO),
212.4(CO), 205.8(b, CO), 127-
138(Ph), 85.8, 85.3(Cp),
35.8(Me)

* The $^{13}$C NMR spectrum was taken in the presence
of 7 equivalents of PPh$_3$ to retard decomposi-
tion of 40.

k. Reaction of 33 with PEt$_3$

Using the procedure
in "j" above, 33 (0.20 g, 0.40 mmol) and PEt$_3$ (0.070 mL,
0.47 mmol) were stirred for 1.5 hours. Crystallization
from CH$_2$Cl$_2$ (3 mL)/hexane (20 mL), at -20°C, gave 0.16 g
(68% yield) of grayish-black crystals of Cp$_2$Fe$_2$Co(PEt$_3$)-
(CO)$_2$(\mu-CO)$_2$(\mu$_3$-CSMe)$_2$, 35. Crystalline 35 has a dp of 95°C
and is stable indefinitely under nitrogen at -20°C. Solu-
tions of 35 in CH$_2$Cl$_2$ did not decompose after several
hours.

Anal Calcd for C$_{22}$H$_{28}$O$_4$PSCoFe$_2$:  C: 44.78,
H: 4.78, S: 5.43

Found:  C: 44.77, H: 4.80, S: 5.71

IR(CD$_2$Cl$_2$):  1976(s), 1926(w), 1796(s), 1760(w)

$^1$H(CDC$_3$):  4.85 and 4.38(Cp), 2.77(Me), 1.68
  (b, PCH$_2$), 1.11(b, PCCH$_3$)
1. **Reaction of 33 with PCy$_3$**

Using the procedure for the synthesis of 40, 33 (0.20, 0.40 mmol) and PCy$_3$(0.78 g, 2.8 mmol), were stirred for 12 hours; crystallization at -20°C gave 0.16 g (54% yield) of small black crystals of Cp$_2$Fe$_2$Co(PCy$_3$)(CO)$_2$(μ-CO)$_2$(μ$_3$-CSMe), 41. Crystalline 41 has a dp of 95°C and is stable under nitrogen at -20°C for at least 6 months. In solution, 41 decomposed to a mixture of 33 and 41 within one hour.

IR(CH$_2$Cl$_2$): 1977(s), 1928(w), 1793(s), 1753(w)

$^1$H(CDC$_3$)*: 4.92 and 4.50(Cp), 2.83(Me), 1.26(b, Cy)

*The $^1$H NMR spectrum was taken in the presence of 7 equivalents of PCy$_3$ to retard the decomposition of 41.

m. **Reaction of 33 with PHPh$_2$**

As in procedure "1" above, stirring 33 (0.20 g, 0.40 mmol) and PHPh$_2$(0.30 mL, 1.7 mmol) for 5 hours gave, after workup and crystallization, 0.17 g (63% yield) of black crystals of Cp$_2$Fe$_2$Co(PHPh$_2$)(CO)$_2$(μ-CO)$_2$(μ$_3$-CSMe), 42, having a dp of 90°C.

Anal calcd for C$_{28}$H$_{24}$O$_4$PSCoFe$_2$: C: 51.10, H: 3.68, S: 4.87

Found: C: 50.12, H: 3.69, S: 5.16

IR(CH$_2$Cl$_2$): 1982(s), 1937(w), 1803(s), 1762(w)

$^1$H(CDC$_3$): 7.41(m, Ph)*, 4.86 and 4.24(Cp),
2.78(Me)

*Resonance for Ph is believed to be in this multiplet.

n. Reaction of 33 with PMePh₂

As in the procedure for the synthesis of 40, 33 (0.05 g, 0.1 mmol) and PMePh₂ (0.14 g, 0.70 mmol) gave black crystals of Cp₂Fe₂Co(PMe-Ph₂)(CO)₂(μ-CO)₂(μ₃-CSMe), 43.

IR(CH₂Cl₂): 1979(s), 1928(w), 1796(s), 1755(w)

¹H(CDCl₃): 7.35(Ph), 4.79 and 3.98(Cp), 2.87(SMe), 1.97(d, PMe, J₉H = 6.5 Hz)

o. Reaction of 33 with Ph₂PCH₂PPh₂, dppm

A solution of 33 (0.20 g, 0.40 mmol) and Ph₂PCH₂PPh₂ (0.31 g, 0.81 mmol) in CH₂Cl₂ (15 mL) was stirred for 45 hours. The brown-black residue, obtained after solvent evaporation, was extracted three times with hexane to remove dppm, redissolved in CH₂Cl₂, filtered through anhydrous MgSO₄ and concentrated to 4 mL. Layering with hexane (25 mL) and cooling to -20°C gave a crystalline product contaminated with free dppm. Crushing the product, extracting three times with hexane and recrystallizing from CH₂Cl₂ (4 mL)/hexane (25 mL) at -20°C gave 0.19 g (57% yield) of black crystals of Cp₂Fe₂Co-(dppm)(CO)(μ-CO)(μ₃-CSMe), 44. This product contained no free dppm and has a dpₐ of 90°C.

Anal calcd for C₄₆H₃₅O₃P₂CoFe₂: C: 58.00,
Found:  C: 57.53, H: 4.29, S: 4.32
IR(CH₂Cl₂):  1937(s), 1760(s), 1720(w)

¹H(CDC₁₃):  7.13(m, Ph), 4.38 and 4.39(Cp),
2.85(Me), 1.76(b, CH₂)

³¹P[H](CD₂Cl₂):  72.95(d, P-Fe, Jₚₚ = 81.4 Hz),
46.45(m, br, P-Co)

p. Reaction of 33 with Ph₂PCH₂CH₂PPh₂ Stirring 33
(0.010 g, 0.020 mmol) in CH₂Cl₂ (10 mL) with a 10 fold
excess of Ph₂PCH₂CH₂PPh₂ (dppe) gave, after 1.5 hours, a
product with IR spectral bands at 1980(s), 1930(w), 1795(s)
and 1755(w) cm⁻¹. Continued stirring for 24 hours showed
no further change in the IR spectrum. This IR spectrum is
similar to other monodentate phosphine derivatives of 33,
which tentatively identifies this product as Cp₂Fe₂Co(η'-
dppe)(CO)₂(μ-CO)(μ₃-CSMe), 45; the compound was not iso-
lated.

q. Reaction of 33 with P(OPh)₃ A CH₂Cl₂ (10 mL)
solution of 33 (0.020 g, 0.040 mmol) was stirred with a tenold excess of P(OPh)₃ for 2 hours to give a solution of a
product tentatively identified as Cp₂Fe₂Co[P(OPh)₃](CO)₂-
(μ-CO)₂(μ₃-SMe), 46. Attempted isolation of the compound
resulted in its decomposition.

IR(CH₂Cl₂):  1987(s), 1947(w), 1810(s), 1780(sh)
r. Reaction of \( 33 \) with \( \text{P(OMe)}_3 \)  As in the procedure for the preparation of \( 46 \), stirring \( 33 \) (0.020 g, 0.040 mmol) and a ten fold excess of \( \text{P(OMe)}_3 \) gave a solution of \( \text{Cp}_2\text{Fe}_2\text{Co[P(OMe)}_3\text{]}(\text{CO})_2(\mu-\text{CO})_2(\mu_3-\text{CSMe}) \), \( 47 \). The compound was not isolated.

\[ \text{IR(}\text{CH}_2\text{Cl}_2\text{)}: \quad 1981(\text{s}), \quad 1937(\text{w}), \quad 1805(\text{s}), \quad 1770(\text{w}) \]

s. Reaction of PPNCN with \( 33 \) Stirring PPNCN (0.45 g, 2.0 mmol) and \( 33 \) (0.20 g, 0.40 mmol) in \( \text{CH}_2\text{Cl}_2 \) (10 mL) for 2 hours gave a brownish-black solution of a product tentatively identified as \( [\text{Cp}_2\text{Fe}_2\text{Co(CN)}(\text{CO})_2(\mu-\text{CO})_2(\mu_3-\text{CSMe})]^- \), \( 48 \).

\[ \text{IR(}\text{CH}_2\text{Cl}_2\text{)}: \quad 2082(\text{w}, \text{CN}), \quad 1967(\text{s}), \quad 1916(\text{m}), \quad 1786(\text{s}), \quad 1745(\text{w}) \]

The reaction mixture was filtered through anhydrous \( \text{MgSO}_4 \) and the solvent evaporated. Attempted crystallization of the product in the presence of PPNCN precipitated both \( 48 \) and PPNCN. Attempted isolation of \( 48 \) from PPNCN decomposed the product.

t. Reaction of \( \text{t-BuNC} \) with \( 33 \) A \( \text{CH}_2\text{Cl}_2 \) (20 mL) solution of \( 33 \) (0.20 g, 0.40 mmol) and \( \text{t-BuNC} \) (0.04 mL, 0.40 mmol) were stirred for 1 hour giving a partial conversion (60%) to a brownish-black solution tentatively identified as \( \text{Cp}_2\text{Fe}_2\text{Co(t-BuNC)(CO)}_2(\mu-\text{CO})_2(\mu_3-\text{CSMe}) \), \( 49 \).

\[ \text{IR(}\text{CH}_2\text{Cl}_2\text{)}: \quad 2130(\text{s}, \text{CN}), \quad 1982(\text{s}), \quad 1939(\text{m}), \]
Addition of excess t-BuNC (2.0 mmol) gave a product tentatively identified as Cp$_2$Fe$_2$Co(t-BuNC)$_2$(CO)(μ-CO)$_2$(μ$_3$-CSMe),

IR(CH$_2$Cl$_2$): 2120(s, CN), 1930(s), 1780(s), 1740(w)

The reaction mixture was filtered through anhydrous MgSO$_4$, concentrated to 5 mL and layered with hexane (20 mL). Crystallization at -20°C resulted in product decomposition.

u. Reaction of 33 with other nucleophiles In qualitative experiments, the reaction of 33 in CH$_2$Cl$_2$ with NEt$_3$, NHEt$_2$, NH$_2$Bu, pyridine, 4-dimethylaminopyridine, SbPh$_3$, AsPh$_3$, CO, H$_2$, Me$_2$S, SPh$_3$, ONMe$_3$, PhS$^-$, I$^-$, N$_3^-$, NO$_2^-$, MeI, PhC=CPH, PhC=CH, cyclohexene, fumaronitrile and CS$_2$ gave no reaction after 1 hour at room temperature.

5. Synthesis and reactivity of the bridging thiocarbyne radical, Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CSMe), 51

a. Preparation of 51 by bulk electrolysis A typical procedure used the apparatus shown in Figure 5, the PAR 173 potentiostat/galvanostat and the PAR 178 high impedance voltage follower. Electrolyte solution (0.1 M NBu$_4$PF$_6$/CH$_3$CN) was added to each compartment (30 mL to the sample compartment, 10 mL to the auxiliary compartment and to the
electrolyte bridge, and the middle compartment was filled completely) and deoxygenated. After cooling to 0°C, the electrolyte solution was electrolized at -0.8 V versus the Ag/AgCl reference electrode until the background current was approximately 0.2 mA. After turning the voltage off, 2 (0.053 g, 0.10 mmol) was added to the sample compartment, dissolved, deoxygenated and electrolized at -0.8 V. Electrolysis for ca. 15 minutes (> 90% conversion to radical) gave a brilliant emerald green solution characteristic of the radical, 51.

\[
\text{IR(CH}_3\text{CN/0.1 M NBu}_4\text{PF}_6): 1973(s), 1933(m), 1760(m)
\]

Solutions of 51 were air sensitive and thermally unstable. Maintained at 0°C, solutions of the radical slowly turned brown over a 1 hour period; at -80°C the frozen radical solution turns completely brown after about 24 hours.

Coulombic runs were performed using the same apparatus as the bulk electrolysis experiments, except that the PAR 179 digital coulometer was interfaced with the PAR 173 potentiostat/galvanostat. The procedure was the same as the bulk electrolysis experiments above, except that electrolysis was continued until a constant residual current was achieved. The number of coulombs used was read directly from the PAR 179 digital coulometer. Coulometric values
were corrected through the use of a blank consisting of only the electrolyte solution run under the same conditions as the samples of 2. These results are summarized in Table 9 given in Section C of the RESULTS AND DISCUSSION.

b. Preparation of 51 from sodium naphthalide (NaNP)
A THF solution of NaNP (0.19 mmol/ml) was titrated into a THF (10 mL) suspension of 2 (0.25 g, 0.47 mmol) at 0°C. Since 2 is insoluble in THF, this addition was made slowly to prevent further reduction of 51. Addition of NaNP was terminated when little or none of the fine red precipitate of 2 could be observed. The emerald green radical in THF at -80°C slowly turned brown over a 10 hour period.

\[ \text{IR(THF): 1978(s), 1944(m), 1772(m)} \]

c. Reaction of 51 with Co\(_2\)(CO)\(_8\)
Addition of Co\(_2\)(CO)\(_8\) (0.015 g, 0.044 mmol) to the electrogenerated radical (0.087 mmol) at 0°C, gave an immediate reaction forming Co(CO)\(_4\)^- (\(\nu_{CO}=1890 \text{ cm}^{-1}\))\(^{79}\) and 2. Stirring the solution for 2 hours gave no further reaction between Co(CO)\(_4\)^- and 2 to form 33.

d. Reaction of 51 with Mn\(_2\)(CO)\(_{10}\)
Addition of Mn\(_2\)(CO)\(_{10}\) (0.017 g, 0.043 mmol) to the electrogenerated radical (0.087 mmol) at 0°C gave, within 10 minutes, a brown solution. IR spectral analysis shows carbonyl bands for Mn\(_2\)(CO)\(_{10}\) (\(\nu_{CO}=2045(\text{m}), 2015(\text{s}), 1980(\text{w}) \text{ cm}^{-1}\))\(^{92}\) and
Mn(CO)\textsubscript{5}\textsuperscript{-} (\nu CO = 1905, 1865 cm\textsuperscript{-1}).\textsuperscript{81} Stirring the reaction for 30 minutes gave no further reaction. Bubbling air through the reaction mixture gave products that exhibit an IR spectrum of Mn\textsubscript{2}(CO)\textsubscript{10} and a small amount of 2.

e. Reaction of 51 with Re\textsubscript{2}(CO)\textsubscript{10} Addition of Re\textsubscript{2}(CO)\textsubscript{10} (0.029 g, 0.045 mmol) to the electrogenerated radical (0.091 mmol) solution at 0\degree C showed no immediate reaction. A slow fading of the green radical solution occurred over 45 minutes to give a brown solution. IR spectral analysis shows carbonyl bands for Re\textsubscript{2}(CO)\textsubscript{10} (\nu CO = 2060(m), 2000(s), 1960(m) cm\textsuperscript{-1}); bands for the carbyne cation are absent. The solvent was evaporated in vacuo and the resulting residue extracted with hexane to remove Re\textsubscript{2}-(CO)\textsubscript{10}. The remaining residue (in CH\textsubscript{3}CN) shows a spectrum typical of decomposed 51.

IR(CH\textsubscript{3}CN): 2020-1970(b), 1930(sh), 1800-1765(b)

f. Reaction of 51 with PhCH\textsubscript{2}Br Addition of benzyl bromide (0.012 mL, 0.096 mmol) to the electrogenerated radical (0.096 mmol) solution at 0\degree C gave, in 10 minutes, a reddish-brown solution. IR spectral analysis shows carbonyl bands for 2 and 24 (1977(s), 1940(m), 1790(m) cm\textsuperscript{-1}). Evaporation of the solvent and extraction of the residue with 20 mL of a 50:50 mixture of hexane:CH\textsubscript{2}Cl\textsubscript{2}, gave two solution phases. The top layer was collected, filtered,
evaporated to dryness and redissolved in CH$_3$CN (5 mL) to give a brown solution of 24. This product was not pure and contained a significant amount of electrolyte.

**IR(CH$_3$CN)**: 1975(s), 1945(m), 1788(m)

g. **Reaction of 51 with Mn(CO)$_5$Br**: Addition of electrogenerated radical (0.022 mmol) to Mn(CO)$_5$Br (0.003 g, 0.01 mmol) gave an immediate reaction to form a reddish-orange solution. IR spectral analysis shows carbonyl bands for residual Mn(CO)$_5$Br$^{100}$ and Mn(CO)$_5$-. No further reaction occurred after 0.5 hour of stirring. Bubbling air through the reaction mixture gave a solution containing Mn$_2$(CO)$_{10}$, 2, and residual Mn(CO)$_5$Br.

h. **Reaction of 51 with [Cp$_2$Fe][FeCl$_4$]**: Addition of electrogenerated radical (0.009 mmol) to [Cp$_2$Fe][FeCl$_4$] (0.003 g, 0.009 mmol) gave an immediate reaction, forming a reddish-orange solution. IR spectral analysis indicated a clean reaction had occurred yielding 2. The co-product of the reaction was presumed to be ferrocene.

i. **Reaction of 51 with PhSSPh**: Addition of PhSSPh (0.051 g, 0.24 mmol) to the chemically generated radical (0.47 mmol) at 0°C gave an immediate reaction forming a purple-brown reaction mixture. The solvent was removed under vacuum, and the resulting residue extracted with hexane to remove naphthalene and some of the co-product,
12. The remaining residue was extracted with CH$_2$Cl$_2$, filtered through Celite, concentrated to 4 mL and layered with hexane (20 mL). Crystallization at -20$^\circ$C gave 0.080 g (35% yield) of brownish-black crystals of Cp$_2$Fe$_2$(SPh)(CO)(\mu-CO)(\mu-CSMe), 38. Under the same conditions 51 failed to react with CH$_3$SSCH$_3$ and PhCH$_2$SSCH$_2$Ph.

IR(CH$_2$Cl$_2$): 1988(s), 1809(s)

$^1$H(CDC$_3$): 7.26(m, Ph), 4.84 and 4.80(Cp), 3.39(Me)

j. Reaction of 51 with PhSeSePh

Diphenyldiselenide, PhSeSePh, (0.035 g, 0.11 mmol) was added to the chemically generated radical (0.19 mmol) at -80$^\circ$C. Warming the solution to approximately -20$^\circ$C and recooling to -80$^\circ$C, gave a purple solution. The IR spectrum of this solution was similar to other \mu-carbene complexes (11, 12, 15, 16) prepared in this study and tentatively identifies the product as Cp$_2$Fe$_2$(CO)$_2$(\mu-CO)(\mu-C(SMe)SePh), 23.

IR(THF): 1982(s), 1952(m), 1790(s)

The purple solution turned brown after warming to room temperature. IR spectral analysis of the solution at this point shows, predominantly, the formation of 22.

IR(THF): 1980(s), 1950(w), 1804(s), 1790(sh)

The residue remaining after solvent removal, was washed with hexane, redissolved in CH$_2$Cl$_2$ (20 mL) and filtered through
Celite. Concentrating to 4 mL, layering with hexane (20 mL) and storing overnight at -20°C gave 0.030 g (31% yield) of 22.

IR(CH₃CN): 1978(s), 1800(s)

k. Reaction of 51 with organic peroxides

Addition of (t-BuO)₂ (ca. 0.015 g, 0.10 mmol) to the chemically generated radical (0.057 mmol) immediately gave 2 and, presumably, t-BuO⁻. A similar reaction occurred with [PhC(O)O]₂.

1. Electron-transfer-catalyzed substitution reactions of 2

Carbon monoxide substitution reactions of [Cp₂Fe₂-(CO)₂(µ-CO)(µ-CSMe)]⁺, 2, by PEt₃, PMePh₂, PMe₂Ph, PPh₃ and t-BuNC, catalyzed by electrogenerated 51 were studied. These experiments used the cell and apparatus used for the coulometric experiments described in Section II.B.5.a. A 3.0 x 10⁻³ M solution of 2 was prepared by dissolving 0.32 g of 2 in 200 mL of CH₃CN containing 0.1 M NBu₄PF₆. A typical procedure for these experiments is reported in detail for the PEt₃ case. A 20.0 mL aliquot of the 3.0 x 10⁻³ M solution of 2 (0.060 mmol) was placed in the sample compartment of the electrolysis cell and deoxygenated with argon at 0°C for 20 minutes. After adding PEt₃ (0.018 mL, 0.12 mmol), the solution was stirred at 0°C under an argon atmosphere for 1 hour. Infrared spectral analysis of the
reaction mixture, at this point, verified that no reaction had occurred. The solution was then electrolyzed, with stirring, under argon at -0.525 V. When the cathodic current had dropped to 20 μA or less, the coulometer was reset and the solution reduced at a controlled current of 1 mA. The electrical potential at this point was approximately -0.68 V. After about 150 seconds the potential rose to -0.77 V. During this time the brownish-orange sample solution did not change color. After this time, the potential rose rapidly towards -1.0 V, and the reaction solution changed color to yellowish-green. The current to the cell was shut off at -0.8 V and the coulometer reading was taken. Infrared spectral analysis of the final reaction mixture shows a complete reaction giving Cp₂Fe₂(PET₃)(CO)(μ-CO)(μ-CSMe)⁺, B: IR (0.1 M NBu₄PF₆/CH₃CN) 1987(s), 1818(s). Similar results were obtained for PMePh₂, PMe₂Ph and t-BuNC giving the corresponding substituted products. In the PPh₃ reaction, more than 20 minutes were required to reach a potential of -0.80 V. At this potential the reaction solution was a deep emerald green indicative of the radical 51. The IR spectrum of the solution showed 51, 2 and the PPh₃ substituted product. An absorbance versus concentration curve (Beer Law Plot) for 2 in 0.1 M NBu₄PF₆/CH₃CN was used to determine the residual concentra-
tion of 2 in the PPh₃ reaction. These results are summarized in Table 10 in the RESULTS AND DISCUSSION Section.

m. Reaction of the radical 5₁ with ¹³CO: CO exchange experiment. A THF solution (10 mL) of 2 (0.023 g, 0.050 mmol) was frozen in liquid nitrogen under vacuum, then exposed to a ¹³CO atmosphere (190 torr, ca. 2 mmol). In the presence of this ¹³CO atmosphere, the frozen solution was warmed to 25°C then stirred vigorously for 15 minutes. IR spectral analysis of the solution shows bands for 2 at 2052(s), 2010(w) and 1855(m) cm⁻¹. No bands for the ¹³CO exchange product of 2 were observed at approximately 2007, 1965 and 1814 cm⁻¹.

The solution was purged with nitrogen, cooled to 0°C and titrated with NaNp (ca. 0.05 mmol/mL in THF) to convert 2 to the radical, 5₁. After freezing with liquid nitrogen under vacuum, the frozen solution was exposed to a ¹³CO atmosphere (190 torr, ca. 2 mmol), warmed to 0°C and stirred vigorously for 15 minutes. The radical was then oxidized with I₂ (0.007 mg, 0.03 mmol) giving an orange-brown solution of 2. The solution was taken to dryness and the resulting residue washed with hexane (20 mL) and extracted with benzene (10 mL). The extract was evaporated to dryness and the resulting residue washed with Et₂O (10 mL) and dried. IR spectral analysis of the residue shows bands at
1996 and 1811 cm\(^{-1}\) for the \(^{13}\)CO exchange product of 2. The \(^1\)H NMR shows the sample to be >95% \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^+\); the \(^{13}\)CO spectrum has two carbonyl resonances at 252.0 and 207.3 ppm (1:2 ratio) which are at least twice as intense as the Cp resonances.

\[
\begin{align*}
\text{IR}(\text{CH}_3\text{CN}) & : 2043(\text{s}), 1994(\text{s}), 1974(\text{sh}), 1852(\text{m}), \\
 & 1811(\text{m}) \\
\text{\(^1\)H}(\text{CD}_3\text{CN}) & : 5.42 \text{ and } 5.38(\text{Cp}), 3.60(\text{Me}) \\
\text{\(^{13}\)C}(\text{CD}_3\text{CN}) & : 252.0(\mu-\text{CO}), 207.3(\text{CO}), 92.7 \text{ and } 92.0(\text{Cp})
\end{align*}
\]

6. **Crystallographic summary** for \(\text{Cp}_2\text{Fe}_2\text{Co}(\text{CO})_3(\mu-\text{CO})_2(\mu_3-\text{CSMe})\), 33, and \(\text{Cp}_2\text{Fe}_2\text{Co}(\text{PPh}_3)(\text{CO})_2(\mu-\text{CO})_2(\mu_3-\text{CSMe})\), 40

a. **Summary for 33**

Mol. Wt. 499.95 g/mol, monoclinic \(P2_1/c\), \(a = 7.057(1) \, \text{Å}, \ b = 14.767(2) \, \text{Å}, \ c = 17.674(3) \, \text{Å}, \ \beta = 99.86(3)^\circ, \ V = 1814.7(4) \, \text{Å}^3, \ \rho(\text{calcd}) = 1.83 \, \text{g/cm}^3, \ \rho(\text{found}) = 1.74 \, \text{g/cm}^3, \ \mu = 4, \ \mu_{\text{abs}} = 29.01 \, \text{cm}^{-1} \) for Mo-K\(\alpha\) radiation, \(\lambda = 0.71034 \, \text{Å}\).

A brownish-purple needle crystal of 33 with approximate dimensions 0.10 x 0.12 x 0.40 mm was mounted on a glass fiber and positioned on a standard goniometer head. Preliminary \(\omega\)-oscillation photographs gave 12 independent reflections \((6^\circ \leq 2\theta \leq 19^\circ)\) which were input into the automatic indexing program (BLIND).\(^{101}\) The resulting re-
duced-cell scalars indicated monoclinic symmetry. Unit cell parameters were determined by a least squares refinement utilizing the tuned 20 values \((23^\circ \leq 2\theta \leq 36^\circ)\) of 23 independent reflections.

X-ray intensity data were collected at 25°C, using an automated four-circle diffractometer designed and built in the Ames Laboratory. Graphite monochromated Mo-K\(\alpha\) \((\lambda = 0.71034 \AA)\) radiation was used for data collection. All data (3779 reflections) within the range of \(0^\circ \leq 2\theta \leq 50^\circ\) from the octants hkl and \(\overline{h}\overline{k}\overline{l}\) were measured using a \(\omega\)-scan technique. Throughout data collection, three near axial standard reflections \((28^\circ \leq 2\theta \leq 36^\circ)\) were monitored every 75 reflections. The intensities showed no systematic variation, and hence no decay corrections were applied. From the systematic extinctions of h01 \((l = 2n+1)\) and 0k0 \((k = 2n+1)\) the space group was determined to be \(P2_1/c\). A phi scan about the reflection \(-5,0,2\) \((\chi = 90^\circ)\) showed insignificant intensity variations; therefore, no absorption correction was applied.

These data, corrected for Lorentz and polarization effects, gave 2942 observed reflections with \(I(\text{obs}) > 3\sigma(I)\). The estimated error in each intensity was calculated by:

\[
(I)^2 = C_T + K_tC_B + (0.03 C_T)^2 + (0.03 C_B)^2
\]
where $C_T, K_t$ and $C_B$ represent the total count, counting
time factor and background count, respectively; the factor
0.03 represents an estimate of the nonstatistical errors.
The estimated standard deviations in the structure factors
($F$) were calculated by the finite difference method. \textsuperscript{103}
Equivalent reflections were averaged, yielding 2304 unique
observed reflections.

The positions of the cobalt and iron atoms were deter-
mined by Harker vector analysis of a three-dimensional
Patterson map. All remaining non-hydrogen atoms were found
by successive electron density map calculations. \textsuperscript{104} The
positional and anisotropic thermal parameters for the non-
hydrogen atoms were refined by a combination of block
matrix/full matrix least squares calculations. \textsuperscript{105} The
positional parameters for the Cp hydrogens were refined
using fixed isotropic temperature factors. The final con-
ventional residual index, $(R = \sum |F_O| - |F_C| / \sum |F_O|)$, was
0.044 with a corresponding weighted index, $[(R_w = \sum w(|F_O| -
|F_C|)^2 / \sum wF_O^2)^{1/2}]$, of 0.051, and the function minimized in
the least-squares refinement was $\sum w(|F_O| - |F_C|)^2$, where $w$ is
$1/\sigma(F)^2$. The final difference map was featureless. The
scattering factors were those from the International Ta-
bles; \textsuperscript{106} those for cobalt, iron and sulfur were modified
for the real and imaginary parts of anomalous disper-
Final positional parameters for non-hydrogen atoms, thermal parameters and structure factors are given in Appendices 1, 2 and 3, respectively. Tables 14 and 15 in the RESULTS AND DISCUSSION Section present selected interatomic distances and angles, respectively.

b. Crystallographic summary for $\text{Cp}_2\text{Fe}_2\text{Co}(\text{PPh}_3)(\text{CO})_2(\mu-\text{CO})_2(\mu_3-\text{CSMe})$, 40

Mol. wt. 734.24 g/mol, monoclinic $P2_1/n$, $a = 13.388(3)$ Å, $b = 23.188(6)$ Å, $c = 10.126(2)$ Å, $\beta = 100.11(2)\degree$, $V = 3095(2)$ Å$^3$, $\rho$ (calcd) = 1.58 g/cm$^3$, $\rho$ (found) = 1.59 g/cm$^3$, $Z = 4$, $\mu_{\text{abs}} = 16.54$ cm$^{-1}$ for Mo-$K\alpha$ radiation, $\lambda = 0.71069$ Å.

A black rhombohedral crystal of 40 of approximate dimensions 0.28 x 0.28 x 0.18 mm was mounted and indexed as for 33. The resulting reduced cell scalars indicated monoclinic symmetry. Unit cell parameters were determined, as for 33, for 20 independent reflections ($17\degree \leq 2\theta \leq 31\degree$).

X-ray intensity data were collected at 25°C on a Syntex $P2_1$ four-circle diffractometer. Graphite-monochromated Mo-$K\alpha$ (0.71069 Å) radiation was used for all data collection. All data (8902 reflections) within the range $4\degree \leq 2\theta \leq 50\degree$ from the octants $hkl$, $h\bar{k}l$, $\bar{h}k1$, $\bar{h}\bar{k}1$, were measured using the $\omega$-scan technique. A standard reflection monitored every 100 reflections showed no systematic variation during data collection; hence, no decay correction was
applied. Systematic extinctions of Ok0 (k = 2n) and h01 (h + 1 = 2n) determined the space group to be P21/n.

The 8902 measured reflections were corrected for Lorentz and polarization effects, and absorption (via an empirical absorption correction technique) giving 2127 observed reflections, I(obs) ≥ 3σ(I). The estimated errors in the intensities and standard deviations in the structure factors were calculated as for 33. Equivalent reflections were averaged, yielding 1088 independent observed reflections in the range 4° ≤ 2θ ≤ 50°.

The five heavy atoms were determined using an automatic Harker analysis program (ORGES) from a superposition map. All remaining non-hydrogen atoms were found by successive electron density map calculations. The positional and anisotropic thermal parameters for the non-hydrogen atoms were refined by the method used for 33. However, the atoms C2, C5, C8-C16, C21, C26, C28-C30 and C35 could not be anisotropically refined. The rapid decrease in intensity as a function of sinθ/λ, and the relatively low observation to parameter ratio, also indicate that such anisotropic refinement is not warranted. The final conventional and weighted residuals, defined as for 33, were R = 0.067 and R_w = 0.068. The final difference map was featureless. The scattering factors were
those from the International Tables; those of cobalt, iron, sulfur and phosphorus were modified for the real and imaginary parts of anomalous dispersion. Final positional parameters, thermal parameters and structure factors are given in Appendices 4, 5 and 6, respectively. Interatomic distances and angles are given in Table 14 and 15, respectively, in the RESULTS AND DISCUSSION section.
III. RESULTS AND DISCUSSION

A. Syntheses and Properties of Bridging Thiocarbyne Complexes

1. Preparation and properties of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSR})^+ \) complexes

   a. Reaction of alkyl halides with \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CS}), 1 \) The preparation of \( [\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})]^{+}\text{PF}_6, 2 \), previously reported by Quick and Angelici,\(^{50}\) was accomplished by stirring \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CS}), 1 \), in neat MeI to obtain \( [\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})]^{+}\text{I} \), which was then converted by ion exchange chromatography to the \( \text{PF}_6^- \) salt, 2. Since the primary purpose of this work was to study the reactivity of 2 and its analogues, it was advantageous to shorten the procedures used to obtain these thiocarbyne cations. The thiocarbonyl complex, 1, is prepared\(^{76}\) by the stepwise reaction of \( \text{CpFe}(\text{CO})_2^- \) with \( (\text{PhO})_2\text{CS} \) (Eqn 37). The second iron anion can attack at either the thioester carbon or Fe to give approximately equal quantities of 1 and \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})_2 \). Quick\(^{71}\) thoroughly investigated alternative routes to 1, but no other method gave yields as high as in equation 37. Therefore, efforts to shorten the procedure focused on workup
and subsequent alkylation of 1.

\[
\begin{align*}
\text{CpFe(CO)}_2^{-} & \quad \text{S} \\
\text{(PhO)}_2CS & \quad \text{--->} \\
\text{CpFe(CO)}_2CO\text{Ph}
\end{align*}
\]

\[
\begin{align*}
\text{S} & \quad \text{--->} \quad \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})_2 \\
\text{CpFe(CO)}_2C-\text{OPh} & \quad \text{--->} \quad \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CS})
\end{align*}
\]

Purification of 1 requires its separation from large quantities of \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})_2\), unreacted \((\text{PhO})_2CS\), Hg-[CpFe(CO)]_2, NaOPh and other unknown products. A fraction containing 1 and the first three compounds is obtained by taking the crude product mixture to dryness, extracting with CS\(_2\) and filtering through Celite. Because of the low solubility of \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})_2\) in CS\(_2\), some of this co-product is removed in this step; evaporation of this CS\(_2\) filtrate to half its volume precipitates more \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})_2\). Filtration and subsequent chromatography on Florisil, eluting with CS\(_2\) (100 mL) and 1/5, CH\(_2\)Cl\(_2\)/CS\(_2\), purportedly gives purified 1.

Quick's chromatographic purification, as summarized above, is time consuming, laborious and does not give good band separation. An orange fraction, which presumably
contains Hg[CpFe(CO)₂]₂ and (PhO)₂CS, elutes first but is quickly followed by a dark fraction consisting of both 1 and Cp₂Fe₂(CO)₂(μ-CO)₂. In order to obtain pure 1, this fraction had to be rechromatographed using a 30/1 (w/w) ratio of Florisil to sample and a 4.0 x 25 cm column. Elution with CS₂ separates a fraction containing 1. Contamination of 1 by Cp₂Fe₂(CO)₂(μ-CO)₂ does not occur until about 2/3 of 1 has eluted from the column. Because of this obvious loss, the eventual yield of 2 from purified 1 is only 16%.

Elimination of the chromatographic separation procedure and direct alkylation with MeI of the first CS₂ filtrate would be advantageous. This does appear feasible since 1) alkylation of Cp₂Fe₂(CO)₂(μ-CO)₂ does not occur unless it is activated by phosphine substituents; and 2) because other products in the reaction mixture, e.g. Hg[CpFe-(CO)₂]₂, which may react with MeI, would give soluble [(CpFe(CO)₂CH₃)],²⁷ HgI₂¹⁰⁹] products. The reaction of neat MeI with the residue after evaporation of the CS₂ filtrate, yields [Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe)]I. The only other carbonyl bands present in the IR spectrum of the reaction mixture are those of Cp₂Fe₂(CO)₂(μ-CO)₂. Precipitation of the iodide salt, [Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe)]I, with ether, followed by filtering and further ether washing, removes
unreacted \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})_2 \) and other soluble impurities. The iodide salt is dissolved in acetone and filtered from a small amount of dark material which is insoluble in all common organic solvents. After ion exchange and crystallization the product, 2, is obtained in 22% yield as air-stable, reddish-brown crystals.

Because it saves time and gives higher yields, the direct methylation procedure is clearly advantageous for synthesizing 2 and other analogous thiocarbyne cations. However, further procedure modification causes problems. If the original product mixture from equation 37 is taken to dryness and reacted with MeI, only a 5.6% yield of 2 is obtained. Either the alkylation reaction is inefficient in this medium or other impurities react with \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})]I\) to form unstable products. Two equivalents of PhO\textsuperscript{-} are present in this mixture and they may react with \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})]I\) to give a bridging carbene complex which may then decompose (Eqn 38). The reaction

\[
\text{NaOPh} \rightarrow \begin{array}{c}
\text{MeS} \\
\text{OPh}
\end{array}
\begin{array}{c}
\text{C} \\
\text{Fe(\text{CO})Cp}
\end{array}
\]

other products
between 2 and sodium phenoxide does indeed give an unstable product. Upon being mixed, this reaction gives a cloudy solution which could not be characterized by IR spectroscopy. The brown oil, recovered from this reaction upon solvent removal, did show broad terminal (2035-1945 cm\(^{-1}\)) and bridging (1850-1750 cm\(^{-1}\)) carbonyl bands in the IR spectrum indicative of either \(\mu\)-carbene and/or dimer products such as 1 and \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2\). However, the oil is unstable, decomposing upon attempted crystallization to leave a brown oil and a supernatant containing numerous products, but mostly \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2\). Quick\(^{71}\) also observed \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2\) as the major product for the reaction of NaOMe with 2.

Preparations of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CSCH}_2\text{Ph})]\text{PF}_6\), 3, and \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CSCH}_2\text{CH}=\text{CH}_2)]\text{PF}_6\), 4, are also achieved by direct alkylation reactions of the CS\(_2\) filtrate as shown in equation 37. These products are air-stable,

\[
\begin{align*}
\text{Cp}(\text{CO})\text{Fe} & \quad \text{SCH}_2\text{Ph} \\
\text{C} & \quad \text{C}
\end{align*}
\quad \text{Br} \rightarrow \text{Cp}(\text{CO})\text{Fe} \quad \text{S} \\
\text{C} & \quad \text{C}
\quad \text{Fe}(\text{CO})\text{Cp} + \text{PhCH}_2\text{Br}
\]

reddish-brown microcrystals. The yield of 4 (28%) is com-
parable to 2 (22%). The low yield (13%) observed for 3 may be due to reversion of the bromide salt to 1 and PhCH₂Br (Eqn 39) prior to the PF₆⁻ ion exchange procedure.

The IR spectra (Table 1) of 2, 3 and 4, synthesized by the direct alkylation procedure, agree with those observed using purified Cp₂Fe₂(CO)₂(μ-CO)(μ-CS), 1; strong, weak and medium carbonyl bands are observed at about 2040, 2010 and 1850 cm⁻¹. This band pattern is independent of solvent and resembles the spectrum of 1 in CH₃CN [i.e. cis-Cp₂Fe₂-(CO)₂(μ-CO)(μ-CS)], indicating that 2, 3 and 4 exist only as the cis isomers. (In this and in all subsequent discussions, the designation cis and trans refer to the position of the Cp ligands in relation to the Fe-Fe bond.)

\[
\text{cis-2, 3 and 4}
\]

The ¹H NMR spectra of 2, 3 and 4 are given in Table 2. Two separate Cp resonances are observed for each of these complexes in d⁶-acetone. Quick previously reported that 3 has two separate Cp resonances in d⁶-acetone, while 2 and 4 had single, broadened Cp resonances. The difference in
Table 1. Infrared stretching frequencies (cm\(^{-1}\)) for metal complexes discussed in Section III.A

<table>
<thead>
<tr>
<th>Compound(^a)</th>
<th>Solvent</th>
<th>(\nu_{\text{CO}})(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Fe}^*(\mu-\text{CO})_2)</td>
<td>CH(_2\text{Cl}_2)</td>
<td>2000(s), 1956(m), 1778(m)</td>
</tr>
<tr>
<td>(\text{Fe}^*(\mu-\text{CO}) (\mu-\text{CS}), 1^c)</td>
<td>Hexane</td>
<td>2012(vs), 1972(vs), 1813(s)</td>
</tr>
<tr>
<td></td>
<td>CH(_2\text{Cl}_2)</td>
<td>2004(vs), 1968(m), 1805(m), 1124(m)(^d)</td>
</tr>
<tr>
<td></td>
<td>CH(_3\text{CN})</td>
<td>1999(vs), 1962(w), 1803(m), 1120(m)(^d)</td>
</tr>
<tr>
<td>([\text{Fe}^*(\mu-\text{CO}) (\mu-\text{CSMe})]I)</td>
<td>CH(_3\text{CN})</td>
<td>2043(s), 2012(w), 1853(m)</td>
</tr>
<tr>
<td>([\text{Fe}^*(\mu-\text{CO}) (\mu-\text{CSMe})]PF_6, 2)</td>
<td>CH(_3\text{CN})</td>
<td>2044(s), 2013(w), 1853(m)</td>
</tr>
<tr>
<td>([\text{Fe}^*(\mu-\text{CO}) (\mu-\text{CSCH}^2\text{Ph})]PF_6, 3)</td>
<td>CH(_3\text{CN})</td>
<td>2040(s), 2010(w), 1850(m)</td>
</tr>
</tbody>
</table>
\[
\begin{array}{lcl}
[\text{Fe}^*(\mu-\text{CO})(\mu-\text{CSCH}_2\text{CH}=\text{CH}_2)]\text{PF}_6, & 4 & \text{CH}_3\text{CN} \\
2040(s), 2015(w), & & 1853(m) \\
[\text{Fe}^*(\mu-\text{CO})[\mu-\text{CSCH}_2\text{C(\text{CH}_3)_3}]]\text{SO}_3\text{CF}_3, & 5 & \text{CH}_3\text{CN} \\
2043(s), 2020(\text{sh}), & & 1850(m) \\
[\text{Fe}^'(\text{CH}_3\text{CN})(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})]\text{PF}_6, & 6 & \text{CH}_3\text{CN} \\
1998(s), 1827(s) & & \\
[\text{Fe}^'(\text{CH}_3\text{CN})_2(\mu-\text{CO})(\mu-\text{CSMe})]\text{PF}_6, & 7 & \text{CH}_3\text{CN} \\
1805(s) & & \\
[\text{Fe}^'(\text{PEt}_3)(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})]\text{PF}_6, & 8 & \text{CH}_2\text{Cl}_2 \\
1988(s), 1820(s) & & 1008(m)^d \\
[\text{Fe}^'(\text{PMe}_2\text{Ph})(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})]\text{PF}_6, & 9 & \text{CH}_3\text{CN} \\
1995(s), 1815(s) & & \\
\text{Fe}^*(\text{I})(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe}), & 10 & \text{CH}_2\text{Cl}_2 \\
1995(s), 1810(s) & & \\
\end{array}
\]

\(^a\) Abbreviations: \(\text{Fe}^* = \text{Cp}_2\text{Fe}_2(\text{CO})_2\), \(\text{Fe}^' = \text{Cp}_2\text{Fe}_2\).

\(^b\) Abbreviations: \(s = \text{strong}, m = \text{medium}, w = \text{weak}, \text{sh} = \text{shoulder}\).

\(^c\) Data from reference 71.

\(^d\) \(\nu_{\text{CS}}\) stretch.
Table 2. $^1$H NMR chemical shifts (ppm) for metal complexes discussed in Section III.A

<table>
<thead>
<tr>
<th>Compound$^a$</th>
<th>Solvent</th>
<th>Cp$^b$$\delta$</th>
<th>Others$^b$$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe*(μ-CO) (μ-CS), 1</td>
<td>d$^6$-acetone</td>
<td>5.01</td>
<td></td>
</tr>
<tr>
<td>[Fe*(μ-CO) (μ-CSMe)]I</td>
<td>CD$_3$CN</td>
<td>5.42(br)</td>
<td>3.60(Me)</td>
</tr>
<tr>
<td>[Fe*(μ-CO) (μ-CSMe)]PF$_6$, 2</td>
<td>d$^6$-acetone</td>
<td>5.72, 5.63</td>
<td>3.80(Me)</td>
</tr>
<tr>
<td>[Fe*(μ-CO) (μ-CSCH$_2$Ph)]PF$_6$, 3</td>
<td>d$^6$-acetone</td>
<td>5.75, 5.62</td>
<td>7.50(m, Ph), 5.43(CH$_2$)</td>
</tr>
<tr>
<td>Fe*(μ-CO) (μ-CSCH$_2$CH=CH$_2$)]PF$_6$, 4</td>
<td>d$^6$-acetone</td>
<td>5.70, 5.65</td>
<td>6.18(m, vinyl), 4.96(t, CH$<em>2$, J$</em>{vinyl, H}$ = 7.8 Hz)</td>
</tr>
<tr>
<td>[Fe'(CO) (CH$_3$CN) (μ-CO) (μ-CSMe)]PF$_6$, 6</td>
<td>CD$_3$NO$_2$</td>
<td>5.19, 5.03</td>
<td>3.72, 1.91(CH$_3$CN)</td>
</tr>
<tr>
<td>Fe'(I) (CO) (μ-CO) (μ-CSMe), 10</td>
<td>d$^6$-acetone</td>
<td>4.86, 4.84</td>
<td>3.74(Me)</td>
</tr>
</tbody>
</table>

$^a$ Abbreviations: Fe* = Cp$_2$Fe$_2$(CO)$_2$, Fe' = Cp$_2$Fe$_2$.

$^b$ Abbreviations: b = broad, d = doublet, m = multiplet, t = triplet.

$^c$ Data from reference 71.
our data for complexes 2 and 4 is probably due, 1) to the higher resolution of the JOEL FX-90Q (90 MHz) NMR spectrometer used in this work versus the Varian A-60 (60 MHz) spectrometer used by Quick, and/or 2) to a higher ambient NMR probe temperature in Quick's work which may have resulted in coalescence of the Cp resonances (see below). The broadened Cp resonances observed by Quick for 2 and 4 was attributed to either inversion of the sulfur atom or possibly rotation about the \( \text{C}_{\text{carbyne}}-\text{S} \) bond which becomes rapid at or near room temperature (Eqn 40). In this work the two

\[
\text{Cp(CO)} \text{Fe} \text{Me}_2 \text{Me}_2 \text{Fe(CO)Cp} \rightleftharpoons \text{Cp(CO)} \text{Fe} \text{Me}_2 \text{Me}_2 \text{Fe(CO)Cp} \quad (40)
\]

Cp resonances of 2 coalesce at 38°C in CD3CN (Figure 6). The coalescence temperature for \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CS-CH}_2\text{Ph})^+ \), 3, occurs at 48°C. This result indicates that the size of the \( R \) substituent on the carbyne carbon has a significant effect on the rate of the process depicted in equation 40. It is tempting to suggest that the cis configuration found in thiocarbyne cations is the result of steric requirements. With both Cp ligands in the cis configuration a rotational path about the \( \text{C}_{\text{carbyne}}-\text{S} \) bond could
Figure 6. Variable-temperature $^1$H NMR spectrum study of Cp ligands in $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})]\text{PF}_6$ in CD$_3$CN (JOEL FX-90Q)
occur without close contact between the R group and the Cp ligands (Figure 7). The trans configuration would have steric interactions in both rotational directions. However, preference for the cis configuration may be purely electronic, since \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CH})^+ \) exists in the cis form, and in this example, there is no obvious steric preference for the cis configuration.\(^{29}\)

A unique case of cis/trans isomerization (activation energy = 22.5 kcal/mol; no error limits provided) was observed for the \( \mu \)-carbyne complex, \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})[\mu-\text{C}(1\text{-cyclopentene})]^+ \).\(^{35}\) Although this trans to cis isomerization shows a \( K_{\text{eq}} = 7.32 \) at 32°C, no evidence for a trans isomer is observed for 2 up to 90°C in CD\(_3\)NO\(_2\).

The \( ^{13}\text{C} \) NMR spectrum of 2 reported by Quick\(^{71}\) is in error. The methyl resonance occurs at 38.2 ppm in CD\(_3\)CN and not at 83.0 ppm (apparently a typographical error). The carbyne carbon resonance, not previously reported, occurs at 408.3 ppm. In comparison, chemical shifts for the carbyne carbon resonance occur at 403.1 and 407.9 ppm in \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSCH}_2\text{Ph})^+ \), 3 and \( \text{Cp}_2\text{Fe}_2(\text{PET}_3)(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})^+ \), 8, respectively.\(^{50}\) Other \( ^{13}\text{C} \) resonances for 2 are at 92.8 and 92.1 ppm for the Cp ligands, 207.4 ppm for the terminal CO and 252.3 for the bridging CO ligand.
Figure 7. Rotation about the C_{carbene-S} bond in the cis/trans isomers of [Cp_2Fe_2(CO)_2(μ-CO)-(μ-CSR)]PF_6 complexes
b. **Attempted preparation of** \( \text{Cp}_2\text{Fe}_2(\mu-\text{CO})_2(\mu-\text{CO})[\mu-\text{CSCH}_2\text{C(CH}_3)_3]^+ \), \( \text{5} \) **Alkylation of the sulfur atom of** \( \text{Cp}_2\text{Fe}_2(\mu-\text{CO})_2(\mu-\text{CO})(\mu-\text{CS}) \) **is dependent on the reactivity of the alkylating agent** (\( \text{ROSO}_2\text{F, [R}_3\text{O]BF}_4 \gg \text{PhCH}_2\text{Br, AllylBr} \gg \text{MeI} \gg \text{BuI} \)) **and the steric bulk of the alkyl substituent.**

Reaction of \( \text{i} \) with the strong alkylating agent, neopentyl triflate, \( \text{90} \) (Eqn 41) appears to form the neopentyl thiocarbyne cation \( \text{5} \) since the reddish oil obtained shows characteristic IR spectral bands at 2043(s), 2020(sh) and 1850(m) cm\(^{-1}\) in CH\(_3\)CN. However, the \( ^1\text{H} \) NMR spectrum of this oil lacks resonances for a neopentyl group. The proposed product may be unstable for several reasons: 1) the steric bulk of the neopentyl group may cause the reaction in equation 41 to reverse; and 2) the neopentyl carbonium ion may rearrange to form a tertiary carbonium ion (Eqn 42) \( \text{110} \) which would have even greater steric hindrance.
than the neopentyl group.

\[ CH_3-C-CH_2^+ \quad \rightarrow \quad CH_3-C=CH_2CH_3 \quad (42) \]

2. Preparation and properties of \textit{Cp}_2Fe_2(L)(CO)(\mu-CO)(\mu-CSMe)^+ complexes

The photoinduced substitution of CO in 2 by CH\textsubscript{3}CN is a slow reaction that gives both \textit{Cp}_2Fe_2(CH\textsubscript{3}CN)(CO)(\mu-CO)(\mu-CSMe)^+, \textit{6}, and presumably \textit{Cp}_2Fe_2(CH\textsubscript{3}CN)_2(\mu-CO)(\mu-CSMe)^+, \textit{7}, in approximately equal quantities. The bis-acetonitrile product is unstable. The mono-substituted product, isolated by column chromatography, was contaminated by the decomposition products of \textit{Cp}_2Fe_2(CH\textsubscript{3}CN)_2(\mu-CO)(\mu-CSMe)^+. A clean reaction to substitute only one carbonyl occurs when 2 is titrated with an acetonitrile solution of Me\textsubscript{3}NO (Eqn. 43). This brown colored complex is stable for at least

\[ \text{Cp}_2Fe_2(CO)_2(\mu-CO)(\mu-CSMe)^+ \quad \rightarrow \quad \text{Me}_3\text{NO} \quad \text{CH}_3\text{CN} \quad \text{Cp}_2Fe \quad \text{Fe} \quad \text{CO} \quad \text{SMe} \quad \text{Me}_3\text{NO} \quad \text{CH}_3\text{CN} \quad \text{Cp} \quad \text{Cp} \quad \text{O} \quad \text{Me}_3\text{NO} \quad \text{CO}_2 \quad (43) \]

\[ \textit{6} + \text{NMe}_3 + \text{CO}_2 \]
a week under nitrogen. Since a brown oil was obtained on attempted crystallization, this compound is characterized by its IR and \(^1\)H NMR spectra only. The IR spectrum (in CH\(_3\)CN) is characteristic of mono-substituted Cp\(_2\)Fe\(_2\)(L)(CO)-(μ-CO)-(μ-CSMe)\(^+\) complexes having one terminal (1998 cm\(^{-1}\)) and one bridging carbonyl (1827 cm\(^{-1}\)) band; because CH\(_3\)CN is a weak donor ligand these bands are at slightly higher energy than those of the phosphine complex Cp\(_2\)Fe\(_2\)(PMe\(_2\)Ph)(CO)(μ-CO)(μ-CSMe)\(^+\), 9, (CH\(_3\)CN: 1995 and 1815 cm\(^{-1}\)). The \(^1\)H NMR spectrum exhibits two Cp resonances at 5.19 and 5.03 ppm, a resonance at 3.72 ppm for the SMe group and a singlet at 1.91 ppm for the coordinated CH\(_3\)CN ligand. The absence of a large singlet between 2 and 4 ppm indicates that the product is, indeed, an acetonitrile complex and not one containing coordinated NMe\(_3\) or an adduct similar to [Cp\(_2\)Fe\(_2\)(CO)\(_2\)(μ-CO)(μ-C(H)NMe\(_3\))]PF\(_6\).\(^5^8\)

The phosphine derivatives of 2, [Cp\(_2\)Fe\(_2\)(PEt\(_3\))(CO)(μ-CO)(μ-CSMe)]PF\(_6\), 8, and [Cp\(_2\)Fe\(_2\)(PMe\(_2\)Ph)(CO)(μ-CO)(μ-CSMe)]PF\(_6\), 9, were originally prepared by Quick and Angelici.\(^5^0\) In this work the products, 8 and 9, were obtained as green microcrystals in 51% and 79% yields, respectively. The products are stable indefinitely under nitrogen at -20°C. The IR spectral data for 8 and 9 (Table 1) agree with reported values.\(^5^0\) Reactions of [Cp\(_2\)Fe\(_2\)-
(CO)$_2$(μ-CO)(μ-CSMe)]SO$_3$F with PEt$_3$ or PMe$_2$Ph in acetonitrile are reported to occur rapidly at room temperature. Substitution reactions using the PF$_6$ salt of 2 are supposed to occur even faster.$^{50}$ The syntheses of 8 and 9 from 2 reported here, were found to be quite slow (in CH$_3$CN) at room temperature. A possible explanation for this discrepancy is that a small amount of reducing agent may have been present in Quick and Angelici's reactions which would have generated a catalytic amount of the Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CSMe) radical. As will be discussed in Section III.C, this radical catalyzes substitution reactions of 2.

3. Preparation and properties of Cp$_2$Fe$_2$(I)(CO)(μ-CO)(μ-CSMe), 10

An alternative procedure for preparing Cp$_2$Fe$_2$(CO)(I)-(μ-CO)(μ-CSMe), 10,$^{50}$ is to reflux Cp$_2$Fe$_2$(CH$_3$CN)(CO)(μ-CO)-(μ-CSMe)$^+$, 6, with NaI for 6 hours. The yield, 76%, is somewhat less than the 91% obtained by Quick.$^{50}$ Complex 10 is obtained as a brown, crystalline material which is stable indefinitely at 25°C. Although the $^1$H NMR chemical shifts in d$_6$-acetone (4.86, 4.84 ppm) for the Cp ligand of 10 are shifted significantly upfield compared to that of cationic complex 2 (5.72, 5.13 ppm), the shift for the methyl group (3.74 ppm) is approximately the same as in
B. Products of Thiocarbyne Cation Reactions with Nucleophiles

1. Bridging dithiocarbene and selenothiocarbene complexes
   a. Preparation and properties

   Treatment of \( \text{Cp}_2\text{Fe}_2(\mu-\text{CO})(\mu-\text{CSMe})^+ \), 2, with mercaptides (RS\(^-\)) and selenides (RSe\(^-\)) effects a rapid addition of the RS\(^-\) or RSe\(^-\) group to the carbyne carbon to generate bridging carbene complexes (Eqn 44). Excellent yields are obtained for 11 and 12. No yield was obtained for 13 since it was prepared on a micro-scale; this compound was identified by

\[
\text{Cp}_2\text{Fe}_2(\mu-\text{CO})(\mu-\text{CSMe})^+ + \text{RY}^- \xrightarrow{\text{THF or CH}_3\text{CN}} \ 0 - 20^\circ\text{C} \]

\[
\text{Cp}_2\text{Fe}_2(\mu-\text{CO})(\mu-\text{CSMe})^+ + \text{RY}^- \xrightarrow{\text{THF or CH}_3\text{CN}} \ 0 - 20^\circ\text{C} \]

\[
\text{MeS} \quad \text{RY} \quad \text{MeS} \quad \text{RY} \]

\[
\text{Cp(CO)Fe} \quad \text{Fe(CO)Cp} \quad \text{Cp(CO)Fe} \quad \text{Fe(CO)Cp} \]

\[
\text{R}_Y = \text{MeS} \ (11, \ 80\%) \\
\text{R}_Y = \text{PhS} \ (12, \ 75\%) \\
\text{R}_Y = \text{PhCH}_2\text{S} \ (13) \\
\text{R}_Y = \text{PhSe} \ (23)
its similarity to 11 and 12 (color and IR spectrum, see Table 3). The purple selenothiocarbene complex, 23, which has a similar IR spectrum (Table 3) to 11-13, was not isolated because it decomposes at 0°C (especially under vacuum) to give the μ-carbyne complex, \( \text{Cp}_2\text{Fe}_2(\text{SePh})(\text{CO})\left(\mu-\text{CO}\right)\left(\mu-\text{CSMe}\right) \), 22 (see Section d.3 for further discussion), and \( \text{Cp}_2\text{Fe}_2(\text{CO})_2\left(\mu-\text{CO}\right)\left(\mu-\text{CS}\right) \), 1. The dithiocarbene complexes are dark purple, crystalline solids, soluble in most organic solvents (only slightly soluble in hexane) and stable indefinitely under nitrogen at -20°C. Complex 11 is air-stable in the solid state. Solutions of 11, are more susceptible to decomposition by water than air oxidation. Bubbling \( \text{O}_2 \) through a \( \text{CH}_2\text{Cl}_2 \) solution of 11 at 25°C for 0.5 hour, does not appear to cause decomposition. Exposure to water, under nitrogen atmosphere, decomposes 11 to insoluble products within several hours. Water may act as an acid to produce a bridging hydroxy(methylthio)carbene complex and MeSH (Eqn 45). Analogous to the phenoxide reac-

\[
\begin{align*}
\text{OC} & \quad \text{MeS} \quad \text{SMe} \\
\text{Fe} & \quad \text{C} \quad \text{Fe} \quad \text{CO} \\
\text{Cp} & \quad \parallel \quad \text{Cp} \\
\ O & \quad \parallel \quad \ O
\end{align*}
\]

\[\text{H}_2\text{O} \quad \text{OC} \quad \text{HO} \quad \text{SMe} \quad \text{CO} \]

\[\begin{align*}
\text{OC} & \quad \text{Fe} \quad \text{C} \quad \text{Fe} \quad \text{CO} \\
\text{Cp} & \quad \parallel \quad \text{Cp} \\
\ O & \quad \parallel \quad \ O
\end{align*}\]

\[+ \text{MeSH}\]

(45)
tion with \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^+ \) in equation 38, the hydroxy(methylthio)carbene complex may be unstable. After several months at room temperature, crystals of 12 decompose to give the bridging ca-byne complex, \( \text{Cp}_2\text{Fe}_2-(\text{SPh})(\text{CO})(\mu-\text{CO})(\mu-\text{SMe}) \), 38, and some insoluble products.

b. Spectroscopic properties

The bridging dithio-carbene complexes exist as mixtures of isomers which could not be separated by silica gel column chromatography or fractional crystallization. The isomers of 11 and 12 can be distinguished by their spectroscopic properties:

IR (Table 3), \(^1\text{H} \text{NMR} \) (Table 4) and \(^{13}\text{C} \text{NMR} \) (Table 5).

The bridging bis(methylthio)carbene complex 11 has two possible isomers:

![cis-11 and trans-11 structures](image)

The \(^1\text{H} \text{NMR} \) of 11 in \( \text{CD}_2\text{Cl}_2 \), gives a singlet for the Cp protons of the cis isomer (4.89 ppm) and a less intense singlet (4.90 ppm) for the trans isomer. The chemical shifts for the methyl protons of the cis isomer occur as
<table>
<thead>
<tr>
<th>Compounda</th>
<th>Solvent</th>
<th>$\nu_{CO}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe*($\mu$-CO)[$\mu$-C(SMe)$_2$], 11</td>
<td>Nujol</td>
<td>1980(s, b), 1948(m), 1785(s), 1780(sh)</td>
</tr>
<tr>
<td></td>
<td>Hexane</td>
<td>1996(s), 1968(s), 1960(m), 1779(s)</td>
</tr>
<tr>
<td></td>
<td>CH$_2$Cl$_2$</td>
<td>1985(s), 1952(m), 1786(m)</td>
</tr>
<tr>
<td></td>
<td>CH$_3$CN</td>
<td>1980(s), 1948(m), 1783(m)</td>
</tr>
<tr>
<td>Fe*($\mu$-CO)[$\mu$-C(SMe)SPh], 12</td>
<td>CHCl$_3$</td>
<td>1993(s), 1959(m), 1783(m)</td>
</tr>
<tr>
<td></td>
<td>CH$_2$Cl$_2$</td>
<td>1987(s), 1957(m), 1788(m)</td>
</tr>
<tr>
<td></td>
<td>CH$_3$CN</td>
<td>1985(s), 1952(w), 1786(m)</td>
</tr>
<tr>
<td>Fe*($\mu$-CO)[$\mu$-C(SMe)SCH$_2$Ph], 13</td>
<td>CH$_3$CN</td>
<td>1980(s), 1949(m), 1785(m)</td>
</tr>
</tbody>
</table>

Table 3. Infrared stretching frequencies (cm$^{-1}$) for metal complexes discussed in Section III.B
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>νC=O (cm⁻¹)</th>
<th>νC≡N (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-Fe*(µ-CO)[µ-C(H)SMe] 14^c</td>
<td>CH₂Cl₂</td>
<td>1997(s), 1962(w), 1780(m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃CN</td>
<td>1977(s), 1938(w), 1780(m)</td>
<td></td>
</tr>
<tr>
<td>cis-Fe*(µ-CO)[µ-C(H)SMe] 15</td>
<td>Hexane</td>
<td>2000(s), 1968(w), 1955(w), 1805(m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CDCl₃</td>
<td>1989(s), 1951(m), 1780(m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₂Cl₂</td>
<td>1987(s), 1949(w), 1783(m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃CN</td>
<td>1977(s), 1938(w), 1780(m)</td>
<td></td>
</tr>
<tr>
<td>cis-Fe*(µ-CO)[µ-C(H)SCH₂Ph] 16</td>
<td>Hexane</td>
<td>1998(s), 1965(w), 1955(w), 1802(m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₂Cl₂</td>
<td>1985(s), 1977(w), 1780(m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃CN</td>
<td>1975(s), 1938(w), 1780(m)</td>
<td></td>
</tr>
</tbody>
</table>

---

^a Abbreviations: Fe* = Cp₂Fe₂(CO)₂, Fe' = Cp₂Fe₂.
b Abbreviations: s = strong, m = medium, w = weak, sh = shoulder.
c Mixture of cis and trans isomers.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\nu_{CO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}^+ (\mu\text{-CO}) [\mu\text{-C(H)}\text{SCH}_2\text{CH}]=\text{CH}_2$, 17</td>
<td>$\text{CH}_2\text{Cl}_2$</td>
<td>1993(s), 1957(sh), 1793(m)</td>
</tr>
<tr>
<td>$\text{Fe}^+ (\text{CH}_3\text{CN}) (\text{CO}) (\mu\text{-CO}) [\mu\text{-C(H)}\text{SMe}]$, 18</td>
<td>$\text{CH}_3\text{CN}$</td>
<td>1930(s), 1759(m)</td>
</tr>
<tr>
<td>$\text{Fe}^+ (\text{PMe}_2\text{Ph}) (\text{CO}) (\mu\text{-CO}) [\mu\text{-C(H)}\text{SMe}]$, 19</td>
<td>$\text{CH}_3\text{CN}$</td>
<td>1917(s), 1735(s)</td>
</tr>
<tr>
<td>$[\text{Fe}^+ (4\text{-DMAP}) (\text{CO}) (\mu\text{-CO}) (\mu\text{-CSMe})]\text{PF}_6$, 20</td>
<td>$\text{CH}_3\text{CN}$</td>
<td>2000(s), 1815(s)</td>
</tr>
<tr>
<td>$\text{Fe}^+ (4\text{-DMAP}) (\text{CO}) (\mu\text{-CO}) (\mu\text{-CSMe})$, 21</td>
<td>$\text{CH}_2\text{Cl}_2$</td>
<td>2007(s), 1817(s)</td>
</tr>
<tr>
<td>$[\text{Fe}^+ (\text{SePh}) (\text{CO}) (\mu\text{-CO}) (\mu\text{-CSCH}_2\text{Ph})]\text{PF}_6$, 22</td>
<td>$\text{CH}_3\text{CN}$</td>
<td>1978(s), 1800(s)</td>
</tr>
<tr>
<td>$\text{Fe}^+ (\mu\text{-CO}) [\mu\text{-C(SMe)}\text{SePh}]$, 23</td>
<td>THF</td>
<td>1982(s), 1952(m), 1790(s)</td>
</tr>
<tr>
<td>$\text{Fe}^+ (\mu\text{-CO}) [\mu\text{-C(SMe)}\text{CH}_2\text{Ph}]$, 24</td>
<td>hexane</td>
<td>1996(s), 1992(sh), 1964(sh), 1952(s), 1801(m), 1796(sh)</td>
</tr>
<tr>
<td>Compound</td>
<td>Solvent</td>
<td>ν (cm⁻¹)</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>---------</td>
<td>----------</td>
</tr>
<tr>
<td>Fe'(SMe)(CO)(μ-CO)(μ-CNMe₂), 25</td>
<td>CH₂Cl₂</td>
<td>1983(s), 1945(s), 1782(m)</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>1975(s), 1950(s), 1800(s)</td>
</tr>
<tr>
<td></td>
<td>CH₃CN</td>
<td>1977(s), 1940(m), 1782(m)</td>
</tr>
<tr>
<td>Fe'(SMe)(CO)(μ-CO)[μ-CN(CH₂)₄], 26</td>
<td>CH₃CN</td>
<td>1938(s), 1768(s)</td>
</tr>
<tr>
<td>Fe'(SMe)(CO)(μ-CO)[μ-CN(H)Me], 27</td>
<td>CH₃CN</td>
<td>1940(s), 1767(s)</td>
</tr>
<tr>
<td>Fe'(SMe)(CO)(μ-CO)[μ-CN(H)Bu⁰], 28</td>
<td>CH₃CN</td>
<td>1940(s), 1768(s)</td>
</tr>
<tr>
<td>Fe'(SMe)(CO)(μ-CO)[μ-CN(H)(CH₂)₂NH₂], 29</td>
<td>CH₃CN</td>
<td>1948(s), 1770(s)</td>
</tr>
<tr>
<td>Fe'(SMe)(CO)(μ-CO)[μ-CN(H)(CH₂)₃NH₂], 30</td>
<td>CH₃CN</td>
<td>1945(s), 1770(s)</td>
</tr>
<tr>
<td>Fe'(SMe)(CO)(μ-CO)[μ-CN(CH₃)(CH₂)₃N(H)CH₃], 31</td>
<td>CH₃CN</td>
<td>1945(s), 1770(s)</td>
</tr>
<tr>
<td>Fe'(SMe)(CO)(μ-CO)[μ-CN(H)(CH₂)₂OH], 32</td>
<td>CH₃CN</td>
<td>1945(s), 1770(s)</td>
</tr>
<tr>
<td>Compound(^a)</td>
<td>Solvent</td>
<td>(\nu_{\text{CO}})^(^b)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>---------</td>
<td>-------------------------------------------------------</td>
</tr>
<tr>
<td>([\text{Fe}^*(\mu-\text{CO}) (\mu-\text{CSPh})]BF_4), 36</td>
<td>CH(_3)CN</td>
<td>2049(s), 2017(sh), 1856(m)</td>
</tr>
<tr>
<td>(\text{Fe}^*(\mu-\text{CO}) [\mu-\text{C(H)} \text{SPh}], 37)</td>
<td>CH(_3)CN</td>
<td>1978(s), 1942(w), 1784(m)</td>
</tr>
<tr>
<td>(\text{Fe'} (\text{SPh})(\text{CO}) (\mu-\text{CO}) (\mu-\text{CSMe}), 38)</td>
<td>CH(_2)Cl(_2)</td>
<td>1988(s), 1807(s)</td>
</tr>
<tr>
<td>([\text{Fe}^*(\mu-\text{CO}) [\mu-\text{C(H)} \text{PPh}_3]]BF_4, 39)</td>
<td>CH(_2)Cl(_2)</td>
<td>1995(s), 1960(sh), 1817(m)</td>
</tr>
</tbody>
</table>

\(^{39d}\) Data from reference 27.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\delta_{Cp}$</th>
<th>Others $\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Fe*(μ-CO)(μ-C(SMe)$_2$), 11</td>
<td>CD$_2$Cl$_2$</td>
<td>4.89</td>
<td>7.58 (m, Ph), 2.78, 2.57 and 2.41 (Me)</td>
</tr>
<tr>
<td>trans-Fe*(μ-CO)(μ-C(SMe)$_2$), 11</td>
<td>CD$_2$Cl$_2$</td>
<td>4.90</td>
<td>7.58 (m, Ph), 2.78, 2.57 and 2.41 (Me)</td>
</tr>
<tr>
<td>Fe*(μ-CO)(μ-C(SMe)SPh), 12$^c$</td>
<td>CDCl$_3$</td>
<td>4.95, 4.93</td>
<td>7.58 (m, Ph), 2.78, 2.57 and 2.41 (Me)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.78, 5.00</td>
<td>2.78, 2.57 and 2.41 (Me)</td>
</tr>
<tr>
<td>trans-Fe*(μ-CO)(μ-C(H)SMe), 14$^e$</td>
<td>CDCl$_3$</td>
<td>4.94, 4.83</td>
<td>10.03 (methine), 2.72 (Me)</td>
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<tr>
<td></td>
<td>d$_6$-acetone</td>
<td>4.84</td>
<td>11.64 (methine), 2.80 (Me)</td>
</tr>
<tr>
<td>cis-Fe*(μ-CO)(μ-C(H)SMe), 15</td>
<td>CDCl$_3$</td>
<td>4.77</td>
<td>11.48 (methine), 2.82 (Me)</td>
</tr>
<tr>
<td>Reference</td>
<td>Solvent</td>
<td>δ ( ppm)</td>
<td>Description</td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>15</td>
<td>d⁶-acetone</td>
<td>4.88</td>
<td>11.65 (methine), 2.77 (Me)</td>
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<tr>
<td>15</td>
<td>CDCl₃</td>
<td>4.82</td>
<td>11.59 (methine), 2.78 (Me)</td>
</tr>
<tr>
<td>cis-Fp*(μ-CO) [μ-C(H)SCH₂Ph], 16</td>
<td>CDCl₃</td>
<td>4.53</td>
<td>11.43 (methine), 7.43 (m, Ph), 4.34 (CH₂)</td>
</tr>
<tr>
<td>16</td>
<td>d⁶-acetone</td>
<td>4.72</td>
<td>11.68 (methine), 7.44 (m, Ph), 4.39 (CH₂)</td>
</tr>
<tr>
<td>Fe*(μ-CO) [μ-C(H)SCH₂CH=CH₂], 17</td>
<td>CDCl₃</td>
<td>4.78, 4.77, 4.74, 4.72</td>
<td>11.61, 11.37 and 11.21 (methine), 3.24 (b, vinyl), 2.11 (m, b, CH₂)</td>
</tr>
<tr>
<td>Fe'(PMe₂Ph)(CO)(μ-CO) [μ-C(H)SMe], 19f</td>
<td>CDCl₃</td>
<td>4.54, 4.37</td>
<td>10.91 (methine), 2.70 (d, SMe, Jₚₗ = 9.3 Hz)</td>
</tr>
</tbody>
</table>

**Abbreviations:**
- Fe* = Cp₂Fe₂(CO)₂, Fe' = Cp₂Fe₂.
- Abbreviations: b = broad, d = doublet, m = multiplet, t = triplet.
- 25°C, mixture of cis-12A, cis-12B and trans-12, see text.
- 0°C, mixture same as in c.
Table 4. (Continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Cp^δ</th>
<th>Others^δ</th>
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</thead>
<tbody>
<tr>
<td>[Fe'(4-DMAP)(CO)(μ-CO)(μ-CSMe)]PF_6, 20</td>
<td>d^6-acetone</td>
<td>5.34, 5.07</td>
<td>7.76(d, py, J_HH = 7.5 Hz), 6.36(d, py, J_HH = 7.5 Hz), 3.85(SMe), 2.95(NCH_3)</td>
</tr>
<tr>
<td>[Fe'(4-DMAP)(CO)(μ-CO)(μ-CSCH_2Ph)]PF_6, 21</td>
<td>d^6-acetone</td>
<td>5.39, 5.10</td>
<td>7.79(d, py, J_HH = 7.5 Hz), 7.45(m, Ph), 6.39(d, py, J_HH = 7.5 Hz), 5.60(CH_2), 2.94(CH_3)</td>
</tr>
<tr>
<td>Fe'(SePh)(CO)(μ-CO)(μ-CSMe), 22</td>
<td>CDCl_3</td>
<td>4.84, 4.75</td>
<td>3.39, 7.32(m, Ph), 3.39(Me)</td>
</tr>
<tr>
<td>Fe*(u-CO)[μ-C(SMe)CH_2Ph], 24</td>
<td>CD_3CN</td>
<td>4.84</td>
<td>7.29(Ph), 3.79 (CH_2), 2.81(Me)</td>
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<tr>
<td>cis-Fe'(SMe)(CO)(μ-CO)(μ-CNMe_2), 25</td>
<td>CDCl_3</td>
<td>4.72, 4.54</td>
<td>3.45 and 3.37 (μ-CNMe_2), 1.53(SMe)</td>
</tr>
<tr>
<td>Compound</td>
<td>Solvent</td>
<td>δ (ppm) 1</td>
<td>δ (ppm) 2</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>---------------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>trans-Fe'(SMe)(CO)(μ-CO)(μ-CNMe₂), 25</td>
<td>CDCl₃</td>
<td>4.69, 4.50</td>
<td>3.24 and 3.19 (μ-CNMe₂), 1.53(SMe)</td>
</tr>
<tr>
<td>Fe'(SMe)(CO)(μ-CO)u-CNCH₂CH₂CH₂CH₂f, 26</td>
<td>CDCl₃</td>
<td>4.73, 4.53</td>
<td>3.06(b, NCH₂), 1.87(b, CH₂), 1.53(SMe)</td>
</tr>
<tr>
<td>[Fe*(μ-CO)(μ-CSPh)]BF₄, 36</td>
<td>d⁶-acetone</td>
<td>5.72, 5.14</td>
<td>7.8(m, Ar)</td>
</tr>
<tr>
<td>Fe'(SPh)(CO)(μ-CO)(μ-CSMe), 38</td>
<td>CDCl₃</td>
<td>4.84, 4.80</td>
<td>3.39</td>
</tr>
</tbody>
</table>

\(^e\) This product contains about 20% of the cis isomer, 15.

\(^f\) The expected Ph and Me resonances for coordinated PMe₂Ph are masked by resonances at 7.4 ppm (Ph) and 1.6 ppm (Me) for free PMe₂Ph in the sample.
### Table 5. $^{13}$C NMR chemical shifts (ppm) for metal complexes

<table>
<thead>
<tr>
<th>Compound $^a$</th>
<th>Solvent</th>
<th>$\delta$ Cp $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe*(μ-CO)(μ-CSMe)]PF$_6$, 2</td>
<td>CD$_3$CN</td>
<td>92.8, 92.1</td>
</tr>
<tr>
<td>cis-Fe*(μ-CO)[μ-C(SMe)$_2$], 11</td>
<td>CD$_2$Cl$_2$</td>
<td>90.2</td>
</tr>
<tr>
<td>trans-Fe*(μ-CO)[μ-C(SMe)$_2$], 11</td>
<td>CD$_2$Cl$_2$</td>
<td>91.1</td>
</tr>
<tr>
<td>cis-Fe* (μ-CO)[μ-C(H)SMe], 15</td>
<td>CD$_2$Cl$_2$</td>
<td>87.5</td>
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<tr>
<td>cis-Fe*(μ-CO)[μ-C(H)SCH$_2$Ph], 16</td>
<td>CD$_2$Cl$_2$</td>
<td>86.9</td>
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<td>Fe'(4-DMAP)(CO)(μ-CO)(μ-CSMe), 20</td>
<td>CD$_3$CN</td>
<td>90.7</td>
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<td>Fe'(SePh)(CO)(μ-CO))(μ-CSMe), 22</td>
<td>CD$_2$Cl$_2$</td>
<td>88.9, 87.0</td>
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<tr>
<td>Fe'Co(CO)$_3$(μ-CO)$_2$(μ$_3$-CSMe), 33</td>
<td>CD$_2$Cl$_2$</td>
<td>86.6, 86.3</td>
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<tr>
<td>Fe'Co(PPh$_3$)(CO)$_2$(μ-CO)$_2$(μ$_3$-CSMe), 40</td>
<td>CD$_2$Cl$_2$</td>
<td>85.8, 85.3</td>
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</tbody>
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$^a$ Abbreviations: Fe* = Cp$_2$Fe$_2$(CO)$_2$, Fe' = Cp$_2$Fe$_2$.

$^b$ Bridging carbene or carbyne carbon.
<table>
<thead>
<tr>
<th>δ R</th>
<th>δ CO</th>
<th>δ μ-CO</th>
<th>δ μ-C</th>
</tr>
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<tr>
<td>38.2(Me)</td>
<td>207.4</td>
<td>252.3</td>
<td>408.3(μ-carbyne C)</td>
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<tr>
<td>25.6 and 24.1(Me)</td>
<td>210.9</td>
<td>270.9</td>
<td>186.9(μ-carbene C)</td>
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<tr>
<td>26.2(Me)</td>
<td>210.4</td>
<td>271.7</td>
<td>189.2(μ-carbene C)</td>
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<tr>
<td>27.5(Me)</td>
<td>211.5</td>
<td>272.7</td>
<td>169.9(μ-carbene C)</td>
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<tr>
<td>46.8(CH₂), 138.6, 128.8, 128.3 and 126.6(Ph)</td>
<td>210.9</td>
<td>272.5</td>
<td>163.7(μ-carbene C)</td>
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<tr>
<td>36.0(SMe), 39.0(NCH₃), 210.5 155.1, 153.5 and 108.9(py)</td>
<td>267.0</td>
<td></td>
<td>407.1(μ-carbyne C)</td>
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<td>32.8(Me), 135.3, 134.2, 127.1 and 124.2(Ph)</td>
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<td>261.3</td>
<td>403.3(μ-carbyne C)</td>
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<td>36.6</td>
<td>211.3, 262.1, 322.0(μ-carbyne C)</td>
<td>207.7(b), 252.1(b)</td>
<td>201.7(b)</td>
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<td>35.8(Me), 127-138(Ph)</td>
<td>212.4, 262.2, 317.7(d, J₀C = 15.9 Hz, μ-carbyne C)</td>
<td>205.8(b)</td>
<td>253.7(b)</td>
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</table>
two, equal intensity, singlets (2.71 and 2.55 ppm); the equivalent methyl groups of the trans isomer appear as a singlet (2.77 ppm). Integration of the methyl resonances shows a 2.7:1.0 ratio of cis:trans isomers.

The $^{13}$C NMR spectrum in CD$_2$Cl$_2$ (Figure 8) displays resonances at 186.9 (cis) and 189.2 (trans) ppm which, are characteristic of the $\mu$-C$_{\text{carbene}}$ in di-iron bridging carbene complexes. Other resonances in the spectrum are assigned to bridging carbonyls (271.7, 270.9 ppm), terminal carbonyls (210.9, 210.4 ppm), cyclopentadienyl (91.1, 90.2 ppm) and methyl carbons (26.2, 25.6, 24.1 ppm). Assignment of $^{13}$C resonances to a particular isomer is easily made on the basis of relative intensities. The magnetically nonequivalent methyl carbons of the cis isomer appear as two, equal intensity resonances at 24.1 and 25.6 ppm. Downfield from these, at 26.2 ppm, is the less intense methyl resonance for the trans isomer. Except for the terminal carbonyl, the trans isomer resonances all occur downfield from the cis isomer. Based on the relative intensities of the methyl resonances, the isomer ratio is 3.2:1.0 in favor of the cis form; approximately the same ratio, 2.7:1.0, was obtained in the proton spectra.

Complex 12, because it has two different mercaptan groups bonded to the $\mu$-carbene, may have three possible
Figure 8. The $^{13}$C NMR spectrum of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{C(SMe)}_2)$, 11, in $\text{CD}_2\text{Cl}_2$.
The relative stabilities of the isomers are expected to depend on the size of the SR substituents and the minimization of their interaction with the bulky Cp ligands. The larger Phenyl group should dictate the relative stability order: cis-12A > trans-12 > cis-12B.

The $^1$H NMR spectrum of 12 (in CDCl$_3$) shows three methyl resonances at 2.78, 2.57 and 2.41 ppm; their relative intensities decrease in the order 2.57 > 2.78 > 2.41. Based on the above argument, the structure assignments, cis-12A, trans-12 and cis-12B, respectively, are made. As in complex 11, the methyl resonance of the trans isomer is
downfield from the cis isomers' methyl resonances. The Cp resonances for cis-12A and cis-12B are at 4.95 and 4.93 ppm, respectively; the trans-12 Cp resonances apparently are coincident with the cis-12 Cp resonances.

The relative abundance of the cis and trans isomers for 11 and 12 vary with solvent polarity, with the cis configuration favored in polar solvents. For example, the 1.0:2.7, cis:trans, methyl resonance ratio for 11 in d^6-benzene becomes 2.7:1.0 in CDCl₃ and 5.2:1.0 in CD₃CN. The preference for cis-12 in polar solvents is illustrated by the ¹H NMR spectra shown in Figure 9. In these spectra the methyl resonance ratio (cis-12A + cis-12B)/trans-12 varies with solvent: 1.9:1.0 (CDCl₃), 3.7:1.0 (CD₂Cl₂), 10:1.0 (CD₃CN). Variation of the cis:trans ratio was also observed for Cp₂Fe₂(CO)₂(μ-CO)[μ-CMe₂] and Cp₂Fe₂(CO)₂(μ-CO)[μ-C(H)Me], where the ratios changed from 0.8:1.0 and 4:1 in d^6-toluene, to 2:1 and 13:1 in d^6-acetone, respectively. The greater preference for cis-Cp₂Fe₂(CO)₂(μ-CO)[μ-C(H)Me] in polar solvents is attributed to the large relative size difference of the carbene carbon substituents, which favors a cis configuration with the Me group anti to the Cp ligands as shown below:
FIGURE 9. The IR and 1H NMR spectra of \( \text{CP}_2\text{Fe}_2(\text{CO})_2(\text{p}-\text{co})\text{p}-\text{(SME)sp}[\text{I}2] \). In various solvents.
cis-$\text{Cp}_2\text{Fe}_2\text{(CO)}_2(\mu-\text{CO})[\mu-\text{C(H)Me}]$

However, this steric argument is not totally consistent with the results observed for 12. Although 12, with a bulky SPh substituent, shows a greater preference than 11 for a cis-configuration in polar solvents, the spectra in Figure 9 show that a significant amount of the sterically unfavored cis-12B isomer is present even in CD$_3$CN (cis-12A:cis-12B, 3:1). Thus, it would appear that other effects, which are not obvious, may also favor cis isomers in polar solvents.

These results discussed thus far, imply the existence of a cis $\leftrightarrow$ trans equilibrium. In CDCl$_3$, the equilibrium for 11 does not shift detectibly as the temperature is varied from $-50^\circ$C to $20^\circ$C. In CDCl$_3$, the methyl resonance ratio, (cis-12A + cis-12B)/trans-12, varies with temperature mainly due to changes in the relative amounts of the cis-12B and trans-12 isomers (Figure 10). At $0^\circ$C the (cis-12A + cis-12B)/trans-12 ratio is 2:3 and trans-12 is
Figure 10. Variable-temperature $^1$H NMR spectrum of the methyl resonances in Cp$_2$Fe$_2$(CO)$_2$(μ-C)[μ-C(SMe)SPh], 12, in CDCl$_3$. 
slightly more abundant than cis-12B. At 50°C the ratio is 1:4 and trans-12 is approximately twice as abundant as cis-12B. Equilibrium shifts towards the trans isomer with increasing temperature, have been reported for other di-iron μ-carbene complexes. For example, the cis:trans ratio for Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)Me) and Cp₂Fe₂(CO)₂(μ-CO)(μ-CMe₂) (in d⁸-toluene) decrease from 4.6:1.0 and 0.9:1.0 at 0°C to 2.2:1.0 (at 105°C) and 0.7:1.0 (at 75°C), respectively. Resonances for the Cp and Me groups of the cis and trans isomers of Cp₂Fe₂(CO)₂(μ-CO)(μ-CMe₂) coalesce at 114°C. Complex 11 rapidly decomposes to unidentified products above 80°C, without showing any signs of coalescence.

Above 25°C in CDCl₃, the Cp resonances for the trans-12 isomer are coincident with the cis-12A and cis-12B Cp resonances. At 0°C or lower the trans Cp ligands are observed as two singlets (5.00 and 4.78 ppm). This behavior may be due to an equilibrium between the syn and anti isomers shown in equation 46. These isomers may be caused by restricted rotation about the C_carbene-SPh bond. Terminal dithiocarbene complexes, Cp(CO)₂Fe[C(SR)SR']⁺, exhibit syn and anti isomers caused by the partial multiple bond character of the C_carbene-S bonds. In 12, greater
anti syn

trans-12

$^{\text{C}^{\text{carbene}}} - S$ pi bonding may occur for the PhS substituent due to its extended pi orbital system.$^{114}$

If the equilibrium in equation 46 favors the syn configuration at low temperature, the phenyl ring may spend a significant portion of its time in a position perpendicular to the Fe-Fe bond. This may result in a diamagnetic isotropic effect which causes the adjacent Cp ligand resonance to shift upfield by 0.2 ppm. The absence of Cp resonances for the syn configuration at 25°C may mean that the equilibrium
in equation 46 strongly favors the anti configuration at this temperature.

The IR spectra (Table 3) of the dithiocarbene and selenothiocarbene complexes show that both cis and trans isomers are present in solution, and that their relative abundance is dependent on the polarity (dielectric constant) of the solvent. This can be seen by reference to Figures 11 and 9, which display the IR spectra of 11 and 12, respectively. The spectra of 11 and 12 in CH$_3$CN (Figures 11a and 9a) are consistent with cis isomers. One strong and one weak, IR active, terminal carbonyl band is predicted for the cis isomer (C$_g$ symmetry), arising from the symmetric and antisymmetric stretching of this pair of carbonyls. In less polar solvents, a corresponding increase in the weak terminal carbonyl band is observed in Figures 11b and 9b (in CH$_2$Cl$_2$) and again in Figure 9c (in CHCl$_3$). For the trans isomer (local C$_2$ symmetry), only one IR active, terminal carbonyl band is predicted for the anti-symmetric stretching of the terminal carbonyl ligands. The growth of the low energy terminal CO band, in passing from Figures 11a and 9a to Figure 9c, can be attributed to an increase in the proportion of the trans isomer, whose single, terminal carbonyl band is degenerate with the weak band of the cis isomer. The bridging carbonyl bands of the
Figure 11. The infrared spectra of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO}) - \) [\( \mu-\text{C(SMe)}_2 \)], 11, in various solvents.
cis and trans isomers are of similar frequency. Figure 9 also shows that as the single terminal band for the trans isomer increases in less polar solvents, the trans-12 methyl resonance also increases.

In hexane, the antisymmetric band of the trans isomer of 11 (Figure 11c) is observed as a strong, separate, carbonyl band. The isomer ratio in the nujol spectrum of 11 (Table 3) is similar to Figure 11c, which may indicate that the hexane spectrum reflects the cis:trans isomer ratio in the solid state. After refluxing 11 in hexane for one hour, some of cis-11 is converted to trans-11, as evidenced by the decreased intensity of the terminal bands of cis-11 (Figure 11d). Conversion to the trans isomer does not occur (or is slow) upon stirring 11 in hexane for one hour at 25°C. Thus, it would appear that the cis and trans isomers are not at equilibrium at 25°C in hexane. The IR spectrum of 11 does not change significantly after refluxing 11 in CH₂Cl₂ for one hour. Apparently, the isomers of 11 achieve equilibrium rapidly in CH₂Cl₂.

c. **Interconversion of isomers** The spectral data show that all the possible isomers of 11 and 12 are observed in solution. Since 2 exists only as the cis isomer, the complexes 11 and 12, should be formed, initially, as the cis isomers, with the trans isomers being formed by
subsequent isomerization. The Adams-Cotton mechanism has been used to explain cis-trans isomerization of dinuclear metal systems with bridging ligands, including μ-carbene complexes. This mechanism (Figure 12) also adequately explains the cis-trans isomerization of 11. The cis form of 11 first undergoes a concerted bridge opening reaction to give a transient terminal carbene complex, which then may rotate about the metal-metal bond to bring the Cp ligands trans to each other. Bridge closure then generates the trans isomer.

A further explanation is required to account for the two cis isomers of 12, cis-12A and cis-12B. From equation 47, steric arguments would suggest that PhS⁻ attacks opposite the Cp ligands of 2 to give the cis-12A configuration. The Adams-Cotton mechanism, as discussed for 11, allows isomerization of cis-12A to trans-12. The third isomer observed, cis-12B, may have formed by PhS⁻ attack on the same side as the Cp ligands of 2 (Eqn 48). However,
Figure 12. Adams-Cotton mechanism for cis/trans isomerization of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{C(SMe)}_2)$, 11
this route may be sterically confining. Alternatively, cis-12B may form via the Adams-Cotton mechanism if the intermediate formed from cis-12A rotates the terminal carbene ligand to change the orientation of the SMe and OC groups relative to the Cp ligands (Figure 13). An Adams-Cotton mechanism involving rotation of the terminal carbene ligand during the unbridged intermediate stage, has been invoked to explain the coalescence of the methyl resonance (singlet and doublet \( J_{P,H} = 4 \text{Hz} \)) in \( \text{Cp}_2\text{Ru}_2^-(\text{PMe}_2\text{Ph})(\text{CO})(\mu-\text{CO})(\mu-\text{CMe}_2) \).^67

\[ \text{cis-12B} \]

\[ \text{2} \]

d. Reactivity of 11 and 12

1) With \( \text{HBF}_4-\text{Et}_2\text{O} \) Reaction of 11 with \( \text{HBF}_4-\text{Et}_2\text{O} \) gives cis-\( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^+ \), 2. Although trans-11 is approximately 33% abundant in \( \text{CH}_2\text{Cl}_2 \), no trans-2 is produced. Either trans-2 rapidly converts to cis-2 or trans-11 rapidly isomerizes to allow Et\(_2\)OH\(^+\) to attack the SMe group opposite the cis Cp ligand of cis-11.
Figure 13. Isomerization of cis-12A to cis-12B
The reaction of $^{12}$ with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ gives 2 and $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSPh})^+$, 36 (Eqn 49). This reaction is solvent dependent. In $\text{CH}_3\text{CN}$, where the cis-$^{12A}$ isomer predominates over the cis-$^{12B}$ isomer by a 3:1 ratio, the reaction gives by $^1\text{H}$ NMR a 50/50 mixture of 36 and 2. In $\text{CH}_2\text{Cl}_2$, all three isomers are present in significant amounts (trans-$^{12}$:cis-$^{12A}$:cis-$^{12B}$, ca. 1:2:1), and the product yield is 7:1 in favor of 36. Based on the pKa value$^{116}$ of MeSH (10.3) and PhSH (6.5), the MeS group might be expected to bond more strongly to the carbene carbon than the PhS group, resulting in 2 being the favored product in equation 49. Alternatively, the pKa values suggest that the MeS group would have a greater affinity for the
Et₂OH⁺ than the PhS group, which would favor production of 36. The affinity of the MeS group for Et₂OH⁺ may be enhanced, if an extended pi orbital system through the C_carbene-SPh portion of 12 results in greater interaction of the PhS group with the carbene carbon. If preferred attack is at the MeS group, then the product ratio obtained in CH₃CN is low; this may be due to steric effects. If attack by Et₂OH⁺ at the MeS group is sterically hindered, but not prevented, by the bulky Cp ligand in cis-12A, then attack at PhS may compete with the reaction at MeS group. Alternatively, if reaction at SMe is prevented, isomerization to cis-12B has to occur, where displacement of the SMe group will be less sterically hindered.

The greater production of 36 in CH₂Cl₂ may be the result of 1) less cis-12A initially present, 2) isomerization of cis-12A and trans-12 to cis-12B, which allows attack by Et₂OH⁺ at a less sterically confining SMe group and 3) less polar solvents which may retard dissociation of the ion pair reagent, Et₂OH⁺-BF₄⁻,¹¹⁷ allowing the above isomerization to proceed further than in CH₃CN.

Complex 36, which was not isolated, has the typical IR spectrum observed for other μ-thiocarbyne cations; CH₃CN: 2049(s), 2017(sh), 1856(m) cm⁻¹. The ¹H NMR spectrum of 36 (in d⁶-acetone) has a larger chemical shift difference
(0.58 ppm) for the Cp resonances than in other thiocarbyne cations: 2 (0.09 ppm), 3 (0.13 ppm) and 4 (0.05 ppm). The secondary carbon, bound to the sulfur atom in 36, obviously has greater steric requirements than the primary carbon in 2, 3 and 4. An extended pi orbital system may exist in 36, which hinders free rotation about the S-C(phenyl) and C_{carbene}-S bond, causing the phenyl ring to spend a significant portion of its time in the Fe(μ-C_{carbene})Fe plane. This orientation, which is sterically more confining than if free rotation is allowed, brings the Cp and Ph rings closer together, resulting in a greater magnetic nonequivalence for the Cp resonances in 36 compared to other thiocarbyne cations. However, the phenyl ring itself could cause the large chemical shift difference for the Cp resonance.

2) Oxidation reaction of 11 and 12

The cyclic voltammograms of 11 and 12 have irreversible oxidation waves at 0.43 V and 0.48 V, respectively. Chemical oxidation of 11 and 12 (in CH₂Cl₂) with I₂, C₇H₇⁺, Ph₃C⁺ and Cp₂Fe⁺ give clean reactions (by IR analysis) to produce Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe)⁺, 2. An odor indicative of CH₃SSCH₃ was produced in the oxidation of 11, while the ¹H NMR spectrum for the reaction of 12 with I₂ shows a multiplet at 7.1 to 7.6 ppm for PhSSPh. Even though all three isomers of 12 are present in CH₂Cl₂ (trans-12:cis-12A:cis-
12B, ca. 1:2:1), oxidation of 12 did not produce Cp₂Fe₂-(CO)₂(μ-CO)(μ-CSPh)⁺, 36. If steric effects limited the oxidation reactions to the cis isomers of 12, then both 2 and 36 should have been formed. The fact that 36 is not produced, indicates that the PhS group is preferentially oxidized. This result may be explained if the oxidation reaction takes place in two steps: 1) an electron transfer from the bridging dithiocarbene complex to the oxidant that results in the formation of a radical cation, Cp₂Fe₂(CO)₂-(μ-CO)[μ-C(SR)₂]⁺ and 2) subsequent loss of a RS⁺ radical by the radical cation to give a μ-thiocarbyne cation. The RS⁺ radical product could then couple to produce a disulfide. Since PhS⁺ radicals are more stable than MeS⁺ radicals,¹¹⁸ the oxidation of 12 should produce 2 and PhSSPh. A similar mechanism was proposed for the oxidation of Cp₂Ru₂(dppm)(μ-CO)(μ-CH₂).²⁸ Oxidation of this μ-carbene complex is reported to give a radical cation which then loses a hydrogen atom to give Cp₂Ru₂(dppm)(μ-CO)(μ-CH)⁺.

Oxidation of 11 and 12 is quite different than the oxidation reaction of Cp(CO)Fe[μ-C(SMe)₂]Co(CO)₂, 52, which gives the terminal carbene product, [CpFe(CO)₂C(SMe)₂]⁺ in 75% yield.¹¹⁹ The difference in reactivity may be due to the special nature of the μ-carbene ligand in 52, which has one of the sulfur substituents coordinated to cobalt.
Donation of electron density from sulfur to cobalt may make 52 less susceptible to oxidation at the C_carbene-S bond and shift the oxidation, instead, to the metal-metal bond.

3) CO substitution reactions of 11, 12 and 23

Photolyzing or refluxing a solution of 12 causes the dithiocarbene complex to lose CO and form the brownish-black μ-carbyne complex, Cp_2Fe_2(SPh)(CO)(μ-CO)(μ-CSMe), 38 (Eqn 50). The thermal reaction gives a higher yield of 38

(54 vs 20%). Photolyzing or refluxing 11 under the conditions of equation 50 results in decomposition products of an unknown nature. The purple μ-carbene complex, Cp_2Fe_2-(CO)_2(μ-CO)[μ-C(SMe)SePh], 23, is even more reactive than 12, transforming at 0°C (especially under vacuum) into the
brownish-black, μ-carbyne complex, Cp₂Fe₂(SePh)(CO)(μ-CO)(μ-CSMe), 22; the yield of 22 is 32%. Crystals of 22 and 38 are stable indefinitely at -20°C under nitrogen. The μ-carbyne products are soluble in most common organic solvents except hexane. Solutions of 22 and 38 are moderately air-sensitive especially if warmed above 40°C.

Single terminal and single bridging carbonyl absorptions in the IR spectra (Table 3) of complexes 22 and 38 are observed at approximately 1983 and 1803 cm⁻¹. The ¹H NMR spectrum of 22 in CDCl₃ shows nonequivalent Cp resonances at 4.84 and 4.75 ppm, and a methyl resonance at 3.39 ppm. A similar spectrum in CDCl₃ (Table 4) was observed for 38; Cp: 4.84 and 4.80 ppm, Me: 3.39 ppm. The downfield methyl resonances at 3.39 ppm for both 22 and 38 are close to the chemical shift (3.74 ppm, d⁶-acetone) observed for the μ-CSMe group of the neutral μ-carbyne complex, Cp₂Fe₂(I)(CO)(μ-CO)(μ-CSMe), 10.

The ¹³C spectrum of 22 (Table 5) does not show a resonance for a μ-carbene carbon between the terminal CO (212.9 ppm) and the phenyl group carbons (124-135 ppm). An extreme downfield resonance does occur at 403.3 ppm for a μ-carbyne carbon. The cation [Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe)]⁺ shows a μ-carbyne carbon resonance at 408.3 ppm. Neutral, heteronuclear μ-carbynes typically show resonances at lower
field than 400 ppm for the carbyne carbon, e.g. \[
\{(C_6H_5)_{\mu}(CO)\Cr(\mu-CO)(\mu-C_6H_4M-4)W(CO)_{2}Cp\},
\]
430.9 ppm. Thus, the NMR data indicate that 22 and 38 are bridging carbyne complexes. Because 10 and other \(\mu\)-carbyne complexes have a cis configuration, 22 and 38 most likely have a cis structure. For steric reasons, a cis structure for 22 and 38 is more favorable than a trans configuration. Molecular models of 22 and 38 show that in the trans isomers, free rotation of the PhS or PhSe group about the Fe-S or Fe-Se bond would be hindered by the bulky Cp ligand on the adjacent Fe atom.

The transformation of the \(\mu\)-carbene complex, 12, to the \(\mu\)-carbyne complex, 38, is interesting because: 1) 12 exists as an isomeric mixture and it converts to essentially one product, cis-Cp_2Fe_2(SPh)(CO)(\(\mu\)-CO)(\(\mu\)-CSMe), and 2) the isomers of 12 rapidly interconvert to maintain an equilibrium mixture during the synthesis of 38. Examination of the \(^1H\) NMR spectrum of 12 in CDCl_3 at 50°C, shows that the 1:2:1 ratio of trans-12:cis-12A:cis-12B does not change over a 2 hour period as 38 grows in. A total of four isomers of 38 could have been produced from the three isomers of 12 (Figure 14). Only small amounts of two other isomers appear to be produced. In the \(^1H\) NMR spectrum of 38 (cis-38A) additional resonances are observed at 4.96 and
Figure 14. Possible isomers obtainable from the conversion of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-C(\text{SMe})\text{SPh}) \), 12, to \( \text{Cp}_2\text{Fe}_2(\text{SPh})(\text{CO})(\mu-\text{CO})(\mu-C(\text{SMe})) \), 38
4.75 ppm (Cp), and 3.55 ppm (Me) for the trans-38A isomer (5%), and at 4.62 and 4.50 ppm (Cp), and 1.50 ppm (Me) for the structural isomer (7%), Cp₂Fe₂(SMe)(CO)(μ-CO)(μ-CSPh). The structure of the trans-38A isomer was assigned on the basis of its similar 1H NMR spectrum to cis-38A. The methyl resonance of the structural isomer has approximately the same chemical shift as the SMe group in CpFe(CO)₂SMe, 1.61 ppm.¹²¹ It is not certain whether the structure is cis-38B or trans-38B. However, the preference for cis configuration in μ-carbyne complexes would favor cis-38B. No other isomers were observed in the 1H NMR spectrum of 22.

Although 12 loses CO to form 38, it does not react in CH₂Cl₂ at 25°C with PEt₃ to form Cp₂Fe₂(PEt₃)(CO)(μ-CO)[μ-C(SMe)SPh]. Surprisingly, in refluxing CH₂Cl₂, the reaction with PEt₃ gives the green carbyne cation Cp₂Fe₂(PEt₃)-(CO)(μ-CO)(μ-CSMe)+, 8, and a small amount of 38. Formation of 8 may be explained by a reaction sequence involving: 1) formation of 38 under refluxing conditions and 2) oxidation of 38 (by adventitious oxygen) in the presence of PEt₃. Independently, 38 does not react with PEt₃ in refluxing CH₂Cl₂ under anaerobic conditions; however, exposure of the reaction mixture to air produces 8 within three minutes. The facile oxidation of 38 is also observed
in its CV which shows a quasi-reversible oxidation wave at + 0.20 V.

2. Bridging hydridothiocarbene complexes
   a. Preparation and properties  Treatment of the thiocarbene cations, Cp₂Fe₂(L)(CO)(μ-CO)(μ-CSR)⁺, (L = CO, CH₃CN; R = CH₃, Ph, CH₂Ph, CH₂CH=CH₂) with NaBH₄ causes a rapid addition of H⁻ to the carbyne carbon to generate bridging hydridothiocarbene complexes (Eqn 51). Depending on the method of crystallization, the complex, Cp₂Fe₂(CO)₂⁺·(μ-CSR)[μ-C(H)SMel], can be obtained as the predominantly (ca. 80%) trans isomer, 14, or as the cis isomer, 15.

\[ \text{Cp}_2\text{Fe}_2(CO)_2 + \text{BH}_4^- \xrightarrow{0^\circ-25^\circ C} \text{Cp}_2\text{Fe}_2(CO)_2(SR) \]

L = CO, R = CH₃ (14, 64%)
L = CO, R = CH₃ (15, 60%)
L = CO, R = CH₂Ph (16, 72%)
L = CO, R = CH₂CH=CH₂ (17, 76%)
L = CO, R = Ph (37)
L = CH₃CN, R = CH₃ (18)
Crystallization from CH$_2$Cl$_2$/hexane at room temperature (18 hours) and then at -20°C (16 hours) gives Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-C(H)SMe] as a mixture of light red (trans) and dark red (cis) crystals; the $^1$H NMR spectrum of this product shows a 1:4 ratio of cis:trans isomers. Shortening the crystallization time at room temperature to six hours gives Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-C(H)SMe] as a 1:1 ratio of 14:15. The cis isomer, 15, is obtained by crystallizing Cp$_2$Fe$_2$(CO)(μ-CO)[μ-C(H)SMe] from acetone/hexane at -20°C. In contrast, Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-C(H)SCH$_2$Ph], 16, is obtained only as the cis isomer even though it is crystallized from CH$_2$Cl$_2$/hexane at room temperature. Apparently, the bulky benzyl group favors a cis configuration so much that other isomers are not formed in significant amounts to precipitate. The ability to separate the cis isomers, 15 and 16, is unusual for di-iron u-carbene complexes. In other di-iron systems [Cp$_2$Fe$_2$(CO)$_2$(μ-C(R)R')], R = H, alkyl; R' = alkyl; Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-C(H)OME]] the cis/ trans isomerization is so rapid in solution that separation of the isomers is not possible. The allyl complex, Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-C(H)SCH$_2$CH=CH$_2$], 17, also crystallizes (from CH$_2$Cl$_2$/hexane) as several different forms, apparently, due to the presence of several different isomers. Reasonable yields are obtained for the complexes 14, 15, 16 and 17. No yield
was determined for 37 since it was synthesized on a microscale. Its red color and similar IR spectrum in CH$_3$CN to those of 14, 15, 16 and 17 (Table 3), identifies 37 as the $\mu$-hydridothiocarbene complex, Cp$_2$Fe$_2$ (CO)$_2$ ($\mu$-CO) ($\mu$-C(H) SPh). The brown complex, 18, Cp$_2$Fe$_2$ (CH$_3$CN) (CO) ($\mu$-CO) ($\mu$-C(H) SMMe), was not isolated since it was used as an intermediate to prepare the PMe$_2$Ph derivative of 15, Cp$_2$Fe$_2$ (PMe$_2$Ph) (CO) ($\mu$-CO) ($\mu$-C(H) SMMe). The bridging hydridothiocarbene complexes 14, 15, 16, 17 and 37 are light to dark red, crystalline solids, soluble in most common organic solvents (CH$_3$CN, acetone, CH$_2$Cl$_2$, CHCl$_3$ and benzene) and are stable indefinitely at -20°C under nitrogen. Crystals of trans-Cp$_2$Fe$_2$ (CO)$_2$ ($\mu$-CO) ($\mu$-C(H) SMMe) decompose to insoluble products after several months at 25°C under nitrogen. Crystals of the cis isomer are stable under the same conditions.

b. Spectroscopic properties

The two different substituents on the carbene carbon and the possibility of hindered rotation about the C$_{carbene}$-S bond, make it necessary to consider the possible existence of six isomers of the Cp$_2$Fe$_2$ (CO)$_2$ ($\mu$-CO) ($\mu$-C(H) R) complexes. These are shown in Figure 15. Based on the steric interactions between Cp ligands and the SR groups (observed from molecular models), the stability order should be cis-syn > cis-anti > trans-syn > trans-anti > cis$\text{I}$-syn > cis$\text{I}$-anti. Because of the
stability order: cis-syn > cis-anti > trans-syn >
trans-anti > cis-syn > cis-anti

Figure 15. The six possible isomers of the μ-hydridothio-carbene complexes, Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)SR)
steric requirements of the sulfur atom's free electron pairs, the trans-anti configuration may become more stable than the trans-syn configuration when the size of the R substituent decreases to that of a methyl group. The cisᵢ isomers are the expected initial products resulting from attack by BH₄⁻ on the carbyne carbon on the side opposite the Cp ligands of the thiocarbyne cations in equation 51. Methine ¹H NMR resonances for the cisᵢ isomers should occur at approximately 8.5 ppm. However, since the reactions are performed in acetonitrile, and the fact that the ¹H NMR of Cp₂Fe₂(CO)₂(μ-CO)[μ-C(H)SR] complexes in d⁶-acetone or CD₃CN give spectra indicative of cis isomers with methine resonances at approximately 11.6 ppm, the cisᵢ isomer most likely converts to the cis-syn configuration during the reaction. Because of their relative instability, the cisᵢ isomers are probably not observed.

The IR and ¹H NMR data for the hydridothiocarbene complexes are presented in Tables 3 and 4, respectively. The noteworthy feature of the ¹H NMR spectra is the downfield resonance between 10-12 ppm, which is characteristic for the methine proton of di-iron μ-carbene complexes. As was the case for the IR spectra of μ-dithiocarbene complexes, the weak terminal and bridging carbonyl bands of the hydridothiocarbene cis isomers are nearly
degenerate with the single terminal bridging carbonyl bands of their trans isomer. In CH$_3$CN, the complexes 14, 15, 16, 17 and 37 show a strong, weak and medium carbonyl band pattern with $\nu$(CO) absorptions in the regions 1978-1973, 1942-1937 and 1784-1778 cm$^{-1}$. This band pattern is in agreement with a cis configuration (C$_s$ symmetry) for these complexes in polar solvents (acetone and CH$_3$CN). The $^1$H NMR spectra of 14, 15 and 16 in either of these solvents supports this, since they all show a single methine resonance at approximately 11.6 ppm and a singlet for the equivalent protons of Cp ligands. Based on the stability order presented in Figure 15, these cis isomers are probably of the cis-syn configuration. It is important to note that trans-Cp$_2$Fe$_2$(CO)$_2$($\mu$-CO)[($\mu$-C(H)SMe), 14 gives the same IR and $^1$H NMR spectra as 15, cis-Cp$_2$Fe$_2$(CO)$_2$($\mu$-CO)[($\mu$-C(H)SMe]. Since these spectra were taken immediately after dissolution, the isomerization from trans to cis must be thermodynamically favorable and rapid ($<<$ 5 min.) in CH$_3$CN and acetone. This behavior has been observed in other di-iron $\mu$-carbene complexes, including the $\mu$-dithiocarbene complexes discussed in Section III.B.1. In contrast to the $\mu$-dithiocarbene complexes, the large relative size difference of the carbene substituents in Cp$_2$Fe$_2$(CO)$_2$($\mu$-CO)[($\mu$-C(H)SMe] and Cp$_2$Fe$_2$(CO)$_2$($\mu$-CO)[($\mu$-C(H)SCH$_2$Ph] results in a much
greater preference for the cis configuration in polar solvents (i.e. complete conversion). The IR spectra of 15 and 16 maintain the strong, weak and medium, carbonyl pattern consistent with the cis configuration in CH₂Cl₂ and hexane. In CDCl₃, the ¹H NMR spectra of 15 and 16 still show single methine and Cp resonances. Thus, the IR and ¹H NMR data for 15 and 16 indicate that cis-syn isomers of Cp₂Fe₂(CO)₂(μ-C(H)SMe) and Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)SCH₂Ph) do not rapidly isomerize to trans isomers in less polar solvents (see Section c. below for slow isomerization in this solvent). This behavior is unusual for di-iron bridging carbene complexes. In general, these complexes, including Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)OMe)²⁷ and μ-dithiocarbene complexes (e.g. Cp₂Fe₂(CO)₂(μ-CO)(μ-C(SMe)₂)), undergo rapid cis/trans isomerization in most solvents (the μ-dithiocarbene complex Cp₂Fe₂(CO)₂(μ-CO)(μ-C(SMe)₂) isomerizes slowly in hexane) with the equilibrium shifting towards the trans isomer in less polar solvents. The behavior of μ-hydridothiocarbene complexes is similar to the μ-vinylidene complex, Cp₂Fe₂(CO)₂(μ-CO)(μ-CH=CH₂), which undergoes cis/trans isomerization slowly (in toluene) at room temperature, and at a significant rate only at 110°C.³⁰

The ¹H NMR spectra of 14 and 17 show isomeric mixtures in CDCl₃. Besides resonances for a small amount of the cis
isomer (i.e. 15), the spectrum of trans-Cp₂Fe₂(CO)₂(μ-CO)[μ-C(H)SMe], 14, exhibits resonances at 10.03 (methine), 4.94 and 4.83 (Cp), and 2.72 (Me) ppm. It should be emphasized that the resonances for 15 observed in the ¹H NMR spectrum of 14 are due to a small amount of 15 which is isolated with 14 (mixture of light red (trans) and dark red (cis) crystals), and not due to isomerization of 14 to 15. Thus, in contrast to the rapid trans to cis isomerization which occurs for Cp₂Fe₂(CO)₂(μ-CO)[μ-C(H)SMe] in polar solvents, the trans to cis isomerization is slow in less polar solvents. Based on the order of isomer stability presented in Figure 15, 14 might be the trans-syn isomer. However, the data from the ¹H NMR temperature study presented in part c below, indicates that 14 has the trans-anti configuration. The allyl complex, Cp₂Fe₂(CO)₂(μ-CO)[μ-C(H)SCH₂-CH=CH₂], 17, shows three methine resonances in CDCl₃ at 11.61, 11.37 and 11.21 ppm, which are similar to the methine chemical shifts of cis-15 and 16 in CDCl₃. Therefore, two of the three methine peaks may correspond to the cis-syn and cis-anti isomers of 17. Because of the large relative size difference of the carbene substituents, another cis configuration with the allyl group syn to the Cp ligands is unlikely. Expansion of the ¹H NMR spectrum of 17 in the Cp region, though, reveals four signals, two
of which are of equal intensity at 4.78 and 4.77 ppm. Because of this and the observation that the IR spectrum of 17 in CDCl₃ shows a medium intensity carbonyl band at 1957 cm⁻¹ for the trans isomer, one of the methine resonances must be due to trans-Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)SCH₂CH=CH₂). Since 37 was prepared on a micro-scale, no ¹H NMR data were obtained. Complexes 14 and 17 have broad and asymmetric IR bands in CH₂Cl₂. The broadness and asymmetry of the bands is apparently due to the presence of several isomers. The near degeneracy of the carbonyl bands makes interpretation of the spectra difficult. However, it is obvious from comparing the spectra of 14 and 15 in CH₂Cl₂, that cis/trans isomerization is slow in this solvent also.

The ¹³C NMR data for cis-Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)SMe), 15, and cis-Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)SCH₂Ph), 16, are presented in Table 5. The resonances at 169.9 ppm for 15 and at 163.7 ppm for 16 are characteristic of μ-carbene carbons in di-iron μ-carbene complexes.¹¹¹ The carbene chemical shifts for 15 and 16 occur at higher field than the carbene chemical shifts of Cp₂Fe₂(CO)₂(μ-CO)(μ-C(SMe))₂ (cis, 186.9 ppm; trans, 189.2 ppm) and of μ-alkylidene complexes Cp₂Fe₂(CO)₂(μ-CO)(μ-(H)R) [R = CH₃ (173 ppm), Et (183 ppm), Bz (178 ppm)], and at significantly higher field compared to Cp₂(CO)₂(μ-CO)(μ-C(H)OMe) (cis, 216.7 ppm; trans, 214.0
The carbene chemical shifts for 15 and 16 however, occur at lower field than the carbene chemical shift of \( \text{Cp}_2\text{Fe}_2(\mu-\text{CO})_2(\mu-\text{CH}_2) \), 142 ppm.\(^{27}\) Thus, the order of decreasing chemical shifts for these carbene complexes is: \( \mu-\text{C(H)OMe} > \mu-\text{C(SMc)}_2 > \mu-\text{C(H)R} > \mu-\text{C(H)SR} > \mu-\text{CH}_2 \). For terminal carbene complexes of iron, \( \text{Cp}(\text{CO})_2\text{Fe}=\text{C}(\text{X})\text{Y}^+ \) (where \( \text{X} \) and \( \text{Y} = \text{H, NR}_2, \text{OR, SR, and/or SeR} \)), the decreasing chemical shifts order is: \( \text{C(H)SR} = \text{C(SR)(SeR)} \) (320 ppm) > \( \text{C(SR)}_2 \) (308 ppm) > \( \text{C(OR)SR} \) (300 ppm) > \( \text{C(OR)}_2 \) (250 ppm) > \( \text{C(NR}_2)_2 \) (200 ppm). The hydridothiocarbene and dithiocarbene complexes which are common to both orders, have opposite relative positions for their carbene chemical shifts. This order reversal for bridging and terminal carbene chemical shifts was observed by Matachek.\(^{122}\)

c. Isomerization of hydridothiocarbene complexes

Complexes 15 and 16 are unique di-iron \( \mu \)-carbene complexes; these are the first reported examples of di-iron \( \mu \)-carbene complexes that have been isolated (by crystallization) as one isomeric configuration. The ability to separate these isomers may be attributed to a stable cis-syn configuration and slow cis/trans isomerization in non-coordinating solvents (e.g. \( \text{CH}_2\text{Cl}_2 \), hexane). It is likely that the Adams-Cotton mechanism for cis/trans isomerization proposed for \( \mu \)-dithiocarbene complexes (Figures 12 and 13), applies to
cis/trans isomerization of μ-hydridothiocarbene complexes. However, μ-dithiocarbene complexes undergo rapid cis/trans isomerization in most solvents (except hexane), while μ-hydridothiocarbene complexes isomerize rapidly only in CH₃CN and acetone. Di-iron complexes which are assumed to undergo cis/trans isomerization via the Adams-Cotton mechanism are known to do so at different rates depending upon the nature of the μ-ligands. Qualitatively, the isomerization rate (in toluene or benzene) decreases in the order

\[
\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})_2 > \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CS}) > \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CMe}_2) > \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{C}=\text{CH}_2)\].^{30,71,111}

Thus, μ-dithiocarbenes behave similarly to other μ-carbene systems and the μ-hydridothiocarbenes act more like μ-vinylidenes. This feature may be attributed to the ease with which the dithiocarbene ligand leaves the bridging mode, compared to the hydridothiocarbene ligand, and may be related to the relative stability of the terminal carbene intermediate formed during the Adams-Cotton mechanism. In the case of terminal carbene compounds, CpFe(CO)₂=C(X)SR⁺ (X = H, SR), the dithiocarbene complexes (X = SR) are known to be quite stable relative to the hydridothiocarbene complexes (X = H).^{113,123} If the same order of stability applies to the μ-carbene systems, then cis/trans isomerization for μ-hydridothiocarbene complexes may be slower than
the μ-dithiocarbene complexes; this may be attributed to a thermodynamically less favorable terminal carbene intermediate stage. However, rapid cis/trans isomerization in CH₃CN and acetone may be caused by interactions of these solvents with the carbene carbon during the terminal carbene intermediate stage, resulting in stabilization of this intermediate. That this may be so, is evidenced by the weak interaction of CH₃CN with CpFe(CO)$_2$C(H)SMe$, and the fact that adducts of {CpFe(CO)$_2$[CH(SMe)L]$^+$} with Lewis bases such as phosphine, phosphite and pyridine are stable compounds.$^{123}$

In an effort to observe the slow cis/trans isomerization of 15 and 16, the $^1$H NMR spectra of these complexes were taken as a function of time and temperature. The data, presented in Tables 6 and 7 for 15 and 16, respectively, show two types of isomerization: 1) a slow cis/trans isomerization and 2) a faster cis-syn/cis-anti isomerization. After 2 hours at 45°C, 16 shows significant isomerization between two cis configurations. Based on the isomer order of stability presented in Figure 15, this conversion is from cis-syn (methine resonance at 11.43 ppm) to cis-anti (methine resonance at 10.57 ppm), and is probably the result of rotation about the C$_{carbene}$-S bond. Rotation about this bond may be hindered due to partial
Table 6. Variation of the $^1$H NMR of 15 in CDCl$_3$ with time and temperature

<table>
<thead>
<tr>
<th>°C (time)$^a$</th>
<th>Cp (ppm)</th>
<th>Methine$^b$ (ppm)</th>
<th>Methine Ratio$^c$</th>
<th>cis:trans$^d$</th>
<th>syn:anti$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (start)</td>
<td>4.77</td>
<td>11.47</td>
<td>-</td>
<td>very large</td>
<td>very large</td>
</tr>
<tr>
<td>30 (1 hr)</td>
<td>4.77(cis)$^f$</td>
<td>11.47, 10.57</td>
<td>15:2.9:1.0</td>
<td>18</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>4.80(trans)$^g$</td>
<td>9.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 (2 hr)</td>
<td>4.77(cis)$^f$</td>
<td>11.47, 10.57</td>
<td>9.7:2.3:1.0</td>
<td>13</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>4.80, 4.79 (trans)</td>
<td>9.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 (1.5 hr)</td>
<td>4.77(cis)$^f$</td>
<td>11.47, 10.57</td>
<td>7.1:2.3:1.0</td>
<td>9.4</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>4.80, 4.79 (trans)</td>
<td>9.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 (1 hr)</td>
<td>4.77(cis)$^f$</td>
<td>11.47, 10.57</td>
<td>7.0:2.3:1.0</td>
<td>9.3</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>4.80(trans)$^g$</td>
<td>9.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------</td>
<td>---------------</td>
<td>-------------------</td>
<td>-------</td>
<td>-------------------</td>
</tr>
<tr>
<td>0 (0.5 hrs)</td>
<td>4.77 (cis)</td>
<td>11.47, 10.57</td>
<td>8.0:2.8:1.0</td>
<td>11</td>
<td>2.9</td>
</tr>
<tr>
<td>4.80, 4.79 (trans)</td>
<td>9.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 (4 days)</td>
<td>4.77 (cis)</td>
<td>11.47, 10.57</td>
<td>2.0:1.0:6.0</td>
<td>0.5</td>
<td>2.0</td>
</tr>
<tr>
<td>4.94, 4.83</td>
<td>10.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Length of time sample was at indicated temperature before spectrum was taken.
b) Methine resonance assignments: 11.47 (cis-syn), 10.57 (cis-anti), 9.18 (trans-syn), 10.03 (trans-anti).
c) Ratio of cis-syn:cis-anti:trans-syn or anti.
d) Ratio of (cis-syn + cis-anti):trans-syn or anti.
e) Ratio of cis-syn:cis anti.
f) Cp resonances of cis-syn and cis-anti isomers are not resolvable.
g) Nonequivalent Cp resonances of trans-syn isomer are not resolvable.
h) Sample sat at 25°C (ca. 2 days) and then at -20°C (ca. 2 days) prior to obtaining spectrum.
i) Spectra taken 0.5 hours after cooling from 50°C to 0°C.
Table 7. Isomerization of 16 in CDCl$_3$ at 45°C

<table>
<thead>
<tr>
<th>hours</th>
<th>Cp (ppm)</th>
<th>Methine$^a$ (ppm)</th>
<th>Methine Ratio$^b$</th>
<th>cis:trans$^c$</th>
<th>syn:anti$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.53</td>
<td>11.43</td>
<td>-----</td>
<td>very large</td>
<td>very large</td>
</tr>
<tr>
<td>2</td>
<td>4.53, 4.50</td>
<td>11.43, 10.57</td>
<td>-----</td>
<td>very large</td>
<td>5.8</td>
</tr>
<tr>
<td>4</td>
<td>4.53, 4.50(cis) 11.43, 10.57</td>
<td>8.7:2.2:1.0</td>
<td>11</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.68, 4.63(trans) 9.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.53, 4.50(cis) 11.43, 10.57</td>
<td>6.5:1.8:1.0</td>
<td>8.3</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.68, 4.63(trans) 9.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Isomer assignment: 11.43 (cis-syn), 10.57 (cis-anti), 9.20 (trans-syn).


$^c$ Ratio of (cis-syn + cis-anti):trans-syn.

$^d$ Ratio of cis-syn:cis-anti.
multiple bond character brought about by an 'sp\(^2\)' hybridized sulfur donating a free pair of electrons into the 'p' acceptor orbital of the carbene carbon:

\[
\begin{array}{c}
\text{Fe} \\
\text{Fe} \\
\end{array}
\begin{array}{c}
\text{C} \\
\text{S} \\
\end{array}
\begin{array}{c}
\text{H} \\
\text{R} \\
\end{array}
\]

The last column in Table 7 shows that the product ratio cis-syn:cis-anti decreases with time, indicating that the configurations are not at equilibrium even after 5 hours. After four hours, resonances for a trans isomer of 16 are observed and continues to increase in intensity after five hours. This isomer is most probably the trans-syn isomer of 16 (see Figure 15) because this configuration has significantly fewer steric interactions (as observed from molecular models) between the SCH\(_2\)Ph group and an adjacent Cp ligand compared to the trans-anti isomer. If the cis-anti and trans-syn isomers form directly from the cis-syn isomer, then the syn/anti isomerization occurs faster than cis/trans isomerization. This might be expected, since the activation energy needed for rotation about the C\(_{\text{carbene-S}}\) bond, is probably less than the activation energy (ca. 20
169

kcal/mol) required for cis/ trans isomerization of di-iron bridging carbene complexes (e.g. \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CMe}_2) \)). The methine resonances, which appear on warming 15 in CDCl\(_3\) (Table 6), have very similar chemical shifts to those observed for 16. Thus, the isomeric changes that occur for 16, most probably, apply to 15: slow conversion from the cis-syn isomer (methine resonance at 11.47 ppm) to a cis-anti isomer (methine resonance at 10.57 ppm) and a slower cis/trans isomerization to give the trans-syn isomer (methine resonance at 9.18 ppm).

The second to the last set of data in Table 6 shows that the isomeric changes that occur at higher temperatures (30-50°C) are not readily reversible on cooling to 0°C. The cis/trans ratio does show an increase from 9.3 at 50°C to 11 at 0°C. However, the syn:anti ratio shows a small decrease, indicating that isomerization toward the cis-anti isomer is still occurring. The last set of data in Table 6 is quite interesting, since it shows a significant amount of the trans-anti isomer (methine resonance at 10.03 ppm) of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{C(H)SMe}) \), 14. This isomer formed by allowing the CDCl\(_3\) solution of 15 to sit for 4 days (2 days at 25°C and 2 days at -20°C). The dominant trans-anti methine resonance in this spectrum, and the absence of a trans-syn methine resonance at 9.19 ppm, indicates that
conversion to a trans configuration is favored in CDCl₃, and that the trans-anti isomer of Cp₂Fe₂(CO)₂(μ-CO)[μ-C(H)SMe] is more stable than the trans-syn isomer:

(Note: for clarity, the electron pair on sulfur involved in bonding to the carbene carbon is not shown in these structures.)

It has been shown in this work, and by others,¹¹¹ that trans isomers of μ-carbene complexes of iron are favored over cis isomers in low polarity (non-coordinating) solvents (i.e. CHCl₃, benzene, hexane). However, it is not obvious why the trans-anti isomer of Cp₂Fe₂(CO)₂(μ-CO)[μ-C(H)SMe] should be more favorable than the trans-syn isomer. Possible explanations are 1) that the steric interactions between the Cp ligand and the Me group in the trans-anti isomer are less than the interactions of the Cp ligand with a free electron pair on sulfur in the trans-syn isomer, or 2) that solvent/molecule interactions may be more
favorable with the trans-anti isomer compared to the trans-syn isomer, or 3) that the syn-anti isomer might be less polar than a trans-syn isomer and therefore favored in less polar solvents. The large steric interaction between an adjacent Cp ligand and a benzyl group probably precludes a trans-anti isomer for 16.

d. Reactivity of μ-dihydridothiocarbene complexes

1) Preparation of \( \text{Cp}_2\text{Fe}_2(\text{PMe}_2\text{Ph})(\text{CO})(\mu-\text{CO})(\mu-\text{C(H)SMe}) \), 19

Trimethylamine oxide does not react with \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{C(H)SMe}) \) (in \( \text{CH}_2\text{Cl}_2 \)) at room temperature or under reflux. The μ-carbene complex is also inert to carbonyl substitution by PMe₂Ph at room temperature. A phosphine substituted product is not produced by reacting \( [\text{Cp}_2\text{Fe}_2(\text{PMe}_2\text{Ph})(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})]^+ \), 9, with NaBH₄. However, a fast reaction (Eqn 51) between \( \text{Cp}_2\text{Fe}_2(\text{CH}_3\text{CN})(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})]^+ \), 6, and NaBH₄ gives \( \text{Cp}_2\text{Fe}_2(\text{CH}_3\text{CN})(\text{CO})(\mu-\text{CO})(\mu-\text{C(H)(SMe)}) \), 18, which readily reacts with PMe₂Ph to give \( \text{Cp}_2\text{Fe}_2(\text{PMe}_2\text{Ph})(\text{CO})(\mu-\text{CO})(\mu-\text{C(H)(SMe)}) \), 19, (Eqn 52).

Green crystals of 19, obtained in 38% yield, are soluble
in common organic solvents (only slightly soluble in hexane) and are stable indefinitely under nitrogen at -20°C. The IR spectrum of 19 in CH$_3$CN shows two strong $\nu$(CO) absorptions at 1917 and 1735 cm$^{-1}$ for the terminal and bridging carbonyl ligand, respectively. The $^1$H NMR spectrum (Table 4) in CDCl$_3$ shows that the product is contaminated with free PMe$_2$Ph (resonances at 7.4(Ph) and 1.6(Me) ppm), which masks the resonances for coordinated PMe$_2$Ph. The protons of the SMe group (2.70 ppm) are coupled to phosphorous ($J_{P,H} = 9.3$ Hz). The methine resonances at 10.91 ppm is only shifted 0.57 ppm upfield from its position in the unsubstituted complex, cis-Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-C(H)SMe], 15. This suggests that 19 has a cis configuration with the SMe group and PMe$_2$Ph ligand adjacent to each other:

![Diagram of complex 19](image)

This is in contrast to Cp$_2$Fe$_2$[P(n-Bu)$_3$](CO)(μ-CO)[μ-C(H)Me], 53, (THF: 1920 and 1730 cm$^{-1}$), which shows a methine resonance at 8.59 ppm (d$_6$-acetone), 3.01 ppm upfield from the methine resonances in the unsubstituted
complex, cis-Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)Me). The methine chemical shift in 53 is in the range expected for a cis configuration (see Figure 15). The bulky P(n-Bu)₃ ligand, apparently, requires a configuration nonadjacent to the larger carbon substituent:

\[
\begin{align*}
\text{P(n-Bu)₃} & \\
\text{P(n-Bu)₃} & \\
\end{align*}
\]

2) HBF₄-Et₂O and oxidation reactions of

Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)SCH₂Ph), 16 Reaction of 16 with HBF₄-Et₂O in CH₂Cl₂ gives the unstable methyldyne complex, [Cp₂Fe₂(CO)₂(μ-CO)(μ-CH)]⁺, which in the presence of PPh₃, forms the adduct [Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)PPPh₃)]BF₄⁻. Oxidation of 16 with I₂ and [Ph₃C]BF₄ gives unstable products presumably due to the formation of a radical cation, Cp₂Fe₂(CO)₂(μ-CO)(μ-C(H)SCH₂Ph)⁺, which loses a SCH₂Ph⁺ radical to give the unstable methyldyne cation.

3. Preparation and properties of Cp₂Fe₂(CO)₂(μ-CO)(μ-C(SMe)CH₂Ph), 24

a. Synthesis Addition of the Grignard reagent, PhCH₂MgCl, to a THF suspension of Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe)⁺, 2, results in an exothermic reaction to give the
bridging carbene complex, 24, in 27% yield (Eqn 53). The reaction also produces a significant amount of unstable and unidentified brown products and gives off the smell of MeSH. These materials are probably decomposition products of 24, caused by the heat generated from the exothermic reaction. Separation of 24 from other reaction products requires column chromatography (silica gel); the product is eluted with CH₂Cl₂. Crystallization (CH₂Cl₂/hexane) gives 24 as a red crystalline material which is stable indefinitely under nitrogen at -20°C and is soluble in common organic solvents.

b. **Spectroscopic properties** The IR spectrum of 24 in CH₃CN (Table 3) has a strong, medium, medium carbonyl band pattern, similar to the spectra of the μ-dithiocarbene complexes, 11 and 12. The medium intensity, low energy,
terminal CO band at 1940 cm$^{-1}$ implies the presence of some trans isomer. However, the intensity of this band is apparently an anomaly, since the $^1$H NMR spectrum in CD$_3$CN (Table 4) shows only a single resonance (4.84 ppm) for the equivalent protons of the two Cp rings of a cis isomer. Because there are two different carbene substituents, two cis isomers are possible:

![cis-24A](image1.png)  

![cis-24B](image2.png)

Molecular models of 24 show that the shorter C$_{\text{carbene}}$-CH$_2$ [1.514(5) Å]$^{124}$ and CH$_2$-C$_{\text{Ph}}$ [1.515(5) Å]$^{40}$ bonds compared to longer C$_{\text{carbene}}$-S [1.770(2) Å]$^{120}$ and S-CH$_3$ [1.810(3) Å]$^{120}$ bonds, results in greater steric interaction of the bulky CH$_2$Ph group with the Cp ligands in cis-24B, than does the SMe group in cis-24A. Apparently, the steric interactions in cis-24B are great enough such that only one isomer, cis-24A, is observed in the $^1$H NMR spectrum. A strong, low energy terminal CO band at 1950 cm$^{-1}$ in THF and at 1952 cm$^{-1}$ in hexane does indicate that a trans isomer of 24 is present in less polar solvents.
4. Reactions of μ-thiocarbyne cations with 4-dimethylamino-pyridine (4-DMAP)

a. Preparation and properties of Cp₂Fe₂(4-DMAP)(CO)⁻(μ-CO)(μ-CSR)⁺ complexes

The methylidyne complex, Cp₂Fe₂(CO)₂(μ-CO)(μ-CH)⁺, forms adducts with CO, NMe₃ and PPh₃. Tri-n-butyl phosphine reacts with Cp₂Fe₂(CO)₂(μ-CO)(μ-CCH₃)⁺ to give Cp₂Fe₂(CO)₂(μ-CO)[μ-C(CH₃)P(n-Bu)₃]⁺. No adducts of μ-thiocarbyne cations have been synthesized, nor have any been observed as intermediates during the synthesis of CO substituted complexes such as [Cp₂Fe₂(PEt₃)(CO)(μ-CO)(μ-CSMe)]⁺, 8, and [Cp₂Fe₂(PMe₂Ph)(CO)(μ-CO)(μ-CSMe)]⁺, 9. Bulky and less nucleophilic ligands [PPh₃, P(OPh)₃] do not react with Cp₂Fe₂(CO)₂(μ-COSMe)⁺, 2. The bulky but more nucleophilic phosphine, P(n-Bu)₃, also fails to react with 2. Pyridine (Py) forms the unstable product, Cp₂Fe₂(Py)(CO)(μ-CO)(μ-CSMe)⁺, under refluxing conditions. Using 4-dimethylaminopyridine (4-DMAP), which is a stronger nucleophile than pyridine, it was hoped that an adduct of 2 and other thiocarbyne cations could be obtained at room temperature. The reaction (Eqn 54) of excess 4-DMAP (6 equivalents) with either Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe)⁺, 2, or Cp₂Fe₂(CO)₂(μ-CO)(μ-CSCH₂Ph)⁺, 3, gives the CO substituted cations, Cp₂Fe₂(4-DMAP)(CO)(μ-CO)(μ-CSMe)⁺, 20, and Cp₂Fe₂(4-DMAP)(CO)(μ-CO)(μ-CSCH₂Ph)⁺,
21. Although these reactions take 6 to 24 hours to complete, no adduct intermediates, such as Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-C(SMe)4-DMAP]$^+$, are observed. The product, 20, is a black, air stable, crystalline solid, which was obtained in excellent yield (81%). Complex 21 is a brown solid, stable indefinitely under nitrogen at -20°C. Both 20 and 21 are soluble in polar solvents (CH$_3$CN, acetone) and insoluble in hexane, benzene and ether. The yield of 21 is only 36% and the product is contaminated with a small amount of a yellow crystalline material. The low yields for 21 may be due to the reaction shown in equation 55, which would compete with the synthesis of 21. The evidence for this reaction is the production of significant amounts of Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CS), which is extracted from the reaction mixture containing 21. The yellow compound that crystallized with 21 may be the pyridine salt, [1-benzyl-4-dimethylaminopyridinium]-
PF$_6$· The reaction in equation 55 is similar to the equilibrium between benzyl bromide and Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CS) shown in equation 39.\(^50\)

\[
\begin{array}{c}
\text{OCFe} \quad \text{CFeCO}
\end{array}
\]

b. **Spectroscopic properties** The single terminal and single bridging ν(CO) absorptions in the infrared spectra of 20 and 21 (Table 3) are consistent for CO substituted thiocarbyne cations, Cp$_2$Fe$_2$(L)(CO)(μ-CO)(μ-CSR)$^+; the frequencies of these bands (ca. 2000 and 1815 cm$^{-1}$) are similar to those of 6, 8 and 9. Supporting evidence for this structure comes from the $^{13}$C NMR spectrum (Table 5) of 20, which shows a resonance at 407.1 ppm for a μ-carbyme carbon. The resonance for this carbon has approximately the same chemical shift as the carbyme carbon
of 2, 408.3 ppm. In contrast, the NMe$_3$ adduct, Cp$_2$Fe$_2$–
(CO)$_2$(μ-CO)[μ-C(H)NMe$_3$]$^+$, has a $^{13}$C resonance at 191.0 ppm,
which is more typical of a μ-carbene complex, and is shift­
ed 299 ppm upfield from the parent methyldyne compound,
Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CH)$^+$.58

5. Amine reactions with Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CSMe)$^+$, 2
   a. Preparation and properties Addition of a large
   excess of primary and secondary amines to 2 (Eqn 56) gives
   a reaction that produces unstable products identified as μ-
   aminocarbony complexes, Cp$_2$Fe$_2$(SMe)(CO)(μ-CO)(μ-CNR$_2$).

\[
\text{HNRR'} = \text{HNMe}_2 \quad (25) \\
= \text{HN(CH}_2)_4 \quad (26) \\
= \text{H}_2\text{NMe} \quad (27) \\
= \text{H}_2\text{N(n-Bu)} \quad (28) \\
= \text{H}_2\text{N(CH}_2)_2\text{NH}_2 \quad (29) \\
= \text{H}_2\text{N(CH}_2)_3\text{NH}_2 \quad (30) \\
= \text{CH}_3\text{N(H)(CH}_2)_3\text{(H)NCH}_3 \quad (31) \\
= \text{H}_2\text{N(CH}_2)_2\text{OH} \quad (32)
\]
In the absence of a large excess of amine, these reactions are extremely slow. For example, the reaction of 2 with one equivalent of pyrrolidine shows, by IR analysis, that less than 10% of 2 is consumed after 5 hours. Progressively increasing the pyrrolidine concentration to 2, 3, 4 and 5 equivalents, causes an incrementally greater reaction to occur (ca. 40% 2 reacted). Complete consumption of 2 required 15 equivalents of pyrrolidine and one hour of stirring. The reaction of 2 with the other primary and secondary amines in equation 56 required 10-20 fold excess of amine and reaction times of 10-30 minutes to completely consume 2. The brown μ-aminocarbyne complexes, 25-32, are air sensitive and thermally unstable. Because of their instability, none of the products were isolated for chemical analysis. Attempted isolation of 25 and 26 by crystallization resulted in their decomposition. The reaction mixture residue containing 25, shows no trace of the μ-aminocarbyne product after sitting for 3 days under nitrogen at 25°C. The neutral μ-aminocarbyne complexes, 25-32, are less stable than similar cationic complexes previously prepared; the complexes, Cp₂Fe₂(L)(CO)(μ-CO)(μ-CNR₂)⁺ (L = CO, CNR; R = alkyl), are air stable solids which decompose in solution,¹²⁵ while Cp₂Fe₂(CO)(CNMe)(μ-CNMe₂)(μ-CSMe)²⁺ is reported to be an air stable solid which, apparently, is
stable in solution.\textsuperscript{71}

The instability of the \(\mu\)-aminocarbyne product may be related to the inability of \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})[\mu\text{-C(SMe)}_2]\) to convert to a \(\mu\)-carbyne, and the propensity of the \(\text{Cp}_2\text{Fe}_2-(\text{CO})_2(\mu\text{-CO})(\mu\text{-C(SMe)}(\text{XPh}))\) \((X = S, Se)\) complexes to convert to \(\mu\)-carbynes by \text{XPh} rather than \text{SMe} transfer. A possible explanation, is the facile oxidation of the \(\text{Cp}_2\text{Fe}_2(\text{XPh})-(\text{CO})(\mu\text{-CO})(\mu\text{-CSMe})\) \((X = S, Se)\) complexes in solution when exposed to air (see Section III.B.2.d). It may be that the \(\mu\)-aminocarbyne products, with their \text{SMe} group coordinated to iron, are even more easily oxidized.

b. \textbf{Spectroscopic properties}  Complexes 25 and 26 were characterized by their IR (Table 3) and \textsuperscript{1}H NMR (Table 4) spectra. The IR spectra of 25 and 26 (CH\textsubscript{3}CN) both show single terminal and single bridging \(\nu(\text{CO})\) absorptions at about 1940 and 1768 cm\(^{-1}\), consistent with the proposed \(\mu\)-aminocarbyne structure, \(\text{Cp}_2\text{Fe}_2(\text{SMe})(\text{CO})(\mu\text{-CO})(\mu\text{-CNR}_2)\). The \textsuperscript{1}H NMR data (CDCl\textsubscript{3}) also support this type of structure. For 25, two isomers are formed in approximately a 4:1 ratio, which may be cis and trans isomers:
The major isomer, presumably cis-25, has two resonances for the nonequivalent Cp ligands at 4.72 and 4.54 ppm and three approximately equal intensity methyl resonances at 3.45 and 3.37 ppm (μ-CNMe₂), and 1.53 ppm (SMe). The minor isomer, trans-25, has the corresponding resonances at 4.69, 4.58, 3.24, 3.19 and 1.53 ppm (coincident with cis isomer SMe resonance). The chemical shifts for the Cp and μ-CNMe₂ ligands in the neutral complex, 25, are upfield, as expected, compared to the ligands in cis-[Cp₂Fe₂(CNMe)(CO)(μ-CO)- (μ-CNMe₂)]⁺: CDCl₃, 5.26 and 5.20 ppm (Cp), 4.42 and 4.35 ppm (μ-CNMe₂). The chemical shift of the SMe resonance is similar to that observed in CpFe(CO)₂SMe (1.61 ppm). The ¹H NMR spectrum of the pyrrolidine product, 26, shows only the cis isomer: 4.73 and 4.53 ppm (Cp), 3.06 ppm (b, NCH₂), 1.89 ppm (b, CH₂) and 1.53 (SMe) ppm. The pyrrolidine proton resonances at 3.06 and 1.89 ppm are broad peaks which are not resolvable. The other μ-aminocarbonyl complexes, 27-32, were characterized only by the IR spectra (Table 3), which are all similar to the spectra of 25 and 26 in having two ν(CO) absorptions in the region 1940-1945 and 1767-1780 cm⁻¹.

c. Mechanism The reactions between 2 and amines gave products which decompose to completely insoluble materials during crystallization. As such, the following dis-
discussion is conjecture based on the available spectroscopic data. The reaction of dimethylamine with \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^+ \) is shown in Figure 16. This reaction scheme presumably applies to reactions of the other dialkyl and monoalkylamines. Because the reaction sequence contains a deprotonation step, trialkylamines should not react. However, \( \text{Me}_2\text{N}(\text{CH}_2)_3\text{NMe}_2 \) does show a slow and incomplete reaction. Since all of the reactions require a large excess of amine, the limited reaction for \( \text{Me}_2\text{N}(\text{CH}_2)_3\text{Me}_2 \) may be due to dialkyl and monoalkylamine impurities present in commercial trialkylamines.

Because no adducts of 2 are observed as intermediates during phosphine or 4-DMAP reactions, it is very likely that the first equilibrium reaction in Figure 16 lies far to the left. This unfavorable equilibrium requires that large excesses of 1° and 2° amines be used. The initial adduct, \( A \), is not observable due to its low concentration. Any formed is quickly deprotonated by excess amine present to give the \( \mu \)-carbene intermediate, \( B \), which is observed during the reaction (IR bands at 1972 and 1780 cm\(^{-1}\), \( \text{HNMe}_2 \) reaction). These terminal and bridging carbonyl bands have energies and intensities similar to the \( \mu \)-dithiocarbene and \( \mu \)-hydridothiocarbene complexes. A low energy, terminal CO band for \( B \) is probably coincident with the 1938(s) cm\(^{-1}\).
Figure 16. Mechanism for the reaction of HNMe$_2$ with 
Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CSMe)$^+$, 2
band of the \( \mu \)-aminocarbyne product, 25. Likewise, the \( \mu \)-CO bands for B and 25 are nearly coincident at 1770-1780 cm\(^{-1}\). If the volatile dimethylamine is the reactant, and the reaction is taken to dryness under vacuum, then only 25 and 2 are obtained. This behavior is observed even if large excesses of HNMe\(_2\) are used and reaction times are long enough to completely consume 2; only B and 25 are present prior to drying. These results show that \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^+ \) is in equilibrium with B and that 25 is not the trans isomer of B. The irreversibility of 25 is the result of a \( C_{\text{carbene}}-S \) bond rupture and subsequent coordination of the SMe group to iron accompanied by CO loss. Formation of 25 is reminiscent of the carbene-to-carbyne conversion observed for 12 and 23. Pertinent to the present reaction is the fact that mononuclear carbenes that convert to carbynes are aminocarbenes.\(^{91,126}\)

C. A \( \mu \)-Carbyne Radical: \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^+ \)

1. Synthesis and characterization

The cyclic voltammogram of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^+ \), 2, shown in Figure 17, has two reduction waves at -0.78 and -1.70 V. The anodic portion of the irreversible second reduction wave interferes with the first reduction wave. A scan between the voltage limits, 0 to -1.50 V, eliminates
Figure 17. The cyclic voltammogram of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})]\text{PF}_6\), 2, in 0.1 M \(\text{NBu}_4\text{PF}_6/\text{CH}_3\text{CN}\).
this problem and shows an apparent reversible process for the first reduction step; the ratio of anodic to cathodic peak currents ($i^a_p/i^c_p$) is near unity. However, the peak to peak separation, 75 mV, is greater than predicted for Nernstian behavior. The data in Table 8 show that this wave is in fact quasi-reversible; it shows little, if any, change in the reduction potential ($E_p$) with scan rate ($v$); 2) the peak potential difference ($E^c_p - E^a_p$) decreases towards 59 mV/n (n = number of electrons) as the scan rate is lowered; and 3) the $i^c_p/v^{1/2}$ is constant.

Controlled potential coulometry (Table 9) at -0.80V and 0°C, gives an "n" value of 1.00 ± 0.06 electrons. Thus, the electrochemical data indicate that the electrode process at the first reduction wave is:

$$\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^+ + e^- \leftrightarrow \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^-$$

During the course of the electrolysis, the color of the solution changes from brownish-orange to a deep emerald green, indicative of the radical, $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^-$, 51. In the electrolyte solution (0.1 M NBu$_4$PF$_6$/CH$_3$CN) at 0°C, the emerald green color of 51 slowly fades to brown in an hour. The radical decomposes to numerous products, one of which is identified as $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-C(H)SMe)$, 15. At -80°C, the frozen radical solution
Table 8. Cyclic voltammetry data for 2

<table>
<thead>
<tr>
<th>Scan rate (v) (mV/sec)</th>
<th>E_p (V)</th>
<th>E_c^* - E_p (mV)</th>
<th>i_c^* (µA)</th>
<th>i_a^* (µA)</th>
<th>i_c^<em>/i_a^</em></th>
<th>i_c^*/v^{1/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>500^a</td>
<td>-0.787</td>
<td>83</td>
<td>18.2</td>
<td>12.8</td>
<td>1.42</td>
<td>---</td>
</tr>
<tr>
<td>300^b</td>
<td>-0.783</td>
<td>75</td>
<td>33</td>
<td>26.8</td>
<td>1.23</td>
<td>---</td>
</tr>
<tr>
<td>200</td>
<td>-0.785</td>
<td>70</td>
<td>15.2</td>
<td>12.1</td>
<td>1.26</td>
<td>1.07</td>
</tr>
<tr>
<td>100</td>
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<td>62</td>
<td>10.6</td>
<td>9.3</td>
<td>1.14</td>
<td>1.06</td>
</tr>
<tr>
<td>50</td>
<td>-0.785</td>
<td>59</td>
<td>7.5</td>
<td>7.3</td>
<td>1.03</td>
<td>1.06</td>
</tr>
</tbody>
</table>

^a A separate experiment at a different concentration.

^b From Figure 17.
Table 9. Controlled Potential Coulometry\(^a\) for 2

<table>
<thead>
<tr>
<th>Sample (mg)</th>
<th>(Q_T)^(b)</th>
<th>(Q_O)^(c)</th>
<th>(Q_O - B)^(d)</th>
<th>(n)^(e)</th>
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<tbody>
<tr>
<td>49.5</td>
<td>9.02</td>
<td>8.74</td>
<td>8.60</td>
<td>0.95</td>
</tr>
<tr>
<td>46.4</td>
<td>8.02</td>
<td>8.15</td>
<td>8.01</td>
<td>0.95</td>
</tr>
<tr>
<td>47.9</td>
<td>8.72</td>
<td>9.63</td>
<td>9.49</td>
<td>1.09</td>
</tr>
</tbody>
</table>

\(^a\) Performed at \(-0.80 \text{ V vs Ag/AgCl reference electrodes}\) in \(0.1 \text{ M } \text{NBu}_4\text{PF}_6/\text{CH}_3\text{CN}\).

\(^b\) Theoretical number of coulombs for a \(1 \text{ e}^-\) reduction.

\(^c\) Number of coulombs used to reach a steady residual current.

\(^d\) \(B = \text{blank} = 0.14 \text{ }Q\).

\(^e\) \(n = \text{electron change on reduction}, \frac{Q_O - B}{Q_T}\).
decomposes over a 24 hour period. Chemical reduction of 2 in THF with sodium naphthalide gives the same green color observed by electrolytic reduction. In this solvent the radical decomposes over a 10 hour period at -80°C. Isolation of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^+ \) as a solid is not possible; on concentrating, the THF/radical solution turns brown. The resulting residue after complete evaporation of THF contains numerous products and does not give 2 on reoxidation with \( \text{I}_2 \).

2. Spectroscopic properties

In the CH\(_3\)CN/electrolyte solution the IR spectrum of 51 (Figure 18) has carbonyl bands at 1973(s), 1933(m) and 1760(m) cm\(^{-1}\). Other bands in this spectrum are due to unreduced \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^+ \). As in the syntheses of the bridging carbene complexes (see Section III.B), a shift to lower frequencies (\( \Delta = 70-90 \text{ cm}^{-1} \)) on going from 2 to 51 is expected for the change in charge. The relative intensities of the carbonyl bands of 51 are similar to those of cis-\( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{C(H)SMe}) \), indicating that 51 probably has a cis configuration in 0.1 M \( \text{NBu}_4\text{PF}_6/\text{CH}_3\text{CN} \). The IR spectrum of chemically generated 51 (THF: 1978(s), 1944(m), 1772(m) cm\(^{-1}\)) has a carbonyl band pattern similar to the spectrum taken in CH\(_3\)CN (Figure 17) except that the
Figure 18. The infrared spectrum of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})-(\mu-\text{CSMe})$, 51, in 0.1 M $\text{NBu}_4\text{PF}_6/\text{CH}_3\text{CN}$
absorptions occur at higher energy. Since much of the work with 51 (stoichiometric and catalytic reactions) is performed in CH₃CN, it is significant that three carbonyl bands are observed, because it eliminates the possible intermediacy of CH₃CN substituted radicals [i.e. Cp₂Fe₂-(CH₃CN)(CO)(μ-CO)(μ-CSMe)*]. This information, combined with the fact that oxidation of electrogenerated 51 with [Cp₂Fe₂][FeCl₄] at 0°C in CH₃CN gives 2, shows that 51 is a tricarbonyl species.

The UV-visible spectrum of 51, shown in Figure 19, has a low energy band at 602 nm (ε = 588 ± 6 M⁻¹cm⁻¹) which is red shifted by approximately 90 nm from the low energy band of 2 (500 nm; ε = 666 ± 6 M⁻¹cm⁻¹). These extinction coefficients are experimental values including any overlap of the low energy band by a much stronger (ε > 15,000 M⁻¹cm⁻¹) near UV band. These spectra are similar to those of other dinuclear metal-metal bonded complexes, such as Cp₂Fe₂(CO)₂(μ-CO)₂ and Cp(CO)₃WCo(CO)₄, which have a low intensity band (ε = 500-700 M⁻¹cm⁻¹) at about 500 nm and a high intensity band (ε = 8000-12000 M⁻¹cm⁻¹) at 300-400 nm.¹²⁸

The electron spin resonance (EPR) spectrum of 51 (Figure 20), taken in THF at 183 K, gives a singlet with a "g" value of 1.956 ± 0.002. No hyperfine coupling to the
Figure 19. The UV-visible spectra of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})$, 51 (-), and $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})]\text{PF}_6$, 2 (-·), in 0.1 M $\text{NBu}_4\text{PF}_6/\text{CH}_3\text{CN}$
Figure 20. The EPR spectrum of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe}) \), 51 in THF at 183 K.
protons on either the Cp rings or the methyl group is observed. Molecular orbital calculations on bridging carbyne cations show that the LUMO is composed mainly of the out-of-plane 'p' orbital located on the carbyne carbon, and some out-of-plane contribution (antibonding) from donor orbitals of the M₂ fragment. Thus, reduction of Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe)⁺ to a radical would possibly place an electron in this orbital; if so, delocalization of unpaired electron density onto the sulfur atom may occur:

\[ \text{Organic radicals having a similar structural unit as 51 are stabilized by delocalization of unpaired electron density onto sulfur:} \]

\[ R = \text{CH}_3, \text{C}_2\text{H}_5, \text{i-C}_3\text{H}_7 \]
\[ R' = \text{H, alkyl} \]
Electron spin resonance spectra of these organic radicals show hyperfine coupling constants of 1.5-3.25 Gauss with protons at the gamma position and "g" values in the range 2.0046-2.0049.\textsuperscript{130,131} Since the resonance signal in Figure 20 is approximately 10 Gauss wide, any coupling greater than 1 Gauss should be noticeable. Thus, the absence of any hyperfine coupling suggests that delocalization of electron density onto the metal fragment may be more important than delocalization onto sulfur. This should be feasible since the orbital involved does possess some M\textsubscript{2} fragment character (see above). Because of a lack of literature data, comparison of the EPR spectrum of \textit{51} to oxidized or reduced forms of Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{2}(\mu-CO)\textsubscript{2} type compounds is not possible. However, the EPR spectrum of Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{2}(\mu-SCH\textsubscript{3})\textsubscript{2}\textsuperscript{+} does not exhibit hyperfine coupling.\textsuperscript{132} Structural studies for this compound show that the unpaired electron resides in an M-M antibonding orbital.\textsuperscript{133,134} Likewise, the radical anions, R\textsubscript{2}C\textsubscript{2}Co\textsubscript{2}(CO)\textsubscript{6}\textsuperscript{−} [R = Ph, Si(CH\textsubscript{3})\textsubscript{3}, H, CH\textsubscript{3}, CF\textsubscript{3}, t-Bu], show only hyperfine coupling to cobalt.\textsuperscript{135} The unpaired electron density here also resides in a predominantly M-M antibonding orbital.

3. \textbf{Comparative stabilities of thiocarbyne radicals}

The reduction potentials required to form radical anions such as R\textsubscript{2}C\textsubscript{2}Co\textsubscript{2}(CO)\textsubscript{6}\textsuperscript{−}, and their stabilities, are
dependent on the electron donating ability of the R substituents. Thus, when R = t-Bu (electron donating) the reduction potential is -1.03 V and the lifetime of the radical is only 70 ms at 25°C. When R = CF₃ (electron withdrawing) the radical forms at -0.51 V and exists for several hours at 25°C. Terminal ligands show similar behavior; e.g. phosphines shift the reduction to more negative potentials and destabilize the radical. Terminal ligands of thiocarbyne cations produce the same effects. Thus, the cyclic voltammogram of Cp₂Fe₂(PMe₂Ph)(CO)(μ-CO)(μ-CSMe)⁺, 9, shows an irreversible reduction at -1.06 V, 0.31 V more negative than 2. However, the reduction potential of thiocarbyne cations appear to be insensitive to the electronic effects of the μ-thiocarbyne ligand; the cyclic voltammograms of the methyl (2), benzyl (3) and allyl (4) thiocarbyne cations all reduce at -0.78 V. While this reduction wave is quasi-reversible for 2, the reduction waves for 3 and 4 are irreversible. The irreversibility of 3 and 4 may reflect an alternate path for decomposition of their radicals which possibly does not involve metal-metal fragmentation. This path may involve formation of Cp₂Fe₂(CO)₂(μ-CO)(μ-CS), 1, and the relatively stable benzyl and allyl radicals, which may scavenge H (from
the solvent) to form toluene and propene. Evidence for this decomposition pathway may come from the reactions of 3 and 4 with Na[Co(CO)₄] (discussed in Section III.D), which result in redox reactions to give 1 as a major product. In contrast, the reaction of 2 with Na[Co(CO)₄] under thermal conditions, gives less 1 at a slower rate. The relative instability of a methyl radical makes this path less favorable for 51. ¹³⁷

4. Reactivity of the Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe) radical, 51
   a. As a reductant in redox reactions

   Electrogenated 51 reacts instantly with Co₂(CO)₈ at 0°C to give 2 and Co(CO)₄⁻. Under the same conditions, the reaction of Mn₂(CO)₁₀ and 51 gives, after 10 minutes, 2 and Mn(CO)₅⁻. Production of Mn(CO)₅⁻ is unexpected since this anion and 2 are known to react quickly to form Mn₂(CO)₁₀ and 51 (see Section III.D). This apparent anomaly is due to the electrolyte (NBu₄PF₆) present in the reaction mixture, which was required for electrogeneating 51. The high concentration of the bulky NBu₄⁺ counter ion, apparently, stabilizes the Mn(CO)₅⁻ anion, preventing it from acting as a reductant. ¹³⁸ The failure of Re₂(CO)₁₀ to react with 51 under these conditions reflects its much higher reduction potential. ¹³⁹

   Homolytic scission of a C-Br bond appears to occur
when electrogeneated 51 reacts with PhCH₂Br to apparently
give (by IR analysis), within 10 minutes at 0°C, [Cp₂Fe₂-
(CO)₂(μ-CO)(μ-CSMe)]Br and Cp₂Fe₂(CO)₂(μ-CO)[μ-C(CH₂Ph)-
SMe], 24. However, reaction of Mn(CO)₅Br under the same
conditions results in a redox reaction to give 2 and
Mn(CO)₅⁻.

Radicals are known to attack the Cp rings of Cp₂Fe⁺
(Eqn 57).¹⁴⁰ Reaction of 51 with Cp₂Fe⁺ gives 2 and pre-
sumably Cp₂Fe.

\[ \text{Fe} + \text{R}^- \rightarrow \text{Fe} + \text{H}^+ \] (57)

b. Reaction of 51 with ¹³CO A THF solution of the
chemically generated radical undergoes an exchange reaction
when it is stirred under an atmosphere of ¹³CO for 15 min-
utes at 0°C. The exchanged product was oxidized with I₂ to
convert it to the stable carbyne cation, Cp₂Fe₂(CO)₂(μ-CO)-
(μ-CSMe)⁺, 2, which by itself was found not to undergo CO
ligand exchange. The IR spectrum (in CH₃CN) of the recov-
ered cation shows spectral bands for unlabeled 2 at 2043(s)
and 1852(m) cm⁻¹ and for the ¹³CO exchanged product at
1994(s) and 1811(m) cm⁻¹. The weak CO bands at 2012 cm⁻¹
(unlabeled) and 1966 cm⁻¹ (labeled) were not resolved in
this spectrum. The energies of the observed $^{13}$CO bands agree with the calculated values of 1996 and 1811 cm$^{-1}$ (these were calculated using the band position of unlabeled 2: 2043 and 1852 cm$^{-1}$). The NMR data lend support for the presence of a labeled product; the $^1$H NMR spectrum shows resonances for essentially only one type of product, Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CSMe)$^+$, and the $^{13}$C NMR spectrum exhibits strongly enhanced bridging (252.0 ppm) and terminal (207.3 ppm) carbonyl resonances for 2. These results indicate that the carbonyl ligands of 51 are significantly more labile than those of 2. Though the possibility exists that the weak nucleophile, $^{13}$CO, may attack 51 directly to give the exchange product, it is more likely that the exchange product is formed by a dissociative mechanism involving the equilibrium reaction shown in equation 58. Thus, 51 undergoes the equilibrium reaction shown in equation 58. Because the IR spectrum of the radical (in CH$_3$CN or THF)

\[
\begin{align*}
\text{OC} & \quad \text{SMe} \\
\text{Cp} & \quad \text{Fe} \\
\text{C} & \quad \text{Cp} \\
\text{CO} & \\
\text{Cp} & \quad \text{Fe} \\
\text{OC} & \quad \text{SMe} \\
\end{align*}
\]

shows a three carbonyl band pattern expected for a species
like 51, the equilibrium in equation 58 probably strongly favors 51. The carbonyl ligands are apparently fluxional, because both terminal and bridging sites underwent exchange. It is not obvious how this fluxionality occurs, but two possible mechanisms are 1) a two-site exchange mechanism:

\[
\begin{align*}
\text{OC}^* & \text{Fe} & \text{C} & \text{Fe} & \text{CO} \\
\text{Cp} & & & \text{Cp} & & \text{SMe} \\
\end{align*}
\]

or 2) a mechanism involving an intermediate that does not contain a metal-metal bond:

\[
\begin{align*}
\text{OC}^* & \text{Fe} & \text{C} & \text{Fe} & \text{CO} \\
\text{Cp} & & & \text{Cp} & & \text{SMe} \\
\end{align*}
\]

Non-metal-metal bonded intermediates have been proposed for the radical anion, \(R_2C_2Co(CO)_6^-\). A choice between the
above mechanisms for CO fluxionality in 51 is not possible with the data presently available.

c. Reaction of 51 with diphenyldisulfide and diphenylldiselenide. Chemically generated 51 reacts with diphenylldiselenide at -20°C to give the purple μ-carbene complex, Cp_2Fe_2(CO)_2(μ-CO)[μ-C(SMe)SePh], 23 (Eqn 59).

This product is unstable, decomposing in solution between 0-25°C to give a 31% yield of Cp_2Fe_2(SePh)(CO)(μ-CO)(μ-CSMe), 22. Addition of PhSeSePh to a THF solution of 51 at 0°C (Eqn 59) immediately gives a purple-brown reaction mixture, which yields 22 upon solvent removal at 0°C; no
yield was determined for this reaction. Because the purple complex, 23, converts to 22 relatively slowly at 0°C in the absence of a vacuum [see Section III.B.d.3]), the purple-brown reaction mixture observed in this reaction suggests that 22 and 23 were formed simultaneously.

These reactions can be explained by assuming that the undissociated radical, 51, is the dominant reactive species at -20°C and gives the carbene product; and that both 51 and the dissociated radical, 54, which gives the carbyne product, (see Eqn 58) are reactive at 0°C. This suggests that either the equilibrium in equation 58 shifts towards 51 at lower temperature, or that 54 is less reactive than 51. However, because 54 has an open coordination site it might be expected to be more reactive than 51.142

The stoichiometric reaction of 51 with PhSSPh at 0°C gives predominantly (5:1) the μ-carbyne product, Cp₂Fe₂-(SPh)(CO)(μ-CO)(μ-CSMe), 38 (Eqn 60), which is isolated in

![Chemical structures](image-url)

major product (60)
35% yield. With excess PhSSPh, approximately equal amounts of 12 and 38 are produced. The product ratio, 38:12, under excess PhSSPh conditions, is essentially the same: 1) at 0°C or 25°C, or 2) if the PhSSPh addition is made immediately or delayed 15 minutes after radical formation. Since 12 does not convert to 38 at a significant rate below 40°C, these products are probably the result of PhSSPh reacting with both 51 (to give 12) and 54 (to give 38). If 51 and 54 are in equilibrium (Eqn 58), then delaying the PhSSPh addition should have no effect on the 38:12 product ratio, which it does not. The fact that the relative amount of 12 increases under excess PhSSPh conditions, suggests that the rate of this reaction is dependent on both 51 and PhSSPh concentration, while the rate for 38 production is independent of PhSSPh concentration. This behavior could be attributed to the equilibrium between 51 and 54 which may strongly favor 51. Because a large concentration of 51 is present, a bimolecular reaction between 51 and PhSSPh may not be effected by the 51/54 equilibrium. However, reaction of 54 with PhSSPh may depend on the rate which 54 is produced by the 51/54 equilibrium reaction. The invariance of the 38:12 product ratio with temperature is unexpected, but may mean that the 51/54 equilibrium does not shift significantly over this temperature range (0-25°C).
Diphenyldisulfide does not react with the radical at -20°C. This contrasts with PhSeSePh reaction at -20°C, which gives the μ-carbene product, 23. Apparently, the reactions of 51 and 54 with PhSSPh are much slower at this temperature. This may be attributed to several factors including 1) the higher S-S bond energy (63 kcal/mol) compared to Se-Se bond energy (38 kcal/mol) and 2) attack at the smaller sulfur atom may be more sterically hindered.

Chemically generated 51 fails to react with CH₃SSCH₃ and PhCH₂SSCH₂Ph at 0°C; no reaction, except radical decomposition, occurs on warming the reaction mixture to 25°C. The difference in reactivity of 51 between these dialkyldisulfide substrates and PhSSPh is surprising. However, relatively stable organic radicals show the same selectivity, which has been attributed to stronger S-S bonds in dialkyldisulfides compared to diphenylsulfides. The organic peroxides, (t-BuO)₂ and (PhC(O)O)₂, rapidly oxidize 51 (chemically generated) to the cation (Eqn 61).

\[
\begin{align*}
\text{2} & \text{OC}_\text{Fe}^+\text{C}_\text{Fe} & \text{C}_\text{O} \quad \text{THF} \\
& \text{Cp} & \text{Cp} \quad 0^\circ\text{C} \\
\text{51} & \rightarrow \text{2} & \text{OC}_\text{Fe}^\text{+} & \text{C}_\text{Fe} & \text{C}_\text{O} + 2\text{RO}^- \quad \text{2} \quad \text{(61)} \\
& & & & \\
\text{R} = \text{PhC(O)}, \text{t-Bu}
\end{align*}
\]
5. Catalysis by $\text{M}^+$

a) **Ligand substitution reactions of $\text{M}$ catalyzed by chemically generated $\text{M}^+$**  

Metal carbonyl radicals have been used to catalyze ligand substitution reactions.\textsuperscript{142,145} The catalytic effect results from the radical inducing a chain process for the substitution reaction. A generalized mechanism for a radical cation is shown in equations 62-64.

\[ \text{MCO} \longrightarrow \text{MCO}^+ + e^- \quad (62) \]
\[ \text{MCO}^+ + \text{L} \longrightarrow \text{ML}^+ + \text{CO} \quad (63) \]
\[ \text{MK}^+ + \text{MCO} \longrightarrow \text{ML} + \text{MCO}^+ \quad (64) \]

The kinetically labile radical, $\text{MCO}^+$, generated (Eqn 62) by chemical or electrochemical methods, undergoes the ligand (L) substitution reaction shown in equation 63. A spontaneous electron transfer step (Eqn 64) gives the stable product, $\text{ML}^+$, and regenerates the radical cation, $\text{MCO}^+$. Radical cation and neutral 17 electron species, in general, undergo the associative ligand exchange step shown in equation 63.\textsuperscript{145} For 19 electron species it is not known whether an associative or dissociative ligand substitution process occurs.\textsuperscript{145} Recently, dinuclear radical anions were proposed to undergo molecular rearrangement prior to ligand substitution.\textsuperscript{142} The catalytic properties of neutral,
dinuclear radicals have so far not been explored. For this reason the qualitative experiments described here were performed. Addition of 0.01 mmol of chemically generated 51, to a THF suspension of 2 (0.1 mmol) and excess PEt₃ (> 3 equivalents) at 0°C, affords an instantaneous reaction to completely dissolve 2 and give a yellow-green reaction solution. IR analysis shows a complete (no 2 remains unreacted) and clean reaction to give Cp₂Fe₂(PET₃)⁻(CO)(μ-CO)(μ-CSMe)⁺, 8. No attempt was made to separate the product. This reaction shows that 10 moles of 8 were produced per mole of catalyst added. Presumably a greater ratio could be obtained by using higher amounts of 2 or less 51. With poor nucleophiles the reaction is less complete. Addition of 0.01 mmol of chemically generated 51 to a THF suspension of 2 (0.1 mmol) and 3 equivalents of 4-DMAP at 0°C, reacts approximately 60% of 2 within 5 minutes to give Cp₂Fe₂(4-DMAP)(CO)(μ-CO)(μ-CSMe)⁺, 20. Compared to the PEt₃ reaction above, this reaction is much slower. As a consequence, the catalyst probably undergoes greater decomposition during the 4-DMAP reaction, resulting in fewer chain propagating steps; this ultimately may account for the 60% yield in this reaction. This is an improvement over the thermal reaction which takes 6 hours in CH₃CN at 25°C.
b. **Ligand exchange reactions of 2, catalyzed by electrogenerated 51**

Ligand exchange reactions of 2 catalyzed by electrogenerated 51 are conveniently studied by passing a small cathodic current through a stirred solution of 2 containing added ligands. Data for these reactions are presented in Table 10. Because the reduction potentials of the products are more negative than that of 2, the reactions can be conveniently monitored by following the sudden and rapid change toward more negative potentials (under constant current conditions of 1 mA), as the catalytic process occurs. The current to the cell is cut off when the potential reaches -0.80 V (reduction potential of 2 is -0.78 V). During the rapid rise to more negative potentials, the reaction solution's color rapidly changes from the brownish-orange of 2, to the yellowish-green of the substituted product. Infrared analysis of the final reaction solution shows that all of the ligands, except PPh₃, react completely (0.060 mmols of 2 consumed) and cleanly to give the monosubstituted cations. The triphenylphosphine case is only marginally catalytic, giving Cp₂Fe₂(PPh₃)(CO)(μ-CO)(μ-CSMe)⁺, unreacted 2, and other unknown products from the decomposition of 51. In contrast to the other systems, the PPh₃ case shows a color change to emerald green during electrolysis, indicative of a large
<table>
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<tr>
<th>Ligand</th>
<th>Product IR</th>
<th>Reduction Potential (V)</th>
<th>Time (sec)</th>
<th>Coulombs</th>
<th>Current Efficiency (m/n)</th>
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</thead>
<tbody>
<tr>
<td>PEt₃</td>
<td>1987(s), 1818(s)</td>
<td>-1.12</td>
<td>180</td>
<td>0.1825</td>
<td>32.1</td>
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<td>PMePh₂</td>
<td>2005(s), 1811(s)</td>
<td>-1.10</td>
<td>146</td>
<td>0.1466</td>
<td>46.1</td>
</tr>
<tr>
<td>PMe₂Ph</td>
<td>1993(s), 1814(s)</td>
<td>-1.14</td>
<td>150</td>
<td>0.1443</td>
<td>40.8</td>
</tr>
<tr>
<td>PPh₃</td>
<td>2010(s), 1810(s)</td>
<td>-1.02 &gt;20min.</td>
<td>1.728</td>
<td>2.38</td>
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</tr>
<tr>
<td>t-BuNC</td>
<td>2010(s), 1837(s)</td>
<td>-1.12</td>
<td>165</td>
<td>0.1591</td>
<td>36.9</td>
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<td>----</td>
<td>----&lt;5</td>
<td>0.0023</td>
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<td></td>
</tr>
</tbody>
</table>

[^a]: 0.060 mmol of 2 in 20 mL of 0.1 M NBu₄PF₆/CH₃CN.
[^b]: 2 equivalents.
[^c]: Product infrared bands agree with those reported in this work (PEt₃, PMe₂Ph) and reference 50.
[^d]: Cyclic voltammogram of an authentic sample of \([\text{Cp}_2\text{Fe}_2(\text{PMe}_2\text{Ph})(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})]^+\) had a reduction potential of -1.14 V.
[^e]: Time and number of coulombs needed to reach a potential of -0.8 V at constant current of 1 mA.
[^f]: Current efficiency = m/n = moles of 2 consumed per Faraday of charge passed through cell.
[^g]: Other products present plus unreacted 2.
[^h]: Value corrected for the 0.0174 mmol of unreacted 2.
concentration of 51. The current efficiency for a substitution reaction is given by the ratio of m/n which is defined as the number of moles (m) of 2 consumed per Faraday (n) of charge passed through the solution.\(^\text{145}\) For all but the PPh\(_3\) case, current efficiencies of 30-40 represent significant catalysis of the substitution reaction; approximately 40 molecules of 2 are converted to product per molecule of 51 formed. In comparison, reactions of (CF\(_3\))\(_2\)C\(_2\)(CO)\(_6\) with phosphines and phosphites, catalyzed by the radical anions, (CF\(_3\))\(_2\)C\(_2\)CO\(_2\)(CO)\(_6\)\(^-\) (at 20°C using a similar electrochemical procedure and a ligand: (CF\(_3\))\(_2\)C\(_2\)CO\(_2\)(CO)\(_6\) ratio of 1.5:1), have rates which are approximately 25 times faster and give current efficiencies of 100-3000.\(^\text{142}\) The smaller current efficiencies in this work may be due to arbitrarily stopping the catalytic reaction as the potential reached -0.80 V. Perhaps a more optimum, less negative potential would have been better. However, since the potential rise is quite rapid from -0.77 V to -1.00 V, this difference may not be significant. The low current efficiency for PPh\(_3\) may be due to the weak Lewis basicity and greater steric requirements of this ligand. It should be noted that no reaction occurs in any of these systems at 0°C in the absence of 51.

These results show that substitution reactions of 2 in
CH$_3$CN occur slowly at $0^\circ$C by simple dissociative or associative mechanisms involving only diamagnetic intermediates. However, a much faster ligand substitution reaction occurs by a chain process which involves the intermediacy of the neutral radical, 51. A mechanism might be proposed at this point to explain the catalyzed nucleophilic substitution reactions. Such a mechanism might include a step generating 51, followed by the equilibrium reaction of 51 with 54. The next step is uncertain, since the nucleophile has two choices, reaction with 51 (associative process) or 54 (dissociative process). To answer some of these questions the CV experiments presented below were performed.

c. Cyclic voltammetry of 2 in the presence of nucleophiles The cyclic voltammograms (CV) of 2 in the presence of various ligands show two basic types of current/voltage profiles. For those ligands which are good nucleophiles (PEt$_3$, PMe$_2$Ph, PMePh$_2$, t-BuNC), the scan shown in Figure 21b for the PMe$_2$Ph case is typical. For comparison, Figure 21a shows the scan for 2 at the same concentration and scan rate (300 mV/sec). With the addition of 1 equivalent of PMe$_2$Ph, the quasi-reversible reduction of 2 at -0.78 V is still observed, but another chemically quasi-reversible reduction wave occurs at -1.14 V. A CV of an authentic sample of Cp$_2$Fe$_2$(PMe$_2$Ph)(CO)(µ-CO)(µ-CSMe)$^+$, 9,
Figure 21. Cyclic voltammograms of 2 (3.0 x 10^{-2} M) in the presence of PMe₂Ph; scan rate 300 mV/sec, 0.1 M NBu₄PF₆, 0°C
Figure 22. Cyclic voltammogram of 2 (3.0 x 10^{-2} M) in the presence of PEt_3 and 4-DMAP; scan rate 300 mV/sec, 0.1 M NBu_4PF_6, 0°C
confirmed that the second wave was due to the reduction of 9. The CV's in Figure 21 are repetitive scans 3-10 scans). On the first cycle (Figure 21b) the cathodic wave of 2 is slightly larger than the cathodic wave for 9. The second and subsequent cycles see a diminished cathodic wave for 2 and a slightly larger reduction wave for 9. A stirred CV for this system does not show the corresponding anodic waves for either cathodic peak, indicating that electrode adsorption is not responsible for this effect. Therefore, the electrode-generated species are able to escape into the diffusion layer and into the bulk of the solution to effectively participate in the catalytic reaction. The CV of 2 in the presence of 4 equivalents of PMe$_2$Ph (Figure 21c) or 2 with 8 equivalents of PEt$_3$ (Figure 22a) are similar. The invariance of the initial cathodic waves for 2 as the concentration of the nucleophile increases suggests, that nucleophilic attack does not occur with 51. However, the large cathodic peak at -1.14 V on the first cycle shows that 9 is being generated in high yield on the time scale of the CV scan. Thus, one is inclined to conclude that 51 converts relatively slowly to another reactive species, presumably 54, which is responsible for catalyzing the ligand substitution reaction. If 54 is highly reactive and present in only small amounts (see discussion of equa-
tion 58), then its concentration can be estimated by the steady state approximation, and the electrochemical mechanism for the PMe2Ph case might be given by equations 65-70.

\[
\begin{align*}
2 + e^- & \xrightleftharpoons[k_2]{[k_1]} 51 \\
51 & \xrightarrow[k_2^{-1}]{k_2} 54 + CO \\
54 + PMe2Ph & \xrightarrow[k_3]{k_3} 9^* \\
9^* & \xrightarrow[k_4]{k_4} 9 + e^- \\
9^* + 2 & \xrightarrow[k_5]{k_5} 51 + 9 \\
9 & \xrightarrow[51]{v_1^{-1}v_1} 9^* 
\end{align*}
\]

Steps 65 and 70 are the quasi-reversible electrode processes at -0.78 and -1.14 V, respectively. Steps 68 and 69 are spontaneous electron transfer reactions that take place at the electrode and in solution, respectively, to oxidize \(\text{Cp}_2\text{Fe}_2(\text{PMe}_2\text{Ph})(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})^*\), \(9^*\), to 9 prior to its reduction at -1.14 V. At potentials more positive then -1.14 V, step 68 is considered fast; however, the homogeneous solution phase electron transfer in step 69 is probably much faster. Thus, formation of 9 is dependent
on the substitution reaction in step 67; the rate of formation of 9 is given by equation 71:

\[
\frac{d[9]}{dt} = k_3[54][\text{PMe}_2\text{Ph}]
\]  

(71)

Applying the steady state approximation for the concentration of 54 gives:

\[
[54] = \frac{k_2[51]}{k_{-2}[\text{CO}] + k_3[\text{PMe}_2\text{Ph}]} \tag{72}
\]

which when substituted into (71) gives:

\[
\frac{d[9]}{dt} = \frac{k_3k_2[51][\text{PMe}_2\text{Ph}]}{k_{-2}[\text{CO}] + k_3[\text{PMe}_2\text{Ph}]} \tag{73}
\]

Because a significant reduction wave is observed for 9 (Figure 21b, c), the limiting case \(k_3 \gg k_{-2}\) gives:

\[
\frac{d[9]}{dt} = k_2[51] \tag{74}
\]

Likewise, the rate equation for [51] is:

\[
\frac{d[51]}{dt} = \nu_1[2] - k_2[51] + k_{-2}[54] \tag{75}
\]

where \(\nu_1\) is the scan rate. Because of the steady state assumption, the third term is insignificant:
Thus the proposed model predicts that the initial reduction wave will be independent of the nucleophile concentration.

This model also predicts the other type of CV observed for 2 in the presence of weak nucleophiles (L). In the limit where \( k_2 \gg k_3 \), equation 73 reduces to:

\[
\frac{d[n]}{dt} = k_3 k_2 [51][L] \quad k_{-2}[CO]
\]

The second reduction wave should therefore show a ligand dependence; this is indeed the case. Figure 22b, c shows the CV of 2 in the presence of 4-DMAP. The reduction wave at \(-1.02\) V for \(\text{Cp}_2\text{Fe}_2(4\text{-DMAP})(\text{CO})(\mu\text{-CO})(\mu\text{-CSMe})^+\), 20, is only obvious at high concentrations (10 equivalents) of 4-DMAP. Alternatively, because of the high concentration of 4-DMAP present, the small cathodic peak for 20 may be due to an equilibrium shift towards 20. However, the cyclovoltammograms with either 1 or 10 equivalents of 4-DMAP have first cycle cathodic waves for 2 of equal height, which indicates that an uncatalyzed reaction between 2 and 4-DMAP is not occurring during these experiments (the uncatalyzed thermal reaction normally takes 6 hours at a 1:6 equivalent
ratio of 2:4-DMAP). Under catalytic conditions, because the reaction between 54 and 4-DMAP is coupled to spontaneous electron transfer reactions (at potentials less than -1.02 V, the reduction potential of 20), observation of a cathodic wave for 20 should not be limited by thermodynamics. Thus, the small cathodic wave observed in Figure 22c is probably due to a kinetic effect.

Lastly, some comment should be made as to why the cathodic wave for 2 does not disappear on subsequent scans. If nucleophilic attack occurs directly with 51, or if conversion from 51 to 54 is rapid enough so as not to effect a subsequent reaction with a nucleophile, then the cathodic peak for 2 should decrease with each successive scan, the rate of decrease being a function of the specific nucleophile, its concentration and scan rate. The fact that the cathodic wave for 2 in Figures 21b, c and 22a, c reaches constant current values after the first scan, indicates that neither nucleophilic attack on 51, nor rapid conversion to 54 occurs. The constant value obtained indicates that there is a process that limits complete consumption of 2 (by the catalytic reaction) in the vicinity of the electrode (not just the diffusion layer next to the electrode); this process, according to the mechanism proposed, is the relatively slow conversion of 51 to 54. It
should be noted that computer simulated CV's for mechanisms like that proposed in equations 65-70 are similar to those obtained in this work.\textsuperscript{147}

A summary of the CV results is shown in Table 11. These results correlate with the known ability of 2 to react with the various ligands. Ligands that produce a strong reduction wave for \(\text{Cp}_2\text{Fe}_2(L)(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})^+\), are found either in this work or by Quick and Angelici\textsuperscript{50} to substitute a CO on 2 giving stable products. Where the reduction wave for \(\text{Cp}_2\text{Fe}_2(L)(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})^+\) is weak or medium, excess nucleophile and long reaction time are required for substitution (PPh\textsubscript{3}, Py, 4-DMAP).

The CV results support a dissociative mechanism for radical catalyzed ligand substitution reactions of 2, the dissociative step involving the equilibrium behavior between 51 and 54 (Eqn 66). A comparison of the current efficiencies given in Table 10, with the reduction potentials of the \(\text{Cp}_2\text{Fe}_2(L)(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})^+\) products given in Table 11, shows that more efficient catalysis occurs as the reduction potential of the product becomes more negative. If the reduction potential is a measure of charge density in the \(\text{Cp}_2\text{Fe}_2(L)(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})^+\) products, this in turn, may be related to the basicity of the ligand (L).\textsuperscript{148} Thus, a correlation can be drawn between the basicity of the
Table 11. Summary of reduction potentials observed for \( \text{Cp}_2\text{Fe}_2(L)(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe})^+ \) products produced during the CV scan of 2 in the presence of L

<table>
<thead>
<tr>
<th>Ligand (L)</th>
<th>Reduction Potential (V)</th>
<th>Intensity of the Product Reduction Wave, (Equ)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEt(_3)</td>
<td>-1.12</td>
<td>Strong (1)</td>
</tr>
<tr>
<td>PMe(_2)Ph</td>
<td>-1.14</td>
<td>Strong (1)</td>
</tr>
<tr>
<td>PMePh(_2)</td>
<td>-1.10</td>
<td>Strong (1)</td>
</tr>
<tr>
<td>PPh(_3)</td>
<td>-1.02</td>
<td>Weak (&gt;10)</td>
</tr>
<tr>
<td>t-BuNC</td>
<td>-1.12</td>
<td>Strong (1)</td>
</tr>
<tr>
<td>Pyridine</td>
<td>-----</td>
<td>not observed (10)</td>
</tr>
<tr>
<td>4-DMAP</td>
<td>-1.02</td>
<td>Medium (10)</td>
</tr>
<tr>
<td>PhC=CPH</td>
<td>-----</td>
<td>not observed (10)</td>
</tr>
<tr>
<td>NCC(H)=C(H)CN</td>
<td>-----</td>
<td>not observed (10)</td>
</tr>
<tr>
<td>Fe(CO)(_3)NO(^-)</td>
<td>-----</td>
<td>not observed (1)</td>
</tr>
</tbody>
</table>

\(^a\) Number of equivalents of L used.
nucleophile and catalytic efficiency, the more basic the	nucleophile the more efficient the catalytic reaction.
This correlation is in agreement with nucleophilic attack
on 54. Because 54 has an open coordination site, its
reactions with nucleophiles should be more dependent upon
electronic effects than steric effects. Thus, basic nucleo-
philes react quickly with 54 and the efficiency of the
catalytic reaction is dependent on the prior dissociation
of CO from 51 (forward reaction in Eqn 66). Weak nucleo-
philes react slowly with 54, and the reaction becomes
dependent, not only on the dissociative equilibrium (Eqn
66), but also on the rate of reaction of nucleophile with
54 (Eqn 67). In Table 10, the current efficiencies for
strong nucleophiles are all about the same (m/n = 32-46).
The consistency of these values, is probably due to the
dissociative step (Eqn 66) in the proposed mechanism (Eqns
65-70). Because strong nucleophilic systems are dependent
on dissociation of CO from 51, this reaction "levels" the
catalytic effect for these nucleophiles. In addition, the
slow dissociative step may cause relatively low current
efficiencies because, while 51 is "waiting around" to lose
CO, it may also be decomposing (i.e. disproportionation,
fragmentation, etc.), resulting in fewer chain propagation
steps. However, it should be noted that CO dissociation
may also be a decomposition pathway.

D. Reactions of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})]PF_6$ with Metal Carbonyl Anions

1. Reaction of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})]PF_6$, 2, with $\text{Na}[\text{Co}(\text{CO})_4]$

   a. Synthesis and spectroscopic properties

   Reaction of the bridging thiocarbyne complex, 2, with excess $\text{Na}[\text{Co}(\text{CO})_4]$ in THF under ultraviolet photolysis gives an 80% yield of the unusual bridging carbyne complex, $\text{Cp}_2\text{Fe}_2-\text{Co(CO)}_3(\mu-\text{CO})_2(\mu_3-\text{CSMe})$, 33, (Eqn 78). The product is an air-stable, brownish-purple solid, soluble in most organic solvents forming brown solutions which are photo-stable but
susceptible to air oxidation. The IR spectrum of 33 (in CH₂Cl₂) shows bands characteristic of terminal (2023, 1981 and 1951 cm⁻¹) and bridging (1818 and 1781 cm⁻¹) CO groups. The ¹H NMR spectrum (in CD₂Cl₂) exhibits three resonances with relative intensities of 5:5:3, having chemical shifts assignable to the cyclopentadienyl and CSMe ligands. The ¹³C NMR spectrum (in CD₂Cl₂) shows resonances for a methyl group (36.63 ppm), two Cp ligands (86.31 and 86.57 ppm), three terminal carbonyls (201.7, 207.7 and 211.3 ppm), two bridging carbonyls (252.1 and 262.1 ppm) and a triply bridging carbyne carbon (322.0 ppm). The resonances at 201.7, 207.7 and 252.1 ppm are carbonyl ligands coordinated to cobalt since they are broadened by the cobalt quadru-pole. The chemical shift of the carbyne carbon is similar to those observed for other μ₃-carbyne complexes: CpFe₃-(CO)₆(μ-CO)₂(μ₃-CMe), 333.0 ppm;¹⁴⁹ Fe₃(CO)₉(μ₃-OMe)(μ₃-CMe), 334.0 ppm.¹⁵⁰ Although these spectral data are consistent with the observed unsymmetrical structure, they do not exclude other similar structures; for that reason the X-ray diffraction study described in Section III.D.6 was undertaken.

The photolytic preparation of 33, according to equation 78, is free from side products. When performed under thermal conditions (25-81°C) using either Na[Co(CO)₄] or PPN[Co-
(CO)$_4$], the reaction gives low yields (< 12%) of 33 for the following reasons: 1) a competing reaction occurs to give Cp$_2$Fe$_2$(CO)$_3$CS, 1, and an unknown cobalt product; 2) higher temperatures decompose the desired product, 33; 3) the mixture obtained under thermal conditions requires chromatographic separation with loss of product.

b. Possible mechanism  
Addition of a THF solution of Na[Co(CO)$_4$] to 2 greatly increases the solubility of the carbyne salt in THF; the color of the reaction mixture changes from light orange to brownish-purple. However, the IR spectrum shows no change from that of the starting materials, suggesting the formation of the ion pair [Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CSMe)$^+$(μ-CSMe)$^-$][Co(CO)$_4^-$]. The color change is presumably due to a charge transfer absorption between the cation and anion as observed for Tl[Co(CO)$_4^-$]. The slowness of the reaction from this point to give 33 may be due to the weak nucleophilicity of Co(CO)$_4^-$.

Since 2 forms μ-carbene complexes with nucleophiles (see Section III.B), formation of 33 might be expected to go through the μ-carbene intermediate, Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-C(SMe)][Co(CO)$_4$]. However, characteristic IR spectral bands for this type of product [e.g. Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-C(SMe)$_2$], has carbonyl bands at 1985(s), 1952(m) and 1786(s) cm$^{-1}$], or any other intermediate species, were absent during the
Alternatively, under UV photolysis, three types of unsaturated iron centers may be formed from 2: 1) 55, which is the result of direct CO loss from 2; 2) 56, a rearranged form of 2 which does not have an Fe-Fe bond and is held together by three bridging ligands; and 3) 57, a rearranged cation of 2 containing no Fe-Fe bond and held together by only the μ-thiocarbyne ligand.

As was mentioned above, no intermediates are observed during the synthesis of 33, thus, formation of any of these species, 55-57, would probably involve slow reactions followed by rapid addition of Co(CO)₄⁻ to give 33. The inter-
mediate, 55, may not be possible, since the utilization of 
Cp₂Fe₂(CH₃CN)₃(CO)(μ-CO)(μ-CSMe)⁺, 6, which has an easily
displaced CH₃CN ligand, did not appear to give a faster
reaction than 2 under the conditions of equation 78.

Cleavage of metal-metal bonds by photolysis is a syn-
thetic pathway for making mixed-metal dimers.¹²⁸,¹⁵³ Thus,
photolysis of the metal-metal bond in 2, to give 56 or 57,
may be a viable path to 33. A precedent for an interme-
diate similar to 56, is the synthesis of Cp₂Fe₂(μ-CO)₃, 58,
by UV photolysis of Cp₂Fe₂(CO)₂(μ-CO)₂ in a hydrocarbon
matrix at 77 K. However, the extreme conditions for syn-
thesesizing 58 compared to the conditions of equation 78, and
the fact that 2 exists only as a cis isomer and 58 is
formed only from trans-Cp₂Fe₂(CO)₂(μ-CO)₂, would probably
preclude intermediate 56 during the synthesis of 33.

Recently, photoreactions (λ = 366-505 nm; in THF at
25°C) of Cp₂Fe₂(CO)₂(μ-CO)₂ with phosphines (PR₃) to give
Cp₂Fe₂(PR₃)(CO)(μ-CO)₂ products, were found to go through the intermediate, Cp(CO)Fe(μ-CO)Fe(CO)₂Cp, which contains a single bridging ligand and no Fe-Fe bond. The difference between Cp(CO)Fe(μ-CO)Fe(CO)₂Cp and 57, is that 57 is bridged by a thiocarbyne ligand and is charged. Because bridging carbyne complexes of the type Cp₂Fe₂(CO)₃(μ-R)⁺, have high activation energies for cis/trans isomerization, and the fact that 2 shows no evidence for this type of isomerization up to 90°C, suggests that the carbyne (thiocarbyne) ligand strongly favors a bridging position. Thus, photolysis of 2 may rupture the Fe-Fe bond and subsequently give 57. The greater stability of the thiocarbyne ligand in the bridging position may also prevent fragmentation of 57. The similarity between conditions for the photoinduced substitution reaction of CpFe₂(CO)₂(μ-CO)₂ and the synthesis of 33, strongly suggests that 57 is formed prior to reaction with Co(CO)₄⁻. Reaction of Co(CO)₄⁻ at the unsaturated iron site in 57 to give a trinuclear intermediate, may occur either by nucleophilic attack, or possibly by an electron transfer reaction, to give the reactive radicals, Co(CO)₄⁺ and Cp(CO)Fe(μ-CSMe)Fe(CO)₂Cp⁺, which could rapidly couple. A radical path, though, may allow Cp₂Fe₂(CO)₂(μ-CO)(μ-CS), 1, to form. Since 1 is not observed in this reaction under
photolytic conditions, a radical path may not be of any significance. The resulting trinuclear species would quickly lose CO to give 33. This is actually observed in the photoinduced phosphine (PR₃) substitution reactions of Cp₂Fe₂(CO)₂(μ-CO)₂; when carried out at -78°C, the product, Cp(PR₃)(CO)Fe(μ-CO)Fe(CO)₂Cp, was isolated. This species, which has a (μ-CO) and no Fe-Fe bond, rapidly loses CO above -78°C to give the Cp₂Fe₂PR₃(CO)(μ-CO)₂ products.

The mechanism for the synthesis of 33, under photolytic conditions, might be described by Figure 23. This mechanism may explain the results obtained from the reaction of Cp₂Fe₂(PET₃)(CO)(μ-CO)(μ-CSMe), 8, with Na[Co(CO)₄] under photolytic conditions. The reaction requires about 10 hours for completion, and gives a mixture of 33 and Cp₂Fe₂-CoPET₃(CO)₂(μ-CO)(μ-CSMe), 35. An intermediate analogous to 57 formed in this reaction would be 59:

![Figure 23](image_url)

Electron donation by phosphine would stabilize the unsaturated iron center. However, steric crowding by phosphine
Figure 23. Proposed mechanism for the reaction of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^+ \) with Na[Co(CO)]_4.
about the iron center may account for the longer reaction time. In addition, the resulting tri-nuclear intermediate

\[35^*\]

would have to lose \(\text{PET}_3\) and CO to give the cluster product, 33. Free \(\text{PET}_3\) then may react with 33 to give 35.

Because 2 can be reduced to \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})^*\), radical mechanisms also have to be considered. Electron transfer from Co(CO)\(_4\)^− to 2 may give a pair of radicals, Co(CO)\(_4^*\) and 51. Under UV photolysis, these radicals may lose CO, opening coordination sites on the metal centers; subsequent coupling of the unsaturated radicals could form 33. Metal carbonyl radicals are known to labilize CO, especially upon irradiation.\(^{155,156}\) In addition, radical coupling reactions have been shown to be quite rapid.\(^{128}\) Since Co(CO)\(_4^*\) is a weak reductant,\(^{139,152}\) the rate-limiting step in this process would probably be the electron transfer reaction. In this vein, addition of 51 to the reaction, may catalyze the synthesis of 33. Figures 24 and 25 compare the IR spectra of the reaction, with and without
Figure 24. Infrared spectra (in THF) of the photolytic reaction of 2 with Na[Co(CO)$_4$] with time, uncatalyzed reaction.
Figure 25. Infrared spectra (in THF) of the photolysis reaction of 2 with Na[Co(CO)₄] with time, catalyzed with 0.1 eq. of chemically generated 51
the addition of 0.1 equivalent of 51. These spectra show a small but definite enhancement of 33 production in the presence of 51. A comparison of the relative intensities of the 1975 cm\(^{-1}\) IR spectral band with time, indicates that the enhancement is temporary. Thus, 51 may have some initial catalytic effect which sets the reaction ahead of the uncatalyzed reaction. Considering the poor nucleophilicity of Co(CO)\(_4\)^-, it is not surprising that the catalytic effect is poor. Decomposition of 51, especially at 25°C and under photolytic conditions,\(^{155,156}\) probably competes with nucleophilic substitution.

The lack of a sustained catalytic effect when 51 is introduced into the reaction of 2 with NaCo(CO)\(_4\), probably indicates that a radical mechanism is not a major route to 33 under photolytic conditions (However, a radical mechanism may account for the formation of 33 under thermal conditions). Because there is precedence for forming intermediates like 57 under photolytic conditions similar to those in equation 78, and the fact that these intermediates react with nucleophiles and subsequently lose CO rapidly to give metal-metal bonded products, the mechanism in Figure 23 is probably the best description currently proposed for the synthesis of 33.
2. Reactions of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSCH}_2\text{Ph})]\)PF_6, 3, and \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSCH}_2\text{CH}=\text{CH}_2)]\)PF_6, 4 with Na[Co(CO)_4]

Preparation of \(\text{Cp}_2\text{Fe}_2\text{Co(CO)}_3(\mu-\text{CO})_2(\mu_3-\text{CSCH}_2\text{Ph})\), 34, from 3 and Na[Co(CO)_4], under the conditions of equation 78, results in low yields (<13%) due to the facile formation of 1. At 12°C, higher yields (28%) are obtained. Under thermal conditions (25°C), the IR spectrum of the reaction mixture shows that 34 is formed as a minor product (ca. <10%); the other product formed is 1. Product 34 is a brownish-purple solid which has a shelf-life under a nitrogen atmosphere of less than a month. The similarity of its IR (Table 13) and \(^1\text{H NMR}\) (Table 12) spectra to those of 33, established it as having the same basic structure.

Reaction of 4 with Co(CO)_4\(^-\) gives substantial amounts of 1 under thermal conditions. Because none of the allyl analogue of 33 appears to form, the prospects of isolating \(\text{Cp}_2\text{Fe}_2\text{Co(CO)}_3(\mu-\text{CO})_2(\mu-\text{CSCH}_2\text{CH}=\text{CH}_2)\) under photolytic conditions were minimal, thus, this synthesis was not pursued.

3. Reactions of other metal carbonyl anions with \([\text{CpFe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSMe})]\)PF_6, 2

Other metallate anion reactions with 2 are less successful. Three types of results are observed. In the first, the anions Mn(CO)_5\(^-\), Re(CO)_5\(^-\), CpFe(CO)_2\(^-\) and CpMo-
Table 12. Infrared stretching frequencies (cm\(^{-1}\)) for metal complexes discussed in Section III.D

<table>
<thead>
<tr>
<th>Compound(^a)</th>
<th>Solvent</th>
<th>(\nu_{CO})(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe'Co(CO)(_3) (µ-CO)(_2) (µ-CSMe), 33</td>
<td>CH(_2)Cl(_2)</td>
<td>2023 (s), 1981 (s), 1951 (w), 1818 (s), 1781 (w)</td>
</tr>
<tr>
<td>Fe'Co(CO)(_3) (µ-CO)(_2) (µ-CSCH(_2)Ph), 34</td>
<td>CH(_2)Cl(_2)</td>
<td>2024 (s), 1982 (s), 1950 (w), 1820 (s), 1752 (w)</td>
</tr>
<tr>
<td>Fe'Co(PBT(_3)) (CO)(_2) (µ-CO)(_2) (µ(_3)-CSMe), 35</td>
<td>CH(_2)Cl(_2)</td>
<td>1976 (s), 1926 (w), 1796 (s), 1760 (w)</td>
</tr>
<tr>
<td>Fe'Co(PPh(_3)) (CO)(_2) (µ-CO)(_2) (µ(_3)-CSMe), 40</td>
<td>CH(_2)Cl(_2)</td>
<td>1980 (s), 1930 (w), 1798 (s), 1760 (w)</td>
</tr>
<tr>
<td>Fe'Co(PCy(_3)) (CO)(_2) (µ-CO)(_2) (µ(_3)-CSMe), 41</td>
<td>CH(_2)Cl(_2)</td>
<td>1977 (s), 1928 (w), 1793 (s), 1753 (w)</td>
</tr>
<tr>
<td>Fe'Co(PHPh(_2)) (CO)(_2) (µ-CO)(_2) (µ(_3)-CSMe), 42</td>
<td>CH(_2)Cl(_2)</td>
<td>1982 (s), 1937 (w), 1803 (s), 1762 (w)</td>
</tr>
<tr>
<td>Fe'Co(PMePh(_2)) (CO)(_2) (µ-CO)(_2) (µ(_3)-CSMe), 43</td>
<td>CH(_2)Cl(_2)</td>
<td>1979 (s), 1928 (w), 1796 (s), 1755 (w)</td>
</tr>
<tr>
<td>Compound</td>
<td>Solvent</td>
<td>ν(CO) - cm⁻¹</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>---------</td>
<td>--------------</td>
</tr>
<tr>
<td>$\text{Fe}^\prime\text{Co(dppm)}(\text{CO})_2(\mu-\text{CO})_2(\mu_3-\text{CSMe})$, 44</td>
<td>CH₂Cl₂</td>
<td>1937(s), 1760(s), 1720(w)</td>
</tr>
<tr>
<td>$\text{Fe}^\prime(\eta^1-\text{dppe})(\text{CO})_2(\mu-\text{CO})_2(\mu_3-\text{CSMe})$, 45</td>
<td>CH₂Cl₂</td>
<td>1980(s), 1930(w), 1795(s), 1755(w)</td>
</tr>
<tr>
<td>$\text{Fe}^\prime\text{Co[P(OMe)_3]}(\text{CO})_2(\mu-\text{CO})_2(\mu_3-\text{CSMe})$, 46</td>
<td>CH₂Cl₂</td>
<td>1987(s), 1947(w), 1810(s), 1780(w)</td>
</tr>
<tr>
<td>$\text{PPN[Fe}^\prime\text{Co(CN)}(\text{CO})_2(\mu-\text{CO})_2(\mu-\text{CSMe})]$, 48</td>
<td>CH₂Cl₂</td>
<td>1967(s), 1916(m), 1786(s), 1745(w), 2082(w)c</td>
</tr>
<tr>
<td>$\text{Fe}^\prime\text{Co(t-BuNC)}(\text{CO})_2(\mu-\text{CO})_2(\mu-\text{CSMe})$, 49</td>
<td>CH₂Cl₂</td>
<td>1982(s), 1939(m), 1800(s), 1765(w), 2130(s)d</td>
</tr>
<tr>
<td>$\text{Fe}^\prime\text{Co(t-BuNC)}_2(\text{CO})_2(\mu-\text{CO})_2(\mu-\text{CSMe})$, 50</td>
<td>CH₂Cl₂</td>
<td>1930(s), 1780(s), 1740(w), 2120(s)d</td>
</tr>
</tbody>
</table>

a. Abbreviations: $\text{Fe}^\prime = \text{Cp}_2\text{Fe}_2(\text{CO})_2$, $\text{Fe}^\prime = \text{Cp}_2\text{Fe}_2$.
b. Abbreviations: s = strong, m = medium, w = weak, sh = shoulder.
c. ν(CN) stretch.

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Table 13. $^1$H NMR chemical shifts (ppm) for metal complexes discussed in Section III.D

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Cp δ</th>
<th>Others&lt;sup&gt;b&lt;/sup&gt; δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe'Co(CO)$_3$(μ-CO)$_2$(μ$_3$-CSMe)$_2$, 33</td>
<td>CDCl$_3$</td>
<td>4.83, 4.42</td>
<td>2.75(Me)</td>
</tr>
<tr>
<td>Fe'Co(CO)$_3$(μ-CO)$_2$(μ$_3$-CSCH$_2$Ph)$_2$, 34</td>
<td>CDCl$_3$</td>
<td>4.92, 4.50</td>
<td>7.54(m, Ph)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fe'Co(PPh)$_3$(CO)$_2$(μ-CO)$_2$(μ$_3$-CSMe)$_2$, 35</td>
<td>CDCl$_3$</td>
<td>4.85, 4.38</td>
<td>2.77(SMe), 1.67(b, PCH$_2$), 1.11(b, PCCH$_3$)</td>
</tr>
<tr>
<td>Fe'Co(PPh)$_3$(CO)$_2$(μ-CO)$_2$(μ$_3$-CSMe)$_2$, 40</td>
<td>CDCl$_3$</td>
<td>4.87, 3.97</td>
<td>7.56(m, Ph), 2.80(Me)</td>
</tr>
<tr>
<td>Fe'Co(PCy)$_3$(CO)$_2$(μ-CO)$_2$(μ$_3$-CSMe)$_2$, 41&lt;sup&gt;d&lt;/sup&gt;</td>
<td>CDCl$_3$</td>
<td>4.92, 4.50</td>
<td>2.83(SMe), 1.26(b, Cy)</td>
</tr>
<tr>
<td>Fe'Co(PPh)$_2$(CO)$_2$(μ-CO)$_2$(μ$_3$-CSMe)$_2$, 42</td>
<td>CDCl$_3$</td>
<td>4.86, 4.24</td>
<td>7.41(m, Ph)&lt;sup&gt;e&lt;/sup&gt;, 2.78(Me)</td>
</tr>
</tbody>
</table>
Fe'Co(PMePh₂)(CO)₂(μ-CO)₂(μ₃-CSMe), 43  CDCl₃  4.79, 3.98  7.35(Ph),
2.87(SMe),
1.97(d, PMe,
JₚH = 6.5 Hz)

Fe'Co(dppm)(CO)(μ-CO)₂(μ₃-CSMe), 44  CDCl₃  4.38, 4.39  7.13(m, Ph),
2.85(Me),
1.76(b, CH₂)

^Abbreviations: Fe* = Cp₂Fe₂(CO)₂, Fe' = Cp₂Fe₂.
^Abbreviations: b = broad, d = doublet, m = multiplet, t = triplet.
^CH₂ resonance not observed, but possibly lies under Cp resonance
at 4.50 ppm.
^Spectrum taken in the presence of 7 equivalents of PCy₃.
^PH resonance not observed, but possibly lies under Ph resonance.
(CO)$\text{}_3$ give redox reactions. This is most evident in the Re, Fe, and Mn cases, which produce the deep emerald green color typical of the radical, 51, on mixing with 2. Products isolated from these reactions include Re$_2$(CO)$_{10}$, Cp$_2$Fe$_2$(CO)$_4$, Mn$_2$(CO)$_{10}$, Cp$_2$Fe$_2$(CO)$_3$CS and (CO)$_5$ReFe(CO)$_2$Cp. Efforts to control these reactions by using the PPN salts of the carbonyl anions,\textsuperscript{138} or lowering the reaction temperature, are not successful. Pentacarbonyl rhenate forms the radical immediately even at -70°C. The weakest reductant of this group,\textsuperscript{152} CpMo(CO)$_3$-, does not produce a green radical solution. However, its reactions with 2 or 6 under thermal and photolytic conditions gives products 1 and Cp$_2$Mo$_2$(CO)$_6$, which can be ascribed to a redox reaction. In the second type, the metal anions, Fe(CO)$_3$NO$^-$, Cr(CO)$_5$- and W(CO)$_4$(CS)I$^-$, are such poor nucleophiles\textsuperscript{139} that they do not react. A CV of 2 in the presence of 1 equivalent of Fe(CO)$_3$NO$^-$ (see Table 11), shows no hint of another reduction wave. The third class of metal anion reactions includes only [HFe(CO)$_4$]$^-$ and Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-C(H)SMe), 15, (ca. 11% yield), which indicates that [HFe(CO)$_4$]$^-$ acts partially as a H$^-$ donor; its other functions are not obvious.
4. **Attempted reactions of \( \text{Cp}_2\text{Fe}_2(I)(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe}) \),** 10

Attempts to obtain clusters by halide substitution (Eqn 79) on \( \text{Cp}_2\text{Fe}_2(I)(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe}) \), 10, were unsuccessful. With \( \text{CpMo(CO)}_3^- \) no reaction occurs at room temperature, while refluxing in THF gives \( \text{Cp}_2\text{Mo}_2(\text{CO})_6 \) and \( \text{CpMo(CO)}_3\text{CH}_3 \). Alternatively, reacting electrophilic metal fragments with 1 are unsuccessful (Eqn 80).

![Chemical structure](image1)

\[
\text{Cp}_2\text{Fe}_2(I)(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe}) + M(\text{CO})_x^- \xrightarrow{\text{THF}} \text{Cp}_2\text{Fe}_2(I)(\text{CO})(\mu-\text{CO})(\mu-\text{CSMe}) + M(\text{CO})_y \]

(Eqn 79)

5. **Reactions of 33**

Addition of seven equivalents of \( \text{PPh}_3 \) to a \( \text{CH}_2\text{Cl}_2 \) solution of 33 results in the formation of the black, crystalline, air-stable solid, \( \text{Cp}_2\text{Fe}_2\text{Co(PPh}_3)(\text{CO})_2(\mu-\text{CO})_2(\mu_3-\text{CSMe}) \), 40, in 93% yield (Eqn 81). It was anticipated that a product resulting from the \( \text{PPh}_3 \) displacement of the \( \text{SMe} \) bonded to the Co would be obtained; an X-ray
diffraction study (vide infra) of 40 shows, instead, that a CO group on Co was replaced by phosphine. The $^{13}$C spectrum of 40 (Figure 26 and 27) shows one sharp (212.4 ppm) and one broad (205.8 ppm) resonance, which may be assigned to the single terminal CO ligands on the Fe and Co, respec-

$$\text{Cp}_2\text{Fe}_2\text{Co(CO)}_3(\mu-\text{CO})_2(\mu_3-\text{CSMe}) + \text{PPh}_3 \xrightarrow{25°C, 9 \text{ hrs}} \text{CH}_2\text{Cl}_2$$

33

$$\text{OC} \quad \text{S} \quad \text{C} \quad \text{Fe} \quad \text{Cp} \quad \text{Me}$$

$$\text{PPh}_3\text{Co} \quad \text{C} \quad \text{Fe} \quad \text{Cp} \quad \text{OC}$$

40

tively; the Co-CO resonance is broadened by the Co quadrupole. In addition, two bridging carbonyls at 253.7 ppm, Fe(\mu-\text{CO})Co, and 262.2 ppm, Fe(\mu-\text{CO})Fe, and a resonance at 317.7 ppm due to the \mu_3-C ligand were observed. The high field \mu-CO resonance is so broad that P coupling could not be resolved. The chemical shift of the carbyne carbon is shifted upfield by 4.3 ppm compared to the parent complex, 33. In addition, this resonance occurs as a doublet, $J_{PC} = 15.9 \text{ Hz}$, which is in the range observed for other \mu_3-carbynes: \{FePtW(Cp)(CO)_5(PMe_2Ph)_2(\mu-CO)(\mu_3-CC_6H_4Me-4)\},
Figure 26. The $^{13}$C NMR spectrum of \( \text{Cp}_2\text{Fe}_2\text{Co}({\text{PPh}_3})\text{(CO)}_2(\mu-\text{CO})_2(\mu_3-\text{CSMe}) \), 40, taken in CD$_2$Cl$_2$ in the presence of 7 equivalents of PPh$_3$. 
Figure 27. Expansion of Figure 26 in the region 205-320 ppm
$J_{PC} = 27.0\text{ Hz;}\ [\text{FePtW(Cp)(CO)}_6(\text{PMePh}_2)(\mu_3-\text{CC}_6\text{H}_4\text{Me}-4)], J_{PC} = 7.0\text{ Hz}.\text{51}$

The $^1H$ NMR spectrum of 40 (Table 13) has four resonances assignable to the aromatic, cyclopentadienyl and CSMe ligands. The chemical shift of one Cp resonance is essentially the same in 33 and 40; the other Cp resonance of 40 is $0.45\text{ ppm}$ upfield from that in 33. The crystal structure of 40 (Figure 29) shows the phenyl ring of the PPh$_3$ ligand positioned orthogonal to the Cp ring of Fe(1). This phenyl orientation is probably favored for steric reasons and may result in diamagnetic anisotropic shielding, causing an upfield shift of the Cp resonance. Upfield shifts of $0.18\text{ ppm}$ and $0.44\text{ ppm}$ are also observed for the PHPh$_2$ and PMePh$_2$ derivatives, 42 and 43, respectively. The smaller upfield shift for the PHPh$_2$ complex is probably due to the lower steric requirements of this ligand,\textsuperscript{157} which may not require as strict an orthogonal configuration of the Ph and Cp rings.

Excess PPh$_3$ is necessary to drive the reaction in equation 82 to completion and to prevent decomposition of 40 back to 33. Apparently, 40 decomposes by PPh$_3$ dissociation, giving an unsaturated species which scavenges free CO liberated by some decomposition of 40. A sample of 40, when recrystallized in the absence of PPh$_3$, gives an ap-
proximately equal mixture of 33 and 40. The IR spectrum of a solution of 40 reverts after 20 hours to a spectrum that is similar to that obtained from a mixture of 1 equivalent each of PPh₃ and 33.

The reaction of a slight excess of PEt₃ with 33 is essentially complete after 1 hour, giving a 67% yield of the black, crystalline solid, Cp₂Fe₂(PET₃)(CO)₂(μ-CO)₂(μ₃-CSMe), 35. Due to the limited solubility of 35, a ¹³C NMR spectrum was not obtained. The ¹H NMR spectrum (Table 13), shows Cp and SMe resonances with chemical shifts similar to those of the parent complex, 33. Resonances for the CH₂ (1.68 ppm) and CH₃ (1.11 ppm) protons of the PEt₃ ligand are unresolved, broadened multiplets. Similar resolution problems were observed for the methyl protons of the PMe₂Ph ligands coordinated to cobalt in [CpCo₂W(μ₃-CC₆H₄Me-4)(CO)₆(PMe₂Ph)₂]. Solutions of 35 show only slight reversion to 33 after 5 hours. The greater stability of 35 compared to 40, may be due to the higher basicity of PEt₃ over PPh₃. However, steric effects may also be important. In the crystal structure (Figure 29) of 40, the Co-P-C(18) angle is about 5° smaller than the other two Co-P-C angles, while the Fe(1)-Co-P angle is 10° larger than the Fe(1)-Co-C(7) angle in 33. Although these differences are small, they do indicate some steric strain in the phosphine
complexes.

Steric factors affecting the stability of the phosphine substituted complexes are more evident for the PCy$_3$ derivative. Reaction of seven equivalents of PCy$_3$ with 33 for 12 hours gives a 54% yield of black, crystalline, Cp$_2$Fe$_2$Co(PCy$_3$)(CO)$_2$(μ-CO)$_2$(μ$_3$-CSMe), 41. In the solid state, 41 is stable for at least 6 months under nitrogen at -20°C; however, solutions of 41 are very unstable. The IR spectrum (Table 12) of a solution of 41 reverts, within one hour, to a spectrum similar to one obtained upon mixing 1 equivalent each of PCy$_3$ and 33. Whereas the $^1$H NMR spectrum (Table 13) of 40 can be obtained without significant decomposition, the spectrum of 41 can only be obtained in the presence of excess (seven equivalents) PCy$_3$.

The phosphines, PHPh$_2$ and PMePh$_2$, react with 33 to give the black, crystalline products, Cp$_2$Fe$_2$Co(PHPh$_2$)(CO)$_2$(μ-CO)$_2$(μ$_3$-CSMe), 42 and Cp$_2$Fe$_2$Co(PMMePh$_2$)(CO)$_2$(μ-CO)$_2$(μ$_3$-CSMe), 43, respectively. Solutions of 42 and 43 are approximately as stable as the PPh$_3$ derivative, i.e. IR (Table 12) and $^1$H NMR (Table 13) spectra of 42 and 43 are obtainable with little or no excess phosphine being present. Two equivalents of dppm react with 33 to give a 57% yield of Cp$_2$Fe$_2$Co(CO)(μ-CO)$_2$(dppm)(μ$_3$-CSMe), 44. The IR spectrum shows evidence for one terminal (1937 cm$^{-1}$) and
two bridging (1760 and 1720 cm\(^{-1}\)) CO ligands. The \(^{31}\)P[H] spectrum has a broad resonance at 46.45 ppm and a sharp doublet at 72.95 ppm (\(J_{pp} = 81.4\) Hz), indicating phosphine substitution at Co and Fe, respectively.\(^{158-160}\) In comparison, the \(^{31}\)P resonance for free dppm is at -23.6 ppm.\(^{161}\)

A possible structure for 44 is shown below. This structure assumes that the metal core remains intact with

![Structure 44](image)

the dppm ligand bridging the Co-Fe(2) distance of about 3.5 Å (Table 14). The ability of dppm to coordinate to two widely separated metals is demonstrated in "A-frame" complexes [e.g. \(\text{Pd}_2(\text{dppm})_2(\mu-\text{SO}_2)\text{Cl}_2\) (Pd-Pd = 3.38(4) Å)].\(^{162-164}\) Although the probable Co-Fe(2) distance (ca. 3.50 Å) in 44 is about 0.12 Å longer, an intra-ligand P-P distance of 3.429 Å has been observed in the complex, \(\text{Rh}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{Cl})(\text{dppm})_2^+\).\(^{165}\)

The IR spectrum of the dppm reaction after 11 hours
shows carbonyl bands at 1980(s), 1937(w), 1795(s) and 1760(w) cm\(^{-1}\), which are similar to the monodentate products, 35, 40-43. This would indicate initial coordination of one of the dppm ligands to cobalt. An additional 35 hours is required to convert this intermediate to 44. With a large excess of dppm, the reaction gives the intermediate product within an hour, but formation of the final product still requires an additional 24 hours of stirring. The shorter reaction time is of no advantage since excess dppm is difficult to separate from 44 during work up. The solid product is stable under nitrogen for less than 2 months at room temperature. Solutions of 44 are stable over several hours under nitrogen at room temperature. However, they decompose to insoluble products when exposed to heat and oxygen.

In a qualitative experiment, Ph\(_2\)PCH\(_2\)CH\(_2\)PPh\(_2\) (dppe) reacts with 33, to give a product, 45, having IR spectral carbonyl bands at 1980(s), 1930(w), 1795(s) and 1755(w) cm\(^{-1}\) that correspond to coordination of one end of the dppe ligand to cobalt. Unlike the dppm case, long reaction times (24 hours) show no further reaction to give a product similar to 44. Either the "bite" of this ligand is unsatisfactory for bridging between the Co and Fe(2) atoms, or dppe forms a dimeric species by substituting a carbonyl on
the cobalt of two 33 molecules.

Complex 33 reacts with P(OPh)$_3$, P(OMe)$_3$, CN$^-$ and t-
BuNC to give the monosubstituted products, 46-49, respec-
tively. The similarity of their IR spectra (Table 12) to
the phosphine derivatives', 35 and 40-43, indicates that a
CO on cobalt was substituted. Isolation of the products
free of excess ligand was not possible without product
decomposition. With excess t-BuNC a disubstituted product,
50, with an IR similar (CH$_2$Cl$_2$: 1930(s), 1780(s), 1740(w)
cm$^{-1}$) to 44 (see Table 12) is observed but not isolatable.

Treatment of 33 in CH$_2$Cl$_2$ with excess NEt$_3$, NHEt$_2$,
NH$_2$Bu, pyridine, 4-dimethylaminopyridine, SbPh$_3$, AsPh$_3$, CO,
H$_2$, Me$_2$S, SPh$_3$, ONMe$_3$, PhS$^-$, I$^-$, N$_3^-$, NO$_2^-$, MeI, PhC=CH,
cylohexene, fumaronitrile and CS$_2$ shows no reaction at
room temperature after 1 hour.

Addition of HBF$_4$-Et$_2$O to 33 gives 2 as the only stable
carbonyl containing product. Dark colored products are
also observed which readily decompose to insoluble mater-
ial. Surprisingly, CH$_3$SO$_3$F does not react with 33. The
monodentate phosphine derivatives, 40 and 35, react with
HBF$_4$-Et$_2$O to give 2 as the only stable carbonyl containing
product. The bidentate complex, 44, reacts with HBF$_4$-Et$_2$O
giving a product with carbonyl bands in the IR at 1990(s)
and 1815(s) cm$^{-1}$. Since these bands are similar to those
observed for phosphine derivatives of $2,^{50}$ this product is most likely $[\text{Cp}_2\text{Fe}_2(\text{CO})(\eta^1-\text{dppm})(\mu-\text{CO})(\mu-\text{CSMe})]\text{BF}_4$.  

Oxidation of $33$ in $\text{CH}_2\text{Cl}_2$ with $\text{Ag}^+$, $\text{Ph}_3\text{C}^+$, $I_2$ or $\text{NOPF}_6$ gives $2$ within 10 minutes; with $\text{NOPF}_6$ (2 equivalents) the yield of $2$ is $>90\%$. A stable cobalt product containing carbonyl ligands was not observed. Oxidation with $I_2$ in the presence of excess $\text{PPh}_3$ did not trap the expected $\text{Co(CO)}_2^+$ product as $\text{ICo(CO)}_2(\text{PPh}_3)_2$.\textsuperscript{119} Chemical oxidation ($\text{Ag}^+$, halogens) of $\mu_3$-carbyne clusters of cobalt, $[\{\text{(CO)}_9-n(X)_n\text{Co(\mu}_3\text{-CMe)}]\}; \ X = \text{phosphine}; \ n = 1-3$ also yields unstable cobalt products.\textsuperscript{166,167} In a similar reaction, $52$, which contains a bridging carbene that is also coordinated to cobalt through sulfur, reacts with oxidants to give the stable terminal carbene complex, $\text{CpFe(CO)}_2(\text{C-(SMe)}_2)_2^+$.\textsuperscript{119,120} In this case, the $\text{Co(CO)}_2^+$ product was trapped as $\text{ICo(CO)}_2(\text{PPh}_3)_2$ when the $I_2$ oxidation was performed in the presence of excess $\text{PPh}_3$. Thus, the oxida-
tion of 33 is very similar to the oxidation of 52 in that a Co(CO)$_2$ group is removed from both.

6. Molecular structures of Cp$_2$Fe$_2$Co(CO)$_3$(μ-CO)$_2$(μ$_3$-CSMe)$_3$, 33, and Cp$_2$Fe$_2$Co(CO)$_2$(PPh$_3$)(μ-CO)$_2$(μ$_3$-CSMe)$_4$, 40

The atom labeling scheme and molecular geometry of the bridged thiocarbyne complexes, 33 and 40, are shown in Figures 28 and 29, respectively. Selected bond lengths and angles of both compounds are compared in Tables 14 and 15. Since the structures are similar and the bond distances and angles are more precise for 33, this discussion will focus mainly on the unsubstituted complex, 33.

The crystallographically determined structure of 33 has a trinuclear core that is approximately "L" shaped with a Co-Fe(1)-Fe(2) angle of 88.38°; there is no metal-metal bond between Co and Fe(2), (3.511(1) Å). The bridging thiocarbyne ligand bonds to all three metals through the carbyne carbon, and, in addition, coordinated to cobalt through the sulfur atom. A similar type of coordination is observed for the μ$_3$-COMe ligand in the complex, Fe$_4$-(CO)$_{12}$(μ-H)(μ$_3$-COMe)$_4$. The "open" triangular structure observed for 33 is unusual for μ$_3$-carbyne complexes in that most complexes of this type have a "closed" structure with metal-metal bonds between the three metal
Figure 28. ORTEP drawing of $\text{Cp}_2\text{Fe}_2\text{Co(CO)}_3(\mu-\text{CO})_2(\mu_3-\text{CSMe})$, 33
Figure 29. ORTEP drawing of $\text{Cp}_2\text{Fe}_2\text{Co(PPh}_3\text{)}(\text{CO})_2(\mu-\text{CO})_2(-\text{Fe}(\mu_3-\text{CSMe}))$, 40
Table 14. Selected bond distances\(^a\) for Cp\(_2\)Fe\(_2\)Co(CO)\(_3\)-
\((\mu^-\text{CO})\(_2\)(\mu^-_3\text{-CSMe}), 33, and Cp\(_2\)Fe\(_2\)Co(PPH\(_3\))(CO)\(_2\)-
\((\mu^-\text{CO})\(_2\)(\mu\_3\text{CSMe}), 40

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\(^a\) The number in the parentheses are the estimated standard deviations in the last significant digits.
\(^b\) Atoms are labeled in agreement with Figures 28 and 29.
Table 14 (Continued)

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Table 15. Selected bond angles\(^a\) for Cp\(_2\)Fe\(_2\)Co(CO)\(_3\)(\(\mu\)-CO)\(_2\)(\(\mu_3\)-CSMe), 33 and Cp\(_2\)Fe\(_2\)Co(PPh\(_3\))(CO)\(_2\)\(^-\)(\(\mu\)-CO)\(_2\)(\(\mu_3\)-CSMe), 40

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<td>47.4(2)</td>
<td>46.8(7)</td>
</tr>
</tbody>
</table>

\(^a\) The number in parentheses are the estimated standard deviation in the last significant digits.

\(^b\) Atoms are labeled in agreement with Figures 28 and 29.
<table>
<thead>
<tr>
<th>Type</th>
<th>Angle, deg (33)</th>
<th>Angle, deg (40)</th>
</tr>
</thead>
<tbody>
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<td>Co-S-C1</td>
<td>54.4(2)</td>
<td>52.0(8)</td>
</tr>
<tr>
<td>Cl-Co-C7</td>
<td>144.8(3)</td>
<td>-</td>
</tr>
<tr>
<td>Cl-Co-P</td>
<td>-</td>
<td>141.6(8)</td>
</tr>
<tr>
<td>Fe1-Fe2-C4</td>
<td>104.7(2)</td>
<td>-</td>
</tr>
<tr>
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<td>132.7(3)</td>
<td>129.1(9)</td>
</tr>
<tr>
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<td>115.9(2)</td>
<td>-</td>
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<tr>
<td>Fe1-Co-P</td>
<td>-</td>
<td>125.1(3)</td>
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<tr>
<td>C3-Co-P</td>
<td>-</td>
<td>99.4(9)</td>
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<td>Co-P-C18</td>
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<td>117.5(8)</td>
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<tr>
<td>Co-P-C20</td>
<td>-</td>
<td>117.1(8)</td>
</tr>
</tbody>
</table>
Other "open" triangular \(\mu_3\)-carbyne complexes include \([(CO)_3Fe]_3(\mu_3-CMe)(\mu_3-OMe)\)\(^{150}\), \(60\), and the Pt and W complexes derived from \(\text{L}_2\text{Pt}(\mu-\text{CC}_6\text{H}_4\text{Me}-4)\text{W}(\text{CO})_2\text{Cp}\) (\(\text{L} = \text{CO or phosphine}\)) such as \([\text{Pt}_2\text{W}(\mu_3-\text{CC}_6\text{H}_4\text{Me}-4)(\text{CO})_4(\text{PMePh}_2)_2(\text{Cp})]\)\(^{55,169}\).

Complex \(60\) is, to my knowledge, the only other triply bridging carbyne complex with an "open" triangular cluster of first row transition metals. This complex has an \(\text{Fe}(1)-\text{Fe}(2)-\text{Fe}(3)\) angle of \(76.7^\circ\) and an \(\text{Fe}(1)-\text{Fe}(3)\) distance of \(3.059(4)\) \(\AA\). The \(\text{Fe}(1)-\text{Fe}(2)\) distance (\(2.537(1)\) \(\AA\)) in \(33\) is longer than either \(\text{Fe}-\text{Fe}\) distance (\(2.472(3)\) \(\AA\), \(2.459(3)\) \(\AA\)) in \(60\). However, it is similar to the corresponding distances in \(\text{Cp}_2\text{Fe}_2(\mu-\text{CO})_2(\text{CO})_2\) (\(2.531(2)\) \(\AA\))\(^96\) and \([\text{Fe}_2\text{W}(\mu_3-\text{CC}_6\text{H}_4\text{Me}=4)(\mu-\text{CO})(\text{CO})_8\text{Cp}\]) (\(2.538(2)\) \(\AA\)).\(^41\) The \(\text{Fe}(1)-\text{Co}\) distance (\(2.500(1)\) \(\AA\)) is the same as in \(\text{Cp}(\text{CO})\text{Fe}(\mu-\text{CO})[\mu-\text{C(SMe)}_2]\text{Co}(\text{CO})_2\), \(52\), (\(2.502(1)\) \(\AA\))\(^{120}\) but is shorter than in the carbonyl-bridged complex \((\text{CO})_3\text{Co}(\mu-\text{CO})_2\text{Fe}(\text{CO})\text{Cp}\) (\(2.545(1)\) \(\AA\)).\(^{170}\)

The dihedral angle formed by the planes \(\text{Fe}(1)-\text{C}(1)-\text{Fe}(2)\) and \(\text{Fe}(1)-\text{C}(5)-\text{Fe}(2)\) is \(150.8^\circ\); this compares with \(164^\circ\) found between the two \(\mu-\text{CO}\) \(\text{Fe}\) planes in \(\text{Cp}_2\text{Fe}_2(\mu-\text{CO})_2(\text{CO})_2\).\(^96\) The planes, \(\text{Co}-\text{C}(1)-\text{Fe}(1)\) and \(\text{Co}-\text{C}(6)-\text{Fe}(1)\), make a dihedral angle of \(140.9^\circ\); this compares with dihedral angles between the \(\mu-\text{CO}\) \(\text{Co}\) planes found in
(CO)$_3$Co($\mu$-CO)$_2$Fe(CO)Cp (143.5°)$^{170}$ and ($\eta^5$-C$_9$H$_7$)(CO)Fe($\mu$-
CO)$_2$Co(CO)$_3$ (148.0°)$^{171}$ Relative to the metal-to-bridge-
carbon distance in cis-Cp$_2$Fe$_2$($\mu$-CO)$_2$(CO)$_2$$^{96}$ and Co$_2$-
(CO)$_8$$^{172}$ the Co-(\mu-CO) distance is reduced slightly from
1.92(1) \AA to 1.897(7) \AA, while the Fe(1)-(\mu-CO) distance
had lengthened from 1.917(4) \AA to 1.951(7) \AA. Likewise,
the \mu-CO between the iron atoms is shifted towards Fe(1),
Fe(1)-(\mu-CO) = 1.867(7) \AA, Fe(2)-(\mu-CO) = 1.998(7) \AA.

The geometry about the bridging carbyne carbon is
unusual in that it lies only 0.724 \AA off the metal plane,
substantially less than the 1.25 \AA observed for the
"closed" metal triangular carbyne complex, (CO)$_9$Co$_3$(\mu$_3$-
CMe)$^{173}$ Relative to the metal triangle, the \mu$_3$-Carbon
sits approximately over the mid-point of the line between
Co and Fe(2). A similar geometry is observed for the \mu$_3$-
nitride complex, Mo$_3$(\mu$_3$-N)(O)(CO)$_4$Cp$_3$.$^{174}$ The atoms Co,
S, C(1) and Fe(2) are nearly coplanar; the sum of the
angles around C(1) to S, Co and Fe(2) are 354.8° with C(1)
being only 0.220 \AA out of the S, Co, Fe(2) plane towards
the Fe(1) atom. The Fe(1)-C(1) and Fe(2)-C(1) distances
(1.895(6) \AA and 1.877(6) \AA), are slightly shorter than the
CpFe-(\mu$_3$-CMe) distances in [CpFe$_3$(CO)$_6$(\mu-CO)$_2$(\mu$_3$-CMe)]
(1.902(3) \AA).$^{149}$ The Co-C(1) distance (1.921(6) \AA) com-
pares with (CO)$_3$Co-(\mu$_3$-C) distances found in the following
bridging carbyne complexes with "closed" triangular metal cores: [CpCo₂W(CO)₈(μ₃-CC₆H₄Me-4)], 1.953(6) Å, [CpCo₂-Mo(CO)₈(μ₃-CPh)], 1.933(5) Å, and [(C₅Me₅)₂Co(CO)₃(μ-CO)(μ₃-CMe)], 1.932(6) Å. The Co-C(1) distance is slightly longer than the Co-[μ-C(SMe)₂] distance in 52, 1.916(2) Å.

The Co-C(1)-Fe(1) and Fe(1)-C(1)-Fe(2) angles of 81.8° and 84.5°, respectively, are in the range observed for closed μ₃-carbyne complexes. The plane defined by Co-C(1)-Fe(1) makes a dihedral angle of 128.9° with the Co-C(1)-S plane. The Co-C(1)-S triangle has a C-S distance of 1.740(6) Å, substantially shorter than the C(2)-S distance, 1.837(7) Å, and shorter than that observed in 52, 1.789(2) Å. It is much less than the C-S single bonds in ethylene sulfide, 1.819(1) Å and tetrahydrothiophene, 1.839(1) Å. It is slightly shorter than Cₛᵖ²-S bonds (1.75-1.78 Å), but longer than the C-S bond in thiophene, 1.718(5) Å. Thus, it would appear that the C-S bond in 33 has some double bond character. Molecular orbital calculations on 52, suggest that the Co-C-S triangle is stabilized by sigma bonding from 'p' orbitals on carbon and sulfur and back donation from cobalt 'd' orbitals into the π* orbital located mainly on these two atoms. The bonding in the Co-C(1)-S triangle of 33 is probably very similar.
The stability of this triangle in both 33 and 52, may account for their reactions with phosphines, which lead to the replacement of a CO group on the Co rather than displacement of the coordinated sulfur (Eqn 81 and reference 120).

As can be seen in Figures 28 and 29, the basic geometries of 33 and 40 are very similar. The greater electron density provided by PPh₃ substitution causes shortening of the Co-CO bonds (Co-C(3), 1.67(3) Å; Co-C(6), 1.80(2) Å in 40 versus 1.780(8) Å and 1.897(7) Å, respectively in 33). In addition, the Co-C(1) distance is about 0.06 Å shorter in 40, possibly as a result of greater d-π* back-bonding into the C-SMe fragment. As a consequence, the Fe(2)-C(1) distance is about 0.04 Å longer. The greater steric requirement of PPh₃ as compared with CO is probably responsible for the Fe(1)-Co-P angle (125.1°) being larger than the Fe(1)-Co-C(7) angle (115.9°) in 33.
IV. SUMMARY

The thiocarbyne cations, \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{CSR})^+ \) (\( R = \text{Me, Bz, All} \)), have been prepared using a modification of the procedure previously described for their syntheses. Reaction of the thiocarbyne cations with a variety of nucleophiles (\( \text{Nuc} = \text{BH}_4^- , \text{MeS}^- , \text{PhS}^- , \text{BzS}^- , \text{PhSe}^- \) and \( \text{BzMgCl} \)) yield bridging carbene complexes, \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})[\mu-\text{C(SR)Nuc}] \).

Bridging hydridothiocarbene complexes, \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})[\mu-\text{C(H)SR}] \) (\( R = \text{Me, Bz} \)), can be isolated as the cis-syn isomers. In \( \text{CDCl}_3 \), these compounds undergo: 1) a slow cis-syn to cis-anti interconversion resulting from rotation about the \( \text{C}_{\text{carbene-S}} \) bond and 2) an even slower cis-syn to trans-syn isomerization. The complex, \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})[\mu-\text{C(H)SMe}] \), which can be observed spectroscopically in four different isomeric forms (cis-syn, cis-anti, trans-syn and trans-anti) can be isolated in 80% isomeric purity as the trans-anti isomer. The trans-anti isomer rapidly isomerizes (\(< 5 \text{ minutes}) in \( \text{CH}_3\text{CN} \) and acetone to give the cis-syn isomer.

Solutions of \( \mu \)-dithiocarbene complexes, \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})[\mu-\text{C(SMe)SR}] \), rapidly form equilibrium mixtures of all possible cis and trans isomers when dissolved in common
organic solvents (benzene, CH₂Cl₂, CH₃CN, acetone) except hexane. Except for the Cp₂Fe₂(CO)₂(μ-CO)[μ-C(SMe)SPh] complex at low temperature, separate syn and anti isomers are not observed for the μ-dithiocarbene complexes.

Oxidations of Cp₂Fe₂(CO)₂(μ-CO)[μ-C(H)SCH₂Ph] and Cp₂Fe₂(CO)₂(μ-CO)[μ-C(SMe)SPh] with I₂ and Ph₂C⁺ are presumed to go through radical cations [e.g. Cp₂Fe₂(CO)₂(μ-CO)[μ-C(SMe)SPh]⁺] which lose the stable radicals, PhCH₂S⁺ and PhS⁺ respectively, to give the carbonye cations, Cp₂Fe₂-(CO)₂(μ-CO)(μ-CH)⁺ and Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe)⁺.

The μ-selenothiocarbene complex, Cp₂Fe₂(CO)₂(μ-CO)[μ-C(SMe)SePh], cannot be isolated since it rapidly transforms (at 0°C) to a μ-carbyne complex, Cp₂Fe₂(SePh)(CO)(μ-CO)(μ-CSMe). The μ-dithiocarbene complex, Cp₂Fe₂(CO)₂(μ-CO)[μ-C(SMe)SPh], converts to a μ-carbyne complex, Cp₂Fe₂-(SPh)(CO)(μ-CO)(μ-CSMe), at 40°C.

Unstable complexes of the type Cp₂Fe₂(SMe)(CO)(μ-CO)(μ-CNR₂) are obtained from reactions of Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe)⁺ with primary and secondary amines. A large excess of amine is required for these reactions to: 1) shift the presumably unfavorable equilibrium reaction between Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe)⁺ and the amines towards the adducts Cp₂Fe₂(CO)₂(μ-CO)[μ-C(SMe)HNR₂]⁺ and 2) deprotonate the adducts to form an intermediate carbene complex,
Cp₂Fe₂(CO)₂(μ-CO)(μ-C(SMe)NR₂). Because of the deprotonation step, tertiary amines do not react.

The thiocarbonyl complex, Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe), can be reduced to form a relatively stable radical, Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe)⁺, which was characterized by IR, EPR and UV-visible spectroscopy. A ¹³CO exchange experiment shows that the deep emerald green radical exchanges both its terminal and bridging CO ligands. Presumably, dissociative loss of a terminal CO ligand accounts for exchange at the terminal position; fluxionality of the terminal and bridging position accounts for exchange at the bridging position. Ligand exchange reactions of Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe)⁺ are catalyzed by the radical via the proposed mechanism:
Reaction of Na[Co(CO)₄] with Cp₂Fe₂(CO)₂(μ-CO)(μ-CSMe)⁺ under UV photolysis gives a high yield of Cp₂Fe₂Co-(CO)₃(μ-CO)₂(μ₃-CSMe). An x-ray diffraction study of this cluster shows that it has an L-shaped triangular structure, but there is no Co-Fe bond on one edge of the triangle. The CSMe group bonds through the carbyne carbon to all three metals, and in addition the sulfur coordinates to the cobalt atom. This complex reacts with phosphine to substitute a CO on cobalt. An x-ray diffraction study of Cp₂Fe₂-Co(PPh₃)(CO)₂(μ-CO)₂(μ₃-CSMe) shows that this compound has the same basic structure as Cp₂Fe₂Co(CO)₃(μ-CO)₂(μ₃-CSMe).
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VI. APPENDIX 1

ATOMIC COORDINATES\(^a\) AND AVERAGE TEMPERATURE FACTORS\(^b\)
FOR Cp\(_2\)Fe\(_2\)Co(CO)\(_3\)(\(\mu\)-CO)\(_2\)(\(\mu_3\)-CSMe), 33

<table>
<thead>
<tr>
<th>Atom(^c)</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>(\bar{U})(^{(\text{ave})}), (\AA^2)</th>
</tr>
</thead>
<tbody>
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<td>33</td>
</tr>
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<td>8739.7(5)</td>
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<td>1746(1)</td>
<td>3142.6(9)</td>
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</tr>
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</tr>
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<td>3397(3)</td>
<td>4917(3)</td>
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<td>63</td>
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<td>1292(6)</td>
<td>5116(5)</td>
<td>55</td>
</tr>
<tr>
<td>C17</td>
<td>223(11)</td>
<td>2184(6)</td>
<td>5184(4)</td>
<td>52</td>
</tr>
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</table>

\(a\) Values are \(x 10^4\). The numbers in parentheses are the estimated standard deviations in the last significant digits.

\(b\) Values are \(x 10^3\). \(\bar{U}\)\(^{(\text{ave})}\) = average of \(U_{11}\), \(U_{22}\) and \(U_{33}\).

\(c\) Atoms are labeled in agreement with Figure 28.
VII. APPENDIX 2

ANISOTROPIC THERMAL PARAMETERS ($\times 10^3$) FOR \( \text{Cp}_2\text{Fe}_2\text{Co(CO)}_3-(\mu-\text{CO})_2(\mu_3-\text{CSMe}) \), 33

<table>
<thead>
<tr>
<th>Atom</th>
<th>( U_{11} )</th>
<th>( U_{22} )</th>
<th>( U_{33} )</th>
<th>( U_{12} )</th>
<th>( U_{13} )</th>
<th>( U_{23} )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>34.0(5)</td>
<td>26.9(4)</td>
<td>38.0(5)</td>
<td>1.1(4)</td>
<td>5.0(4)</td>
<td>-3.2(4)</td>
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<tr>
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<td>29.8(5)</td>
<td>32.9(5)</td>
<td>33.9(5)</td>
<td>-1.5(4)</td>
<td>6.1(4)</td>
<td>-1.7(4)</td>
</tr>
<tr>
<td>Fe2</td>
<td>33.0(5)</td>
<td>27.3(5)</td>
<td>43.4(5)</td>
<td>1.8(4)</td>
<td>9.5(4)</td>
<td>2.1(4)</td>
</tr>
<tr>
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<td>31.4(8)</td>
<td>36.8(9)</td>
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<td>0.3(7)</td>
</tr>
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<td>113(5)</td>
<td>94(5)</td>
<td>76(4)</td>
<td>13(4)</td>
<td>49(4)</td>
<td>-9(4)</td>
</tr>
<tr>
<td>O2</td>
<td>62(4)</td>
<td>86(4)</td>
<td>72(4)</td>
<td>-6(3)</td>
<td>42(3)</td>
<td>-1(3)</td>
</tr>
<tr>
<td>O3</td>
<td>43(3)</td>
<td>55(3)</td>
<td>74(4)</td>
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</tr>
<tr>
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<td>12(2)</td>
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<td>-7(3)</td>
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<td>81(4)</td>
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</tr>
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<td>-2(3)</td>
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VIII. APPENDIX 3

STRUCTURE FACTORS (x 10) FOR

\[ \text{Cp}_2 \text{Fe}_2 \text{Co(CO)}_3 (\mu\text{-CO})_2 (\mu_3\text{-CSMe}), 33 \]
### IX. APPENDIX 4

**ATOMIC COORDINATES\(^a\) AND TEMPERATURE FACTORS FOR**

\[
\text{Cp}_2\text{Fe}_2\text{Co(PPh}_3\text{)(CO)}_2(\mu-\text{CO})_2(\mu_3-\text{CSMe}), \quad 40
\]

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\(^a\) Values are x \(10^4\). The numbers in parentheses are the estimated standard deviations in the last significant digits.

\(^b\) Atoms are labeled in agreement with Figure 29.

\(^c\) Values are x \(10^3\). Atoms refined isotropically have the estimated standard deviation in parentheses. For all other atoms U = average of \(U_{11}\), \(U_{22}\) and \(U_{33}\).
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X. APPENDIX 5

**ANISOTROPIC THERMAL PARAMETERS (x 10^3) FOR Cp₂Fe₂Co-(PPh₃)(CO)₂(μ-CO)₂(μ₃-CSMe), 40**

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**a** Thermal parameters for isotropic atoms C2, C5, C8-C16, C21, C26, C28-C30 and C35 are given in APPENDIX 4.

**b** Atoms are labeled in agreement with Figure 29.
XI. APPENDIX 6

STRUCTURE FACTORS FOR $\text{Cp}_2\text{Fe}_2(\text{PPh}_3)(\text{CO})_2(\mu-\text{CO})_2(\mu_3-\text{CSMe})$, 40
XII. ACKNOWLEDGMENTS

I am deeply indebted to Dr. Robert J. Angelici for his guidance, encouragement and support throughout the course of this work. I wish to thank Dr. Robert E. McCarley, Dr. Glenn L. Schrader, Dr. Dennis C. Johnson and Dr. Donald M. Kurtz for their assistance over the years, their service on the committee and their review of this dissertation. I wish to thank Jim Richardson and Sue-Lein Wang for their helpful assistance on X-ray studies. I gratefully acknowledge the efforts of Barbara F. Smith, my wife, who typed this manuscript. It has been a distinct pleasure working with Dan Plummer, Siu-Yeung Yu, Nan Sauer and Mohan Singh and others in our research group. Finally, to quote Michael Harry Quick, "regarding the dissertation itself (with which I have developed something of an adversary relationship over the past four months), I share the sentiments of the 18th-century printer who, upon receiving the final pages of Samuel Johnson's voluminous Dictionary, was heard to exclaim, 'Thank God I have done with him!'"