Synthesis and reactions of a thiocarbonyl-bridged complex, dicarbonylbis([eta]-cyclopentadienyl)-[mu]-carbonyl-[mu]-thiocarbonyldiiron

Michael Harry Quick
Iowa State University
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IOWA STATE UNIVERSITY, PH.D., 1978

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Synthesis and reactions of a thiocarbonyl-bridged complex, dicarbonylbis(η-cyclopentadienyl)-μ-carbonyl-μ-thiocarbonyldiiron

by

Michael Harry Quick

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the degree of

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For the Major Department

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Iowa State University
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1978
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<tr>
<td>acac</td>
<td>acetylacetonato ligand</td>
</tr>
<tr>
<td>All</td>
<td>allyl</td>
</tr>
<tr>
<td>Bu</td>
<td>butyl</td>
</tr>
<tr>
<td>Bz</td>
<td>benzyl</td>
</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
</tr>
<tr>
<td>Cy</td>
<td>cyclohexyl</td>
</tr>
<tr>
<td>decalin</td>
<td>decahydronaphthalene</td>
</tr>
<tr>
<td>diphos</td>
<td>1,2-bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>L</td>
<td>donor ligand</td>
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<tr>
<td>M</td>
<td>metal atom</td>
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<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>PPN⁺</td>
<td>μ-azidobis(triphenylphosphorus) cation</td>
</tr>
<tr>
<td>Pr</td>
<td>propyl</td>
</tr>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>R</td>
<td>organic substituent</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>tetramethyilsilane</td>
</tr>
<tr>
<td>X</td>
<td>halogen or chalcogen</td>
</tr>
<tr>
<td>ν</td>
<td>infrared stretching frequency or mode</td>
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INTRODUCTION

General Comments

One of the more interesting recent developments in transition metal organometallic chemistry is the synthesis of complexes containing the thiocarbonyl ligand, CS. These compounds are analogous to the well-known metal carbonyls. However, metal carbonyls were known and studied for more than 75 years before the first report of a metal thiocarbonyl appeared in 1966. About 100 such compounds are now known, the majority having been reported within the last seven years.

The major impediment to the development of metal thiocarbonyl chemistry was — and remains — the chemical nature of CS. Carbon monosulfide, unlike carbon monoxide, is not a stable compound under normal conditions. As a result, the CS ligand must be incorporated into a complex by indirect methods. At present only a few such methods are known, and introduction of more than one CS group is not possible in most cases. Further, thiocarbonyl analogs of other well-known types of metal carbonyls, such as bridging carbonyls and carbonyl anions, are still very uncommon. It is apparent that the study of metal thiocarbonyls will continue to provide challenging problems in organometallic synthesis.

While the search for additional preparative methods is still of primary interest, other aspects of metal
thiocarbonyl chemistry are also being investigated. Experimental and theoretical studies have been conducted to elucidate the similarities and differences in the bonding of CS and CO to metals. Other studies have shown that the coordinated CS group has a pronounced effect on the reactivity of a metal thiocarbonyl complex, and also that the CS ligand itself often is unusually reactive. Metal thiocarbonyls are also of interest because, in some cases, the introduction of a CS ligand results in, or facilitates, formation of a chiral metal center. Finally, the increasing interest in metal carbonyls as catalysts and organic synthesis reagents suggests that similar special uses for some metal thiocarbonyls will eventually be found. Therefore, it is anticipated that metal thiocarbonyl chemistry will remain an active and fruitful research area for some time to come.

The remainder of this introductory chapter is devoted to various aspects of the chemistry of CS and metal thiocarbonyls. Coverage is intended to be representative only, with emphasis on relatively new work, inasmuch as two recent reviews on the subject are available.¹²

Carbon Monosulfide

The difference in the stabilities of free and coordinated CS are so striking that it is worthwhile to review the properties of carbon monosulfide itself prior to any discussion of thiocarbonyl complexes. Also remarkable is
the contrast between the properties of CS and CO.

Carbon monosulfide was first prepared in 1910, but only in recent years has it been obtained in macroscopic quantities. Of the numerous reactions known to produce CS, the majority involve pyrolysis, photolysis or electrolysis of CS₂. The compound is best prepared in usable amounts by passage of a high-voltage ac discharge through CS₂ at liquid nitrogen temperatures. This procedure apparently gives a mixture of CS, CS₂ and C₃S₂; pure CS has never been isolated because of its high reactivity (see below). Naturally-occurring CS has been detected in the upper atmosphere and in interstellar space.

Above -160°C, carbon monosulfide undergoes a highly exothermic and often violent polymerization, giving a brown-black solid. The reaction has been studied for both condensed CS⁴ and CS vapor, and is not a simple polymerization. Products commonly observed are CS₂, free sulfur and a "copolymer" of CS and C₃S₂. The nature and composition of the products obtained depend on the method and reaction conditions used.

Despite the difficulties involved in the preparation and handling of CS, many physicochemical studies of the molecule have been conducted. Spectroscopic methods employed in the study of CS include infrared, uv absorption and emission, uv PES and microwave. Reported thermodynamic parameters vary considerably. Various molecular
properties of CS determined in these studies are given in Table 1; corresponding properties of CO are shown for comparison.

Table 1. Molecular properties of CS and CO

<table>
<thead>
<tr>
<th>Property</th>
<th>CS</th>
<th>Ref.</th>
<th>CO</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>μ, D</td>
<td>1.958 (-CS+)</td>
<td>(15)</td>
<td>0.112 (-CO+)</td>
<td>(21)</td>
</tr>
<tr>
<td>ν&lt;sub&gt;CX&lt;/sub&gt;, cm&lt;sup&gt;-1&lt;/sup&gt; (k, mdyne/Å)</td>
<td>1274 (8.4)</td>
<td>(9)</td>
<td>2143 (19.0)</td>
<td>(22)</td>
</tr>
<tr>
<td>C-X distance, Å</td>
<td>1.535</td>
<td>(13)</td>
<td>1.128</td>
<td>(22)</td>
</tr>
<tr>
<td>Bond energy, kcal/mol</td>
<td>166</td>
<td>(17)</td>
<td>256</td>
<td>(23)</td>
</tr>
<tr>
<td>Bond order (estimated)</td>
<td>2.2</td>
<td>(4)</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>1st IP, eV</td>
<td>11.34</td>
<td>(12)</td>
<td>14.01</td>
<td>(22)</td>
</tr>
</tbody>
</table>

The chemistry of carbon monosulfide has also been investigated to some extent. Reaction with halogens gives thiocarbonyl halides, X<sub>2</sub>CS,<sup>4,24</sup> or trihalomethyl sulfenyl halides, X<sub>3</sub>CSX.<sup>5</sup> Similarly, HCl and HBr react with CS to give thioformyl halides, HXCS; CS also reacts with boron halides.<sup>5</sup> In the gas phase CS reacts with selenium and tellurium to form CSSe and CSTe.<sup>4</sup> All of these reactions were, of course, carried out at very low temperatures. On the basis of its reactivity, CS has been classified both as an electrophilic carbene<sup>4</sup> and as a weak Lewis base.<sup>5</sup> Since reaction of CS with electron-rich compounds is not general,<sup>5</sup> the latter description is possibly more accurate.
At present carbon monosulfide appears to have only one practical application. This is in the $\text{CS}_2/O_2$ chemical laser, in which CS is known to be an active species.$^{25,26}$

**Synthesis of Thiocarbonyl Complexes**

Direct synthesis of metal thiocarbonyls from free CS has been attempted, but with little success. Klabunde et al.$^5$ reported that CS did not react with labile complexes such as $\text{RhCl}($$\text{PPh}_3)_3$, $\text{Fe}($$\text{CO})_5$ and $\text{Ni}($$\text{CO})_4$, but this is hardly surprising in view of the very low temperatures at which these reactions were necessarily conducted. Yarbrough et al.$^27$ obtained spectroscopic evidence for $\text{Ni}($$\text{CS})_4$ after the co-condensation of Ni atoms and CS. However, the product was not isolated, and other workers have found the results difficult to reproduce.$^{28}$

Since the use of CS itself has proved impractical, all known metal thiocarbonyls have been synthesized by indirect methods. Most of these procedures are essentially variations of a single method: reaction of an organic thiocarbonyl compound with a metal complex, usually followed by elimination of one or more groups, leaving a CS ligand coordinated to the metal. Nevertheless it is useful to classify these reactions according to the type of thiocarbonyl reagent used. The organic thiocarbonyls discussed here are the only compounds presently known to be useful for the introduction of M-CS bonds.
Carbon disulfide

Most of the reactions which form metal-CS bonds employ CS₂ as the source of CS. Numerous metal complexes form Π-adducts with CS₂.¹ In some cases it is possible to effect elimination of a sulfur atom from such compounds to yield metal thiocarbonyls. Occasionally the elimination occurs spontaneously, but in most syntheses this step must be assisted. Metal carbonyl anions also react with CS₂,²⁹-³² and in a few instances such reactions can be used to introduce a CS ligand.

Baird and Wilkinson obtained the first metal thiocarbonyls during an investigation of metal-Π-CS₂ complexes.³³,³⁴ It was discovered that RhCl(PPh₃)₃ reacts with CS₂ and PPh₃ in methanol to give trans-RhCl(PPh₃)₂CS. Excess PPh₃, which

(1) \( \text{RhCl(PPh₃)₃} + \text{CS₂} + \text{PPh₃} \xrightarrow{\text{MeOH}} \text{RhCl(PPh₃)₂CS} + \text{P₃PS} \)

abstracts a sulfur atom from the Π-CS₂ intermediate, and MeOH are both necessary for maximum yields. The reaction works poorly with IrCl(PPh₃)₃, however, and Kubota and Carey³⁵ found trans-IrCl(PPh₃)₂(N₂) to be a superior starting material for preparation of the iridium analog.

The CS₂/PPh₃ reaction has been used in the synthesis of several other metal thiocarbonyls. Butler and co-workers³⁶,³⁷ obtained CpM(CO)₂CS (M = Mn, Re) by reaction sequence 2 (where L = cis-cyclooctene or THF). Repetition of this
sequence starting with \( \text{CpM(CO)}_2 \text{CS} \) gives \( \text{CpM(CO)}_2 \text{(CS)}_2 \), which are among the few \text{bis} thiocarbonyls known. Upon further reaction of \( \text{CpMn(CO)}_2 \text{(CS)}_2 \) by this process, IR evidence for the \text{tris} thiocarbonyl was obtained. The analogous reaction 3 was used by Jaouen and Dabard\(^3\) to prepare \( \text{(arene)} \text{Cr(CO)}_2 \text{CS} \)

\[
\begin{align*}
\text{(3) (arene)} \text{Cr(CO)}_2 &\text{L} \xrightarrow{\text{CS}_2} \text{(arene)} \text{Cr(CO)}_2 \text{(CS)}_2 \xrightarrow{\text{PPh}_3} \text{(arene)} \text{Cr(CO)}_2 \text{CS} + \text{Ph}_3 \text{PS}
\end{align*}
\]

(where \text{arene} = \text{C}_6\text{H}_6, \text{C}_6\text{H}_5\text{COOMe}). Other group 6B analogs of the arenechromium thiocarbonyls are presently unknown.

The synthesis of the dimeric, chloride-bridged ruthenium thiocarbonyl \([\text{RuCl}_2(\text{PPh}_3)_2 \text{CS}]_2\) does not require \text{PPh}_3; in fact, the presence of added phosphine prevents the

\[
\begin{align*}
\text{(4) RuCl}_2 &\text{(PPh}_3)_4 \xrightarrow{\text{CS}_2} \text{[RuCl}_2(\text{PPh}_3)_2 \text{CS}]_2 \xrightarrow{\text{ reflux}} \text{RuCl}_2(\text{PPh}_3)_2 \text{(CS)}_2
\end{align*}
\]

formation of this product.\(^3\) Upon prolonged reaction, the monomeric \text{bis} thiocarbonyl complex is obtained.\(^4\) Similarly, \( \text{RuBr}_3(\text{PPh}_3)_2 \cdot \text{MeOH} \) gives a thiocarbonyl complex upon reaction with \text{CS}_2 alone.\(^5\) Recently it has been found that reaction 3

\[
\begin{align*}
\text{(5) RuBr}_3 &\text{(PPh}_3)_2 \cdot \text{MeOH} \xrightarrow{\text{CS}_2} \text{reflux} \text{RuBr}_3(\text{PPh}_3)_2 \text{CS}
\end{align*}
\]
above gives higher yields if \( \text{PPh}_3 \) is not present.\(^2\)

Roper and co-workers\(^{42,43}\) recently prepared several metal thiocarbons by alkylation/elimination reactions of certain ruthenium, osmium and iridium \( \pi-\text{CS}_2 \) complexes. The cationic intermediates shown in reactions 6 and 7 contain a \( \text{CS}_5 \) \( \text{MeI} \)

(6) \[
\text{Ru}({\text{CO}})_{2}(\text{PPh}_3)_3 \overset{\text{CS}_2}{\longrightarrow} \text{Ru}({\text{CO}})_{2}(\text{PPh}_3)_2(\pi-\text{CS}_2) \overset{\text{MeI}}{\longrightarrow} \\
[\text{Ru}({\text{CO}})_{2}(\text{PPh}_3)_2(\text{CS}_2\text{Me})]^+ \underset{\text{EtOH, aq. HCl}}{\overset{\text{reflux}}{\longrightarrow}} \\
\text{RuCl}_2({\text{CO}})(\text{PPh}_3)_2\text{CS} + \text{MeSH}
\]

(7) \[
\text{Os}({\text{CO}})_{2}(\text{PPh}_3)_2(\pi-\text{CS}_2) \overset{\text{MeI}}{\longrightarrow} [\text{Os}({\text{CO}})_{2}(\text{PPh}_3)_2(\text{CS}_2\text{Me})]^+ \\
\overset{\text{NaBH}_4}{\underset{\Delta}{\longrightarrow}} \text{Os}({\text{CO}})_{2}(\text{PPh}_3)_2(\text{CS}_2\text{Me})\overset{\Delta}{\longrightarrow} \text{Os}({\text{CO}})_{2}(\text{PPh}_3)_2\text{CS} \\
+ \text{MeSH}
\]

\( \pi \)-bonded \( S \)-methyl dithioester ligand and can be isolated. Usually the group eliminated is methanethiol, although the osmium \( \pi-\text{CS}_2 \) complex in reaction 7 will react directly with HCl, as in 6, to give \( \text{OsCl}_2(\text{CO})(\text{PPh}_3)_2\text{CS} \) and \( \text{H}_2\text{S} \).

Methanethiol elimination was also used by Dombek and Angelici\(^{30}\) to prepare \( \text{CpFe}({\text{CO}})_{2}\text{CS}^+ \). The isolable methyl dithioester intermediate formed in reaction 8 is \( \sigma \)-bonded, in contrast to the preceding examples. Acid cleavage to the
The thiocarbonyl cation is effected by HCl\[^{30}\] or CF\(_3\)SO\(_3\)H.\[^{44}\] Wnuk and Angelici\[^{32}\] recently obtained the analogous ruthenium thiocarbonyl cation by the same method. Unfortunately, this method seems to be applicable only to the very nucleophilic\[^{45,46}\] Fe and Ru carbonyl anions.

At this point it should be noted that a number of metal selenocarbonyls are now known.\[^{2}\] Since at present the only available source of the CSe ligand is CSe\(_2\), the methods just described are also used in the formation of metal-CSe bonds.

**Thiophosgene**

Kubota and Curtis\[^{47}\] found that certain Ir(I) complexes undergo oxidative addition of Cl\(_2\)CS, as in reaction 9, to give Ir(III) thiocarbonyls. This is an unusual "three-fragment" addition, since both groups eliminated from the thiocarbonyl moiety become bonded to the metal atom.

\[(\text{9}) \quad \text{IrCl(PPh}_3\text{)}_3 + \text{Cl}_2\text{CS} \rightarrow \text{IrCl}_3(\text{PPh}_3)_2\text{CS} \]

Dombek and Angelici\[^{48}\] obtained the group 6B thiocarbonyls M(CO)\(_5\)CS (M = Cr, W) by reaction of the dimeric carbonyl
anions with thiophosgene (reaction 10). However, only

\[ \text{M}_2(\text{CO})_{10}^{2-} + \text{Cl}_2\text{CS} \rightarrow \text{M(\text{CO})}_5\text{CS} \]

only W(\text{CO})_5\text{CS} could be obtained in useful amounts. Apparently
the rather high volatility of Cr(\text{CO})_5\text{CS} leads to large product
losses during work-up of the reaction mixture; a higher-yield
synthesis of this compound was recently reported (see below).

\textbf{Alkyl chlorothioformates}

The oxidative addition of methyl chlorothioformate to
\( \text{Pt(PPh}_3)_4 \) was studied by Dobrzynski \textit{et al.} \textit{50} This reaction
yields a thioester intermediate which can be cleaved to give

\[ \text{Pt(PPh}_3)_4 + \text{Cl-C-OMe} \rightarrow \text{trans-PtCl(PPh}_3)_2\text{C-OMe} \]

the \( \text{Pt(II) thiocarbonyl cation} \). The palladium analog was
also obtained, but was too reactive to be purified.

The iron thiocarbonyl cation \( \text{CpFe(CO)}_2\text{CS}^+ \) was originally
obtained from the reaction of \( \text{CpFe(CO)}_2^- \) and ethyl or methyl
chlorothioformate followed by acid cleavage. \textit{51} However,
this method has been supplanted by the \( \text{CS}_2/\text{MeI/H}^+ \) reaction
discussed previously.
Diphenyl thionocarbonate

All of the previously mentioned reactions yield complexes with terminal thiocarbonyl ligands. However, reaction of \( \text{CpFe(CO)}_2^- \) with \((\text{PhO})_2\text{CS}\) gives \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \),\(^{52}\) which contains a bridging CS group. This is the only reaction known to introduce a CS ligand directly into a bridge position. Further discussion of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) will be deferred, since the compound is the subject of this dissertation.

Theoretical Interlude: The Metal-CS Bond

The bonding of CO and CS to metals is believed to result from a synergistic interaction of metal d orbitals with ligand \( \sigma \) (donor) and \( \pi^* \) (acceptor) orbitals.\(^{53}\) Molecular orbital calculations on CS\(^{54}\) and thiocarbonyl complexes\(^{55}\) indicate that CS should be a considerably better \( \pi \)-acceptor than CO, owing to the lower energy of the CS \( \pi^* \) orbitals, and also a slightly better \( \sigma \)-donor. Further, the calculations suggest that CS can also act as a \( \pi \)-donor ligand to some extent. The theoretical studies thus predict that M-CS bonds should be stronger than their CO counterparts. The calculations also predict a smaller positive charge for the thiocarbonyl carbon atom.

The superior \( \pi \)-acceptor ability of CS has been demonstrated by infrared\(^{56}\) and Mössbauer\(^{57}\) studies. Other
experimental evidence (see below) also supports the theoretical predictions regarding the strength of the M-CS bond. Conflicting ionization data reported for several metal thiocarbonyls apparently result from the Π-donor capability of CS, which makes the ligand more responsive than CO to its electronic environment.58

Reactions of Metal Thiocarbonyls

Reactions at the metal

Thiocarbonyl complexes such as RhCl(PPh3)2CS,34 IrCl(PPh3)2CS,59 and Ir(CO)2(PPh3)2CS+60 undergo most of the same oxidative addition reactions characteristic of their carbonyl analogs, e.g., addition of halogens and tetracyanoethylene, but tend to be less reactive toward weaker electrophiles such as H2 and HCl. These results were attributed to a lowering of the metal electron density by the more strongly Π-bonding CS ligand.

Reaction of W(CO)2CS with Br2, followed by addition of PPh3, gives the seven-coordinate W(II) complex W(CO)2(CS)(PPh3)2Br2.61 Unlike its tricarbonyl analog, the compound does not readily lose a CO ligand to form a six-coordinate species. The authors suggested that the more strongly bonding CS, rather than a CO ligand, occupies the unique site in the molecule (a face-capping position) from which dissociation ordinarily would seem most favorable.
Many ligand substitution reactions of metal thiocarbonyls have been reported. As the majority of thiocarbonyl complexes also contain carbonyl ligands, most of these reactions involve replacement of CO by another ligand. It is generally observed, and has been verified by several kinetic studies,48,62 that thiocarbonyl complexes undergo ligand substitution more readily than their carbonyl analogs. Further, simple replacement of CS by another ligand never occurs in such reactions. Thus, the thiocarbonyl not only bonds more strongly, but also has a labilizing effect on other \( \pi \)-bonding ligands such as CO48 and cis-cyclooctene.62 While it is tempting to attribute this effect to the strong \( \pi \)-backbonding of the CS ligand, it should be noted that many kinetic studies of metal carbonyl substitution reactions well illustrate the problems in the use of \( \pi \)-bonding arguments to explain reaction rates.63

Examples of metal thiocarbonyl ligand substitutions are shown in reactions 12-19. Reactions of the cyclopentadienyl

\[
\begin{align*}
(12) \quad & \text{IrCl}(\text{PPh}_3)_2\text{CS} \underset{\text{CO}}{\longrightarrow} \text{Ir}(\text{CO})_2(\text{PPh}_3)_2\text{CS}^+ \underset{\text{PCy}_3}{\longrightarrow} \\
& \text{Ir}(\text{CO})_2(\text{PCy}_3)_2\text{CS}^+ 60
\end{align*}
\]

\[
\begin{align*}
(13) \quad & \text{CpMn}(\text{CO})_2\text{CS} + \text{olefin} \underset{\text{hv}}{\longrightarrow} \text{CpMn}(\text{CO})(\text{CS})(\text{olefin}) \underset{\text{PPh}_3}{\longrightarrow} \\
& \text{CpMn}(\text{CO})(\text{PPh}_3)_2\text{CS} 36
\end{align*}
\]
and arene thiocarbonyls are of interest because a chiral metal center is formed; recently the enantiomers of \((\text{o-Me}_2\text{C}_6\text{H}_4)\text{Cr(CO)(P(0Ph)}_3)\text{CS}\) have been resolved.\(^{67}\) The carbonylation of arenechromium thiocarbonyls (reaction 16) is the best method for preparing \(\text{Cr(CO)}_2\text{CS}\). The \(\text{IW(CO)}_4\text{CS}^-\) reaction (19) is particularly interesting because of its unusual stereoselectivity.

Reactions at the CS ligand

Several metal thiocarbonyl complexes are known to be susceptible to nucleophilic attack at the thiocarbonyl carbon.
Dobrzynski et al.\textsuperscript{50} found that PtCl(PPh\textsubscript{3})\textsubscript{2}CS\textsuperscript{+} reacts readily with water to give PtCl(PPh\textsubscript{3})\textsubscript{2}CO\textsuperscript{+} and H\textsubscript{2}S. The reactions of CpFe(CO)\textsubscript{2}CS\textsuperscript{+} and W(CO)\textsubscript{5}CS with nucleophiles have been studied by Busetto et al.\textsuperscript{68} and Dombek and Angelici.\textsuperscript{69} For these compounds (reactions 20 and 21), reaction occurs preferentially at the CS carbon, even though similar reactions at the carbonyl groups should be possible.\textsuperscript{70,71} This reactivity seems contrary to the anticipated higher electron density.
on the CS carbon, and also to the observation by Mays and Stefanini\(^60\) that methoxide adds to a carbonyl group of Ir(CO)\(_2\)(PPh\(_3\))\(_2\)CS\(^+\). Recently, Lichtenberger and Fenske\(^55\) suggested that such reactions are controlled by the energy of the ligand frontier orbitals rather than the charge density at the CS carbon. In any case, it is not yet known whether reaction with nucleophiles is a general property of thio-
carbonyl ligands.

Metal thiocarbonyls with unusually high electron density
on the CS ligand can undergo electrophilic addition to the
thiocarbonyl sulfur atom. Thus, W(CO)(diphos)\(_2\)CS forms
W(CO)(diphos)\(_2\)CS•W(CO)\(_5\) and [W(CO)(diphos)\(_2\)CS-Me]FSO\(_3\) on reaction with W(CO)\(_5\)(acetone) and MeOSO\(_2\)F, respectively.\(^61\) It appears that \(\nu_{CS}\) of a thiocarbonyl complex must be below ~1200 cm\(^{-1}\) for this type of reaction to occur,\(^72\) although spectroscopic evidence for the compound CpMn(CO)\(_2\)CS•CpMn(CO)\(_2\) was recently reported.\(^37\)

Reactions forming bridging thiocarbonyls

The complex W(CO)(diphos)\(_2\)CS•W(CO)\(_5\) mentioned above
affords an example of an "end-to-end" bridging thiocarbonyl
ligand. The first reported thiocarbonyl complex containing
a "thioketonic" bridge was [CpMn(NO)(CS)]\(_2\), prepared by
Efraty et al.\(^65\) by the reaction of CpMn(NO)(CS)I with Zn
dust. Shortly thereafter, Dunker et al.\(^73\) reported the
synthesis of [CpFe(CO)(CS)]\(_2\) from CpFe(CO)\(_2\)CS\(^+\) and NaH.
Wnuk and Angelici \(^{32}\) recently obtained the ruthenium analog in the same manner; a small amount of the monothiocarbonyl analog \(\text{Cp}_2\text{Ru}_2(\text{CO})_2\text{CS}\) was also isolated. In all of these compounds, the CS ligands occupy bridge positions only. The iron complex reacts with \(\text{MeOSO}_2\text{F}\) to give the isolable derivative \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS-Me})]\text{FSO}_2\)\(^{\text{v}}\), in which one bridging CS has been alkylated.

With the exception of \(\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS}\), which is the subject of this dissertation, these are the only examples of this type of thiocarbonyl complex presently known.

**Characterization of Metal Thiocarbonyls**

**Structural studies**

Several metal thiocarbonyls,\(^{74,75}\) including one bridging thiocarbonyl complex,\(^{73}\) have been investigated by X-ray crystallography. The compounds studied have either structurally equivalent CO and CS ligands, or carbonyl analogs whose structures are known. In all cases save one,\(^{75}\) the M-CS bond is found to be significantly shorter than the corresponding M-CO bonds, in agreement with the expected greater strength of the former. The terminal M-C-S linkage is essentially linear, as is the case for terminal carbonyls. The longest and shortest terminal C-S distances reported differ by about 0.070 Å, which is somewhat larger than the range found for CO ligands. As expected, the C-S bond of the bridging thiocarbonyl ligand is significantly longer
than that of a terminal CS group.

**Spectra**

The CS ligand exhibits a strong infrared absorption resulting from the C-S bond stretching; this band is usually at least as intense as a metal carbonyl $\nu_{CO}$ absorption. While the $\nu_{CO}$ frequency of CO almost always decreases upon coordination, the $\nu_{CS}$ frequency of a CS ligand can be either higher or lower than that of free CS. This is not surprising in view of the considerable electronic differences between the two ligands. The ranges of $\nu_{CS}$ frequencies observed for the various types of metal thiocarbonyls are shown in Table 2. ($\nu_{CS}$ values for certain compounds discussed in this dissertation are not included in the table.) In general, the $\nu_{CS}$ frequency is inversely related to the metal electron density, as is the case for CO frequencies in metal carbonyls. For terminal CS ligands, a linear correlation exists between $\nu_{CS}$ and the C-S distance, showing that changes in the stretching frequency reflect actual strengthening or weakening of the C-S bond.

Numerous $^{13}$C NMR spectra of metal thiocarbonyls have been reported. Thiocarbonyl carbon resonances are readily identified by their positions at extremely low field; the range observed to date (exclusive of compounds discussed in this dissertation) is 286-352 ppm downfield from TMS.
Table 2. IR ranges for $\nu_{CS}$ in metal thiocarbonyls

<table>
<thead>
<tr>
<th>Type</th>
<th>$\nu_{CS}$(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free CS$^a$</td>
<td>1274</td>
</tr>
<tr>
<td>M-CS</td>
<td>1409-1161</td>
</tr>
<tr>
<td>M-C(S)-M$^a$</td>
<td>1150-1118</td>
</tr>
<tr>
<td>M-CS-M$^a$</td>
<td>1106-1063</td>
</tr>
</tbody>
</table>

$^a$In CS$_2$ matrix at -196°C.

$^b$"Thicketonic" bridge.

$^c$"End-to-end" bridge.

(The original assignment of -443 ppm for CpMn(CO)$_2$CS$^{76}$ is apparently erroneous.$^{77}$) At present there is no satisfactory explanation for this large chemical shift. Another unusual feature in the $^{13}$C spectra is that replacement of CO by CS in a complex causes an upfield shift of the remaining CO resonances, whereas substitution of other ligands produces the opposite result.$^2$ This effect is attributable to the greater $\pi$-acceptor character of CS relative to other ligands.

Mass spectra of metal thiocarbonyls generally show an M-CS$^+$ peak resulting from loss of all groups other than the thiocarbonyl.$^2$ This is a further indication of the stronger bonding of the CS ligand.
The Present Research

In the course of investigating various organic thio­
carbonyl compounds as possible reagents for metal thiocarbonyl
synthesis, it was discovered that the reaction of CpFe(CO)$_2$-
with (PhO)$_2$CS gave usable amounts of the thiocarbonyl-
bridged complex Cp$_2$Fe$_2$(CO)$_3$CS. Since such compounds were
(and still are) quite rare, little was known of their
structures, fluxional behavior, reactivity, or any other
aspects of their chemistry. Therefore, it was decided that
the investigation of this new thiocarbonyl complex would be
an interesting and worthwhile research project.
EXPERIMENTAL

General Procedures

All reactions were conducted under prepurified N\textsubscript{2} that was passed through anhydrous Mg(ClO\textsubscript{4})\textsubscript{2} before use. Unless stated otherwise, all reactions were performed at room temperature. Schlenk ware (or similar apparatus) and standard inert atmosphere techniques were used.\textsuperscript{78} Amalgam reductions were carried out in either the common type of amalgam reduction apparatus\textsuperscript{79} or a sidearm round-bottom flask with a drain stopcock attached perpendicular to the flask axis, the latter vessel being more convenient for small-scale reactions. Exchange of PF\textsubscript{6}\textsuperscript{-} for other anions was accomplished with a 1 X 25 cm column of Amberlite IRA-400 resin in methanol or acetone. In the "slow evaporation" technique mentioned below, the compound to be crystallized was dissolved in a suitable solvent, and a higher-boiling solvent in which the compound was less soluble was added; the solution was then evaporated to a small volume (usually 10-15 ml) under reduced pressure (50-60 torr) at room temperature with a rotary evaporator.

Spectra

Infrared spectra were recorded on a Perkin-Elmer 337 or 237B grating spectrophotometer; NaCl cells with a 1 mm path length were used for most spectra. The spectra were
expanded on an auxiliary recorder, and the band positions were determined using CO gas (CO region) and polystyrene (CS region) as references. Band positions are believed accurate to within 2 cm\(^{-1}\).

Proton NMR spectra were obtained with a Varian A-60 spectrometer. Variable-temperature \(^1\)H NMR spectra were run on a Varian HA-100 instrument. All \(^13\)C NMR spectra were recorded on a Bruker HX-90 Fourier transform spectrometer; Cr(acac)\(_3\) (\(~35 \text{ mg/ml}\)) was added to the samples to reduce data collection time. TMS was used as the internal reference for all NMR spectra.

Visible spectra were obtained with a Cary 14 uv-visible spectrophotometer.

Other Physical Measurements

Conductivity measurements were determined in nitromethane using an Industrial Instruments RC-16E2 conductivity bridge and a conductance cell with \(k = 0.348 \text{ cm}^{-1}\). Melting points were obtained with a Thomas Model 40 melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories.

Solvents

Commercial decalin was washed with concentrated H\(_2\)SO\(_4\) and then with water, dried over anhydrous CaSO\(_4\), and fractionally distilled from sodium under N\(_2\) through a
30-cm Vigreux column. Butyronitrile was fractionally distilled under \( N_2 \) from CaH\(_2\) and then from P\(_4\)O\(_{10}\), through a 30-cm Vigreux column. Nitromethane for conductivity measurements was dried over P\(_4\)O\(_{10}\) and then fractionally distilled twice under \( N_2 \) through a 30-cm Vigreux column; the solvent thus obtained had a specific resistance of \( \omega 2 \times 10^5 \) ohms, as recommended for conductivity work.\(^{81}\)

Tetrahydrofuran was distilled from LiAlH\(_4\) or NaK\(_{2.8}\) immediately before use. All other solvents used were commercial reagent grade products. Acetone was stored over CaSO\(_4\); other solvents were kept over Baker type 4A molecular sieves. Solvents were deaerated by flushing with \( N_2 \) before use.

Reagents

**Organic compounds**

Phosphines and phosphites were fractionally distilled or, where appropriate, recrystallized. Amines requiring purification were fractionally distilled from KOH. Impure alkyl halides were shaken with 1 M aqueous Na\(_2\)S\(_2\)O\(_3\) and then dried with CaSO\(_4\). Thiirane,\(^{82}\) methyl isocyanide\(^{83}\) and phenyl isocyanide\(^{84}\) were prepared by literature methods. Commercial [PPN]Cl was crystallized from acetone/Et\(_2\)O; [PPN]N\(_3\) was prepared from [PPN]Cl and NaN\(_3\) by the usual metathesis procedure.\(^{85}\) Commercial Et\(_4\)NBr was dried over
A solution of CH₂N₂ in Et₂O was provided by G. Senatore.

**Inorganic and metal carbonyl compounds**

Sodium amalgam (1%) was stored under N₂ and transferred to reaction vessels by syringe. Commercial NaI, AgPF₆, and AgBF₄ were dried over P₂O₁₀. The complex PtCl₂(PhCN)₂ was obtained by a published method.⁸⁶

The complexes [CpFe(CO)₂]₂ and [(MeC₅H₄)Fe(CO)₂]₂ were recrystallized from 3:1 hexane/CH₂Cl₂ at -20°. The metal carbonyls M₂(CO)₁₀ (M = Mn, Re) were sublimed (70°, 0.01 torr) and used in the preparation of M(CO)₅Br⁸⁷,⁸⁸ and [M(CO)₅(MeCN)]PF₆.⁸⁹ **Trans-**Re(CO)₃(PPh₃)₂Br was obtained by refluxing Re(CO)₅Br with excess Ph₃P under N₂ in toluene for 18 hr. The anionic carbonyl halides Et₄N[M'(CO)₅I] (M' = Cr, Mo, W) were prepared by the literature method;⁹¹ a sample of Bu₄N[IW(CO)₄CS] was kindly provided by W. Greaves. Other metal carbonyl halides used in this work, e.g. CpW(CO)₃Cl and CpFe(CO)₂Cl, were samples prepared several years ago by W. Jetz. The complex [CpFe(CO)₂(THF)]BF₄ was obtained by the published procedure.⁹²

**Other compounds**

All other reagents used in this research (except those mentioned below) were commercial products of the highest purity available and were used as received.
Preparation of Thiocarbonyl Reagents

Technical grade thiocarbonyldiimidazole \([\text{C}_{3}H_{5}N_{2}]_{2}\text{CS}\) was extracted with THF, precipitated with hexane, and then sublimed \(95^\circ, 0.2\) torr. Phenyl chlorothioformate \([\text{Cl-C(S)-OPh}]^{93}\) and diphenyltrithiocarbonate \([\text{(PhS)}_{2}\text{CS}]^{94}\) were obtained in satisfactory yields by literature methods. The published procedures for methyl chlorothioformate \([\text{Cl-C(S)-OMe}]^{95}\) and diphenylthionocarbonate \([\text{(PhO)}_{2}\text{CS}]^{96}\) gave poor yields, and were modified as described below.

**Methyl chlorothioformate**

Thiophosgene \((15.2\ \text{ml, 23.0 g, 0.20 mol})\) was added to a Schlenk tube of about 200 ml capacity, and the vessel and contents were then cooled to \(0^\circ\)C in an ice bath. Methanol \((16.0\ \text{ml, 12.7 g, 0.40 mol})\) was added slowly from a syringe so that a two-layer reaction mixture was obtained. The tube was then immersed in a special water bath. This bath consisted of an inverted polyethylene bottle \((\phi9 \times 25\ \text{cm})\) with the bottom removed, clamped to a ring stand; the neck of the bottle was connected (by rubber tubing to a water tap, so that a continuous stream of water at \(\sim15^\circ\)C flowed around the reaction vessel. The tube was vented to a mineral oil bubbler containing KOH pellets to absorb HCl generated during the reaction. On standing for 5 days, the layers gradually merged to form a yellow-orange solution.
The reaction mixture was poured into 40 ml of ice water in a separatory funnel, and the resulting mixture was extracted twice with 40 ml of Et₂O. The combined extracts were dried over CaSO₄, and the ether was then removed under reduced pressure (aspirator). Distillation of the residual liquid at atmospheric pressure under N₂ through a 10-cm vacuum-jacketed Vigreux column gave three fractions: orange, b.p. 70-73° (unreacted Cl₂CS); bright yellow, b.p. ~90-95° (unknown impurity); light yellow, b.p. ~95-100° (product plus some impurity). Redistillation of the third fraction gave fairly pure Cl-C(S)-OMe as a pale yellow, fuming liquid, b.p. 100-103°, d. ~1.28 g/ml. Yields were typically 25-30%.

NMR(CDCl₃): δ4.17.

**Diphenyl thionocarbonate**

The reaction was conducted under N₂ in a 500-ml 3-neck flask equipped with a motor-driven paddle stirrer. (A magnetic stirring bar is inadequate, as the reaction mixture gradually becomes rather viscous.) Phenol (30.1 g, 0.32 mol) and 350 ml of THF were added, and then NaH (7.68 g of crystalline NaH or 13.5 g of 57% oil dispersion, 0.32 mol) was added in small portions to the stirred solution. (Caution: Vigorous H₂ evolution occurred, and the mixture became warm.) After all the hydride had been added, the mixture was stirred until gas evolution had ceased and the solution had cooled to room temperature (about 2 hr). (If
NaH oil dispersion was used, the NaOPh solution was nearly black at this point. The flask was then equipped with an equipressure dropping funnel and a rubber stopper/thermometer assembly. A solution of Cl₂CS (11.5 ml, 17.3 g, 0.15 mol) in 50 ml of THF was added from the funnel to the stirred phenoxide solution at such a rate that the temperature of the reaction mixture did not exceed 50°; this step required about 1.5 hr. As the reaction proceeded the mixture became light brown and quite thick. When all the Cl₂CS had been added, the funnel was replaced with a condenser, the flask was equipped with a heating mantle, and the mixture was refluxed for 1 hr. The mixture was then cooled and evaporated to dryness under reduced pressure. The residue was extracted with 500 ml of Et₂O, and the mixture was filtered through a 3-cm layer of Celite packed in a coarse frit filter. The filtrate was transferred to a separatory funnel and washed once with 150 ml of 5% aqueous NaOH and twice with 150 ml of water. After drying over CaSO₄, the solution was boiled with 1 g of decolorizing carbon for 5 min, cooled and filtered through Celite as before; the filter material was washed with an additional 100 ml of Et₂O. The filtrate was diluted to 1200 ml with hexane and evaporated to about 350 ml by boiling carefully on a hotplate. On cooling to room temperature, the (PhO)₂CS crystallized as pearly, nearly colorless leaves (m.p. 107°). An additional batch was
obtained by evaporating the filtrate from the first crop to about 90 ml and cooling as before. The combined yield was usually 85-90%.

Substituted aryl thionocarbonates, \((p-XC_6H_4O)_2CS\), were also obtained in good yields by this method (e.g., 65% for \(X = \text{MeO}\) and 78% for \(X = \text{Cl}\)). The \(p-\text{NO}_2\) analog was prepared by T. Wnuk in 75% yield by refluxing stoichiometric amounts of \(p\)-nitrophenol and \(\text{Cl}_2\text{CS}\) with excess \(\text{Na}_2\text{CO}_3\) in THF under \(\text{N}_2\) for 12 hr.

Synthesis and Reactions of Thiocarbonyl Complexes

\textbf{Reaction of Re(CO)}_5^- \text{with CS}_2/\text{MeI}

Dirhenium decacarbonyl (1.50 g, 2.3 mmol) in 30 ml of THF was stirred with 1% \(\text{Na(Hg)}\) (5 ml) for 4 hr to give a clear yellow-orange solution of \(\text{Na[Re(CO)}_5\); the excess amalgam was then drained off. Addition of \(\text{CS}_2\) (5.0 ml, 6.4 g, 84 mmol) caused an immediate color change to deep red. After 20 sec, \(\text{MeI}\) (5.0 ml, 11 g, 78 mmol) was added, giving a deep red-purple solution; in the following 30 sec the color faded somewhat to orange-purple. Evaporation of the mixture gave an orange oil that seemed to consist mainly of \(\text{Re(CO)}_5\text{I}\) (IR bands at 2145 \(\text{w}\), 2010 \(\text{vw}\), 2042 \(\text{vs}\), 1995 \(\text{s}\) in pentane) and another product, possibly the dithioester compound \(\text{Re(CO)}_5\text{CS}_2\text{Me}\) (IR bands at 2072 \(\text{w}\), 1953 \(\text{vs}\), 2000 \(\text{s}\)). However, attempts to isolate this second product were unsuccessful.
Reaction of the orange oil with CF$_3$SO$_2$H in Et$_2$O gave some evidence for the formation of Re(CO)$_5$CS$^+$ (see below), but this was clearly a minor product.

Reaction of Re(CO)$_5^-$ with Cl-C(S)OMe/CF$_3$SO$_2$H

A solution of Na[Re(CO)$_5$] was prepared by reducing Re$_2$(CO)$_{10}$ (1.50 g, 2.50 mmol) in 40 ml of THF with 1% Na(Hg). The solution was transferred by syringe to an equipressure dropping funnel and added over a period of 20 min to a stirred solution of Cl-C(S)-OCH$_3$ (1.0 ml, 1.3 g, 12 mmol) in 10 ml of THF. The mixture was stirred for an additional 30 min and then filtered, giving a white residue (shown by qualitative tests to be NaCl) and an orange solution. A brown oil was obtained upon evaporation of the solvent under reduced pressure. This substance was shown by IR to be a mixture of several products. An attempt to isolate the desired product, Re(CO)$_5$C(S)OMe, by column chromatography was unsuccessful.

The reaction was repeated, and the oily product was dissolved in 40 ml of Et$_2$O to give a dark brown solution. Addition of CF$_3$SO$_2$H (5 ml of a 1 M Et$_2$O solution, 5 mmol) caused the immediate formation of a white precipitate, tentatively identified as [Re(CO)$_5$CS]CF$_3$SO$_2$ by its IR spectrum. After 1 hr the product was filtered off, washed with Et$_2$O and dried in vacuo. Yield: 0.30 g.

IR(CH$_2$Cl$_2$): 2173 w, 2080 s, 2033 m-s, (KBr) 1363 m-s.
The compound decomposed fairly rapidly in solution, as evidenced by the disappearance of the three IR bands and the growth of a new band at 2048 cm$^{-1}$. Reaction with water or atmospheric moisture gave H$_2$S and a yellowish residue. Addition of [PPN]N$_3$ to the compound in CH$_2$Cl$_2$ resulted in vigorous gas evolution and formation of a yellow solution; the IR spectrum showed several new bands, including one at $\sim$2120 cm$^{-1}$ suggesting an NCS or NCO ligand.

**Reaction of Re(CO)$_3$(PPh$_3$)$_2^-$ with CS$_2$/MeI**

Potassium (0.51 g, 13 mmol) was added in small pieces to 5 ml of rapidly-stirred Hg at 60° to form $\sim$0.75% K(Hg). After cooling, the amalgam was transferred by syringe to the reduction flask. A solution of trans-Re(CO)$_3$(PPh$_3$)$_2$Br (0.44 g, 0.50 mmol) in 75 ml of THF was added, and the mixture was stirred vigorously for 6-7 hr, giving a yellow-orange suspension of K[Re(CO)$_3$(PPh$_3$)$_2$]. If the amalgam was more concentrated than $\sim$0.75%, it solidified during the initial stages of the reaction. The identity of the product was established by its reaction with MeI to give trans-Re(CO)$_3$(PPh$_3$)$_2$Me; IR(CHCl$_3$): 2025 vw, 1927 s, 1885 m; $^1$H NMR(CDCl$_3$): 6-0.9 (triplet, Me). The excess amalgam was removed, and then CS$_2$ (1.0 ml, 1.3 g, 17 mmol) was added, giving a turbid grayish-white mixture. After 2 min, MeI (1.0 ml, 2.2 g, 16 mmol) was added, whereupon the mixture became cloudy orange. The reaction mixture was stirred for
an additional 10 min, filtered through Celite, and evaporated to dryness under reduced pressure. Extraction of the residue with CS\textsubscript{2} followed by filtration gave an orange solution, from which an orange solid was precipitated by addition of hexane. The IR spectrum suggested that this product could be the desired compound, \textit{trans}-Re(CO)\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2}CS\textsubscript{2}Me; however, the \textsuperscript{1}H NMR spectrum contained no methyl resonance.

IR(CHCl\textsubscript{3}): 2050 w, 1956 s, 1923 m, (CS\textsubscript{2}) 1237 w.

\textbf{Preparation of CpFe(CO)\textsubscript{2}CS\textsubscript{2}Me and \{CpFe(CO)\textsubscript{2}CS\textsuperscript{+}\}CF\textsubscript{3}SO\textsubscript{3}\}}

Although satisfactory methods for the preparation of CpFe(CO)\textsubscript{2}CS\textsubscript{2}Me and CpFe(CO)\textsubscript{2}CS\textsuperscript{+} are available,\textsuperscript{30} recent improvements in these procedures warrant their inclusion in this dissertation. The use of CF\textsubscript{3}SO\textsubscript{3}H rather than HCl in the synthesis of the thiocarbonyl cation is of particular importance.

Cyclopentadienyliron dicarbonyl dimer (14.2 g, 40.1 mmol) in 230 ml of THF was stirred with \textasciitilde\textasciitilde\textasciitilde Na(Hg) (17 ml, \textasciitilde\textasciitilde\textasciitilde 96 mmol Na) for 1 hr to give a solution of Na[CpFe(CO)\textsubscript{2}]\textsubscript{2}. (A much cleaner reaction mixture was obtained if the amalgam was prepared in a separate flask and then transferred by syringe.) After removal of the excess amalgam, CS\textsubscript{2} (8.2 ml, 9.1 g, 120 mmol) was added to the rapidly-stirred solution. After 15-20 sec (no more than 30 sec), MeI (8.2 ml, 18.1 g, 128 mmol) was added. At this point the mixture was yellow-brown and cloudy, owing to the formation of CpFe(CO)\textsubscript{2}CS\textsubscript{2}Me and
precipitated NaI. (Caution: It was important to use at least the specified amount of THF. On this scale the alkylation step was highly exothermic; if insufficient solvent was used, the reaction mixture boiled violently out of the flask.) The mixture was stirred for an additional 20 min and then evaporated to dryness under reduced pressure. The residue was extracted with 200 ml of Et₂O, and the mixture was filtered through Celite to give a dark yellow-brown solution.

If the dithioester compound was desired, the solution was evaporated to dryness under reduced pressure. The residue was recrystallized from hexane at -20° to give a 60% yield of yellow-brown CpFe(CO)₂CS₂Me.

IR(hexane): 2035 vs, 1988 vs. NMR(CCl₄): 52.50(Me), 4.82(Cp).

If the thiocarbonyl cation was desired, CF₃SO₂H (8.9 ml, 15 g, 100 mmol) was added to the Et₂O solution from an equipressure dropping funnel over a period of 1 hr. The mixture was stirred for an additional 2 hr, and the precipitated [CpFe(CO)₂CS]CF₃SO₂ was filtered off and washed 5 times with Et₂O. The crude product was dissolved in 200 ml of acetone and re-precipitated by slow addition of 600 ml of hexane to give brown-gold crystals of the product in 75-80% yield. The compound is slightly moisture-sensitive, and therefore was stored in a desiccator over CaSO₄, with a small
beaker of Pb(OAc)\textsubscript{2} to absorb any H\textsubscript{2}S evolved.

IR(CH\textsubscript{2}Cl\textsubscript{2}): 2105 s, 2071 s, 1353 s. NMR(d\textsubscript{6}-acetone): 66.05.

**Preparation of Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{2}CS**

A solution of Na[CpFe(CO)\textsubscript{2}] was prepared by stirring [CpFe(CO)\textsubscript{2}]\textsubscript{2} (11.5 g, 31.5 mmol) with 1% Na(Hg) (14 ml, \approx 80 mmol Na) in 130 ml of THF for 45 min. After the excess amalgam was drained off, a solution of (PhO)\textsubscript{2}CS (6.90 g, 30.0 mmol) was added to the stirred reaction mixture from an equipressure dropping funnel over a period of 5-10 min. A mildly exothermic reaction with vigorous evolution of CO occurred, giving a dark brown solution. The mixture was stirred for an additional 10 min and then evaporated to a moist residue under reduced pressure; the residue was dried in vacuo for 15-20 min. (Evaporation to dryness gave a rock-hard solid that was very difficult to extract.) The residue was stirred with 250 ml of CS\textsubscript{2} for 20 min and the mixture was filtered through Celite; the gummy residual material was washed with another 50 ml of CS\textsubscript{2}. The volume of solution was reduced to about 120 ml, using a rotary evaporator and a room-temperature water bath. Any solid that precipitated at this point was found to consist almost entirely of [CpFe(CO)\textsubscript{2}];\textsubscript{2}, and was separated by filtration through a coarse frit filter. The solution was then chromatographed on a 25 mm X 1 m Florisil column by eluting first with 100 ml
of CS$_2$, and thereafter with a 5:1 CS$_2$/CH$_2$Cl$_2$ mixture. Four bands always developed; in order of elution these were: light orange (identified by IR and NMR spectra as [CpFe(CO)$_2$]$_2$Hg), pale yellow (unreacted (PhO)$_2$CS), black (Cp$_2$Fe$_2$(CO)$_3$CS) and dark red ([CpFe(CO)$_2$]$_2$). Resolution of the thiocarbonyl and dimer bands was never complete, but only a small amount of Cp$_2$Fe$_2$(CO)$_3$CS remained on the column when [CpFe(CO)$_2$]$_2$ began to elute. (In the latter stages of the elution, the composition of the eluate was monitored by IR to prevent contamination of the product with [CpFe(CO)$_2$]$_2$. The thiocarbonyl solution was filtered and then evaporated slowly to give shiny black crystals of Cp$_2$Fe$_2$(CO)$_3$CS. The product was transferred to a frit filter, washed 3 times with cold (0°) pentane, and dried in vacuo. A typical yield was 4.77 g (12.9 mmol, 43%). The analytical sample was recrystallized from hexane at -20°.

IR(CS$_2$): 2005 vs, 1968 s, 1809 m-s, 1130 m. $^1$H NMR(CS$_2$): δ4.65, 4.73 (4:7 ratio). $^{13}$C NMR(CDCl$_3$): δ90.1, 92.1 (Cp, 5:2); 208.5, 209.3 (terminal CO, 5:2); 267.7 (bridge CO); 378.1 (CS). Mass spectrum: parent ion at m/e 370. MP: 159-161°. Anal. Calc. for C$_{14}$H$_{14}$Fe$_2$O$_3$S: C 45.45, H 2.72, S 8.66. Found: C 45.32, H 2.72, S 9.19.

The analogous reactions of CpFe(CO)$_2$ with (p-ClC$_6$H$_4$O)$_2$CS and (p-MeOC$_6$H$_4$O)$_2$CS afforded Cp$_2$Fe$_2$(CO)$_3$CS in 35% and 44%, respectively, while reaction with (p-NO$_2$C$_6$H$_4$O)$_2$CS gave no
thiocarbonyl complex.

Reaction of (MeC_5H_4)Fe(CO)_2^- with (PhO)_2CS in the same manner gave the methylcyclopentadienyl analog. After chromatography, the product was crystallized from hexane at -20° to give purple needles of (MeC_5H_4)_2Fe_2(CO)_3CS in 33% yield.

IR(CS_2): 2001 vs, 1962 s, 1804 m, 1125 m. NMR(d_6-acetone): 62.15 (Me), 4.60-4.85 (multiplet, C_5H_4).

Reactions of CpFe(CO)_2^- with other thiocarbonyl reagents

The anion CpFe(CO)_2^- reacted with Cl-C(S)-OPh (2:1 molar ratio) in THF at 0° to give, after chromatography, Cp_2Fe_2(CO)_3CS in 5-6% yield. The major product of this reaction was [CpFe(CO)_2]_2; if a large excess of the chlorothioformate was used, an appreciable amount of CpFe(CO)_2Cl was also produced. In similar reactions at -78°, (PhS)_2CS and (C_3H_2N)_2CS gave only trace amounts of the thiocarbonyl complex, and Cl_2CS gave none at all. In these reactions the major product was again [CpFe(CO)_2]_2.

Reaction of equimolar amounts of CpFe(CO)_2^- and [CpFe(CO)_2CS]CF_3SO_3 in THF at -78° gave [CpFe(CO)_2]_2 and very small amounts of Cp_2Fe_2(CO)_3CS and [CpFe(CO)(CS)]_2. In contrast, the analogous reaction with CpFe(CO)_2CS_Me at room temperature gave the carbonyl dimer (major product) and a 25% yield of the thiocarbonyl complex.
**Preparation of CpFe(CO)$_2$C(S)OPh**

A solution of NaOPh was prepared by addition of NaH (0.60 g, 25.0 mmol) in small portions to a solution of phenol (2.35 g, 25.0 mmol) in 75 ml of THF. After all the hydride had reacted, [CpFe(CO)$_2$CS]CF$_3$SO$_3$ (9.25 g, 25.0 mmol) was added and the mixture was stirred for 1 hr. The solvent was then removed under reduced pressure, and the residue was extracted with 100 ml of CS$_2$. After filtration, the solvent was evaporated under reduced pressure to give a dark yellow-brown oil which could not be made to crystallize. Attempted purification by chromatography on Florisil resulted in decomposition of the product.

IR(hexane): 2042 vs, 1966 vs.

**Reaction of CpFe(CO)$_2$C(S)OPh with CpFe(CO)$_2$**

The phenylthioester was prepared as above. A solution of Na[CpFe(CO)$_2$], obtained by Na(Hg) reduction of [CpFe(CO)$_2$]$^-$ (6.20 g, 17.5 mmol) in 60 ml of THF, was added from an equipressure dropping funnel to the stirred CpFe(CO)$_2$C(S)OPh solution over a period of 5-10 min. Vigorous evolution of gas occurred, and the mixture became very dark brown. After an additional 10 min, the solvent was removed under reduced pressure. Chromatography of the residue as described previously for the isolation of Cp$_2$Fe$_2$(CO)$_3$CS gave [CpFe(CO)(CS)]$_2$ (green band, yield ~0.2 g),
Cp₂Fe₂(CO)₃CS (36% yield) and [CpFe(CO)₂]₂. The monothiocarbonyl product was slightly contaminated with the bis-thiocarbonyl complex.

**Preparation of [CpFe(CO)₂C(OH)₂]PF₆**

The thioester CpFe(CO)₂C(S)OPh (5.0 mmol), prepared and isolated as before, was dissolved in 30 ml of CH₂Cl₂. Methyl fluorosulfonate (0.50 ml, 0.70 g, 6.2 mmol) was added, and the solution was stirred for 30 min. An IR spectrum of the reaction mixture showed bands at 2059 vs and 2019 s, presumably from the cationic carbene [CpFe(CO)₂C(SMe)(OPh)] FSO₃⁻. The solvent was removed in vacuo, leaving a yellow-brown oil that would not crystallize. Ion exchange in acetone gave the PF₆⁻ salt, which was also an oil. Addition of MeOH caused an immediate reaction, giving solid [CpFe(CO)₂C(OH)₂]PF₆ and MeSH. The product was recrystallized from MeOH at -20° to give small, pale yellow crystals in 44% yield.

IR(CH₂Cl₂): 2068 vs, 2020 s. ¹H NMR(d₆-acetone): δ 4.42 (Me), 5.65 (Cp). ¹³C NMR (d₆-acetone): δ 85.0 (Cp), 207.0 (CO), 248.6 (carbene C), Me resonance obscured by solvent peaks. MP: dec. 200-205°. **Anal. Calc. for C₁₀H₁₁F₆FeO₄P: C 30.33, H 2.80. Found: C 31.78, H 2.98.**

**Reaction of Cp₂Fe₂(CO)₃CS with halogens**

Addition of a saturated solution of Cl₂ in CCl₄ to Cp₂Fe₂(CO)₃CS in CCl₄ at 0° caused the immediate formation
of a gummy brown-black precipitate. Extraction with CH₂Cl₂ gave a brown solution; the bulk of the precipitate was insoluble in all solvents, however. The IR spectrum of the extract showed CO bands at ~2090 w-m, 2060 s and 2030 m, but contained no CS absorption.

The thiocarbonyl complex reacted rapidly with a threefold excess of Br₂ or I₂ in CS₂ to give small amounts of CpFe(CO)₂X and CpFe(CO)(CS)X, which were identified by their IR spectra. However, in both cases the major product was an insoluble black tar much like that obtained in the Cl₂ reaction.

\[
\text{IR of CpFe(CO)(CS)X (CS₂): } X = \text{Br, 2032 s, 1310 vs; } X = \text{I, 2023 s, 1301 vs.}
\]

**Reduction of Cp₂Fe₂(CO)₃CS and preparation of CpFe(CO)(CS)SnPh₃**

A solution of Cp₂Fe₂(CO)₃CS (1.11 g, 3.00 mmol) in 50 ml of THF was stirred vigorously with 1% Na(Hg) (2.0 ml, \(\approx 11 \text{ mmol Na} \)) for 7-8 min to give a red-brown solution of Na[CpFe(CO)(CS)] and Na[CpFe(CO)₂]. The excess amalgam (which had turned into a sand) was drained off, and Ph₃SnCl (2.31 g, 6.00 g) was added, causing an immediate color change to yellow-brown. After 10 min the solvent was evaporated under reduced pressure and the residue was extracted with 30 ml of CS₂. Chromatography on Florisil column (18 X 700 mm) with CS₂ gave a bright yellow band (CpFe(CO)(CS)SnPh₃) followed closely by a pale yellow band (CpFe(CO)₂SnPh₃, plus,
in the later stages of elution, some unreacted \( \text{Ph}_3\text{SnCl} \).
Evaporation of the thiocarbonyl solution gave a sticky yellow-brown residue, which was recrystallized from hexane at \(-20°\) to give golden yellow needles of \( \text{CpFe(CO)(CS)SnPh}_3 \) (58%).

\[
\text{IR(CS}_2\text{): } 1978 \text{ s, 1288 vs. } \text{H NMR(CS}_2\text{): } \delta 4.78 \text{ (Cp), 7.20-7.70 (multiplet, Ph). } \text{13C NMR(CDC}_3\text{): } \delta 84.4 \text{ (Cp), 127.6 (Ph), 136.1 (Ph), 142.9 (Ph), 213.9 (CO), 314.8 (CS). MP: 124-126°. Anal. Calc. for C}_{29}^\text{H}_{20}^\text{FeCSSn: C 55.29, H 3.71, S 5.90. Found: C 55.61, H 3.85, S 6.19.}
\]

The analogous reaction with \( \text{Ph}_3\text{GeBr} \) gave yellow \( \text{CpFe(CO)(CS)GePh}_3 \) in 11% yield.

\[
\text{IR(CS}_2\text{): } 1982 \text{ s, 1289 vs. } \text{NMR(CS}_2\text{): } \delta 4.69 \text{ (Cp), 7.15-7.60 (multiplet, Ph).}
\]

**Reaction of \( \text{CpFe(CO)(CS)^-} \) with other organometallic halides**

The thiocarbonyl anion appeared to react with \( \text{PhHgCl} \) and \( \text{Ph}_3\text{PbCl} \) to give the desired arylmetal derivatives. However, these products were not stable to chromatography and could not be isolated. Reaction of \( \text{CpM(CO)}_{\text{3}}^\text{Cl} \) (\( M = \text{Mo, W} \)) with \( \text{CpFe(CO)(CS)^-} \) gave only \( \text{[CpM(CO)}_{\text{3}}^\text{]}_2, \text{Cp}_2\text{Fe}_2(\text{CO)}_{\text{3}}\text{CS}, \text{[CpFe(CO)}_{\text{2}}^\text{]}_2 \) and a small amount of \( \text{[CpFe(CO)(CS)]}_2; there was no evidence of the formation of mixed metal thiocarbonyls.
Reaction of CoFe(CO)(CS)⁻ with MeI and MeOSO₂F

The thiocarbonyl (0.74 g, 2.0 mmol) was reduced with 1% Na(Hg) (1.5 ml, 8.6 mmol Na) in 40 ml of THF. After removal of the excess amalgam, MeI (0.50 ml, 1.1 g, 7.8 mmol) was added, and the solution was stirred for 10 min. The brown reaction mixture was evaporated to dryness under reduced pressure, and the residue was extracted with 30 ml of CS₂. After filtration, the solution was chromatographed on an 18 X 700 mm Florisil column. Development with CS₂ gave six bands: yellow, orange, gray, green black and red. The yellow band was eluted with CS₂ and contained CpFe(CO)₂He, identified by its IR spectrum. The orange band was also eluted with CS₂, and on evaporation yielded 0.1 g of an orange-brown solid, tentatively identified by its spectra as CpFe(CO)(CS-He). Elution of the gray band with 9:1 CS₂/CH₂Cl₂ gave 0.15 g of an unidentified black solid. The three remaining components were eluted with 5:2 CS₂/CH₂Cl₂ and were identified by IR as \([\text{CpFe(CO)(CS)}]_2\), \(\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\) and \([\text{CpFe(CO)}]_2\)₂, respectively; only very small amounts were obtained.

IR of orange compound (CS₂): 1960 vs. NMR(CS₂): 62.53, 4.57 (3:5 ratio).

IR of black product (CS₂): 1963 vs, 1273 m, 1205 m. NMR(CS₂): 62.47, 2.52, 4.62 (3:3:5 ratio).

Use of MeOSO₂F instead of MeI in this reaction gave
CpFe(CO)₂Me, and a black product which appeared to be ionic and was not investigated further.

**Reaction of CpFe(CO)(CS)²⁻ with CS₂/MeI**

The thiocarbonyl complex (0.74 g, 2.0 mmol) was reduced with 1% Na(Hg) (1.5 ml, ~8.6 mmol Na) in 40 ml of THF. Addition of CS₂ (0.50 ml, 0.64 g, 8.4 mmol) followed after 10 sec by MeI (0.50 ml, 1.1 g, 7.8 mmol) gave a dark brown solution, which was stirred for 10 min and then evaporated to dryness. The residue was insoluble in hexane or CS₂. Extraction with CH₂Cl₂, filtration, and evaporation of the solvent in vacuo gave a dark brown solid. This product appeared to be a mixture of two ionic compounds, but the components could not be separated or identified.

IR(CH₂Cl₂): 2023, 1986 s, 1955 s, 1047 w.

**Reaction of CpFe(CO)(CS)SnPh₃ with R-NH₂ (R = Me, Pr, Cy)**

A slow stream of MeNH₂ was bubbled through a solution of CpFe(CO)(CS)SnPh₃ (0.27 g, 0.50 mmol) in 50 ml of Et₂O for 5 min; a green color immediately developed. On stirring the mixture for 3 hr at RT, a yellow solution and a small amount of greenish precipitate were obtained. The mixture was evaporated under reduced pressure, and the residue was extracted with 30 ml of 1:1 hexane/CS₂. The resulting solution was filtered and then eluted through a Florisil column (18 X 500 mm) with the same solvent mixture.
Evaporation of the eluate and slow crystallization (2-3 weeks) of the residue from hexane at -20° gave golden needles of the isocyanide complex, CpFe(CO)(MeNC)SnPh₃, in 74% yield.


Reaction of CpFe(CO)(CS)SnPh₃ (0.10 g, 0.18 mmol) with Pr-NH₂ (0.20 ml, 0.14 g, 2.4 mmol) and pyridine (0.10 ml) in 30 ml of hexane or Et₂O gave CpFe(CO)(PrNC)SnPh₃. The reaction required about 20 hr to reach completion; the yield was not determined.

IR(hexane): 2115 m, 1946 s.

The analogous reaction of the thiocarbonyl (0.10 g, 0.18 mmol) with CyNH₂ (0.30 ml, 0.26 g, 3.0 mmol) and pyridine (0.10 ml) in 30 ml of hexane required 3 days. The product, CpFe(CO)(CyNC)SnPh₃, was isolated as a yellow powder (25%).

IR(hexane): 2115 m, 1947 s.

**Reaction of CpFe(CO)(CS)SnPh₃ with ethylenediamine**

The thiocarbonyl complex (0.27 g, 0.50 mmol) was stirred with ethylenediamine (0.20 ml, 0.18 g, 3.0 mmol) and pyridine (0.10 ml) in 40 ml of Et₂O for 12 hr. Evaporation of the solvent under reduced pressure extraction of the residue with 30 ml of CS₂, and filtration gave a yellow solution of the aminocarbene complex CpFe(CO)(CN₂C₂H₆)SnPh₃. The solvent
was removed in vacuo, and the product was recrystallized from 9:1 hexane/Et₂O at -20° to give small yellow-brown crystals (46%).

**IR(CS₂):** 1893 s. **NMR(CS₂):** δ3.05 (doublet, CH₂), 4.38 (Cp), 5.45 (broad, NH), 7.10-7.60 (multiplet, Ph).


The similar reaction with ethanolamine was much slower (~36 hr), and converted the CS ligand to an isocyanide rather than a carbene. This product was not isolated.

**Reaction of Cp₂Fe₂(CO)₃CS with PET₃ in methylcyclohexane**

A mixture of Cp₂Fe₂(CO)₃CS (0.20 g, 0.54 mmol) and PET₃ (0.15 ml, 0.12 g, 1.0 mmol) in 40 ml of methylcyclohexane was refluxed for 2.5 hr. The resulting dark green solution was evaporated to dryness under reduced pressure at 60°, the residue was extracted with 25 ml of CS₂, and the extract was chromatographed on a 10 X 200 mm Florisil column. Carbon disulfide eluted a yellow compound that was identified by IR and NMR as Cp₂Fe. Elution with 20:1 CS₂/Et₂O gave a deep green solution, which was evaporated under reduced pressure. The residue was redissolved in 20 ml of CH₂Cl₂, and the solution was filtered. Addition of 50 ml of hexane followed by slow evaporation gave black crystals of Cp₂Fe₂(CO)₂(CS)PET₃ (65%). The analytical sample was recrystallized from hexane at -20°.
IR(CS₂): 1945 vs, 1764 s, 1102 m. ¹H NMR(CDCl₃): δ 0.70–1.60 (multiplet, PEt₃), 4.55 (doublet, Cp), 4.80 (Cp).
¹³C NMR(CDCl₃): 67.17 (PET₃), 17.3 (doublet, PEt₃), 88.5 (Cp), 89.7 (Cp), 216.8 (terminal CO), 278.3 (doublet, bridge CO), 396.3 (doublet, CS). MP: 142–144° dec. Anal. Calc. for C₁₉H₂₅Fe₂O₂PS: C 38.74, H 4.55, S 5.17. Found: C 38.80, H 4.55, S 5.03.

Reaction of Cp₂Fe₂(CO)₂CS with PEt₃ in acetonitrile

The thiocarbonyl complex (0.20 g, 0.54 mmol) and PEt₃ (0.12 ml, 0.10 g, 0.82 mmol) were refluxed in 30 ml of CH₃CN for 30 min. The solvent was removed in vacuo, the residue was extracted with 40 ml of CS₂, and the solution was chromatographed on a 10 x 120 mm Florisil column. The product was eluted with 10:1 CS₂/Et₂O. Slow evaporation of a hexane/CH₂Cl₂ solution as before gave an 87% yield of Cp₂Fe₂(CO)₂(CS)PET₃.

Preparation of Cp₂Fe₂(CO)₂(CS)PET₃Ph₂

The thiocarbonyl (0.20 g, 0.54 mmol) was refluxed with PET₃Ph₂ (0.13 ml, 0.13 g, 0.91 mmol) in 30 ml of CH₃CN for 30 min. Isolation as for the PEt₃ analog gave black crystals of the product in 83% yield. The analytical sample was crystallized from 1:1 hexane/Et₂O at -78°.

IR(CS₂): 1950 vs, 1760 s, 1104 m. NMR(CDCl₃): δ 0.91 (doublet, Me), 1.45 (doublet, Me), 4.25 (doublet, Cp), 4.79
(Cp), 7.30-7.60 (multiplet, Ph). MP: 180-183° dec. **Anal.**

Calc. for C_{21}H_{21}Fe_{2}O_{2}PS: C 52.53, H 4.41. Found: C 52.49, H 4.48.

**Preparation of Cp_{2}Fe_{2}(CO)_{2}(CS)P(OMe)_{3}**

A solution of the thiocarbonyl (0.20 g, 0.54 mmol) in 30 ml of CH_{3}CN was refluxed for 8 hr with PMePh_{2} (0.20 ml, 0.20 g, 1.0 mmol). Isolation as before gave the dark green product (60%).

IR(CS_{2}): 1964 vs, 1944 s, 1748 s, 1100 m. NMR(CDCl_{3}): 61.70 (doublet, Me), 4.24 (doublet, Cp), 4.61 (Cp), 7.00-7.50 (multiplet, Ph).

**Preparation of Cp_{2}Fe_{2}(CO)_{2}(CS)P(OiPr)_{3}**

The thiocarbonyl complex (0.20 g, 0.54 mmol) and P(OiPr)_{3} (0.30 ml, 0.30 g, 0.93 mmol) were refluxed in 30 ml of CH_{3}CN for 1.5 hr. Isolation as for the phosphine derivatives gave a 56% yield of the brown product.

IR(CS_{2}): 1956 vs, 1759 s, 1108 m. NMR(CDCl_{3}): 63.58 (doublet, Me), 4.58 (doublet, Cp), 4.74 (Cp).

**Preparation of Cp_{2}Fe_{2}(CO)_{2}(CS)(MeNC)  

A solution of Cp_{2}Fe_{2}(CO)_{2}CS (0.20 g, 0.54 mmol) and MeNC (0.10 ml, 0.071 g, 1.72 mmol) in 30 ml of THF was refluxed for 1 hr. The mixture was evaporated under reduced pressure, the residue was extracted with 30 ml of CS_{2}, and the solution was filtered. Addition of 60 ml of hexane followed by slow
evaporation gave the red-brown isocyanide complex (84%).
The analytical sample was crystallized from 5:1 hexane/Et₂O
at -78°.

IR(CH₂Cl₂): 2164 s, 1996 w(sh), 1961 vs, 1773 s,
1119 s(sh), 1113 s. NMR(CDCl₃): 63.05 (Me), 4.70 (Cp)
4.82 (Cp). δP: 171-174°. Anal. Calc. for C₁₆H₁₃Fe₂N₂O₂S:
C 47.04, H 3.42, N 5.66. Found: C 46.95, H 3.53, N 5.66.

The same complex was obtained in 70% yield by refluxing
Cp₂Fe₂(CO)₃CS with excess MeNC in cyclohexane for 2.5 hr.

Preparation of Cp₂Fe₂(CO)(CS)(MeNC)₂

A mixture of Cp₂Fe₂(CO)₃CS (0.37 g, 1.0 mmol) and MeNC
(0.20 ml, 0.14 g, 3.4 mmol) in 30 ml of CH₃CN was refluxed
for 20 min. The solvent was evaporated under reduced pressure,
the residue was extracted with 40 ml of CS₂, and the solution
was filtered. The filtrate was then stirred for 24 hr at
room temperature. After filtration, 80 ml of hexane was
added, and slow evaporation gave purple crystals of
Cp₂Fe₂(CO)(CS)(MeNC)₂ (78%). The analytical sample was
crystallized from 4:1 hexane/Et₂O at -78°.

IR(CH₂Cl₂): 2155 s, 1955 vs, 1717 s, 1119 m(sh),
1105 m-s. NMR(CDCl₃): 62.96 (Me), 3.72 (Me), 4.67 (Cp),
4.83 (Cp). δP: 130-135°. Anal. Calc. for C₁₆H₁₆N₂O₂S:

In several cases the CS₂ extract of the reaction mixture
was chromatographed on a 10 X 120 mm column of Grade III
Woehlm alumina. Carbon disulfide eluted a green band, which proved to be a small amount of the monosubstituted complex, \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{HNC}) \). Elution with 20:1 \( \text{CS}_2/\text{Et}_2\text{O} \) gave a second green band that contained the major product, \( \text{Cp}_2\text{Fe}_2(\text{CO})(\text{CS})(\text{HNC})_2 \). Continued elution brought down a third green band; this yielded a small amount of a brown-purple compound, which also analyzed as the \textbf{bis}-isocyanide complex but had a different IR spectrum.

\text{IR(CH}_2\text{Cl}_2\text{)}: 2154 \text{ vs}, 1954 \text{ v}, 1751 \text{ s}, 1720 \text{ w}, 1110 \text{ s}.

\text{Anal. Calc. for } \text{C}_{16}\text{H}_{16}\text{Fe}_2\text{N}_2\text{OS}: \text{ C 48.52, H 4.07, N 7.07.}

\text{Found: C 47.80, H 3.98, N 6.92.}

\textbf{Reaction of } \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS with other ligands}

Reaction of the thiocarbonyl complex with \( \text{PBU}_3 \) in refluxing \( \text{CH}_2\text{Cl}_2 \) gave some of the substituted derivative; however, this product was rather unstable and was not isolated. Other potential ligands such as \( \text{PPh}_3 \), \( \text{P(OPh)}_3 \), diphos, \( \text{R-NH}_2 \), \( \text{R}_2\text{NH} \), \( \text{R}_3\text{N} \), pyridine, and \( \text{PhNC} \) gave no evidence of reaction under these conditions. Ultraviolet irradiation of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) with \( \text{PPh}_3 \) or \( \text{P(OPh)}_3 \) in \( \text{Et}_2\text{O} \) gave the mono-substitution products, but the complexes were not isolated owing to their low stabilities. Photolysis with \( \text{PhNC} \) appeared to give a mixture of \textbf{mono} and \textbf{bis} substitution, but attempts to separate the products by chromatography of Florisil resulted in decomposition.
Reaction of Cp₂Fe₂(CO)₃CS with nucleophiles

The thiocarbonyl complex was found to be unreactive toward NaOMe in MeOH or [PPN]H₂ in acetone at room temperature. As mentioned above, amines give no reaction with Cp₂Fe₂(CO)₃CS in refluxing CH₃CN. Thiocarbonyl reacted with KCN in refluxing CH₃CN to give a rather insoluble black product, which was not characterized; NaI, KSCN and KSeCN did not react.

Reaction of Cp₂Fe₂(CO)₃CS with an equimolar amount of MeLi in THF at -20° gave a black solution. Addition of MeOSO₂F followed by removal of the solvent in vacuo gave a black oil. This product appeared to be an ionic compound, but it could not be crystallized and was not isolated.

IR(CH₃CN): 2006 m, 1946 vs, 1777 s.

Reaction of Cp₂Fe₂(CO)₃CS with HX₂ (X = Cl, Br, I)

Mercuric chloride (0.136 g, 0.5000 mmol) was added to a solution of Cp₂Fe₂(CO)₃CS (0.189 g, 0.510 mmol) in 30 ml of CH₂Cl₂, and the mixture was stirred for 5 min. Evaporation of the solvent under reduced pressure gave a dark red residue, which was dried in vacuo for several hours. The product was transferred to a frit filter, washed 10 times with 15 ml of pentane, and again dried in vacuo. Yield of the product, Cp₂Fe₂(CO)₃CS·HgCl₂, was essentially quantitative. To obtain spectra it was necessary to saturate the solvents with HgCl₂, owing to the lability of the adduct; such solutions were deep red.
IR(CH₂Cl₂): 2037 s, 2004 m, 1842 m, 1019 w.


Anal. Calc. for C₁₄H₁₀Cl₂Fe₂HgO₂S: C 26.21, H 1.57, S 5.00.
Found: C 27.93, H 1.85, S 4.67.

The dark red HgBr₂ adduct was prepared in the same manner. As with the HgCl₂ complex, the presence of excess mercuric halide was necessary for observation of spectra.

IR(CH₂Cl₂): 2035 s, 2006 m, 1840 m, 1020 w.

The HgI₂ complex, also dark red, was obtained by the same method, except that acetone was used as the solvent. Spectra of Cp₂Fe₂(CO)₃CS·HgI₂ could not be determined owing to the low solubility of HgI₂ in organic solvents.

H: 125-130° dec. Anal. Calc. for C₁₄H₁₀Fe₂HgI₂O₂S: C 20.40, H 1.22. Found: C 19.87, H 1.34.

Reaction of Cp₂Fe₂(CO)₃CS with BX₃ (X = F, Cl, Br) and AlCl₃

Addition of BBr₃ (0.10 ml, excess) to a solution of Cp₂Fe₂(CO)₃CS (0.20 g, 0.54 mmol) gave a deep red solution. Within a few minutes the thiocarbonyl began to decompose, as evidenced by a color change to orange and the appearance of additional IR bands at 2100 and 2070 cm⁻¹. The adduct, Cp₂Fe₂(CO)₃CS·BBr₃, was very labile and could not be isolated.

IR(CH₂Cl₂): 2039 s, 2006 m, 1842 m, 1002 w. NMR(CDCl₃): 65.20, 5.27 (ν1:2).

Reactions with BCl₃ and BF₃·Et₂O gave IR evidence for Cp₂Fe₂(CO)₃CS·BX₃ adducts, but decomposition of the
thiocarbonyl complex was even more rapid in the presence of these boron halides.

The thiocarbonyl was stable in CH₂Cl₂ solution in the presence of an equimolar amount of AlCl₃. Addition of excess AlCl₃ gave a reddish solution, indicating adduct formation, but also caused rapid decomposition. The adduct was too unstable to be isolated.

**Reaction of Cp₂Fe₂(CO)₂CS with PtCl₂(PhCN)₂**

A solution of the thiocarbonyl complex (0.20 g, 0.54 mmol) and PtCl₂(PhCN)₂ (0.12 g, 0.25 mmol) in 40 ml of CHCl₃ was refluxed for 12 hr, giving a red solution and a red precipitate. The solution was cooled, 50 ml of hexane was added, and the mixture was filtered. The product, tentatively identified as [Cp₂Fe₂(CO)₂CS]₂PtCl₂, was washed 5 times with Et₂O and dried in vacuo. Yield of the red powder was 75%. Attempts to crystallize the product were unsuccessful.

IR(CH₂Cl₂): 2024 vs, 1992 m(sh), 1828 s, 1081 w, 1033 w.

**Preparation of Cp₂Fe₂(CO)₂CS·M(CO)₅ (M = Cr, W)**

A solution of Et₄N[Cr(CO)₅]I (0.229 g, 0.510 mmol) in 30 ml of acetone was cooled to 0°, and then AgBF₄ (0.100 g, 0.513 mmol) in 10 ml of acetone was added over 5 min from an equipressure dropping funnel. After an additional 10 min the mixture was filtered to remove AgI, and the yellow-orange filtrate was again cooled to 0°. Solid
Cp₂Fe₂(CO)₃CS (0.191 g, 0.516 mmol) was added, and the mixture was stirred for 30 min. The solution was warmed to room temperature, and the solvent was evaporated under reduced pressure. Extraction of the residue with 30 ml of 4:1 pentane/acetone and filtration gave a deep red solution, which was evaporated under a slow stream of N₂ to give red-purple needles of Cp₂Fe₂(CO)₃CS·Cr(CO)₅ (60%).

IR(CS₂): 2061 m, 2020 s, 1977 w, 1934 s, 1916 m, 1825 w-m, 1082 w. NMR(d₆-acetone): δ 5.28. MP: 126-129° dec. Anal. Calc. for C₁₉H₁₀CrFe₂O₈S: C 40.60, H 1.79. Found: C 40.01, H 1.94.

The same reaction with Et₄N[Cl(CO)₅] (0.296 g, 0.510 mmol) afforded the Cl analog as red-purple needles in 76% yield.

IR(CS₂): 2067 m, 2022 s, 1992 w, 1977 w, 1931 s, 1911 m, 1827 w-m, 1076 w. NMR(d₆-acetone): δ 5.28. MP: 119-122° dec. Anal. Calc. for C₁₉H₁₀Fe₂O₈S: C 32.89, H 1.45, S 4.62. Found: C 35.08, H 1.14, S 4.68.

Preparation of [Cp₂Fe₂(CO)₃CS·CoFe(CO)₂]BF₄

A mixture of Cp₂Fe₂(CO)₃CS (0.20 g, 0.54 mmol) and [CpFe(CO)₂(THF)]BF₄ (0.17 g, 0.50 mmol) in 35 ml of acetone was refluxed for 1 hr. The solvent was removed in vacuo, and the residue was dried in vacuo overnight. The red solid was transferred to a frit filter and washed 5 times with 20 ml of Et₂O. The product was then recrystallized from 1:1
CH₂Cl₂/hexane at -20° to give small red-brown crystals of the complex (82%).

\[ \text{IR(CH}_2\text{Cl}_2): \ 2049 \text{ vs, } 2025 \text{ s, } 2006 \text{ m, } 1834 \text{ m.} \]

\[ \text{H\textsubscript{13}Cl\textsubscript{g}Cl\textsubscript{2}: } \ 85.45, \ 5.73 \text{ (2:1). Molar conductivity: } \lambda = 77.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}. \text{ MP: dec. 200-205°. Anal. Calc. for } C_{31}H_{15}BF_4Fe_2O_5S: C 39.80, H 2.59, S 5.12. \text{ Found: C 39.00, H 2.37, S 5.12.} \]

**Preparation of CpFe(CO)(CS)CF₃SO₃ and \( [\text{CpFe(CO)}_2\text{CS}]\text{CF₃SO₃} \)**

A quartz Schlenk tube (20 X 170 mm) was charged with \([\text{CpFe(CO)}_2\text{CS}]\text{CF₃SO₃} \) (0.37 g, 1.0 mmol) and 25 ml of CH₂Cl₂. The solution was then irradiated at 254 nm for 6 hr in a small photolysis apparatus (Bradford Scientific Co., modified with a plexiglas bottom so that a magnetic stirrer could be used); the tube was vented to a mineral oil bubbler to permit escape of CO. The resulting red solution was transferred to another Schlenk tube, 40 ml of hexane was added, and the mixture was filtered to give a red solution of CpFe(CO)(CS)CF₃SO₃. The compound was stable only in solution and could not be isolated.

\[ \text{IR(CH}_2\text{Cl}_2): \ 2048 \text{ s, } 1325 \text{ vs.} \]

The solution was refluxed with \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) (0.40 g, 1.1 mmol) for 1 hr, after which the solvent was evaporated under reduced pressure to give a dark red oil. The residue was dissolved in 30 ml of MeOH and the solution was filtered. Addition of Na₂BPh₄ (1.0 g, 3.0 mmol) in 5 ml of MeOH gave
a red precipitate. The mixture was cooled at 0° for several hours; the product was then filtered off and washed 3 times with 20 ml of Et₂O. Recrystallization twice from 2:1 hexane/CH₂Cl₂ at -20° gave small red needles of [Cp₂Fe₂(CO)₂CS•CpFe(CO)(CS)]BPh₄ (71%).

IR(CH₃CN): 2032 s, 2020 s, 1987 v/, 1834 m, (CHCl₃) 1315 m. NMR(d₆-acetone): 65.42, 5.61 (10:7, Cp), 6.90-7.40 (multiplet, Ph).

Reaction of Cp₂Fe₂(CO)₂CS with other metal carbonyl compounds

Spectroscopic evidence for S-adducts was obtained in low-temperature reactions of the thiocarbonyl complex with Mo(CO)₅(acetone), W(CO)₄(CS)(acetone), and Fe(CO)₄(THF), but the complexes were too unstable to be isolated. Similarly, the thiocarbonyl reacted with [M(CO)₅(CH₂CN)]PF₆ (M = Mn, Re) in refluxing THF to give red products, but again the stabilities were too low to permit isolation of the desired complexes. Under the same conditions, CpFe(CO)₂Cl did not react, and Mn(CO)₅Br gave only [Mn(CO)₄Br]₂. Direct thermal or photochemical synthesis of [Cp₂Fe₂(CO)₂CS•CpFe(CO)(CX)]⁺ (X = O, S) from [CpFe(CO)₂(CX)]PF₆ also failed.

Preparation of [Cp₂Fe₂(CO)₂CS•HgMe]PF₆

Methylmercuric chloride (0.13 g, 0.52 mmol) was dissolved in 15 ml of CH₂Cl₂ at 0°, and AgPF₆ (0.13 g, 0.51 mmol) in 10 ml of CH₂Cl₂ was added. The mixture was stirred for 15
min, and the \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) (0.20 g, 0.54 mmol) was added, giving a dark red mixture. After 5 min the solution was filtered to remove AgCl, 30 ml of hexane was added and the solution was evaporated slowly; the crystals obtained were filtered off and washed with Et\(_2\)O. Two more crystallizations in this manner gave a product sufficiently pure for analysis. The yield of small dark red needles was 66%.

**IR(\text{CH}_2\text{Cl}_2):** 2033 s, 1998 m, 1844 m, 1017 w.

**NMR(\text{d}_6-\text{acetone}):** \( \delta 1.33 \) (broad, \( H_e \)), 5.59 (Cp). MP: 155-160° dec. **Anal. Calc.** for \( C_{15}H_{13}Fe_6Fe_2O_8PS \): C 24.66, H 1.79.

**Found:** C 24.99, H 1.86.

**Reaction of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) with RO\(\text{SO}_2\)F (\( R = \text{Me, Et} \))**

Methyl fluorosulfonate (0.20 ml, 0.36 g, 2.5 mmol) was added to a solution of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) (0.40 g, 1.1 mmol) in 20 ml of \( \text{CH}_2\text{Cl}_2 \), and the mixture was stirred for 1 hr. The majority of the product precipitated during this time. Addition of 30 ml of Et\(_2\)O followed by filtration gave tiny dark red crystals of \([\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-}\text{MeFSO}_3] \) (96%). The analytical sample was crystallized from 1:1 acetone/hexane at -20°.

**IR(\text{CH}_2\text{Cl}_2):** 2038 s, 2001 w, 1854 m, v1030 w. Molar conductivity: \( A = 82.1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \). MP: dec. 210-215°.

**Anal. Calc.** for \( C_{15}H_{13}Fe_6Fe_2O_8S_2 \): C 37.22, H 2.71, S 13.25.

**Found:** C 37.10, H 2.73, S 13.42.
The same reaction with EtOSO₂F afforded the Et analog in 86% yield.

**IR(CH₂Cl₂): 2037 s, 2007 w, 1853 m, ~1025 w.**

**Preparation of [C₆F₅Fe₂(CO)₃CS-Et]BF₄**

A mixture of the thiocarbonyl complex (0.20 g, 0.54 mmol) and [Et₃O]BF₄ (0.10 g, 0.55 mmol) in 15 ml of CH₂Cl₂ was stirred for 30 min, giving a red solution. The product was precipitated with 40 ml of Et₂O and recrystallized from 1:1 CH₂Cl₂/hexane at -20° to give red-brown crystals in 80% yield.


The crystals from this preparation were used for the X-ray structure of the compound (see Results and Discussion).

**Reaction of C₆F₅Fe₂(CO)₃CS with MeI**

A mixture of C₆F₅Fe₂(CO)₃CS (0.20 g, 0.54 mmol) and MeI (~3 ml) was stirred for 12 hr, giving a red precipitate. Addition of 40 ml of Et₂O and filtration of the mixture gave the product as a red powder (95%).

**IR(CH₂Cl₂): 2037 s, 2007 w-m, 1853 m, 1031 w.**

The product was dissolved in 150 ml of acetone, and the solution was passed through a PF₆⁻ ion exchange column. The eluate was evaporated to about 50 ml under reduced pressure, 30 ml of heptane (Skelly 'C') was added, and the solution was
slowly evaporated to give small red crystals of
\[ \text{[Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\text{]}\text{PF}_6 \] (93%).

\text{IR(}\text{CH}_2\text{Cl}_2\text{)}: 2040 s, 2012 w, 1856 m, 1028 w.  
\text{\textsuperscript{1}H NMR(}d_6\text{-acetone): } \delta 3.77 (\text{m}), 5.65 (\text{broad, Cp}).  
\text{\textsuperscript{13}C NMR(}d_6\text{-acetone): } \delta 83.0 (\text{m}), 89.9 (\text{Cp}), 90.5 (\text{Cp}), 249.6 (\text{bridge CO}).

\textbf{Reaction of Cp}_2\text{Fe}_2(\text{CO})_3\text{CS with other alkyl halides}

\text{Reaction of Cp}_2\text{Fe}_2(\text{CO})_3\text{CS (0.20 g, 0.54 mmol) with EtI (3 ml) for 24 hr gave [Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Et}]I. Isolation, ion exchange and crystallization as in the MeI reaction above gave red-brown crystals of [Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Et}]\text{PF}_6 in 77% yield.}

\text{IR(}\text{CH}_2\text{Cl}_2\text{)}: 2040 s, 2009 w, 1855 m, 1024 w.  
\text{\textsuperscript{1}H NMR(}d_6\text{-acetone): } \delta 3.69 (\text{triplet, CH}_3), 4.30 (\text{broad quartet, CH}_2), 5.58 (\text{Cp}).  
\text{\textsuperscript{13}C NMR(}d_6\text{-acetone): } \delta 83.0 (\text{m}), 89.9 (\text{Cp}), 90.5 (\text{Cp}), 249.6 (\text{bridge CO}).  
\text{Molar conductivity: } \Lambda = 89.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}.

\text{The same reaction with n-PrI gave dark red [Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Pr}]\text{PF}_6 in 90% yield. The higher solubility of this derivative (and all subsequent derivatives; see below) permitted use of less acetone (30-40 ml) in the ion exchange step.}

\text{IR(}\text{CH}_2\text{Cl}_2\text{)}: 2039 s, 2009 w, 1855 m, 1022 w.  
\text{\textsuperscript{1}H NMR(}d_6\text{-acetone): } \delta 1.20 (\text{triplet, CH}_3), 1.90-2.40 (\text{multiplet, CH}_2), 4.35 (\text{broad quartet, CH}_2), 5.75 (\text{broad, Cp}).  
\text{The dark red butyl analog was obtained in 85% yield in the same manner from n-DuI and the thiocarbonyl.}

\text{IR(}\text{CH}_2\text{Cl}_2\text{)}: 2039 s, 2009 w, 1955 m, 1024 w.
NMR (d<sub>6</sub>-acetone): δ1.05 (broad triplet, CH<sub>3</sub>), 1.35-2.10 (multiplet, CH<sub>2</sub>CH<sub>2</sub>), 4.36 broad quartet, CH<sub>2</sub>, 5.73 (broad, Cp).

To obtain the benzyl derivative, the thiocarbonyl (0.37 g, 1.0 mmol) was stirred with BzBr (3 ml) for 8 hr. (Caution: The reaction was carried out in a hood, since BzBr is a potent lachrymator.) Addition of 40 ml of Et<sub>2</sub>O and filtration gave the dull red Br<sup>-</sup> salt, which was washed 10 times with 20 ml of Et<sub>2</sub>O to remove excess BzBr. Ion exchange and crystallization as before gave red crystals of [Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>CS-Bz]<PF<sub>6</sub> (88%).

IR(CH<sub>2</sub>Cl<sub>2</sub>): 2039 s, 2011 w, 1857 m, 1023 w.

NIR(d<sub>6</sub>-acetone): δ5.43 (possibly CH<sub>2</sub>), 5.60 (broad Cp), 7.48 (multiplet, Ph). ¹³C NMR (d<sub>6</sub>-acetone): δ60.7 (CH<sub>2</sub>), 92.3 (Cp), 92.9 (Cp), 129.6 (Ph), 130.2 (Ph), 133.9 (Ph), 207.4 (terminal CO), 251.6 (bridge CO), 403.1 (CS). Molar conductivity: Λ = 82.4 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. M.P: 185-188° dec.

Anal. Calc. for C<sub>41</sub>H<sub>17</sub>F<sub>6</sub>Fe<sub>2</sub>PSe: C 41.62, H 2.83, S 5.29. Found: C 41.83, H 2.80, S 5.01.

Reaction of the thiocarbonyl in the same manner with AllBr, followed by ion exchange and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane by slow evaporation, gave red-gold [Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>CS-All]<PF<sub>6</sub> (86%).

IR(CH<sub>2</sub>Cl<sub>2</sub>): 2040 s, 2010 w, 1856 m, 1017 w.

NIR(d<sub>6</sub>-acetone): δ4.93 (broad triplet, CH<sub>2</sub>), 5.62 (Cp),
5.20-6.50 (multiplet, vinyl).

The thiocarbonyl was also alkylated by ErCH\textsubscript{2}COOEt under the same conditions used in the BzBr and AlI\textsubscript{2}Br reactions. (Caution: ErCH\textsubscript{2}COOEt is an even stronger lacrymator than BzBr.) Work-up as for the benzyl derivative gave an 81\% yield of red-gold [C\textsubscript{p}\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{5}CS-CH\textsubscript{2}COOEt]PF\textsubscript{6}.

IR(CH\textsubscript{2}Cl\textsubscript{2}): 2043 s, 2014 w, 1859 m, 1739 w, 1015 w.

NMR(d\textsubscript{6}-acetone): 61.32 (triplet, CH\textsubscript{2}), 4.38 (quartet, CH\textsubscript{2}), 5.20 (doublet, CH\textsubscript{2}), 5.80 (Cp). MP: 153-156\(^\circ\) dec. Anal. Calc. for C\textsubscript{18}H\textsubscript{17}F\textsubscript{6}Fe\textsubscript{2}O\textsubscript{5}PS: C 35.91, H 2.85. Found: C 35.62, H 2.90.

Reaction of C\textsubscript{p}Fe(CO)\textsubscript{3}CS with neat CH\textsubscript{2}I\textsubscript{2} for 24 hr, followed by ion exchange and crystallization from acetone/heptane by slow evaporation, gave dark red [C\textsubscript{p}Fe(CO)\textsubscript{3}CS-CH\textsubscript{2}I]PF\textsubscript{6} (37\%).

IR(CH\textsubscript{2}Cl\textsubscript{2}): 2044 s, 2017 w, 1860 m, 1109 w.

NMR(d\textsubscript{6}-acetone): 65.69 (doublet, possibly CH\textsubscript{2}), 5.79 (broad, Cp), 5.87 (broad, Cp).

The thiocarbonyl complex did not react with PzCl, AlCl, MeOCH\textsubscript{2}Cl, PrBr, CyBr, t-BuBr, CH\textsubscript{2}Br\textsubscript{2} or i-PrI.

Reaction of C\textsubscript{p}Fe(CO)\textsubscript{3}CS with ICH\textsubscript{2}COOH

The thiocarbonyl (0.20 g, 0.54 mmol) was stirred with ICH\textsubscript{2}COOH (0.28 g, 1.5 mmol) in 10 ml of CH\textsubscript{2}Cl\textsubscript{2} for 12 hr, giving a red precipitate. Addition of 40 ml of Et\textsubscript{2}O produced a somewhat gummy red product, which was washed 10 times with...
15 ml of Et₂O by decantation and dried in vacuo. The residue was dissolved in 20 ml of acetone and the solution was eluted through a PF₆⁻ ion exchange column. The product was obtained as a red solid (with some difficulty) by slow evaporation of an acetone/hexane solution.

IR(CH₂Cl₂): 2044 s, 2016 w, 1859 m, 1743 w, 1013 w.

If the reaction was carried out with an excess of the thiocarbonyl complex, the product had a very similar IR spectrum, but was insoluble in CH₂Cl₂. The product was soluble in CH₂Cl₂ containing ICH₂COOH or CH₃COOH.

IR(CH₃CN): 2040 s, 2008 w, 1857 m, 1740 w.

Addition of Et₂N to a CH₃CN solution of this compound caused a color shift from yellow-red to red. This change was accompanied by the disappearance of the above IR bands and the appearance of new bands at 1989 s, 1950 m, 1776 s and 1690 w. Acidification with CF₃SO₂H did not reverse this process.

**Acetylation of Cp₂Fe₂(CO)₂CS**

A solution of Ag₂PF₆ (0.17 g, 0.66 mmol) in 15 ml of CH₂Cl₂ was cooled to -40°. Acetyl bromide (0.10 ml, 1.4 mmol) in 10 ml of 10:1 CH₂Cl₂Et₂O was added via syringe, and the mixture was stirred for 30 min. Addition of Cp₂Fe₂(CO)₂CS (0.26 g, 0.70 mmol) in 10 ml of CH₂Cl₂ caused an immediate color change to deep red. After 30 min, the mixture was warmed to room temperature and filtered. Addition of 100 ml
of hexane gave a red precipitate. The mixture was stored at -20° overnight and then filtered to give a red powder.

IR(CH₂Cl₂): 2106 m, 2072 m, 2046 s, 2005 m, 1856 m, 1771 w, 997 w.

Efforts to crystallize the product from CH₂Cl₂/hexane by slow evaporation failed. In fact, after several such treatments a different compound was obtained. The IR spectrum showed no band assignable to an acyl CO stretch, and new CO bands at 2040 s, 2010 w-m and 1855 cm⁻¹ suggested that [Cp₂Fe₂(CO)₃CS-Me]PF₆ had been formed.

Preparation of [Cp₂Fe₂(CO)₂(PEt₃)CS-R]PF₆ (R = Me, Et, Bz)

Triethyl phosphine (0.11 ml, 0.088 g, 0.75 mmol) was added to a stirred solution of [Cp₂Fe₂(CO)₃CS-Me]FSO₃ (0.24 g, 0.50 mmol) in 15 ml of CH₂CN. Evolution of CO commenced immediately, and a yellow-green solution formed. After 30 min the solvent was removed in vacuo at 50°; the residue was extracted with 20 ml of acetone, and the solution was eluted through a PF₆⁻ exchange column. The eluate was evaporated under reduced pressure; the residue was dissolved in 30 ml of CH₂Cl₂, and 20 ml of hexane was added. Slow evaporation gave brown crystals of [Cp₂Fe₂(CO)₂(PEt₃)CS-Me]PF₆ (95%). The analytical sample was crystallized from 1:1 acetone/Et₂O at -20°.

The same compound was obtained by reaction of MeOSO₂F (0.10 ml, 0.14 g, 1.2 mmol) with Cp₂Fe₂(CO)₂(CS)PET₃ (0.23 g,
0.50 mmol) in 20 ml of CH₂Cl₂ for 20 min, followed by ion exchange. The yield was 82%. IR(CH₂Cl₂): 1985 vs, 1818 s, 1006 m. ¹H NMR(d₆-acetone): 80.80-1.80 (multiplet, PEt₃), 3.60 (He), 5.23 (doublet, Cp), 5.45 (Cp). ¹³C NMR(d₆-acetone): 85.70 (PEt₃), 17.1 (doublet, PEt₃), 88.3 (doublet, Cp), 213.4 (terminal CO), 256.4 (doublet, bridge CO), 407.9 (doublet, CS). Molar conductivity: A = 84.6 ohm⁻¹ cm² mol⁻¹. M.P.: 210-214° dec. Anal. Calc. for C₂₀H₂₈Fe₂O₄S²P₂: C 38.74, H 4.55, S 5.17. Found: C 38.80, H 4.55, S 5.03.

To prepare the ethyl analog, a solution of [Cp₂Fe₂(CO)₂CS₂t]PF₆ (0.27 g, 0.50 mmol) was stirred with PEt₃ (0.10 ml, 0.88 g, 0.75 mmol) in 15 ml of CH₂-CN for 1 hr, after which the solvent was removed under reduced pressure at 50°. Slow evaporation of a CH₂Cl₂/hexane solution of the product gave brown needles of [Cp₂Fe₂(CO)₂(PEt₃)CS₂Et]PF₆ (88%). A sample for analysis was crystallized from 1:1 acetone/Et₂O at -20°.

IR(CH₂Cl₂): 1984 vs, 1818 s, 1006 m. NMR(d₆-acetone): 80.80-1.80 (multiplet, PEt₃ and CH₃), 4.23 (broad multiplet, CH₂), 5.23 (doublet, Cp), 5.45 (Cp). M.P.: dec. 225-230°. Anal. Calc. for C₂₁H₃₀F₆Fe₂O₂P₂S: C 39.77, H 4.77. Found: C 40.00, H 4.81.

Addition of PEt₃ to [Cp₂Fe₂(CO)₂CS₂Et]PF₆ in CH₂-CN resulted in dissociation of the benzyl group. To obtain the
S-benzyl compound, \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})\text{PET}_3 \) (0.20 g, 0.54 mmol) was stirred with \( \text{Et}2\text{Br} \) (3 ml) for 3 hr. The product was precipitated with 40 ml of \( \text{Et}_2\text{O} \), filtered off and washed repeatedly with \( \text{Et}_2\text{O} \). Ion exchange in acetone and slow evaporation of a \( \text{CH}_2\text{Cl}_2/\text{hexane} \) solution gave an 89% yield of black \( \text{[Cp}_2\text{Fe}_2(\text{CO})_2(\text{PET}_3)\text{CS-Et}]PF_6 \).

**IR(\text{CH}_2\text{Cl}_2):** 1979 vs, 1809 s, 1031 m, 998 m. **NMR(\text{CD}_3\text{CN}):**

\[ \delta 0.60-1.60 \text{ (multiplet, PET}_3 \), 5.06 \text{ (doublet, Cp), 5.22 (Cp), 7.46 (multiplet, Ph).} \]

**Preparation of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{PMe}_2\text{Ph})\text{CS-Me}]PF_6 \)**

Dimethylphenyl phosphine (0.10 ml, 0.097 g, 0.70 mmol) was added to a solution of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS-Me}]\text{FSO}_3 \) (0.24 g, 0.30 mmol) in 15 ml of \( \text{CH}_2\text{CN} \), and the mixture was stirred for 30 min, giving a yellow-green solution. The solvent was evaporated under reduced pressure at 50°, and the residue was dried at 50° in high vacuum for 1 hr. Work-up as for the PET\(_3\) analog above gave brown needles of the product (95%). A sample for analysis was crystallized from 1:1 acetone/\( \text{Et}_2\text{O} \) at -20°.

**IR(\text{CH}_2\text{Cl}_2):** 1991 vs, 1816 s, 1008 m. **NMR(\text{d}_6\text{-acetone):**

\[ \delta 1.43 \text{ (doublet, Me), 1.68 (doublet, Me), 3.58 (Me), 5.13 (doublet, Cp), 5.46 (Cp), 7.40-7.70 (multiplet, Ph).} \]

**MP:** 220-223°. **Anal. Calc. for C\(_{22}\)H\(_{24}\)F\(_6\)Fe\(_2\)O\(_2\)P\(_2\)S:** C 41.28, H 3.78. **Found:** C 41.59, H 3.94.
Preparation of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{PMePh}_2)\text{CS-i-}e]\text{PF}_6\)

A solution of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS-i-}e]\text{FSO}_3\) (0.24 g, 0.50 mmol) and \(\text{PMePh}_2\) (0.25 ml, 0.24 g, 1.2 mmol) in 15 ml of \(\text{CH}_3\text{CN}\) was refluxed for 4 hr. Work-up as for the \(\text{PMe}_2\text{Ph}\) compound gave a 63\% yield of the greenish-brown product.

IR(\(\text{CH}_2\text{Cl}_2\)): 2003 vs, 1971 w(sh), 1811 s, 1008 m.

\(\text{NMR}(d_6\text{-acetone})\): 62.14 (doublet, \(\text{He}\)), 3.53 (\(\text{Me}\)), 5.13 (doublet, \(\text{Cp}\)), 5.38 (\(\text{Cp}\)), 7.10-7.50 (multiplet, \(\text{Ph}\)).

Preparation of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{P}('\text{O}':\text{e})_3)\text{CS-i-e}]\text{PF}_6\)

A solution of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS-i-}e]\text{FSO}_3\) (0.24 g, 0.50 mmol) and \(\text{P}('\text{O}':\text{e})_3\) (0.12 ml, 0.15 g, 1.0 mmol) in 15 ml of \(\text{CH}_3\text{CN}\) was refluxed for 45 min. Work-up as for the \(\text{PET}_{\beta}\) derivative gave a 56\% yield of the brown \(\text{P}('\text{O}':\text{e})_3\) complex.

IR(\(\text{CH}_2\text{Cl}_2\)): 2004 vs, 1812 s. \(\text{NMR}(d_6\text{-acetone})\): 63.58 (\(\text{He}\)), 3.77 (\(\text{Me}\)), 5.27 (\(\text{Cp}\)), 5.59 (\(\text{Cp}\)).

Preparation of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{MeNC})\text{CS-R}]\text{PF}_6\) (\(\text{R} = \text{He, Et}\))

A solution of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS-Me}]\text{PF}_6\) (0.27 g, 0.51 mmol) and \(\text{MeNC}(0.10 \text{ ml}, 0.071 \text{ g}, 1.8 \text{ mmol})\) in 15 ml of \(\text{CH}_3\text{CN}\) was refluxed for 35 min. The red-brown solution was evaporated under reduced pressure, and the product was crystallized by slow evaporation of a \(\text{CH}_2\text{Cl}_2/\text{hexane}\) solution to give red crystals of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{MeNC})\text{CS-Me}]\text{PF}_6\) (93\%). An analytical sample was obtained from 1:1 acetone/Et\(_2\text{O}\) at -20\°. 
IR(CH\textsubscript{2}Cl\textsubscript{2}): 2196 s, 2004 vs, 1827 s, 1017 m. 
NMR(d\textsubscript{6}-acetone): 63.22 (iHe), 3.67 (H\textsubscript{e}), 5.33 (Cp), 5.42 (Cp).
Anal. Calc. for C\textsubscript{16}H\textsubscript{16}Fe\textsubscript{2}NO\textsubscript{2}PS: C 35.39, H 2.97, N 2.58. 
Found: C 35.59, H 3.06, N 2.63.

The ethyl analog, [Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{2}(MeNC)CS-Et]PF\textsubscript{6}, was obtained as red needles in identical fashion (92%).

IR(CH\textsubscript{2}Cl\textsubscript{2}): 2195 s, 2005 vs, 1833 s, 1016 m. 
NMR(d\textsubscript{6}-acetone): 61.63 (triplet, CH\textsubscript{2}), 3.22 (iHe), 4.18 (broad quartet, CH\textsubscript{2}), 5.31 (Cp), 5.40 (Cp). MP: 206-208° dec. Anal. C 36.65, H 3.26, N 2.51. Found: C 36.80, H 3.31, N 2.52.

The identical compounds were obtained by reaction of Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{2}(CS)(MeNC) with the appropriate alkylating agent in CH\textsubscript{2}Cl\textsubscript{2}.

**Preparation of [Cp\textsubscript{2}Fe\textsubscript{2}(CO)(PhNC)\textsubscript{2}CS-Me]PF\textsubscript{6}**

A solution of [Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{3}CS-Me]PF\textsubscript{6} (0.27 g, 0.51 mmol) and PhNC (0.13 ml, 0.13 g, 1.3 mmol) in 15 ml of CH\textsubscript{3}CH for 1 hr, giving a red-brown solution. The solvent was removed under reduced pressure, and the residue was dried in vacuo at 50° for 2 hr. The somewhat oily product was then washed several times with Et\textsubscript{2}O by decantation. Extraction with 30 ml of CH\textsubscript{2}Cl\textsubscript{2} and filtration gave a red solution. A red solid was obtained by evaporation of the solvent and drying in high vacuum overnight, but the product could not be crystallized. Yield was 85%.
IR(CH\textsubscript{2}Cl\textsubscript{2}): 2133 vs, 2045 w(sh), 2003 s, 1831 s, 1020 m.

NMR(d\textsubscript{6}-acetone): 63.70 (Me), 5.46 (Cy), 7.10-7.70 (multiplet, Ph).

**Preparation of Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{2}(CS-Me)X (X = Cl, Br, I)**

A solution of [Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{3}CS-Me]FSO\textsubscript{3} (0.24 g, 0.50 mmol) and [PPPh\textsubscript{3}]Cl (0.86 g, 1.5 mmol) in 15 ml of CH\textsubscript{3}CN was refluxed for 2 hr, giving a brown solution. The solvent was evaporated under reduced pressure; the residue was then transferred to a frit filter, washed 10 times with warm (40\degree) water to remove excess [PPPh\textsubscript{3}]Cl, and dried overnight in vacuo. Slow evaporation of CH\textsubscript{2}Cl\textsubscript{2}/hexane solution gave Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{2}(CS-Me)Cl as a dark brown solid (50%).

IR(CH\textsubscript{2}Cl\textsubscript{2}): 2000 vs, 1815 s, 1012 m.

To obtain the bromo analog, the S-methyl thiocarbonyl (0.24 g, 0.50 mmol) was refluxed with Et\textsubscript{4}NEt (0.32 g, 1.5 mmol) in 15 ml of CH\textsubscript{3}CN for 4 hr. After evaporation of the solvent, the residue was washed 5 times with water, dried in vacuo, and dissolved in 30 ml of CH\textsubscript{2}Cl\textsubscript{2}. Filtration, addition of hexane and slow evaporation gave dark brown Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{2}(CS-Me)Br (69%).

IR(CH\textsubscript{2}Cl\textsubscript{2}): 1996 vs, 1812 s, 1011 m.

The iodo analog could be obtained similarly from NaI and [Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{3}CS-Me]FSO\textsubscript{3}. However, a somewhat different procedure was found to be superior. A mixture of Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{3}CS (0.40 g, 1.1 mmol), MeI (0.12 ml, 0.28 g,
2.0 mmol) and NaI (0.60 g, 4.0 mmol) in 20 ml of CH₂CN was refluxed for 6 hr. The solvent was evaporated under reduced pressure, the residue was extracted with 40 ml of CH₂Cl₂, and the mixture was filtered. Addition of 30 ml of hexane and slow evaporation gave dark brown crystals of Cp₂Fe₂(CO)₂(CS-Me)I (91%). A sample for analysis was obtained from 1:1 acetone/hexane at -20°.

IR(CH₂Cl₂): 1992 vs, 1807 s, 1011 m. MP: dec. >230°.

Anal. Calc. for C₁₄H₁₃Fe₂I₀₂S: C 34.75, H 2.71, S 6.63.
Found: C 34.43, H 2.84, S 3.90.

Substitution of EtI for MeI in the above reaction gave dark brown Cp₂Fe₂(CO)₂(CS-Et)I (88%). This reaction required 18 hr.

IR(CH₂Cl₂): 1991 vs, 1807 s, 1009 m. ¹H NMR(d₆-acetone): 61.67 (triplet, CH₂), 4.30 (broad quartet, CH₂), 4.82 (Cp), 4.87 (Cp).

**Reaction of [Cp₂Fe₂(CO)₂CS-MeFSO₂] with other ligands**

Refluxing the 2-methyl thiocarbonyl with pyridine in CH₂CN for 10 hr gave the brown complex [Cp₂Fe₂(CO)₂(py)CS-MeFSO₂]. The product could not be crystallized, and decomposed slowly even when stored at -20°.

IR(CH₂Cl₂): 1998 vs, 1806 s, 1010 m.

The analogous reactions with PPh₃, diphos and P(OPh)₃ gave no evidence of substitution. However, these derivatives could be obtained by another method (see below).
The S-methyl thiocarbonyl reacted rapidly with KSeCN in refluxing CH₃CN to give the substitution product; this complex was not isolated. Under the same conditions, KCN and KSCN did not react.

**Preparation of [Cp₂Fe₂(CO)₂(L)CS-Me]PF₆ \( (L = \text{PPh}_3, \text{P(OPh)}_3) \)**

A solution of Cp₂Fe₂(CO)₂(CS-Me)I (0.12 g, 0.25 mmol) in 15 ml of acetone was cooled to 0°, and AgBF₄ (0.049 g, 0.25 mmol) in 5 ml of acetone was added. After 20 min the brown solution was filtered to remove AgI, and PPh₃ (0.10 g, 0.38 mmol) was added. The solution was stirred for 10 min, and the solvent was removed under reduced pressure. The residue was washed 5 times with Et₂O by decantation, dissolved in 30 ml of acetone, and eluted through a PF₆⁻ exchange column. Attempts to crystallize the product from the green eluate failed. The compound could be obtained as a solid by evaporating the solvent and drying the gummy residue in high vacuum for 24 hr, but the product was still somewhat impure with excess ligand. Yield was ~80%.

IR(CH₂Cl₂): 1998 vs, 1801 s, 1007 m.

The same reaction with P(OPh)₃ gave the phosphite complex. This product could be obtained as brown crystals (~70% yield), but was also somewhat impure.

IR(CH₂Cl₂): 2005 vs, 1825 s, 1013 m.
Reaction of $[\text{Cp}_2\text{Fe}_2(\text{CO})_5\text{CS-Me}]\text{PF}_6$ with nucleophiles

Addition of NaOMe to the S-methyl thiocarbonyl complex in MeOH gave a rapid reaction, forming a red-brown solution. The product was identified as $[\text{CpFe}(\text{CO})_2]^2$. In aqueous solution, KOH gave the same product; acidification of this mixture liberated MeSH (detected by its odor).

The S-methyl thiocarbonyl reacted rapidly with MeNH$_2$ and PrNH$_2$ in MeOH or CH$_3$CN to give a brown solution; no gas evolution occurred in this reaction. Two brown products were obtained: one soluble in CS$_2$, the other insoluble in CS$_2$ but soluble in CH$_2$Cl$_2$. Their IR spectra were very similar, and in both cases the broad, weak CS band characteristic of the S-alkyl compounds ($\sim$1020 cm$^{-1}$) was absent. Neither product was stable enough to be purified and characterized.

IR of CS$_2$-soluble product (CS$_2$): 1945 vs, 1787 s, 1646 w.

IR of CH$_2$Cl$_2$-soluble product (CH$_2$Cl$_2$): 1942 vs, 1768 s, 1641 w.

Addition of [PPN]N$_3$ to $[\text{Cp}_2\text{Fe}_2(\text{CO})_5\text{CS-Me}]\text{PF}_6$ in CH$_2$Cl$_2$ instantly gave a deep green solution and vigorous gas evolution. An IR spectrum showed that several products had been formed. On stirring for 24 hr, the solution turned brown and a precipitate formed. The IR spectrum at this time showed one predominant product, with bands at $\sim$1900 vs and 1770 m-s. However, this compound could not be isolated.
Alkylation of Cp₂Fe₂(CO)(CS)(MeNC)₂

To a solution of Cp₂Fe₂(CO)(CS)(MeNC)₂ (0.10 g, 0.25 mmol) in 50 ml of CH₂Cl₂, MeOSO₂F (0.10 ml, 0.14 g, 0.13 mmol) was added, and the reaction mixture was stirred for 9 hr. The solution quickly turned brown, and a greenish precipitate gradually formed. The product was filtered off, washed 3 times with 20 ml of CH₂Cl₂, dissolved in 20 ml of acetone, and eluted through a PF₆⁻ ion exchange column. Addition of heptane (Skelly 'C') and slow evaporation gave a brown solid, which was filtered off and dried in vacuo. Extraction 4 times with 10 ml of water gave a brown solution, which was then cooled to 0° for 2 days. The small brown needles that formed were filtered off, washed once with 5 ml of cold (10°) water, and dried in vacuo overnight. Yield of the product, [Cp₂Fe₂(CO)(MeNC)(Me₂NC)CS-Me](PF₆)₂, was 56%.

IR(CH₂NO₂): 2222 vs, 2038 s, (acetone) 1023 a.

HMP(d₆-acetone): 63.28 (Me), 3.77 (Me), 4.28 (Me), 4.34 (Me), 5.83 (Cp), 5.92 (Cp). Molar conductivity: \( \Lambda = 177 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \). MP: dec. \( \sim 250^° \). Anal. Calc. for C₁₆H₂₂F₁₂Fe₂N₂OP₂S: C 30.19, H 3.10, N 3.91. Found: C 30.21, H 3.13, N 4.79.

Reaction of the bis isocyanide complex (0.10 g, 0.25 mmol) with MeI (0.10 ml, 0.23 g, 1.6 mmol) in 15 ml of CH₂Cl₂ gave a different product. After 30 min the initial purple solution had turned brown. The product was precipitated with 50 ml of Et₂O and filtered off. Ion exchange in acetone followed
by crystallization from 1:1 acetone/Et₂O at -78° gave small brown crystals of the product, [Cp₂Fe₂(CO)(MeNC)₂CS-Me]PF₆ (65%).

IR(CH₂Cl₂): 2190 vs, 1996 w, 1815 s, 1014 m.

Miscellaneous reactions of Cp₂Fe₂(CO)₃CS

Oxidation of Cp₂Fe₂(CO)₃CS with O₂ in acetone in the presence of aqueous HEF₄, followed by addition of KCl, gave CpFe(CO)₂Cl and [Cp₂Fe₂(CO)₃CS·CpFe(CO)₂]BF₄.

When AgPF₆ was added to an acetone solution of the thiocarbonyl complex, Ag⁺ precipitated; the carbonyl product was a red oil that was not identified.

The thiocarbonyl complex gave no evidence of reaction after refluxing with Me₂S₂ in benzene for 3 days.

Evidence was seen for protonation of Cp₂Fe₂(CO)₃CS by CF₃SO₂H in CH₂Cl₂, but the product could not be isolated. The thiocarbonyl did not react with HCl gas in Et₂O or CH₂Cl₂.

No reaction occurred upon stirring solutions of Cp₂Fe₂(CO)₃CS and CH₂N₂, thirane, aziridine or SO₂ for extended periods.
Kinetic Experiments

The reaction of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS} \) with \( \text{PMe}_2\text{Ph} \) was studied in \( \text{BuCN} \) and decalin at several different phosphine concentrations. Reactions were carried out under \( \text{N}_2 \) in 25 ml volumetric flasks capped with rubber septa. In each run, the flask containing the thiocarbonyl solution was placed in a constant-temperature bath for 30 min. The phosphine (at least a 10-fold excess) was then added from a microliter syringe, and the solution was thoroughly agitated. After another 15-20 min, samples were withdrawn at constant intervals for analysis by IR; the progress of the reaction was monitored by the decrease in the intensity of the bridge \( \nu_{\text{CC}} \) band of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS} \). At least two runs were performed at each phosphine concentration, and the reactions were followed to at least 80% completion.

In \( \text{BuCN} \) at 65° at all phosphine concentrations, there was an induction period of about 30 min, after which the substitution occurred very rapidly. Consequently, no data could obtained from these runs. At 80° or below, no reaction occurred.

For reactions in decalin at 115°, graphs of \( \ln(A-A_\infty) \) vs. time for runs at lower \( \text{PMe}_2\text{Ph} \) concentrations were linear with slopes equal to \( k_{\text{obs}} \). At higher phosphine concentrations, the graphs showed a definite curvature, with the slope increasing as the reaction proceeded. Straight lines
could be obtained from the upper portions of the curves, yielding values of $k_{\text{obs}}$ for these reactions. A plot of $k_{\text{obs}}$ vs. $[\text{PMe}_2\text{Ph}]$ was linear, with slope $k_2$ and intercept $k_1$. Appreciable decomposition occurred during all runs. In the absence of phosphine, the rate constant for the decomposition of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$ was found to be about half as large as $k_{\text{obs}}$ at the lower PMe$_2$Ph concentrations.
RESULTS AND DISCUSSION

Attempts to Prepare Rhenium Thiocarbonyls

As one of the more nucleophilic carbonyl anions, \(^{45} \text{Re(CO)}_5^-\) seemed a possible starting material for preparation of thiocarbonyl complexes by reaction with appropriate organosulfur reagents. A previous attempt\(^{97}\) to obtain \(\text{Re(CO)}_5\text{CS}^+\) by the reaction of \(\text{Re(CO)}_5^-\) with \(\text{CS}_2/\text{MeI}\) followed by acid cleavage gave inconsistent results. It was suggested that use of \(\text{CF}_3\text{SO}_2\text{H}\) rather than \(\text{HCl}\) as the acid might improve this synthesis.

In the present work this was found not to be the case. Reaction of \(\text{Re(CO)}_5^-\) with \(\text{CS}_2/\text{MeI}\) did seem to give some of the desired compound, \(\text{Re(CO)}_5\text{CS}_2\text{Me}\). However, addition of \(\text{CF}_3\text{SO}_2\text{H}\) to this product gave little evidence for formation of the thiocarbonyl cation. Efforts to isolate the dithioester intermediate failed; during these attempts it was discovered that the reaction also produced a considerable amount of \(\text{Re(CO)}_5\text{I}\). This result is interesting in view of the recent observation that use of excess \(\text{MeI}\) in the preparation of \(\text{CpRu(CO)}_2\text{CS}_2\text{Me}\) leads to formation of \(\text{CpRu(CO)}_2\text{I}\). The role of the alkylating agent in producing metal carbonyl halides in these reactions is unclear, but it is evident that a large excess of \(\text{MeI}\) should be avoided in any future attempts to prepare \(\text{Re(CO)}_5\text{CS}^+\) by this method.

Better evidence for the thiocarbonyl cation was obtained
in the reaction of Re(CO)$_5^-$ with Cl-C(S)-OMe. This reaction gave an inseparable mixture of several compounds, presumably including the desired product, Re(CO)$_5$C(S)OMe. Addition of CF$_3$SO$_3$H to the crude thioester in Et$_2$O gave a white precipitate. This product undoubtedly contained some Re(CO)$_5$CS$^+$, as shown by its IR spectrum and high reactivity toward water and N$_3^-$. In fact, the product was so reactive that it decomposed rather quickly in solution, even in the absence of air or moisture. These observations are reminiscent of the problems previously encountered in the preparation of trans-PtCl(PPh$_3$)$_2$CS$^+$, and suggest that the isolation of pure Re(CO)$_5$CS$^+$ may be very difficult. It may prove more feasible to attempt reduction of the impure thiocarbonyl cation to Re$_2$(CO)$_8$(CS)$_2$, which should be more stable and have an equally interesting chemistry.

The reaction of Re(CO)$_5^-$ with other thiocarbonyl reagents, such as (PhO)$_2$CS and (C$_3$H$_7$N$_2$)$_2$CS, gave mixtures of many products, and were not investigated further.

Previous work has shown that the majority of metal carbonyl anions are insufficiently nucleophilic to form stable dithioester complexes in the CS$_2$/MeI reaction, presumably because the intermediate M-CS$_2^-$ anions are too labile. Since phosphine-substituted anions should be better nucleophiles, several reactions with these species were attempted. Reaction of Mn(CO)$_4$L$^-$ or Mn(CO)$_3$L$_2^-$
(L = PPh₃, PMe₂Ph) with Cl-C(S)-OCH₃ in THF gave Mn(CO)₄LCl and Mn(CO)₂L₂Cl rather than the thioester derivatives. The anion Re(CO)₃(PPh₃)₂⁻, which apparently had not been prepared before, can be obtained from K(Hg) and trans-Re(CO)₃(PPh₃)₂Br in THF (Na(Hg) reacts, but does not give the anion). The reaction of this species with Cl-C(S)-OMe gave a mixture of products, none of which was identified. Reaction with CS₂/MeI gave an orange compound that did not contain a methyl group. The IR spectrum clearly indicated a trans-Re(CO)₂L₂X derivative (not trans-Re(CO)₃(PPh₃)₂I, which is colorless); a possible formulation of this product is shown below. This trithiocarbonate-bridged structure has been proposed as the intermediate in the reaction of M(CO)₅⁻ (M = Mn, Re) with CS₂ to give the complexes M(CO)₄(S₂C=S)M(CO)₅. Presumably, in the present case the electron-donating phosphine ligands could make loss of CO to form a chelating trithiocarbonate group less favorable.

From the work done thus far on reactions of the less
nucleophilic metal carbonyl anions with thiocarbonyl reagents, certain trends are apparent. Such reactions tend to give several products; evidently the intermediates initially formed are of low stability, permitting undesirable secondary reactions to occur. In many cases a metal carbonyl halide rather than the intended thioester or dithioester is formed. Finally, reactions with phosphine-substituted carbonyl anions are also unsuccessful, indicating that these anions still are not sufficiently nucleophilic. It appears that the future utility of less nucleophilic carbonyl anions in the synthesis of metal thiocarbonyls will require the development of better methods for increasing the nucleophilicity perhaps, (for example, by the use of crown ethers\textsuperscript{101}), or the discovery of more effective thiocarbonyl reagents.

Preparation and Properties of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \)

**Synthesis and isolation**

Certain results discussed above, as well as some previous work,\textsuperscript{50,51} suggested that Cl-C(S)-OMe was a potentially useful reagent for introduction of CS. Unfortunately, the synthesis of this compound is time-consuming and gives rather low yields. Therefore, the reaction of \( \text{CpFe(CO)}_2^- \) with the more easily prepared Cl-C(S)-OPh was investigated to determine whether this chlorothioformate could be used in place of the methyl analog. Contrary to an earlier report,\textsuperscript{97} little evidence was found for the desired thioester,
CpFe(CO)$_2$C(S)OPh. (However, this compound can be obtained by a different method; see below.) Instead, the reaction gave [CpFe(CO)$_2$]$_2$, CpFe(CO)$_2$Cl and a small amount of an unexpected product — the thiocarbonyl-bridged complex Cp$_2$Fe$_2$(CO)$_3$CS.

Since the maximum yield of the thiocarbonyl compound obtainable from Cl-C(S)-OPh was only about 7%, a more efficient synthesis was sought. The most effective thiocarbonyl reagent proved to be diphenyl thionocarbonate, (PhO)$_2$CS; reaction of CpFe(CO)$_2^-$ with (PhO)$_2$CS in a 2:1 molar ratio in THF affords Cp$_2$Fe$_2$(CO)$_3$CS in 40-45% yield. Certain other aryl thionocarbonates, such as (p-ClC$_6$H$_4$O)$_2$CS and (p-MeCC$_6$H$_4$O)$_2$CS, give comparable yields, but offer no advantage over the unsubstituted compound. In contrast, reactions of (p-NO$_2$C$_6$H$_4$O)$_2$CS, (PhS)$_2$CS, (C$_3$H$_7$N$_2$)$_2$CS or Cl$_2$CS with CpFe(CO)$_2^-$ give little or no thiocarbonyl complex.

Formation of Cp$_2$Fe$_2$(CO)$_3$CS from (PhO)$_2$CS and CpFe(CO)$_2^-$ probably occurs by stepwise replacement of phenoxide by the iron anion, as shown in reaction 22. The second CS-bridged

\[
(22) \quad (\text{PhO})_2\text{CS} \xrightarrow{\text{CpFe(CO)$_2^-$}} \text{CpFe(CO)$_2^-$C-OPh} \xrightarrow{\text{S}} \text{CpFe(CO)$_2^-$}
\]

\[
\text{[CpFe(CO)$_2$]$_2$CS} \xrightarrow{\text{-CS}} \text{[CpFe(CO)$_2$]$_2$} \xrightarrow{\text{-CO}} \text{Cp$_2$Fe$_2$(CO)$_3$CS}
\]
intermediate shown could then eliminate either CO or CS to give the two major reaction products, which are always formed in approximately equimolar amounts. Alternatively, the \([\text{CpFe(CO)}_2\]_2 might be formed by attack of the second anion at the Fe atom of the first intermediate, causing elimination of CS and PhO\(^-\). The second of these proposed intermediates was never detected, but the thioester intermediate can be prepared by another route, and does react with \(\text{CpFe(CO)}_2^-\) to give \([\text{CpFe(CO)}_2\]_2 and \(\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS}\) (see below). Reaction 22 also produces a quantity of brown, insoluble material, and the total yield of \(\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS}\) and \([\text{CpFe(CO)}_2\]_2 always accounts for only about 85-90% of the iron originally added as \(\text{CpFe(CO)}_2^-\). Apparently there is a secondary reaction leading to decomposition, but the nature of this process is unknown.

It is not clear why other thiocarbonyl reagents, such as \(\text{Cl}_2\text{CS}, (\text{C}_3\text{H}_7\text{N})_2\text{CS}\) and \((\text{p-NO}_2\text{C}_6\text{H}_4\text{O})_2\text{CS}\), should not react similarly to give the thiocarbonyl complex. Perhaps the initial intermediates obtained with these compounds are so unstable that decomposition to other products occurs before reaction to form \(\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS}\) can take place.

The use of organometallic thiocarbonyl reagents in the preparation of \(\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS}\) was also investigated. As mentioned above, the compound \(\text{CpFe(CO)}_2\text{C(S)OPh}\) cannot be obtained from \(\text{Cl-C(S)-OPh}\) and \(\text{CpFe(CO)}_2^-\); however, the compound can be prepared by the reaction of \([\text{CpFe(CO)}_2\text{CS}]\text{CF}_3\text{SO}_3\)
with NaOPh in THF (reaction 23). It is too unstable to be isolated and purified (see below), but can be generated in situ and reacted with CpFe(CO)_{2}^{-} to give Cp_{2}Fe_{2}(CO)_{3}CS in yields comparable to those obtained with (PhO)_{2}CS.

\[
(23) \quad \text{CpFe(CO)_{2}CS}^{+} + \text{PhO}^{-} \xrightarrow{\text{THF}} \text{CpFe(CO)_{2}C-OPh} \xrightarrow{\text{S}} \text{CpFe(CO)_{2}^{-}}
\]

\[
\text{Cp_{2}Fe_{2}(CO)_{3}CS} + [\text{CpFe(CO)_{2}]_{2}}
\]

Complete reaction of the thioester requires more than one equivalent of CpFe(CO)_{2}^{-}, suggesting that a certain amount of the [CpFe(CO)_{2}]_{2} produced in this reaction, and presumably also in the (PhO)_{2}CS reaction, is formed in a process (perhaps the decomposition reaction mentioned above) unrelated to the formation of Cp_{2}Fe_{2}(CO)_{3}CS. Prepared in this way, the thiocarbonyl complex invariably contains a small amount of [CpFe(CO)(CS)]_{2}, evidently formed by prior reaction of the thiocarbonyl cation with unreacted NaH used in preparing the NaOPh solution. Undoubtedly this disadvantage could be eliminated by the use of a different base, such as MeLi, for deprotonation of the phenol.

The dithioester CpFe(CO)_{2}CS_{2}Me also reacts with CpFe(CO)_{2}^{-} to give Cp_{2}Fe_{2}(CO)_{3}CS. However, the yield obtained by this method (~25%) is somewhat lower, and the compound is always contaminated with a foul-smelling substance (presumably an organosulfur decomposition product) that is difficult to
remove. Nevertheless, this is the most convenient method for the preparation of small quantities (2-3 mmol) of the thiocarbonyl complex, since the dithioester can be easily and rapidly generated in situ for use in the reaction.

The monothiocarbonyl compound cannot be obtained in useful quantities directly from the thiocarbonyl cation. Addition of CpFe(CO)$_2^-$ to CpFe(CO)$_2$CS$^+$ in THF gives [CpFe(CO)$_2$]$_2$ almost exclusively, and reaction of equimolar amounts of CpFe(CO)$_2$CS$^+$ and CpFe(CO)$_2^+$ with NaH in THF gives mainly [CpFe(CO)$_2$]$_2$ and [CpFe(CO)(CS)]$_2^*$. The isolation of Cp$_2$Fe$_2$(CO)$_2$CS is essentially a problem of separating the thiocarbonyl complex from [CpFe(CO)$_2$]$_2^*$. The only practical and efficient method for effecting this separation was found to be column chromatography on Florisil. The eluting solvent must consist of CS$_2$ and a smaller proportion of a stronger eluant, for example 5:1 CS$_2$/CH$_2$Cl$_2$ or 49:1 CS$_2$/Et$_2$O. (The latter mixture is superior from the standpoint of time required for elution, but does not separate the thiocarbonyl complex from contaminants such as (PhO)$_2$CS, [CpFe(CO)$_2$]$_2$Hg and [CpFe(CO)(CS)]$_2^*$. Other solvent mixtures will not resolve the two compounds on a column of manageable length, and also cause significant decomposition of the thiocarbonyl compound on the column.
Properties

The thiocarbonyl complex \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) is an air-stable solid. It forms very dark red crystals that appear black to the unaided eye. The compound dissolves in all common organic solvents, its solubility being greatest in \( \text{CH}_2\text{Cl}_2 \) and acetone, and lowest in aliphatic hydrocarbons. Solutions in nonpolar solvents (e.g., hexane or benzene) are grayish brown, whereas in polar media (e.g., \( \text{CH}_2\text{Cl}_2 \) or \( \text{CH}_3\text{CN} \)) the color is grayish green; the significance of this color difference is discussed in the following section. Solutions of the compound may be handled in air for brief periods, but prolonged contact results in decomposition. In most respects the physical properties of \( \text{Cp}_2\text{Fe}(\text{CO})_3\text{CS} \) are intermediate between those of \( [\text{CpFe(CO)}_2]_2 \) and \( [\text{CpFe(CO)(CS)}]_2 \), as might be expected from its "intermediate" composition.

Spectra and Structure of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \)

Mass spectrum

As with other metal thiocarbonyls,\(^2\) the mass spectrum of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) shows a parent peak (m/e 370) and peaks corresponding to the stepwise loss of the CO ligands (m/e 342, 314 and 286). There is also a ferrocene peak (m/e 186), but no peak arising from dissociation of the CS group.
Visible spectra

The visible spectrum of the thiocarbonyl complex in cyclohexane solution shows absorption maxima at 503 nm (ε = 570) and 592 nm (ε = 500). In CH$_2$CN solution the bands occur at 535 nm (ε = 750) and 615 nm (ε = 530), confirming that the color of Cp$_2$Fe$_2$(CO)$_3$CS in solution is solvent-dependent. The spectra in both solvents also contain a very intense absorption at ~310 nm that is commonly found for metal carbonyls.

IR spectra, NMR spectra and fluxional behavior

Infrared spectra of Cp$_2$Fe$_2$(CO)$_3$CS in solution (Table 3) show three absorptions from the CO ligands and a single ν$_{CS}$ band. Two higher-frequency CO bands suggest the symmetric and antisymmetric stretching of two terminal CO ligands, while the remaining CO band is characteristic of a bridging carbonyl. The low position of the CS stretching frequency indicates that this ligand occupies a bridge position. The absence of any absorptions in the 1400-1200 cm$^{-1}$ region shows that there is no significant amount of any species with a terminal CS group.
Table 3. IR stretching frequencies (cm\(^{-1}\)) for Cp\(_2\)Fe\(_2\)(CO)\(_3\)CS in various solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\nu_{\text{CO}}^a)</th>
<th>(\nu_{\text{CS}}^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>2010 vs, 1975 m(sh), 1971 vs, 1814 s</td>
<td>—</td>
</tr>
<tr>
<td>hexane</td>
<td>2012 vs, 1972 vs, 1813 s</td>
<td>—</td>
</tr>
<tr>
<td>CS(_2)</td>
<td>2006 vs, 1969 s, 1809 m</td>
<td>1130 m</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>2009 vs, 1971 m, 1804 m</td>
<td>—</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>2004 vs, 1968 m, 1805 m</td>
<td>1124 m</td>
</tr>
<tr>
<td>CH(_3)CN</td>
<td>1999 vs, 1962 w, 1803 m</td>
<td>1120 m</td>
</tr>
</tbody>
</table>

\(^a\)Abbreviations: s = strong, m = medium, w = weak, sh = shoulder, v = very.

In the CO region the spectra display a marked dependence on solvent polarity; representative examples are shown in Figure 1. This variation is also observed in the IR spectra of [CpFe(CO)\(_2\)]\(_2\), and may be interpreted in the same way for the thiocarbonyl complex as was done for the carbonyl analog.\(^{103,104}\) The compound exists in solution as a mixture of interconverting cis and trans isomers, the cis form being favored in polar media. Thus, in cyclohexane
solution the band at 2010 vs and the barely perceptible shoulder at 1975 m may be assigned to $v_{\text{sym}}$ and $v_{\text{as}}$ of the terminal carbonyls of the cis form, while the band at 1971 vs can be assigned to $v_{\text{as}}$ of the trans isomer ($v_{\text{sym}}$ being inactive, or only weakly active, because of symmetry); apparently the $v_{\text{CO}}$ frequency of the bridging carbonyl is the same for both isomers. In other solvents the terminal $v_{\text{as}}$ frequencies also are coincident, as are the $v_{\text{CS}}$ bands. In very polar solvents, such as CH$_3$CN, only cis-Cp$_2$Fe$_2$(CO)$_2$CS appears to be present. The cis/trans ratio in a particular solvent is established immediately upon dissolving the compound and does not change with time.

Ambient-temperature $^1$H NMR spectra of Cp$_2$Fe$_2$(CO)$_2$CS in most solvents (Table 4 and Figure 2), show two sharp resonances, corresponding to the Cp groups of the two isomers. The lower-field peak can be assigned to the cis isomer, since its relative intensity increases with increasing solvent polarity. The two Cp resonances observed in C$_6$D$_6$ solution coalesce at about 50°. In very polar media, the spectrum
Figure 1. IR spectra of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$ in various solvents.

CH$_3$CN  CH$_2$Cl$_2$  Cyclohexane
consists of a single peak, indicating that the compound exists solely in the cis form.

Table 4. $^1H$ NMR chemical shifts (ppm) for $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$ in various solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta$ Cp</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_6\text{D}_6$</td>
<td>4.26, 4.33</td>
<td>2:1</td>
</tr>
<tr>
<td>$\text{CS}_2$</td>
<td>4.65, 4.73</td>
<td>4:7</td>
</tr>
<tr>
<td>$\text{CDCl}_3$</td>
<td>4.79, 4.85</td>
<td>2:5</td>
</tr>
<tr>
<td>$\text{d}_6$-acetone</td>
<td>5.01</td>
<td></td>
</tr>
</tbody>
</table>

The $^{13}$C spectra of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$ (Table 5) may be similarly interpreted. In less polar media, the spectra show two Cp resonances and two terminal CO resonances, indicating two isomers; the relative intensities for each pair are about the same as those observed for the two Cp signals in the $^1H$ NMR spectra. The bridging CO and CS ligands each give rise to only one signal, evidently because the chemical shifts of these groups are very nearly the same in both isomers. In the polar solvent acetone, only the cis isomer is present, and all of the ligands give single peaks. However, the most interesting feature of the $^{13}$C NMR spectra of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$ is the chemical shift of the CS carbon ($\delta \sim 380$ ppm), which is the largest shift.
Figure 2. $^1\text{H}$ NMR spectra of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$ in various solvents.
yet reported for a thiocarbonyl ligand. This is particularly striking in view of the fact that the bridging CS peak for \([\text{CpFe(CO)(CS)}]_2\) occurs at higher field by nearly 100 ppm (δ ~287). It is not evident why replacement of CS by CO in the bridge structure should cause such a dramatic downfield shift in the resonance of the remaining CS ligand.

Table 5. \(^{13}\)C NMR chemical shifts (ppm) for \(\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS}\) in various solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>δ Cp</th>
<th>δ CO(^a)</th>
<th>δ CO(^b)</th>
<th>δ CS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_6\text{D}_6)</td>
<td>90.9, 91.6</td>
<td>210.4, 211.2</td>
<td>267.1</td>
<td>—</td>
</tr>
<tr>
<td>(\text{CS}_2/\text{C}_6\text{D}_6)(^c)</td>
<td>90.5, 92.5</td>
<td>208.8, 209.7</td>
<td>265.2</td>
<td>—</td>
</tr>
<tr>
<td>(\text{CDCl}_3)</td>
<td>90.0, 92.1</td>
<td>208.5, 209.3</td>
<td>267.7</td>
<td>378.1</td>
</tr>
<tr>
<td>(\text{d}_6)-acetone</td>
<td>92.1</td>
<td>211.4</td>
<td>268.1</td>
<td>380.8</td>
</tr>
</tbody>
</table>

\(^a\)Terminal CO.

\(^b\)Bridge CO.

\(^c\)9:1 mixture.

The NMR spectra of the monothiocarbonyl complex are quite different from those of its close analogs, \([\text{CpFe(CO)}]_2\)\(^2\) and \([\text{CpFe(CO)(CS)}]_2\). The latter compound is found by IR and NMR to be essentially non-fluxional at ordinary temperatures. In contrast, the all-carbonyl complex undergoes very rapid isomerization; for example, the coalescence temperature for
the Cp signals in the $^1$H NMR is about $-50^\circ$. It is evident that introduction of even one bridging CS ligand decreases the rate of cis-trans isomerization remarkably. This is also found for the Ru analogs of the above compounds.

The isomerization of [CpFe(CO)$_2$]$_2$ has been studied in detail by IR, $^{103,104,106}$ $^1$H NMR $^{105}$ and $^{13}$C NMR $^{107}$ methods. A reasonable mechanism for this process, proposed by Adams and Cotton, $^{108}$ is shown in Figure 3. The essential features of the Adams-Cotton (AC) mechanism involve opening of the bridging groups to form a non-bridged molecule, rotation about the Fe-Fe bond, and re-formation of a bridged structure. This process results in cis-trans isomerization with concomitant exchange of bridge and terminal ligands. As can be seen from the more general scheme shown, the AC mechanism also satisfactorily accounts for the isomerization of Cp$_2$Fe$_2$(CO)$_3$CS. In the latter case, the restriction that the CS ligand remain in a bridge position requires that bridge-terminal CO exchange in either isomer must involve cis-trans interconversion, whereas this is not necessarily true for the trans isomer of [CpFe(CO)$_2$]$_2$.

It should be mentioned at this point that the trans isomer of Cp$_2$Fe$_2$(CO)$_3$CS is actually a pair of enantiomers. However, this fact is of no importance to the spectra or chemistry of the compound and its derivatives.

The preference of the CS ligand for a bridge position
Figure 3. Adams - Cotton isomerization mechanism for 
$[\text{CpFe(CO)}_2]_2$ ($X = 0$) and $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$ ($X = S$).
in \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) and related thiocarbonyl complexes\(^{32, 65, 73}\) is understandable in view of the relative bond strengths in CO and CS. Formation of a "ketonic" or "thioketonic" bridge requires some sacrifice of \( \pi \)-bonding in the \( \text{C} \equiv \text{X} \) bonds. Since this bond is much weaker in CS\(^{17, 23}\) the migration of a CS ligand from a terminal to a bridging position results in little loss in C-S \( \pi \)-bond stabilization. The stabilization gained by forming an additional Fe-CS bond more than compensates for any loss in C-S \( \pi \)-bonding. This also accounts for the slower isomerization observed in \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) and other CS-bridged complexes, since the more stable bridge structure would be expected to dissociate less readily to non-bridged forms required by this process.

A final note of interest concerns the possibility of isolating the two isomers of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \). This separation is easily accomplished for \([\text{CpFe(\text{CO})}_2]_2\)\(^{106}\) and also for \([\text{CpFe(\text{CO})(\text{CS})}]_2\),\(^{32}\) but thus far it has not proved possible for the monothiocarbonyl complex. The compound can be obtained in several different crystal forms, depending on the solvent and temperature used in crystallization. However, all of these products have the same solid-phase IR spectrum. It appears that \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) may exist in the solid state as only one isomer or mixture of isomers. An X-ray crystal structure, currently in progress, may resolve this question.
Reactions of \( \text{CpFe(CO)}_2 \text{C(S)OPh} \)

The synthesis of the thioester complex \( \text{CpFe(CO)}_2 \text{C(S)Ph} \), presumed to be an intermediate in the formation of \( \text{Cp}_2 \text{Fe}_2 \text{(CO)}_3 \text{CS} \), was discussed in the previous section. The compound, which is a dark brown oil, can be identified by IR (Table 6) but is not stable enough to be isolated.

Table 6. IR stretching frequencies (cm\(^{-1}\)) of various cyclopentadienyl iron carbonyl and thiocarbonyl compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>( \nu_{\text{CO}} )</th>
<th>( \nu_{\text{CS}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CpFe(CO)}_2 \text{C(S)OPh} )</td>
<td>hexane</td>
<td>2042 s, 1996 s</td>
<td>—</td>
</tr>
<tr>
<td>( [\text{CpFe(CO)}_2 \text{C(OMe)}_2] \text{PF}_6 )</td>
<td>( \text{CH}_2\text{Cl}_2 )</td>
<td>2068 s, 2020 s</td>
<td>—</td>
</tr>
<tr>
<td>( \text{CpFe(CO)}(\text{CS})\text{Br} )</td>
<td>( \text{CS}_2 )</td>
<td>2032 s</td>
<td>1310 vs</td>
</tr>
<tr>
<td>( \text{CpFe(CO)}(\text{CS})\text{I} )</td>
<td>( \text{CS}_2 )</td>
<td>2023 s</td>
<td>1304 vs</td>
</tr>
<tr>
<td>( \text{CpFe(CO)}(\text{CS})\text{SnPh}_3 )</td>
<td>( \text{CS}_2 )</td>
<td>1978 s</td>
<td>1288 vs</td>
</tr>
<tr>
<td>( \text{CpFe(CO)}(\text{CS})\text{GePh}_3 )</td>
<td>( \text{CS}_2 )</td>
<td>1982 s</td>
<td>1289 vs</td>
</tr>
<tr>
<td>( \text{CpFe(CO)}(\text{MeNC})\text{SnPh}_3 )</td>
<td>hexane</td>
<td>2117 m, 1945 s</td>
<td>—</td>
</tr>
<tr>
<td>( \text{CpFe(CO)}(\text{PrNC})\text{SnPh}_3 )</td>
<td>hexane</td>
<td>2115 m, 1946 s</td>
<td>—</td>
</tr>
<tr>
<td>( \text{CpFe(CO)}(\text{CyNC})\text{SnPh}_3 )</td>
<td>hexane</td>
<td>2115 m, 1947 s</td>
<td>—</td>
</tr>
<tr>
<td>( \text{CpFe(CO)}(\text{N}_2\text{C}_2\text{H}_6)\text{SnPh}_3 )</td>
<td>( \text{CS}_2 )</td>
<td>1893 s</td>
<td>—</td>
</tr>
</tbody>
</table>

\( ^a \)See Table 3, footnote a.

\( ^b \)\( \nu_{\text{CN}} \) absorption.
In addition to its reaction with CpFe(CO)$_2$ to give the monothiocarbonyl compound, the thioester reacts with strong alkylating agents to give cationic thiocarbenes.$^{109}$

The initial product of reaction 24 was detected by IR

\[ \text{CpFe(CO)$_2$C-OPh} \xrightarrow{\text{MeOSO$_2$F}} \text{CpFe(CO)$_2$C(OH) + FSO$_3$} \xrightarrow{1) \text{PF$_6$}^-} \xrightarrow{2) \text{MeOH}} \]

\[ \text{CpFe(CO)$_2$C(OH)$_2$ + PF$_6$}^- + \text{MeSH + PhOH} \]

($\nu_{CO}$ 2059 vs, 2019 s in CH$_2$Cl$_2$), but could not be crystallized. However, addition of MeOH gives the stable, crystalline dimethoxycarbene complex. The IR spectrum (Table 6) and $^1$H NMR spectrum (Table 7) clearly support this formulation. The $^{13}$C spectrum of [CpFe(CO)$_2$C(OH)$_2$]PF$_6$ shows a typical low-field resonance$^{110}$ ($\delta \approx 249$ ppm) for the carbene carbon atom. The stability of this compound is interesting, inasmuch as carbenes of this type cannot be obtained by alkylation of metal alkoxy carbonyl complexes.$^{109}$

No other reactions of CpFe(CO)$_2$C(S)OPh or [CpFe(CO)$_2$C(OH)$_2$]PF$_6$ were attempted, as compounds of this type are currently under investigation by another member of this research group (F. McCormick)$^{111}$.
Table 7. $^1$H NMR chemical shifts (ppm) of various cyclopentadienyl iron carbonyl and thiocarbonyl compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\delta$ Cp</th>
<th>$\delta$ R</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{CpFe(CO)}_2\text{C(OH)}]\text{PF}_6$</td>
<td>$d_6$-acetone</td>
<td>5.65</td>
<td>4.42 (Me)</td>
</tr>
<tr>
<td>$\text{CpFe(CO)(CS)Br}$</td>
<td>$\text{CS}_2$</td>
<td>5.10</td>
<td></td>
</tr>
<tr>
<td>$\text{CpFe(CO)(CS)I}$</td>
<td>$\text{CS}_2$</td>
<td>5.07</td>
<td></td>
</tr>
<tr>
<td>$\text{CpFe(CO)(CS)SnPh}_3$</td>
<td>$\text{CS}_2$</td>
<td>4.78</td>
<td>7.20-7.70 (Ph)</td>
</tr>
<tr>
<td>$\text{CpFe(CO)(CS)GePh}_3$</td>
<td>$\text{CS}_2$</td>
<td>4.69</td>
<td>7.15-7.60 (Ph)</td>
</tr>
<tr>
<td>$\text{CpFe(CO)(MeNC)SnPh}_3$</td>
<td>$\text{CS}_2$</td>
<td>4.48</td>
<td>2.70 (Me), 7.10-7.60 (Ph)</td>
</tr>
<tr>
<td>$\text{CpFe(CO)C(N}_2\text{C}_2\text{H}_6)\text{SnPh}_3$</td>
<td>$\text{CS}_2$</td>
<td>4.38</td>
<td>3.05 (CH$_2$), 5.45 (NH), 7.10-7.60 (Ph)</td>
</tr>
</tbody>
</table>
Cleavage Reactions of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \)

The carbonyl complex \([\text{CpFe(CO)}_2]_2\) undergoes numerous reactions in which the Fe-Fe bond is cleaved. Reaction with halogens, \(X_2\), gives \(\text{CpFe(CO)}_2X\) compounds.\(^{112}\) A more general route to such compounds involves treatment of the dimer with \(O_2\) and aqueous \(\text{HBF}_4\) in acetone; this gives \(\text{CpFe(CO)}_2(\text{H}_2\text{O})^+\), from which \(\text{CpFe(CO)}_2X\) compound may be obtained by reaction with almost any anionic ligand.\(^{113}\) Reduction of the dimer to \(\text{CpFe(CO)}_2^-\) by \(\text{Na(Hg)}\) is another important cleavage reaction.\(^{114}\) As a final example, the reaction of \([\text{CpFe(CO)}_2]_2\) with \(\text{Me}_2\text{S}_2\) in refluxing benzene gives the thiomethoxy-bridged complex \([\text{CpFe(CO)(MeS)}]_2\),\(^{115}\) which can be regarded as a cleavage product because it does not contain a metal-metal bond.

In the present study it was of interest to determine whether \(\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\) would also undergo such reactions. In most instances it is found that the CS ligand exerts a marked influence on the reactivity of the thiocarbonyl complex toward cleavage and on the nature of the products formed.

The thiocarbonyl complex reacts rapidly with \(\text{Cl}_2\) in \(\text{CCl}_4\) at \(0^\circ\), and with \(\text{Br}_2\) and \(\text{I}_2\) in \(\text{CS}_2\) at room temperature. In all cases the major product is an insoluble black tar. The composition of this substance was not determined, but it seems likely that the product may consist in part of polymerized CS. The bromine and iodine reactions do yield
small amounts of the expected cleavage products, CpFe(CO)₂X and CpFe(CO)(CS)X. Infrared spectra of the thiocarbonyl products (Table 6) show the expected single ν₃CO band and the very strong ν₃CS band characteristic of terminal CS ligands. The compounds were also characterized by ¹H NMR (Table 7). It is not clear why the main result of these reactions is destruction of the CS group. This also occurs to some extent in the reactions of [CpFe(CO)(CS)]₂¹₁⁶ and [CpRu(CO)(CS)]₂⁵² with halogens, and so may be characteristic of thiocarbonyl-bridged complexes.

Unlike its carbonyl analog, Cp₂Fe₂(CO)₃CS does not react with Me₂S₂ upon prolonged reflux in benzene. This result is probably attributable to the inability of this relatively weak electrophile to disrupt the more stable bridge structure of the thiocarbonyl complex.

When O₂ is passed through an acetone solution of Cp₂Fe₂(CO)₃CS and aqueous HBF₄, an immediate reaction occurs, giving a red mixture. The thiocarbonyl product obtained is the S-adduct [Cp₂Fe₂(CO)₃CS·CpFe(CO)₂BF₄, which is discussed in a later section. Formation of this product may be explained in the following way. Some of the thiocarbonyl complex first undergoes oxidative cleavage to CpFe(CO)₂(H₂O)⁺ and CpFe(CO)(CS)(H₂O)⁺. The remaining Cp₂Fe₂(CO)₃CS then reacts with these species to form the corresponding S-adducts. Finally, the CpFe(CO)(CS)⁺ adduct is rapidly hydrolyzed to
to the dicarbonyl product, accounting for the H$_2$S produced in the reaction.

The thiocarbonyl complex reacts rapidly with Na(Hg) in THF to give a mixture of Na[CpFe(CO)$_2$] and Na[CpFe(CO)(CS)]. Of the few thiocarbonyl anions known, $^{48,117,118}$ CpFe(CO)(CS)$^-$ is the first to be produced by actual reduction of a thiocarbonyl complex. Initially the solution is red-brown, but prolonged stirring with excess Na(Hg) gives a dark brown mixture and results in gradual destruction of the thiocarbonyl anion. Like the dicarbonyl anion, CpFe(CO)(CS)$^-$ is highly reactive and extremely air-sensitive. Interestingly, exposure of the CpFe(CO)$_2$$^-$/CpFe(CO)(CS)$^-$ solution to air gives mainly Cp$_2$Fe$_2$(CO)$_3$CS rather than, as might be expected, [CpFe(CO)$_2$]$^2^-$ and the more stable [CpFe(CO)(CS)]$_2$. Reactions of the thiocarbonyl anion are discussed in the following section.

Reactions of CpFe(CO)(CS)$^-$ and CpFe(CO)(CS)SnPh$_3$

Addition of MeI to a mixture of CpFe(CO)$_2$$^-$ in THF gives CpFe(CO)$_2$Me and small amounts of two other products, neither of which was particularly stable at room temperature. One of these is an orange compound whose IR spectrum in CS$_2$ shows a single strong CO absorption at 1960 cm$^{-1}$; the $^1$H NMR spectrum shows an Me resonance at 62.53. This Me peak occurs at nearly the same position as the Me resonances of
trans-[W(CO)]_{4}CS-Me^{61} and the recently-prepared
Cp[W(CO)]_{2}CS-Me,^{118} which contain S-alkylated terminal CS
ligands. Therefore, it appears that alkylation of the iron
thiocarbonyl anion gives the S-methyl compound
CpFe(CO)(CS-Me), rather than the expected metal-alkylated
product, CpFe(CO)(CS)Me, for which the Me resonance would
be expected to occur at much higher field (e.g., δ Me of
CpFe(CO)_{2}Me is 0.15 ppm^{119}). The observed product may be

(25) CpFe(CO)(CS)^{-} + MeI^{THF} \rightarrow CpFe(CO)(CS-Me) + I^{-}

regarded either as an S-alkyl thiocarbonylium complex,
M-C=S-R, or as an S-alkyl thiocarbyne^{120} compound, M=C-S-R.
The apparently high nucleophilicity of the CS sulfur atom
in CpFe(CO)(CS)^{-} is probably attributable to the stronger
electron-withdrawing ability of CS and the inherently
greater nucleophilicity of sulfur compared to oxygen.

The other product of this reaction is a black solid.
The IR spectrum in CS_{2} shows a strong ν_{CO} band at 1963 cm^{-1},
while the ^{1}H NMR spectrum shows a single Cp resonance (δ 4.62)
and two Me resonances (δ 2.47, 2.52). The identity of this
compound is not evident. One possibility is a carbene
product resulting from addition of excess MeI across the
Fe≡C bond of the thiocarbyne compound. However, this is
only a speculation, since this compound was never isolated in sufficient quantities for purification and analysis.

As another example of the different reactivities of CpFe(CO)(CS)\textsuperscript{-} and CpFe(CO)\textsubscript{2} \textsuperscript{-}, the reaction of the thio-carbonyl anion with CS\textsubscript{2}/MeI does not give CpFe(CO)(CS)CS\textsubscript{2}Me. Presumably, reaction occurs at the CS sulfur rather than the metal in this case also, but the actual product obtained was not identified. The intent of this reaction was to prepare the dithioester intermediate for subsequent use in the synthesis of CpFe(CO)(CS)\textsubscript{2}\textsuperscript{+}, as shown in reaction 27.

\begin{equation}
(27) \text{CpFe(CO)(CS)}^{-} \xrightarrow{1} \text{CS}_{2} \xrightarrow{2} \text{MeI} \xrightarrow{S_{i}^{+}} \text{CpFe(CO)(CS)C-SMe} \xrightarrow{H^{+}} \text{CpFe(CO)(CS)}_{2}^{+} + \text{MeSH}
\end{equation}

However, it now appears that the \textit{bis}-thiocarbonyl cation will not be accessible from the thio-carbonyl anion.

In contrast to the preceding results, reaction of the thio-carbonyl anion with Ph\textsubscript{3}SnCl and Ph\textsubscript{3}GeBr gives the metal-metal bonded derivatives CpFe(CO)(CS)MPh\textsubscript{3}, as shown by the IR and NMR spectra (Tables 6 and 7) which are typical of CpFe(CO)(CS)X compounds. Other arylmetal compounds, such

\begin{equation}
(28) \text{CpFe(CO)(CS)}^{-} + \text{Ph}_{3}MX \xrightarrow{\text{THF}} \text{CpFe(CO)(CS)MPh}_{3} + X^{-}
\end{equation}
as Ph$_2$PbCl and PhHgCl, appear to react similarly, but these derivatives were too unstable to be isolated. In the case of the tin compound, the higher yield and greater stability, and the fact that the reaction occurs at Fe rather than S, can probably be attributed to the relatively strong Fe-Sn bond found in similar complexes.$^{121}$

A recurrent problem in the study of the reactions of CpFe(CO)(CS)$^-$ is the fact that the reduction of Cp$_2$Fe$_2$(CO)$_3$CS also gives CpFe(CO)$_2^-$, which complicates the separation and purification of products from such reactions. Unfortunately, the thiocarbonyl anion cannot be generated from CpFe(CO)$_2$CS$^+$ or [CpFe(CO)(CS)]$_2$. Attempts to react the two anions selectively—for example, by addition of half an equivalent of MeI, followed by half an equivalent of Ph$_2$SnCl—give mixtures of all possible products. This result indicates that the nucleophilicities of CpFe(CO)(CS)$^-$ and CpFe(CO)$_2^-$ must be comparable.

Reaction of CpFe(CO)(CS)$^-$ with CpM(CO)$_3$Cl (M = Mo, W) gives Cp$_2$Fe$_2$(CO)$_3$CS, [CpFe(CO)(CS)]$_2$, [CpFe(CO)$_2$]$_2$ and [CpM(CO)$_3$]$_2$ rather than mixed-metal thiocarbonyl complexes. This is the usual result of the reaction of a metal carbonyl anion with a metal carbonyl halide whose corresponding anion is less nucleophilic.$^{122}$ Therefore, synthesis of mixed-metal thiocarbonyls may be possible by reactions of CpFe(CO)(CS)X (X = Cl, Br, I) with appropriate carbonyl anions.
The terminal CS ligand in CpFe(CO)(CS)SnPh$_3$, like those in certain other thiocarbonyl complexes,\textsuperscript{68,69} reacts with primary amines to give isocyanide complexes, as indicated by the disappearance of the $\nu_{CS}$ band in the IR spectrum and

\begin{equation}
\text{CpFe(CO)(CS)SnPh}_3 + \text{R-NH}_2 \xrightarrow{\text{Et}_2\text{O}} \text{CpFe(CO)(R-NC)SnPh}_3 + \text{H}_2\text{S}
\end{equation}

the appearance of the isocyanide $\nu_{CN}$ absorption. Methylamine reacts rapidly, but with other aliphatic amines the reaction is very slow. In these cases, addition of pyridine increases the reaction rate to some extent, as was also observed for the similar reactions of W(CO)$_5$CS.\textsuperscript{69} These reactions undoubtedly occur by the same mechanism proposed\textsuperscript{69} for the reaction of W(CO)$_5$CS with amines, in which attack of a hydrogen-bonded amine complex occurs at the thiocarbonyl carbon atom. Infrared and NMR data for isocyanide complexes prepared in these reactions are shown in Tables 6 and 7.

Unlike W(CO)$_5$CS, CpFe(CO)(CS)SnPh$_3$ is unreactive toward secondary amines, presumably because the size of the SnPh$_3$ group prevents close approach of the rather bulky nucleophile. On the other hand, ethylenediamine reacts to give a different type of product, the cyclic diaminocarbene complex CpFe(CO)C(N$_2$C$_2$H$_4$)SnPh$_3$; spectroscopic data for this compound are shown in Tables 6 and 7. There is no IR evidence for
the initial formation of an isocyanide complex, though the reaction presumably involves such an intermediate; apparently the ring closure is very rapid. In contrast, ethanolamine gives an isocyanide complex, evidently because the hydroxy group is insufficiently nucleophilic to promote ring formation.

Substitution Reactions of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \)

**Phosphine and phosphite derivatives**

The thiocarbonyl complex \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) undergoes thermal carbonyl substitution by \( \text{PET}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2 \) and \( \text{P}(\text{OMe})_3 \) to give the monosubstituted complexes \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})L \).

These reactions were tried in several different solvents. No reaction occurs in acetone or THF at reflux. In hydrocarbon solvents the reactions are rather slow below 100°, and considerable decomposition of the thiocarbonyl complex occurs (giving ferrocene and unidentified insoluble products). However, in refluxing \( \text{CH}_3\text{CN} \), substitution proceeds much more rapidly, and with little decomposition. For the above ligands,

\[
(31) \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} + \frac{\text{CH}_3\text{CN}}{\text{reflux}} \xrightarrow{} \text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})\text{PR}_3 + \text{CO}
\]

the observed order of reactivity is \( \text{PET}_3 \approx \text{PMe}_2\text{Ph} > \text{P}(\text{OMe})_3 >> \text{PMePh}_2 \).
Tributyl phosphine also reacts, but the product is rather unstable and was not isolated. Other ligands, such as PPh\(_3\), diphos and P(OPh)\(_3\), gave no evidence of substitution products. Derivatives of these ligands could be obtained by photochemical reactions, but, as with the PBu\(_3\) complex, the products were not very stable.

Substitution reactions of metal carbonyls\(^{63}\) generally follow a rate equation of the form Rate = \( k_1[M] + k_2[M][L] \), where M and L represent the metal carbonyl and ligand, respectively. The first term represents a dissociative reaction independent of the ligand concentration (S\(_{N,1}\)), while the second represents a ligand-dependent associative (S\(_{N,2}\)) process involving attack of the ligand at the metal center. The marked dependence of the above substitution reactions of Cp\(_2\)Fe\(_2\)(CO)\(_3\)CS on the nature of the ligand suggest that these reactions proceed mainly by an associative process. A kinetic study of the reaction of the thiocarbonyl complex with PMe\(_2\)Ph was undertaken to determine if this was the case. In the non-polar solvent decalin at 115°, the rate constants obtained were \( k_1 \sim 2.2 \times 10^{-5} \) sec\(^{-1}\) and \( k_2 \sim 7.6 \times 10^{-4} \) M\(^{-1}\) sec\(^{-1}\), which would seem to indicate that the associative reaction does indeed predominate. (The above value of \( k_1 \) is corrected for the decomposition of Cp\(_2\)Fe\(_2\)(CO)\(_3\)CS, which is assumed to be a first-order process.) However, other results of this study indicate that the actual reaction mechanism may be more complex, since at high
phosphine concentrations (>20-fold excess), the reaction is initially slower than at lower concentrations. It is not clear what sort of interaction of thiocarbonyl complex and phosphine could produce such an effect. Kinetic data for this reaction are shown in Table 7a.

This reaction was also studied in the polar solvent BuCN at 85°C. At all phosphine concentrations there was an induction period of about 20 min, after which the reaction proceeded so rapidly that no kinetic data could be obtained. The reaction appears to be phosphine-independent in this solvent (and presumably also in CH3CN). Therefore, the rate enhancement observed for the reactions in CH3CN could result from a substantial increase in the first-order (dissociative) rate constant, as is sometimes found for other metal carbonyl substitution reactions in coordinating solvents.123 However, as with the reactions in decalin, the peculiarities associated with the reaction prevent an unambiguous interpretation of the results.

Substitution reactions of [CpFe(CO)2]2 with phosphines,124 phosphites124 and primary amines125 have been investigated, and in most cases these reactions occur readily in refluxing benzene. In contrast, the reaction of Cp2Fe2(CO)3CS with
Table 7a. Kinetic data for the reaction of Cp₂Fe₂(CO)₃CS with PMe₂Ph in decalin at 115° a,b

<table>
<thead>
<tr>
<th>[PMe₂Ph], M</th>
<th>kₜₐₜ, sec⁻¹ c,d</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.54 x 10⁻²</td>
<td>1.28 x 10⁻⁴</td>
</tr>
<tr>
<td>5.29 x 10⁻²</td>
<td>1.48 x 10⁻⁴</td>
</tr>
<tr>
<td>7.93 x 10⁻²</td>
<td>1.69 x 10⁻⁴</td>
</tr>
<tr>
<td>10.6 x 10⁻²</td>
<td>1.89 x 10⁻⁴</td>
</tr>
</tbody>
</table>

a [Cp₂Fe₂(CO)₃CS] was 2.53 x 10⁻³ M in all runs.
b In the absence of PMe₂Ph, the thiocarbonyl complex decomposed in decalin at 115°, with kₗₜₜ = 8.60 x 10⁻⁵ sec⁻¹ obtained from slope of ln(A - Aᵦ) vs. time graph.
c Values of kₜₐₜ were obtained from graphs of ln(A - Aᵦ) vs. time (see p. 71); values reported above are averages from at least two runs.
d Graph of kₜₐₜ vs. [PMe₂Ph] was linear, with intercept = k₁ = 1.08 x 10⁻⁴ sec⁻¹ and slope = k₂ = 7.55 x 10⁻⁴ M⁻¹ sec⁻¹; correction for the decomposition of the thiocarbonyl complex gives k₁ = 2.2 x 10⁻⁵ sec⁻¹.

phosphines and phosphites under the same conditions is very slow, and amines fail to react even in refluxing CH₂CN.
The thiocarbonyl complex, unlike [CpFe(CO)]₂,₁₂₆ also fails to undergo ¹³CO exchange at room temperature. Thus,
Cp₂Fe₂(CO)₂CS is the first example of a thiocarbonyl complex which undergoes CO replacement less readily than does its carbonyl analog.⁶¹,⁶²,⁶⁶ These results are surprising in view of the fact that the carbonyl stretching bands occur at higher frequencies in Cp₂Fe₂(CO)₂CS than in [CpFe(CO)₂]₂, which might seem to indicate that the π-backbonding, and hence the Fe-CO bond strength, is somewhat lower in the thiocarbonyl compound. The reason for this apparently anomalous behavior of Cp₂Fe₂(CO)₂CS is not evident. However, it should be pointed out that all previous reports of the labilizing effects of CS concern complexes with terminal thiocarbonyl ligands. It will be interesting to see if the reverse effect is general in thiocarbonyl-bridged compounds.

The phosphine and phosphite derivatives Cp₂Fe₂(CO)₂(CS)L are very dark green or brown crystalline solids. The compounds decompose slowly if stored in air at room temperature, but appear to be indefinitely stable at -20°. They are sparingly soluble in aliphatic hydrocarbons, but more soluble in other organic solvents, and form characteristic deep green solutions. In solution the compounds are somewhat more susceptible to air oxidation and thermal decomposition than is the parent thiocarbonyl.

The IR spectra (Table 8) of all the derivatives except the PMePh₂ compound display one strong terminal CO stretch and also a single strong band for the bridging carbonyl; these
bands occur at lower frequencies than in \( \text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS} \), as would be expected because of the increase in electron density resulting from the introduction of a donor ligand. The CS band is considerably stronger than that of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS} \), undoubtedly because of the lower symmetry of the substituted derivatives. The spectrum of the \( \text{PMePh}_2 \) complex differs from those mentioned above in that in non-polar solvents there are two strong terminal CO absorptions, although the other spectra have much weaker bands in both the terminal and bridging regions. In all of the spectra the \( \nu_{\text{CS}} \) band has a \( \delta \) shoulder on the high-frequency side. These spectra are not noticeably solvent-dependent, again except for that of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})\text{PMePh}_2 \), which shows only one terminal \( \nu_{\text{CO}} \) band in polar solvents.

The IR data are consistent with the presence of cis and trans isomers of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})\text{PR}_3 \) in solution, with only one isomer predominant in most cases. This is also found to be the case for the carbonyl analogs \( \text{Cp}_2\text{Fe}_2(\text{CO})_2\text{PR}_3 \). The cis-trans interconversion of the thiocarbonyl compounds can occur by the AC mechanism if the CS and PR\(_3\) ligands are on the same Fe atom in the non-bridged intermediate, as can be seen by mentally substituting a PR\(_3\) ligand for the appropriate carbonyl in one of the non-bridged isomers shown in Figure 3.

The \( ^1\text{H} \) NMR spectra of the \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})\text{PR}_3 \) complexes
Table 8. IR stretching frequencies (cm\(^{-1}\)) for derivatives of \(\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\)

<table>
<thead>
<tr>
<th>Compound (^a)</th>
<th>Solvent</th>
<th>(\nu_{\text{CO}}^b)</th>
<th>(\nu_{\text{CS}}^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Fe'}\text{CS}(-\text{PEt}_3))</td>
<td>hexane</td>
<td>1945 vs, 1760 s</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>(\text{CS}_2)</td>
<td>1945 vs, 1764 s</td>
<td>1102 m (^c)</td>
</tr>
<tr>
<td></td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>1936 vs, 1748 s</td>
<td>1099 m</td>
</tr>
<tr>
<td>(\text{Fe'}\text{CS}(-\text{PMe}_2\text{Ph}))</td>
<td>hexane</td>
<td>1950 vs, 1758 s</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>(\text{CS}_2)</td>
<td>1950 vs, 1760 s</td>
<td>1104 m</td>
</tr>
<tr>
<td></td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>1940 vs, 1747 s</td>
<td>1100 m</td>
</tr>
<tr>
<td>(\text{Fe'}\text{CS}(-\text{PMePh}_2))</td>
<td>hexane</td>
<td>1970 vs, 1951 s, 1757 s</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>(\text{CS}_2)</td>
<td>1964 vs, 1944 s, 1748 s</td>
<td>1100 m</td>
</tr>
<tr>
<td></td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>1953 vs, 1745 s</td>
<td>1098 m</td>
</tr>
</tbody>
</table>

\(^a\)Abbreviations: \(\text{Fe}^* = \text{Cp}_2\text{Fe}_2(\text{CO})_3\), \(\text{Fe}' = \text{Cp}_2\text{Fe}_2(\text{CO})_2\), \(\text{Fe}'' = \text{Cp}_2\text{Fe}_2(\text{CO})\).

\(^b\)See Table 3, footnote a.

\(^c\)\(\nu_{\text{CS}}\) band for all \(\text{PR}_3\) derivatives has w-m sh at 1120.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\nu_{CO}$</th>
<th>$\nu_{CS}$</th>
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<tr>
<td>Fe'CS(P(OMe)$_3$)</td>
<td>hexane</td>
<td>1972 vs, 1952 m,</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>1765 s</td>
<td></td>
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<tr>
<td>Fe'CS(P(OPh)$_3$)</td>
<td>CS$_2$</td>
<td>1965 vs, 1759 s</td>
<td>1108 m</td>
</tr>
<tr>
<td></td>
<td>CH$_2$Cl$_2$</td>
<td>1959 vs, 1755 s</td>
<td>1106 m</td>
</tr>
<tr>
<td>Fe'CS(MeNC)</td>
<td>hexane</td>
<td>2150 m, d 2005 m,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1965 vs, 1749 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C$_6$H$_6$</td>
<td>2160 s, d 1994 w,</td>
<td>1122 s, 1114 s</td>
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<tr>
<td></td>
<td></td>
<td>1954 s, 1781 vs</td>
<td></td>
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<tr>
<td></td>
<td>CS$_2$</td>
<td>1998 m, 1961 vs,</td>
<td>1119 s, 1113 s</td>
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<td></td>
<td></td>
<td>1784 s</td>
<td></td>
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<tr>
<td></td>
<td>CH$_2$Cl$_2$</td>
<td>2164 s, d 1996 w,</td>
<td>1119 s, 1113 s</td>
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<tr>
<td></td>
<td></td>
<td>1961 vs, 1773 s</td>
<td></td>
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<tr>
<td></td>
<td>CH$_3$CN</td>
<td>2164 s, d 1988 w,</td>
<td>1120 s, 1113 s</td>
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<tr>
<td></td>
<td></td>
<td>1958 vs, 1777 s</td>
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$^d_{\nu_{CN}}$ absorption.

$^e$Recorded in 0.1 mm cell.
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<thead>
<tr>
<th>Compound$^a$</th>
<th>Solvent</th>
<th>$\nu_{CO}^b$</th>
<th>$\nu_{CS}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{II}$CS(MeNC)$_2$f</td>
<td>hexane</td>
<td>2143 m, $^d$ 1960 s, $^d$ 1951 vs, 1723 s$^d$</td>
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<tr>
<td>C$_6$H$_6$</td>
<td>2152 s, $^d$ 1949 vs, 1720 s$^d$</td>
<td>1122 s, 1111 s</td>
<td></td>
</tr>
<tr>
<td>CS$_2$</td>
<td>1954 vs, 1723 s$^d$</td>
<td>1119 s, 1111 s</td>
<td></td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>2155 s, $^d$ 1954 vs, 1720 s$^d$</td>
<td>1120 m(sh), 1105 s</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>2155 s, $^d$ 1952 vs, 1720 s$^d$</td>
<td>1120 m(sh), 1107 s</td>
<td></td>
</tr>
<tr>
<td>Fe$^{II}$CS(MeNC)$_2$E</td>
<td>CS$_2$</td>
<td>1764 s</td>
<td>1103 s</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>2154 vs, $^d$ 1751 s</td>
<td>1110 m-s</td>
<td></td>
</tr>
<tr>
<td>Fe*CS·HgCl$_2$</td>
<td>CH$_2$Cl$_2$</td>
<td>2037 s, 2004 m, $^h$ 1842 m</td>
<td>1019 w</td>
</tr>
</tbody>
</table>

$^f$Bridge-terminal isomer.
$^E$Bis-terminal isomer.
$^h$Saturated with HgX$_2$. 
Table 8. (Continued)

<table>
<thead>
<tr>
<th>Compound(^\text{a})</th>
<th>Solvent</th>
<th>(v_{\text{CO}}^\text{b})</th>
<th>(v_{\text{CS}}^\text{b})</th>
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<tbody>
<tr>
<td>Fe*CS·HgBr(_2)</td>
<td>CH(_2)Cl(_2) (^\text{h})</td>
<td>2035 s, 2006 m, 1840 m</td>
<td>1020 w</td>
</tr>
<tr>
<td>Fe*CS·BBr(_3)</td>
<td>CH(_2)Cl(_2) (^\text{i})</td>
<td>2039 s, 2006 m, 1842 m</td>
<td>1022 w</td>
</tr>
<tr>
<td>Fe*CS·Cr(CO)(_5)</td>
<td>CS(_2)</td>
<td>2061 m, 2020 s, 2005 w, 1977 w, 1934 s, 1916 m, 1825 w-m</td>
<td>1082 w</td>
</tr>
<tr>
<td>Fe*CS·W(CO)(_5)</td>
<td>CS(_2)</td>
<td>2067 m, 2022 s, 1992 w, 1977 w, 1931 s, 1911 m, 1827 w-m</td>
<td>1076 w</td>
</tr>
<tr>
<td>(Fe*CS)(_2)PtCl(_2)</td>
<td>CH(_2)Cl(_2)</td>
<td>2024 vs, 1992 m, 1828 s</td>
<td>1081 w, 1033 w</td>
</tr>
<tr>
<td>[Fe*CS·HgMe]PF(_6)</td>
<td>CH(_2)Cl(_2)</td>
<td>2033 s, 1998 m, 1844 s</td>
<td>1017 w</td>
</tr>
<tr>
<td>[Fe*CS·CpFe(CO)(_2)]BF(_4)</td>
<td>CH(_2)Cl(_2)</td>
<td>2049 vs, 2025 s, 2006 m, 1834 m</td>
<td>—</td>
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\(^{1}\text{Excess BBr}_3\text{ present.}\)
<table>
<thead>
<tr>
<th>Compound(^a)</th>
<th>Solvent</th>
<th>(v_{\text{CO}})</th>
<th>(v_{\text{CS}})</th>
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<tr>
<td>([\text{Fe*CS•CpFe(CO)(CS)}]\text{BPh}_4)</td>
<td>(\text{CH}_2\text{CN})</td>
<td>2032 s, 2020 s, 1987 m, 1834 m</td>
<td>1315 m(^j)</td>
</tr>
<tr>
<td>([\text{Fe*CS-Me}]\text{PF}_6)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>2040 s, 2012 w, 1856 m</td>
<td>1028 w</td>
</tr>
<tr>
<td>([\text{Fe*CS-Et}]\text{PF}_6)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>2040 s, 2009 w, 1855 m</td>
<td>1024 w</td>
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<tr>
<td>([\text{Fe*CS-Pr}]\text{PF}_6)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>2039 s, 2008 w, 1855 m</td>
<td>1022 w</td>
</tr>
<tr>
<td>([\text{Fe*CS-Bu}]\text{PF}_6)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>2039 s, 2009 w, 1855 m</td>
<td>1024 w</td>
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<tr>
<td>([\text{Fe*CS-All}]\text{PF}_6)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
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<td>1017 w</td>
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<tr>
<td>([\text{Fe*CS-Bz}]\text{PF}_6)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>2039 s, 2011 w, 1857 m</td>
<td>1023 w</td>
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<tr>
<td>([\text{Fe*CS-CH}_2\text{I}]\text{PF}_6)</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>2044 s, 2017 w, 1860 m</td>
<td>1009 w</td>
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\(^j\)Terminal \(v_{\text{CS}}\): \(\text{CHCl}_3\) solution.
Table 8. (Continued)

<table>
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<tr>
<th>Compound&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Solvent</th>
<th>(v_{CO})&lt;sup&gt;b&lt;/sup&gt;</th>
<th>(v_{CS})&lt;sup&gt;b&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
<td>([Fe'CS-CH_2COOEt]PF_6)</td>
<td>(CH_2Cl_2)</td>
<td>2043 s, 2014 w, 1859 m, 1739 wk</td>
<td>1015 w</td>
</tr>
<tr>
<td>([Fe'CS-Me(PET_3)]PF_6)</td>
<td>(CH_2Cl_2)</td>
<td>1985 vs, 1818 s</td>
<td>1004 m</td>
</tr>
<tr>
<td>([Fe'CS-Et(PET_3)]PF_6)</td>
<td>(CH_2Cl_2)</td>
<td>1984 vs, 1818 s</td>
<td>1006 m</td>
</tr>
<tr>
<td>([Fe'CS-Bz(PET_3)]PF_6)</td>
<td>(CH_2Cl_2)</td>
<td>1979 vs, 1809 s</td>
<td>998 m</td>
</tr>
<tr>
<td>([Fe'CS-Me(PMe_2Ph)]PF_6)</td>
<td>(CH_2Cl_2)</td>
<td>1991 vs, 1816 s</td>
<td>1008 m</td>
</tr>
<tr>
<td>([Fe'CS-Me(PMePh_2)]PF_6)</td>
<td>(CH_2Cl_2)</td>
<td>2003 vs, 1971 w, 1811 s</td>
<td>1008 m</td>
</tr>
<tr>
<td>([Fe'CS-Me(PPh_3)]PF_6)</td>
<td>(CH_2Cl_2)</td>
<td>1998 vs, 1801 s</td>
<td>1007 m</td>
</tr>
<tr>
<td>([Fe'CS-Me(P(OMe)_3)]PF_6)</td>
<td>(CH_2Cl_2)</td>
<td>2004 vs, 1812 s</td>
<td></td>
</tr>
<tr>
<td>([Fe'CS-Me(P(OPh)_3)]PF_6)</td>
<td>(CH_2Cl_2)</td>
<td>2005 vs, 1825 s</td>
<td>1013 m</td>
</tr>
<tr>
<td>([Fe'CS-Me(py)]PF_6)</td>
<td>(CH_2Cl_2)</td>
<td>1998 vs, 1806 s</td>
<td>1010 m</td>
</tr>
<tr>
<td>([Fe'CS-Me(MeNC)]PF_6)</td>
<td>(CH_2Cl_2)</td>
<td>2196 s&lt;sup&gt;d&lt;/sup&gt;, 2006 vs, 1834 s</td>
<td>1019 m</td>
</tr>
</tbody>
</table>

<sup>k</sup>Ester \(v_{C=O}\) absorption.
Table 8. (Continued)

<table>
<thead>
<tr>
<th>Compounda</th>
<th>Solvent</th>
<th>$\nu_{CO}$b</th>
<th>$\nu_{CS}$b</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe'CS-Et(MeNC)]PF₆</td>
<td>CH₂Cl₂</td>
<td>2195, d 2005 vs, 1833 s</td>
<td>1017 m</td>
</tr>
<tr>
<td>[Fe''CS-He(MeNC)₂]PF₆</td>
<td>CH₂Cl₂</td>
<td>2190 vs, d 1815 s</td>
<td>1014 m</td>
</tr>
<tr>
<td>[Fe''CS-He(PhNC)₂]PF₆</td>
<td>CH₂Cl₂</td>
<td>2133 vs, d 2045 w(sh), d 2003 s, 1831 s</td>
<td>1020 m</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Fe''CS-He(Me₂NC)(MeNC)</a>₂</td>
<td>CH₃NO₂</td>
<td>2222 vs, d 2038 vs, 1620 m-s⁻¹</td>
<td>1023 m⁷</td>
</tr>
<tr>
<td>[Fe'CS-He(Cl)]</td>
<td>CH₂Cl₂</td>
<td>2000 vs, 1815 s</td>
<td>1012 m</td>
</tr>
<tr>
<td>[Fe'CS-He(Br)]</td>
<td>CH₂Cl₂</td>
<td>1996 vs, 1812 s</td>
<td>1011 m</td>
</tr>
<tr>
<td>[Fe'CS-He(I)]</td>
<td>CH₂Cl₂</td>
<td>1992 vs, 1807 s</td>
<td>1011 m</td>
</tr>
<tr>
<td>[Fe'CS-Et(I)]</td>
<td>CH₂Cl₂</td>
<td>1991 vs, 1807 s</td>
<td>1009 m</td>
</tr>
</tbody>
</table>

¹$\nu_{C=N}$ absorption of bridging Me₂NC⁺ ligand; KBr wafer.

mAcetone solution; $\nu_{CS}$ 1043 m in KBr.
(Table 9) also indicate that (in CDCl₃, at least) only one isomer is present. Ambient-temperature NMR spectra reported for the carbonyl analogs are very similar,¹²₄,¹²₆ but these molecules are known to be highly fluxional species.¹²₆ However, it is likely that the thiocarbonyl compounds will isomerize much more slowly, owing to the stabilizing influence of the bridging CS ligand, and hence should give more complicated spectra if both isomers were present. Since this is not observed, it may be concluded that only one of the isomers predominates. (The different signals observed for the Me groups in Cp₂Fe₂(CO)₂(CS)PMe₂Ph arise from non-equivalence rather than the presence of isomers.) It is not possible with the presently available data to determine which of the isomers is favored. For the carbonyl analogs Cp₂Fe₂(CO)₃PR₃ it is known to be the cis form,¹²₆ so it seems likely that this is also the case for the thiocarbonyl compounds.

**Isocyanide derivatives**

Metal isocyanide complexes have been studied extensively for many years.¹²⁷,¹²⁸ Recent work on isocyanide derivatives of [CpFe(CO)₂]₂¹²⁹ is especially relevant to the present research. This compound reacts with MeNC in refluxing THF to give a mixture of the mono-, di- and trisubstituted complexes, all of which have been characterized. Of particular
importance is the fact that isocyanide ligands, like CO and CS, can occupy both terminal and bridge positions. It was of interest to determine whether replacement of one or more carbonyls in \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) with isocyanide ligands would force the CS group into a terminal position.

The monothiocarbonyl complex reacts with excess MeNC in refluxing THF to give only the monosubstitution product, \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{MeNC}) \). However, if the reaction is carried out in refluxing \( \text{CH}_3\text{CN} \), only the bis-isocyanide complex, \( \text{Cp}_2\text{Fe}_2(\text{CO})(\text{CS})(\text{MeNC})_2 \), is obtained. There is no evidence for the formation of a trisubstituted product. These results thus provide a convenient method for selective preparation of the thiocarbonyl derivatives, and also illustrate again the different reactivity of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) compared to that of \( [\text{CpFe(\text{CO})}_2]^2 \). Also, unlike its carbonyl analog,\(^{130}\) the thio-

\[
\begin{align*}
(32) \quad & \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \quad \text{MeNC} \\
& \quad \text{THF} \xrightarrow{\text{reflux}} \text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{MeNC}) \\
& \quad \text{CH}_3\text{CN} \xrightarrow{\text{reflux}} \text{Cp}_2\text{Fe}_2(\text{CO})(\text{CS})(\text{MeNC})_2
\end{align*}
\]

carbonyl complex fails to undergo thermal substitution by PhNC. Evidence of PhNC substitution could be obtained only in photolysis experiments, which gave mixtures of products that proved difficult to separate and characterize.

The monosubstituted complex \( \text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{MeNC}) \) is a
Table 9. $^1$H NMR chemical shifts (ppm) for derivatives of Cp$_2$Fe$_2$(CO)$_3$CS in d$_6$-acetone solution

<table>
<thead>
<tr>
<th>Compound$^a$</th>
<th>$\delta$ Cp</th>
<th>$\delta$ R$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe'CS(PEt$_3$)$^c$</td>
<td>4.53 (d),$^d$ 4.80</td>
<td>0.70-1.60 (m, Et)</td>
</tr>
<tr>
<td>Fe'CS(PMe$_2$Ph)$^c$</td>
<td>4.25 (d),$^d$ 4.79</td>
<td>0.91 (d, Me),$^e$ 7.30-7.90 (m, Ph)</td>
</tr>
<tr>
<td>Fe'CS(PMePh$_2$)$^c$</td>
<td>4.24 (d),$^d$ 4.61</td>
<td>1.70 (d, Me),$^e$ 7.20-7.60 (m, Ph)</td>
</tr>
<tr>
<td>Fe'CS(P(OEt)$_3$)$^c$</td>
<td>4.59 (d),$^f$ 4.74</td>
<td>3.58 (d, Me)$^g$</td>
</tr>
</tbody>
</table>

$^a$See Table 8, footnote a.

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

$^c$CDCl$_3$ solution.

$^d$$^3$J$^{PFeCH}$ = 1.8 Hz.

$^e$$^3$J$^{PCH}$ = 9.0 Hz.

$^f$$^3$J$^{PFeCH}$ = 1.0 Hz.

$^g$$^3$J$^{POCH}$ = 11 Hz.
Table 9. (Continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ Cp</th>
<th>δ R&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe'CS(MeNC)</td>
<td>4.68, 4.80</td>
<td>3.05 (Me)</td>
</tr>
<tr>
<td>Fe'CS(MeNC)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.70, 4.82</td>
<td>3.03 (Me)</td>
</tr>
<tr>
<td>Fe'CS(MeNC)&lt;sup&gt;h&lt;/sup&gt;</td>
<td>4.51, 4.62</td>
<td>3.00 (Me)</td>
</tr>
<tr>
<td>Fe'CS(MeNC)&lt;sup&gt;i&lt;/sup&gt;</td>
<td>4.48, 4.51</td>
<td>1.98 (Me)</td>
</tr>
<tr>
<td>Fe''CS(MeNC)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4.70, 4.86</td>
<td>3.01 (Me),&lt;sup&gt;j&lt;/sup&gt; 3.78 (Me)&lt;sup&gt;k&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fe''CS(MeNC)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.67, 4.83</td>
<td>2.96 (Me),&lt;sup&gt;j&lt;/sup&gt; 3.72 (Me)&lt;sup&gt;k&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fe''CS(MeNC)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;h&lt;/sup&gt;</td>
<td>4.51, 4.67</td>
<td>2.93 (Me),&lt;sup&gt;j&lt;/sup&gt; 3.60 (Me)&lt;sup&gt;k&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fe''CS(MeNC)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;i&lt;/sup&gt;</td>
<td>4.54, 4.60</td>
<td>2.02 (Me),&lt;sup&gt;j&lt;/sup&gt; 3.65 (Me)&lt;sup&gt;k&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>h</sup>CS<sub>2</sub> solution.
<sup>i</sup>C<sub>6</sub>D<sub>6</sub> solution.
<sup>j</sup>Terminal isocyanide.
<sup>k</sup>Bridging isocyanide.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ Cp</th>
<th>$\delta$ R$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe*CS•HgCl$_2$</td>
<td>5.54</td>
<td></td>
</tr>
<tr>
<td>Fe*CS•Cr(CO)$_5$</td>
<td>5.28</td>
<td></td>
</tr>
<tr>
<td>Fe*CS•W(CO)$_5$</td>
<td>5.28</td>
<td></td>
</tr>
<tr>
<td>[Fe*CS-HgMe]PF$_6$</td>
<td>5.59</td>
<td>1.33 (br, Me)</td>
</tr>
<tr>
<td>[Fe*CS•CpFe(CO)$_2$]BF$_4$</td>
<td>5.45, 5.73$^1$</td>
<td></td>
</tr>
<tr>
<td>[Fe*CS•CpFe(CO)(CS)]BPh$_4$</td>
<td>5.42, 5.61$^1$</td>
<td></td>
</tr>
<tr>
<td>[Fe*CS-Me]PF$_6$</td>
<td>5.65 (br)</td>
<td>3.77 (Me)</td>
</tr>
<tr>
<td>[Fe*CS-Et]PF$_6$</td>
<td>5.58</td>
<td>1.69 (t, CH$_3$), 4.30 (br q, CH$_2$)</td>
</tr>
<tr>
<td>[Fe*CS-Pr]PF$_6$</td>
<td>5.75 (br)</td>
<td>1.20 (t, CH$_3$), 1.90-2.40 (m, CH$_2$), 4.35 (br q, CH$_2$)</td>
</tr>
</tbody>
</table>

$^1$Cp of adduct group.
Table 9. (Continued)

<table>
<thead>
<tr>
<th>Compounda</th>
<th>δ Cp</th>
<th>δ Rb</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe*CS-Bu]PF₆</td>
<td>5.73 (br)</td>
<td>1.05 (br t, CH₃),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.34-2.10 (br m, CH₂CH₂),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.36 (br q, CH₂)</td>
</tr>
<tr>
<td>[Fe*CS-All]PF₆</td>
<td>5.62</td>
<td>4.93 (br t, CH₂)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.30-6.50 (m, CH=CH₂)</td>
</tr>
<tr>
<td>[Fe*CS-Bz]PF₆</td>
<td>5.60, 5.72</td>
<td>5.43 (br, CH₂),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.48 (m, Ph)</td>
</tr>
<tr>
<td>[Fe*CS-CH₂I]PF₆</td>
<td>5.79, 5.87</td>
<td>5.69 (br, CH₂).</td>
</tr>
<tr>
<td>[Fe*CS-CH₂COOEt]PF₆</td>
<td>5.80</td>
<td>1.32 (t, CH₃),</td>
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<tr>
<td></td>
<td></td>
<td>4.38 (q, CH₂),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.20 (br, CH₂)</td>
</tr>
<tr>
<td>[Fe'CS-Me(PEt₃)]PF₆</td>
<td>5.23 (d),d 5.43</td>
<td>0.80-1.80 (m, Et),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.60 (Me)</td>
</tr>
<tr>
<td>[Fe'CS-Et(PEt₃)]PF₆</td>
<td>5.23 (d),d 5.45</td>
<td>0.80-1.80 (m, Et and CH₂),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.23 (br, CH₂)</td>
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</table>
Table 9. (Continued)

<table>
<thead>
<tr>
<th>Compound&lt;sup&gt;a&lt;/sup&gt;</th>
<th>δ Cp</th>
<th>δ R&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe⁺CS-Bz(PEt₃)]PF₆&lt;sup&gt;m&lt;/sup&gt;</td>
<td>5.06 (d), 5.22</td>
<td>0.60-1.60 (m, Et), 7.46 (m, Ph)</td>
</tr>
<tr>
<td>[Fe⁺CS-Me(PMe₂Ph)]PF₆</td>
<td>5.12 (d), 5.46</td>
<td>1.43 (d, Me), 1.68 (d, Me), 3.58 (Me), 7.51 (m, Ph)</td>
</tr>
<tr>
<td>[Fe⁺CS-Me(PMePh₂)]PF₆</td>
<td>5.14 (d), 5.38</td>
<td>2.14 (d, Me), 3.53 (Me), 7.10-7.50 (m, Ph)</td>
</tr>
<tr>
<td>[Fe⁺CS-Me(POH₃)]PF₆</td>
<td>5.27, 5.39</td>
<td>3.67 (d, Me and CS-Me)&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
<tr>
<td>[Fe⁺CS-Me(MeNC)]PF₆</td>
<td>5.33, 5.42</td>
<td>3.22 (Me), 3.67 (Me)</td>
</tr>
<tr>
<td>[Fe⁺CS-Et(MeNC)]PF₆</td>
<td>5.31, 5.40</td>
<td>1.63 (t, CH₃), 3.22 (Me), 4.18 (br q, CH₂)</td>
</tr>
<tr>
<td>[Fe⁺CS-Me(MeNC)₂]PF₆</td>
<td>5.07</td>
<td>3.22 (Me), 3.57 (Me)</td>
</tr>
<tr>
<td>[Fe⁺CS-Me(PhNC)₂]PF₆</td>
<td>5.46</td>
<td>3.70 (Me), 7.10-7.80 (br m, Ph)</td>
</tr>
</tbody>
</table>

<sup>m</sup>C₆D₆ solution.

<sup>n</sup>^J<sub>PCH</sub> = Hz.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ Cp</th>
<th>$\delta$ R&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>$<a href="%5Ctext%7BPF%7D_6">^{Fe}^\text{II}CS-\text{Me(Me}_2\text{NC})(\text{MeNC})</a>_2$</td>
<td>5.83, 5.92</td>
<td>3.28 (Me), 3.77 (Me), 4.28 (Me), 4.34 (Me)&lt;sup&gt;o&lt;/sup&gt;</td>
</tr>
<tr>
<td>$[^{Fe}^\text{I}CS-\text{Et(I)}]$&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.82, 4.87</td>
<td>1.67 (t, CH&lt;sub&gt;3&lt;/sub&gt;), 4.30 (br, CH&lt;sub&gt;2&lt;/sub&gt;)</td>
</tr>
</tbody>
</table>

<sup>o</sup>Bridging MeNC<sup>+</sup> group.
red-brown crystalline solid that is slightly air-sensitive in the solid state and somewhat more so in solution. Its solubilities in various solvents are similar to those observed for the phosphine derivatives discussed above. Solutions in benzene are grayish, whereas in hexane and CS$_2$ the color is green; in more polar solvents the compound gives brown or greenish-brown solutions. However, the IR spectra of the compound in various solvents (Table 8) all three strong bands at higher frequencies indicative of a terminal isocyanide, a terminal CO and a bridging CO. These bands arise from the predominant isomer, in which the isocyanide is terminal. Two strong, equally-intense bands in the bridging CS region indicate that cis and trans isomers of the compound must be present, since there is only one CS ligand in the molecule; apparently the CO and CN frequencies for the two isomers are virtually the same and hence are unresolved. Other IR bands (≈2000 w-m, and also ≈1740 w) appear to arise from a small amount of another isomer (or pair of cis-trans isomers) where both CS and MeNC ligands occupy bridge positions. There is no evidence for an isomer with a terminal CS ligand.

The $^1$H NMR spectra of Cp$_2$Fe$_2$(CO)$_2$(CS)(MeNC) (Table 9) show three large peaks (ratio 3:5:5) corresponding to the terminal MeNC ligand and the two non-equivalent Cp groups of the predominant isomer. In most solvents the separation of the Cp signals is ≈7 Hz, and the isocyanide Me resonance occurs
at ~ $53.0^\circ$, whereas in $C_6D_6$ solution the Cp chemical shifts differ by only ~3 Hz, and the Me peak is shifted upfield by almost 1 ppm. However, this effect appears to be peculiar to this solvent, and not an indication of any marked configurational change (see below). In all cases the peaks are quite sharp, and would seem to indicate that only one of the isomers, either the cis or the trans, is present. There are two possible explanations for this observation. The first is that the cis-trans interconversion is fast on the NMR time scale, which seems unlikely in view of the slow isomerization observed for the parent compound $Cp_2Fe_2(CO)_3CS$. The other is that the chemical shifts of all ligands must be almost exactly coincident for both isomers.

The NMR spectra of this compound also show much smaller peaks (e.g., $\delta 3.67$ and 5.00 in $d_5$-acetone) arising from the MeNC ligand and the equivalent Cp groups of the isocyanide-bridged isomer. The proportion of this isomer is appreciable in $d_5$-acetone and $CS_2$ (perhaps 10%), but very small in $C_6D_6$ and $CDCl_3$. This variation in the bridge/terminal isomer ratio may be responsible for the abovementioned color changes of the compound in different solvents.

The analogous carbonyl complex $Cp_2Fe_2(CO)_3(MeNC)$ also exists in terminal isocyanide and isocyanide-bridged forms, but, in contrast to the above observations, the two isomers are present in about equal amounts and interconvert rapidly.
at normal temperatures. This very different behavior of the carbonyl and thiocarbonyl analogs can be explained by consideration of the AC mechanism in Figure 3 for the case in which one of the terminal CO ligands has been replaced by MeNC. For either compound, cis-trans isomerization can occur by this mechanism. However, it can be seen that for Cp₂Fe₂(CO)₃(MeNC) the terminal-bridge isocyanide exchange is also allowed by this process, whereas for Cp₂Fe₂(CO)₂(CS)(MeNC) (which must retain the CS bridge) this isomerization can occur only via an intermediate in which the CS and MeNC ligands are on different Fe atoms. This structure would seem to be less stable than one in which the more strongly back-bonding CS ligand and the electron-donating isocyanide are on the same Fe of the non-bridged form. Thus, for the thiocarbonyl complex the terminal-bridge MeNC exchange should be less favorable, and the observed low proportion of the isocyanide-bridged isomer indicates that this is the case.

The bis-isocyanide complex Cp₂Fe₂(CO)(CS)(MeNC)₂ is a dark purple solid whose air stability and solubility characteristics are similar to those of the monosubstituted compound. It forms green solutions in non-polar solvents but is purple in polar media.

The IR spectra of Cp₂Fe₂(CO)(CS)(MeNC)₂ in various solvents (Table 8) show that the compound exists in two isomeric forms. The first of these is a pair of cis-trans isomers
having a bridging isocyanide and a terminal isocyanide. This is illustrated by the spectrum in hexane, which shows a terminal CN stretching band (2143 cm\(^{-1}\)), two terminal CO bands (1960, 1951 cm\(^{-1}\)) and a bridging isocyanide CN band (1723 cm\(^{-1}\)). In other solvents there is only one terminal carbonyl band (which is, however, slightly unsymmetrical to the higher-frequency side in most cases), but two bridging CS bands can be observed. The other isomer has two terminal MeNC ligands, as shown by its IR spectrum in CH\(_2\)Cl\(_2\) (2154, 1751 and 1110 cm\(^{-1}\)). Interconversion of the two forms is fairly slow, and the isomers can be resolved by column chromatography. However, in solutions containing substantial amounts of both forms, isomerization always proceeds so as to increase the proportion of the bridge-terminal isomer, so that the bis-terminal isomer is never obtained in pure form. The isomerization depicted below shows interconversion of the trans-bis-terminal isomer to the cis-bridge-terminal form. Similarly, the cis-bis-terminal form would be converted to the trans-bridge-terminal isomer. It can
be shown that, subject to the previously-mentioned restriction concerning the stabilities of possible non-bridged intermediates, these are the only two isomerization processes allowed this molecule by the AC mechanism. Stated briefly, bridge-terminal exchange of MeNC and CO ligands is permitted, but the same exchange of two MeNC ligands is not. As a consequence, the cis isomer of one of the forms (either bis-terminal or bridge-terminal) cannot be converted to the trans isomer of that same form.

The $^1$H NMR of $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CS})(\text{MeNC})_2$ in all solvents (Table 9) show four large peaks (3:3:5:5 ratio) for the predominant bridge-terminal isomer. The fact that separate sets of peaks for the cis and trans isomers are not observed can only be attributed to the virtual coincidence of these signals, since, as mentioned above, this isomerization probably does not occur at all (and hence cannot be rapid). The spectrum in $\text{C}_6\text{D}_6$ shows the same upfield shift of the terminal MeNC resonance and decrease in the separation of the Cp signals that was described above for the monosubstituted complex; however, the bridge MeNC peak is not much affected.

The foregoing observations are quite different from the results of a study of the carbonyl analog, $[\text{CpFe(CO)(MeNC)}]_2$. This molecule exists as a trans isomer with bridging and terminal MeNC ligands, and a cis isomer with two bridging isocyanides, which are formed in comparable amounts. Also in
contrast to the behavior of the thiocarbonyl analog, the
two predominant forms do not interconvert. These differences
further illustrate the remarkably strong preference of the CS
ligand for a bridge position.

S-Adducts of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \)

The relatively low stretching frequency of the CS group
in \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) indicates that the bridging thiocarbonyl
ligand is electron-rich. Since in other metal thiocarbonyls
such groups have been shown to form S-adducts, it was antici­
pated that the bridging CS would react similarly.

**Lewis acid adducts**

The thiocarbonyl complex reacts with \( \text{HgX}_2 \) (\( X = \text{Cl, Br, I} \))
in \( \text{CH}_2\text{Cl}_2 \) or acetone to give the S-adducts \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{HgX}_2 \).
These compounds are stable in the solid state, but their IR and
NMR spectra (Tables 8 and 9) can be observed only in the
presence of excess mercury (II) halide, owing to the lability
of the compounds in solution. The IR spectra show two terminal

\[
(33) \quad \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} + \text{HgX}_2 \rightarrow \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{HgX}_2
\]

CO bands and a bridging CO band, all at frequencies higher than
those of the free thiocarbonyl complex. This is the expected
result of adduct formation, since electron density is being
removed from the molecule through the coordinated CS group.
More interesting is the fact that the spectra closely resemble that of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) in \( \text{CH}_3\text{CN} \) (Figure 1), indicating that in the adduct the thiocarbonyl complex is almost entirely in the cis configuration. This appears to be true of all the S-adducts (and S-alkyl derivatives; see below) of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \). The deep red color of these compounds is also characteristic of all such derivatives. The CS absorption appears as a weak, rather broad band about 100 cm\(^{-1}\) lower than \( \nu_{\text{CS}} \) of the free thiocarbonyl.

The \(^1\text{H} \) NMR spectrum of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \cdot \text{HgCl}_2 \) (Table 9) shows a single Cp resonance. As would be expected, this peak occurs at lower field than the Cp resonance of the uncoordinated thiocarbonyl complex. However, the single peak is inconsistent with the anticipated non-linearity of the C-S-Hg group,\(^{73}\) which should result in non-equivalence of the Cp groups. Observation of one Cp resonance where two are expected is another characteristic of the spectra of all S-adducts of the thiocarbonyl complex, and probably results from a rapid dissociation-association process, as shown below. Alternatively, this process may

\[
\begin{align*}
\text{34) } & \quad \text{Fe} \quad \text{Fe} \\
& \quad \text{C} \quad \text{C} \\
& \quad \text{S} \quad \text{S} \\
& \quad \text{M} \quad \text{M}
\end{align*}
\]

be viewed as an inversion of the adduct group about the C-S bond, since this is of course the over-all result (see below).
The reaction of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2\) with \( \text{HgX}_2 \) may be contrasted to the corresponding reaction of \( \left[\text{CpFe}(\text{CO})_2\right]_2 \), which is cleaved to give \( \text{CpFe}(\text{CO})_2\text{X} \) and \( \text{CpFe}(\text{CO})_2\text{HgX} \). However, the carbonyl analog does react with certain Lewis acids, such as \( \text{BX}_3 \) (\( X = \text{Cl}, \text{Br}, \text{I} \)), to give isolable (though rather unstable) adducts on the bridging CO ligands. With \( \text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS} \), these reagents give S-adducts. These products could not be isolated, however, owing to a rapid secondary reaction that results in cleavage of the molecule, as shown by the disappearance of the bridging CO and CS bands in the IR spectrum. The decomposition products were not identified, but the relatively high position of the observed CO bands (>2050 cm\(^{-1}\)) suggests cationic, halide-bridged cyclopentadienyl iron carbonyl compounds.

The thermal reaction of \( \text{Cp}_2\text{Fe}_2(\text{CO})_2\) with \( \text{PtCl}_2(\text{PhCN})_2 \) in \( \text{CHCl}_3 \) gives a red solid, apparently \( \left[\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS}\right]_2\text{PtCl}_2 \). This product was not well characterized because of difficulties encountered in its purification, but the IR spectrum (Table 8) does suggest an S-adduct. Owing to the size of the thiocarbonyl "ligand", the arrangement of groups about the Pt atom presumably is trans.

Addition of \( \text{Ag}^+ \) to the thiocarbonyl complex in acetone causes a redox reaction rather than formation of an adduct. The product, a red oil, was not identified. This result is markedly different from the reaction of \( \text{W}(\text{CO})(\text{diphos})_2\text{CS} \) with \( \text{Ag}^+ \), which gives an S-adduct.
The thiocarbonyl complex does not react with MeHgCl. However, if the chloride is first abstracted with AgPF$_6$, the cationic derivative $[\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS-HgMe}]\text{PF}_6$ is formed. The IR and NMR spectra of this compound (Tables 8 and 9) are typical of the S-adducts.

Metal carbonyl adducts

Several S-adducts of $\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS}$ were obtained in which the adduct moiety is a metal carbonyl group. These compounds may also be viewed as metal carbonyl complexes in which the thiocarbonyl compound functions as a ligand.

The thiocarbonyl complex readily displaces the coordinated solvent of $\text{M(CO)}_5(\text{acetone})$ ($\text{M} = \text{Cr, W}$) to give the red-purple, air-stable derivatives $\text{Cp}_2\text{Fe}_2(\text{CO})_2\text{CS-M(CO)}_5$. Similar reactions with $\text{Mo(CO)}_5(\text{acetone})$ and $\text{W(CO)}_4(\text{CS})(\text{acetone})$ gave evidence of adduct formation, but the products were stable only at low temperatures. In the former case this is probably a result of the generally lower stability of $\text{Mo(CO)}_5\text{L}$ complexes, while in the latter instance the instability is possibly attributable to the high trans-labilizing ability of
The IR spectra of the M(CO)$_5$ adducts (Table 8), as might be expected, resemble the spectrum of a non-carbonyl 
Cp$_2$Fe$_2$(CO)$_3$CS adduct (e.g., the HgCl$_2$ complex) superimposed on that of an M(CO)$_5$L compound. The NMR spectra (Table 9), like that of the HgCl$_2$ adduct, show only one Cp resonance.

Reaction of Cp$_2$Fe$_2$(CO)$_3$CS with [CpFe(CO)$_2$(THF)]BF$_4$ gives the stable cationic adduct [Cp$_2$Fe$_2$(CO)$_3$CS•CpFe(CO)$_2$]BF$_4$. The

\[ \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} + \text{CpFe(CO)}_2(\text{THF})^+ \xrightarrow{\text{THF}} [\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS•CpFe(CO)}_2]^+ \]

thiocarbonyl analog [Cp$_2$Fe$_2$(CO)$_3$CS•CpFe(CO)(CS)]CF$_3$SO$_3$, which is somewhat air-sensitive, can be obtained by a similar method from Cp$_2$Fe$_2$(CO)$_3$CS and CpFe(CO)(CS)CF$_3$SO$_3$. (A report on the utility of CpFe(CO)(CS)CF$_3$SO$_3$ in the synthesis of CpFe(CO)(CS)L$^+$ compounds is forthcoming.) The spectra of these complexes (Tables 8 and 9) are consistent with the proposed formulations.

Formation of metal carbonyl adducts does not, however, appear to be a general property of Cp$_2$Fe$_2$(CO)$_3$CS. Several other metal carbonyl species which normally undergo facile CO substitution, such as CpFe(CO)$_2$Cl, Mn(CO)$_5$Br, Fe(CO)$_4$(THF) and Re(CO)$_5$(CH$_3$CN)$^+$ either failed to react or gave unstable products.
**Displacement reactions of the S-adducts**

As was mentioned above, the HgX₂ adducts dissociate spontaneously in the absence of excess HgX₂. The other adducts are also labile in the presence of most ligands. Addition of $X^-$ to a solution of [Cp₂Fe₂(CO)₃CS-HgMe]⁺ results in slow conversion of the complex to MeHgX and free thiocarbonyl. The other adducts react when warmed with $X^-$ in acetone; for example, Cp₂Fe₂(CO)₃CS·W(CO)₅ gives free thiocarbonyl and W(CO)₅X⁻. The metal carbonyl adducts also react slowly at room temperature with almost any donor ligand (e.g., PPh₃ and py) to give Cp₂Fe₂(CO)₃CS and the corresponding ligand-substituted carbonyl complex. A particularly interesting reaction is that of N₃⁻ with [Cp₂Fe₂(CO)₃CS·CpFe(CO)(CX)]⁺ (X = O, S), in which displacement of the adduct group occurs, giving CpFe(CO)(CX)N₃, rather than, as might be expected, attack at a CO or CS ligand of the cationic moiety.⁶⁸⁻⁷¹ Evidently the thiocarbonyl complex is a rather weakly-coordinating "ligand", which may explain its failure to form stable adducts with many metal carbonyls.

**S-Alkyl Derivatives of Cp₂Fe₂(CO)₃CS**

**General comments**

Several thiocarbonyl complexes are known to undergo S-alkylation,⁶¹ including the CS-bridged compound [CpFe(CO)(CS)]₂,⁷³ which is closely related to Cp₂Fe₂(CO)₃CS.
Such reactions are particularly interesting since they are almost unprecedented in metal carbonyl chemistry, there being only one report in the literature of the alkylation of a bridging carbonyl ligand. Therefore, the reactivity of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) toward numerous alkylation agents was investigated.

The thiocarbonyl compound does not react with alkyl chlorides, most alkyl bromides, or secondary and tertiary alkyl iodides. However, primary iodides and unusually reactive primary bromides (e.g., benzyl) react, as do strong alkylation agents such as alkyl fluorosulfonates. The \( S\)-alkyl derivatives obtained proved to be quite interesting compounds for a number of reasons, which will now be discussed.

**Preparation and properties**

The reaction of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) with alkyl iodides or benzyl bromide in \( \text{CH}_2\text{Cl}_2 \) solution is rather slow. In the latter case the reaction does not go to completion, owing to the lability of the product in the presence of halide ions (see below).

\[
\text{(37) } \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} + \text{BzBr} \quad \text{CH}_2\text{Cl}_2 \quad [\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Bz}]^+ + \text{Br}^- 
\]

However, if the alkyl halide itself is used as the reaction solvent, reaction proceeds much more rapidly to give high yields. The halide salts obtained are solids that do not crystallize.
well, but a simple ion exchange procedure gives the more easily purified $PF_6^-$ salts. The observed order of reactivity for R-I is Me $\gg$ Et $>$ Pr, Bu.

\[
(38) \quad [\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}^\text{R}]^{\text{PF}_6^-} \quad \text{neat R-I} \quad [\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-R}]^{\text{I}} \quad \text{PF}_6^- \quad [\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-R}]^{\text{PF}_6^-}
\]

The best method for preparation of the Me and Et derivatives is reaction with methyl or ethyl fluorosulfonate in CH$_2$Cl$_2$. These compounds are easily purified as the $\text{FSO}_3^-$ salts, but as this anion has IR absorptions in the CS region it is advantageous to carry out $PF_6^-$ exchange. In the case of the substitution products $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{L})\text{CS-R}]\text{FSO}_3$ (see below), the ion exchange is more conveniently accomplished after the substitution, owing to the much greater solubility of these derivatives.

The S-alkyl compounds $[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-R}]\text{PF}_6$ are red, microcrystalline solids that are air-stable both in the solid state and in solution. The Me and Et derivatives are slightly water-soluble, sparingly soluble in CH$_2$Cl$_2$, but somewhat more soluble in acetone and CH$_3$CN. The solubilities are much higher when R...
well, but a simple ion exchange procedure gives the more easily purified PF$_6^-$ salts. The observed order of reactivity for R-I is Me $\gg$ Et $>$ Pr, Bu.

\[
(38) \quad \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \xrightarrow{\text{neat R-I}} [\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-R}]\text{I} \xrightarrow{\text{PF}_6^-} [\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-R}]\text{PF}_6
\]

The best method for preparation of the Me and Et derivatives is reaction with methyl or ethyl fluorosulfonate in CH$_2$Cl$_2$. These compounds are easily purified as the FSO$_3^-$ salts, but as this anion has IR absorptions in the CS region it is advantageous to carry out PF$_6^-$ exchange. In the case of the

\[
(39) \quad \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} + \text{ROSO}_2\text{F} \xrightarrow{\text{CH}_2\text{Cl}_2} [\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-R}]\text{FSO}_3
\]

substitution products [Cp$_2$Fe$_2$(CO)$_2$(L)CS-R]FSO$_3$ (see below), the ion exchange is more conveniently accomplished after the substitution, owing to the much greater solubility of these derivatives.

The S-alkyl compounds [Cp$_2$Fe$_2$(CO)$_2$(CS-R)PF$_6$ are red, microcrystalline solids that are air-stable both in the solid state and in solution. The Me and Et derivatives are slightly water-soluble, sparingly soluble in CH$_2$Cl$_2$, but somewhat more soluble in acetone and CH$_3$CN. The solubilities are much higher when R
is a larger group, particularly for \( R = \text{All and Bz} \). Conductivity measurements verify that the compounds are 1:1 electrolytes in nitromethane.\(^8\)

**Spectra and structure**

The IR spectra of the S-alkyl derivatives (Table 8) all show a characteristic three-band pattern in the CO region, the relative intensities of these bands being strong-weak-medium. These spectra strongly resemble the IR of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) in \( \text{CH}_3\text{CN} \), except that the bands occur at somewhat higher frequencies owing to the cationic nature of the compounds. This band pattern indicates that the S-alkyl compounds are all cis isomers. Interestingly, the same products are obtained even if the alkylation is carried out in a solvent such as benzene or \( \text{CCl}_4 \) in which a substantial amount of trans-\( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) is present. Infrared spectra of the S-alkyl compounds in \( \text{CHCl}_3, \text{CH}_2\text{Cl}_2 \) and \( \text{CH}_3\text{CN} \) are very similar, indicating that the compounds do not undergo cis-trans isomerization. Thus, it must be concluded that only the cis isomer of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) reacts with alkylation agents. It may be recalled that the S-adducts of the thiocarbonyl also appear to be cis isomers. Evidently the more polar cis isomer of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) is also the more nucleophilic, as the reason for the cis preference is not apparent from steric considerations.

The CS stretching frequency of the CS-R\(^+\) bridging group
occurs as a rather broad, weak band. Characteristically it is \(\sim 100 \text{ cm}^{-1}\) lower than the corresponding band in \(\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\), as was also found for the S-adducts discussed above.

Before the present work, the only known compound with an alkylated bridging thiocarbonyl ligand was the methylated bis-thiocarbonyl complex \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})\text{CS-Me}]\text{FSO}_3\).\(^7\) The \(^1\text{H NMR}\) spectrum of this compound shows two Cp resonances, showing that the C-S-Me group is non-linear. In contrast, the NMR spectra of \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})\text{R}]\text{PF}_6\) (Table 9) in general contain only one Cp peak, though this peak is often somewhat broad. Only in cases where the R group is relatively large and rigid (\(R = \text{Bz}, \text{CH}_{2}\text{I}\)) are distinct Cp resonances observed at ambient temperatures. The effect of increasing temperature on the spectrum of the S-benzyl derivative is shown in Figure 4. (Temperatures shown in the Figure are approximate; coalescence of the Cp signals actually occurs at about 48°.) The coalescence of the Cp peaks can be attributed to inversion of the alkyl group about the C-S bond, resulting in equivalence of the Cp ligands.

The analogous process is known to occur in bridging isocyanide ligands,\(^1\) but is much faster. Apparently, for most of the S-alkyl compounds this inversion is just becoming rapid near
Figure 4. Variable-temperature $^1$H NMR spectrum of the complex $[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Bz}]\text{PF}_6$ in CD$_3$CN (Varian HA-100).
room temperature, so that only a single, slightly broadened Cp resonance is observed.

Another interesting feature of these NMR spectra is the position of the Me resonance of the bridging CS-Me ligand. This peak typically occurs at $\sim \delta 3.5-3.7$, and thus has the same chemical shift relationship with the terminal CS-Me ligand (e.g., $\delta 2.53$ for CpFe(CO)CS-Me; see above) that is observed for bridging and terminal MeNC ligands.$^{129,131}$

Carbon-13 NMR spectra of the S-methyl and S-benzyl complexes (Table 10) show two Cp resonances. For the Bz derivative, the Cp peaks broaden as the temperature is raised and coalesce at about 45°. More interesting, however, is the very low-field position of the thiocarbonyl carbon resonance ($\sim \delta 403$ ppm), which is even lower than that found for the parent thiocarbonyl ($\sim \delta 380$). In this respect the bridging CS ligand differs greatly from electron-rich terminal thiocarboxyls. For example, in $\text{W(CO)}_4\text{CS}^-$ the thiocarbonyl carbon resonance undergoes an upfield shift of about the same magnitude upon alkylation of the S atom.$^{61}$ Carbon-13 NMR data for a terminal thiocarbonyl complex, CpFe(CO)(CS)SnPh$_3$, and the carbene compound [CpFe(CO)$_2$C(OMe)$_2$]PF$_6$ are shown in Table 10 for comparison.
Table 10. $^{13}$C NMR chemical shifts (ppm) for cyclopentadienyl iron carbonyl and thiocarbonyl complexes in $d_6$-acetone solution

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ (Cp)</th>
<th>$\delta$ (R)</th>
<th>$\delta$ (CO)</th>
<th>$\delta$ (CS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[{CpFe(CO)}$_2$(OMe)$_2$]PF$_6$</td>
<td>85.0</td>
<td>248.6 (carbene C)</td>
<td>207.0</td>
<td>---</td>
</tr>
<tr>
<td>CpFe(CO)(CS)SnPh$_3$</td>
<td>84.4</td>
<td>127.6, 136.1,</td>
<td>213.9</td>
<td>314.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>142.9 (Ph)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[{Cp$_2$Fe$_2$(CO)}$_3$CS-Me]PF$_6$</td>
<td>89.8, 90.5</td>
<td>83.0 (Me)</td>
<td>249.6$^b$</td>
<td>---</td>
</tr>
<tr>
<td>[{Cp$_2$Fe$_2$(CO)}$_3$CS-Bz]PF$_6$</td>
<td>92.3, 92.9</td>
<td>60.7 (CH$_2$),</td>
<td>207.4$^c$,</td>
<td>403.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>129.6, 130.2,</td>
<td>251.6$^b$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>133.9 (Ph)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp$_2$Fe$_2$(CO)$_2$(CS)PET$_3$ $^a$</td>
<td>88.5, 89.7</td>
<td>7.17 (Et),</td>
<td>216.8$^c$,</td>
<td>396.2 (d)$^e$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.3 (d, Et)$^d$</td>
<td>278.3 (d)$^b,c$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$CDC$_3$ solution.

$^b$Bridging CO.

$^c$Terminal CO.

$^d$J$_{PCH}$ = 23.8 Hz.

$^e$J$_{PFeC}$ = 14.9 Hz.
Table 10. (Continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \delta \text{ Cp} )</th>
<th>( \delta \text{ R} )</th>
<th>( \delta \text{ CO} )</th>
<th>( \delta \text{ CS} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{PET}_3)\text{CS-Me})\text{PF}_6]</td>
<td>88.3(^f)</td>
<td>5.70 (Et), 17.1 (d, Et)(^g)</td>
<td>213.4(^c), 256.4 (d)(^b, h)</td>
<td>407.9 (d)(^h)</td>
</tr>
</tbody>
</table>

\(^{f}\) Center of two peaks.

\(^{g}\) \(J_{\text{PCH}} = 28.3\) Hz.

\(^{h}\) \(J_{\text{PFc}}\) not obtained.
Crystal structure of $\text{[Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Et}]\text{BF}_4$  

In order to verify the cis structure proposed for the S-alkyl compounds, an X-ray crystal structure of the complex $\text{[Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Et}]\text{BF}_4$ was undertaken. Complete details of the structure determination are given in a recent paper. A computer-generated drawing of the molecule is shown in Figure 5. It is found that the bonding parameters not directly associated with the bridge structure are very similar to those in the related molecules cis-$\text{[CpFe(CO)(CS)]}_2$ and cis-$\text{[CpFe(CO)]}_2$. The Fe-Fe bond distance is 2.510 Å, which is between those found in the above molecules (2.482 Å and 2.531 Å, respectively). Bond distances and angles associated with the portion of the molecule that is significantly affected by the CS-Et$^+$ group are shown in Figure 6; the numbers in brackets in the Figure are the corresponding values for $\text{[CpFe(CO)(CS)]}_2$. Addition of Et$^+$ to the bridging CS group lengthens the C-S bond (1.666 Å) from its value in the bis-thiocarbonyl complex (average of 1.590 Å). This presumably results from reduced C-S $\pi$-bonding, which promotes Fe-C $\pi$-bonding, giving the shortened Fe-C distances observed.

Fischer, et al., have described bridging carbyne ligands. If there were no $\pi$-bonding in the C(4)-S bond of the CS-Et$^+$ group, this ligand could be considered a bridging carbyne. However, the C(4)-S distance compares to that of a
Nevertheless, there is significant Fe-C(4) \(\pi\)-bonding, as indicated by the 1.840 and 1.828 Å bond lengths compared to the normal Fe-C bond distance of 2.0-2.1 Å. The CS-R\(^+\) group may be regarded as electronically equivalent to an NO\(^+\) ligand (i.e., 3-electron donor) and structurally equivalent to a bridging isocyanide ligand. However, while several complexes containing a terminal CS-R ligand are known, \(^{61,118}\) there is no evidence that the bridging ligand in \([\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-R}]^+\) compounds can shift to a terminal position.

It is worth noting that substitution of PE\(\text{t}_3\) for CO, as in \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})\text{PEt}_3\), produces about the same effect on the \(^{13}\text{C}\) chemical shift of the bridging CS ligand as does alkylation of the thiocarbonyl sulfur (Table 10). As noted above, alkylation increases the Fe-C \(\pi\)-bonding in the bridging CS group; addition of a donor ligand to the unalkylated molecule would be expected to produce the same result. It appears that this effect is responsible for the larger \(^{13}\text{C}\) shifts observed for these derivatives of \(\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\). In this respect the response of the bridging CS ligand is similar to that of bridging and terminal carbonyls.\(^{145}\)

**Alkylation of substituted derivatives**

The substituted complexes \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})L\) (\(L = \text{PR}_3\)) also react with the above alkylating agents to give the S-alkyl
Figure 5. Computer-generated drawing of $[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Et}]^+$. 
Figure 6. Bond distances and angles in $[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Et}]^+$ affected by the CS-Et ligand.
compounds $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{L})\text{CS-R}]^+$. In fact, these reactions are considerably faster than the corresponding alkylations of the unsubstituted thiocarbonyl complex, presumably because the greater electron density provided by the donor ligand increases the nucleophilicity of the thiocarbonyl sulfur. These compounds are brown, slightly air-sensitive solids that dissolve in polar organic solvents to give yellow-green solutions. Infrared and $^1$H NMR data for these derivatives in Tables 8 and 9. The $^{13}$C NMR data for the PEt$_3$ compound show the expected very low field thiocarbonyl carbon resonance.

The reaction of MeI with $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{MeNC})$ gives the red-brown species $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{MeNC})\text{CS-Me}]^+$. In contrast, the carbonyl analog gives $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{Me}_2\text{NC})]^+$, which contains an alkylated bridging isocyanide. Presumably the alkylation occurs at S in the former instance because, as discussed above, the bridge position is less accessible to the isocyanide ligand in the thiocarbonyl complex.

Alkylation of the bridge-terminal isomer of the bis-isocyanide complex $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CS})(\text{MeNC})_2$ is even more interesting. Reaction of this compound with MeI in CH$_2$Cl$_2$ gives the S-methyl derivative of the bis-terminal isomer, whereas
reaction with MeOSO$_2$F results in alkylation of both the CS ligand and a bridging isocyanide. The identities of these

(42) $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CS})(\text{MeNC})_2$ $\xrightarrow{\text{MeI}} [\text{Cp}_2\text{Fe}_2(\text{CO})(\text{MeNC})_2\text{CS-Me}]^+$
(bridge-terminal) $\text{CH}_2\text{Cl}_2$
(bis-terminal)

(43) $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CS})(\text{MeNC})_2$ $\xrightarrow{\text{MeOSO}_2\text{F}} [\text{Cp}_2\text{Fe}_2(\text{CO})(\text{MeNC})(\text{Me}_2\text{NC})\text{CS-Me}]^{2+}$

products were ascertained from their IR and $^1$H NMR spectra, and from a conductivity measurement that showed the latter compound to be a 1:2 electrolyte. Apparently the bridge-terminal isomer is less nucleophilic than the bis-terminal isomer, and so rearranges to the latter form before reacting with the weaker electrophile MeI, whereas the stronger alkylation agent MeOSO$_2$F reacts immediately at either S or N and thus locks the molecule into a form which can undergo a second alkylation.

Both of these compounds are brown, air-stable solids. The monoalkyl complex dissolves in polar organic solvents to form brown solutions; the dialkyl derivative is insoluble in CH$_2$Cl$_2$, but dissolves in acetone and CH$_3$CN, giving greenish-brown solutions, and is also slightly water-soluble. Infrared and $^1$H NMR data for these compounds are given in Tables 8 and 9.
Substitution reactions

The S-alkyl derivatives $[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-R}]^+ \ (R = \text{Me, Et})$ undergo ligand substitution reactions somewhat more readily than does the parent thiocarbonyl complex, possibly because the increased Fe-C π-bonding to the bridging CS-R⁺ ligand weakens the terminal Fe-CO bonds to some extent. Some of the same products can, of course be obtained as discussed above, but the greater reactivity of the S-alkyl compounds affords a wider range of substitution products than is accessible by the other method.

Very basic phosphines react rapidly with $[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-R}]^+$ at room temperature in THF, acetone, CH₃CN or MeNO₂. Other ligands, such as PMePh₂, P(OMe)₃, MeNC and pyridine also react, but require heating. Surprisingly, PhNC, which does not react at all with $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$, gives the bis-isocyanide derivative, as shown by its $^1\text{H}$ NMR spectrum (Table 9) which contains only one Cp resonance. Extended reflux with other ligands in

(44) $[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Me}]^+ + \text{P} \text{Et}_3 \xrightarrow{\text{CH}_3\text{CN}} \xrightarrow{\text{RT}} [\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{P} \text{Et}_3)\text{CS-Me}]^+ + \text{CO}$

(45) $[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Me}]^+ + 2 \text{PhNC} \xrightarrow{\text{CH}_2\text{CN}} \xrightarrow{\text{reflux}} [\text{Cp}_2\text{Fe}_2(\text{CO})(\text{PhNC})_2\text{CS-Me}]^+ + 2 \text{CO}$
CH$_3$CN results in decomposition rather than disubstitution.

Even halide ions react, giving the interesting compounds Cp$_2$Fe$_2$(CO)$_2$(CS-Me)X. Although formally neutral, these derivatives appear to be dipolar, as they are soluble only in polar organic solvents. The reason for the observed order of reactivity, Cl>$\text{Br}>$I, is not evident. It is also unclear why reaction 46 below, which is the best method for preparation

\[
(46) \quad \text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS-Me})_2 \xrightarrow{\text{MeI, NaI, CH}_3\text{CN, reflux}} \text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS-Me})\text{I}
\]

of the iodo compound, is faster than the direct reaction of [Cp$_2$Fe$_2$(CO)$_3$CS-Me]$^+$ with NaI.

Other ligands, such as PPh$_3$ and P(OPh)$_3$, do not react. However, even these derivatives can be obtained by taking advantage of the lability of the iodide in the above compound, as shown in reaction 47. Undoubtedly this reaction

\[
(47) \quad \text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS-Me})\text{I} \xrightarrow{1) \text{Ag}^+, 2) \text{PPh}_3} [\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{PPh}_3)\text{CS-Me}]^+ + \text{AgI}
\]

could be used to prepare analogous complexes of any other donor ligands which do not react directly with the S-alkyl compound.

Infrared and $^1$H NMR data for the above compounds are shown in Tables 8 and 9.
It should be noted that substituted \textit{S-benzyl} derivatives \textbf{must} be prepared from BzBr and the appropriate \( \text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})L \) compound. The \textit{CS-Bz} group is labile in the presence of halide ions, tertiary amines and other donor ligands. Therefore, the reaction of \( [\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Bz}]^+ \) with any of the above ligands results in de-alkylation rather than replacement of \textit{CO}. The \textit{S-allyl} compound reacts similarly. The more facile dissociation of these alkyl groups thus parallels the unusually high reactivity observed for allylic and benzylic halides.

\textbf{Reaction with nucleophiles}

The \textit{CS-Me} group appears to be susceptible to nucleophilic attack, as might be expected because of its cationic nature. Reaction of \( [\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Me}]^+ \) with NaOMe in MeOH rapidly converts the \textit{S-methyl} thiocarbonyl to \( [\text{CpFe} \text{(CO)}_2]_2 \). Presumably

\begin{equation}
(48) \quad \begin{array}{c}
\text{Fe} \\
\text{C} \\
\text{S} \\
\text{Me}
\end{array}
+ \text{MeO}^- \quad \rightarrow \quad \begin{array}{c}
\text{Fe} \\
\text{C} \\
\text{SMe}
\end{array}
\quad \rightarrow \quad \begin{array}{c}
\text{Fe} \\
\text{C} \\
\text{O}
\end{array}
\quad + \text{Me}_2\text{S}
\end{equation}

this reaction occurs \textbf{via} the neutral carbene-like intermediate shown above. The other proposed product, \textit{Me}_2\text{S}, was not isolated, but the analogous reaction with aqueous NaOH definitely produces \textit{MeSH}, as would be required by the above mechanism.

In other cases the results are less clear. For example,
in the reaction of the same compound with MeNH₂, attack evidently occurs at the CS-Me⁺ ligand, since the characteristic weak IR band at ~1020 cm⁻¹ disappears immediately. Yet the IR spectrum of the final product (1942 vs, 1768 s, 1641 m) suggests that reaction has occurred at a terminal CO ligand, possibly to form a carbamoyl compound.¹⁴⁷ Unfortunately, the instability of this product prevented its further characterization. Additional study is needed to determine the generality of such reactions and the nature of the products obtained.

Other Attempted Reactions of Cp₂Fe₂(CO)₃CS

With nucleophiles

Unlike the terminal CS ligands in some thiocarbonyl complexes,⁶⁸,⁶⁹ the bridging thiocarbonyl in Cp₂Fe₂(CO)₃CS is unreactive toward common nucleophiles such as MeO⁻, MeNH₂ and N₃⁻. However, the reactivity of terminal CS groups toward nucleophiles may be ascribed in part to the weakness of the C-S π-bonding.³² As discussed previously, this weakness in the π-bonding probably also accounts for the strong tendency of the CS ligand to bridge when possible. Hence, the formation of a bridging thiocarbonyl may remove most of the driving force for reaction with nucleophiles.

Methyllithium does react with Cp₂Fe₂(CO)₃CS, but the IR spectrum of the rather unstable product obtained (1946 vs, 1777 s) suggests that the MeLi attacks a terminal CO rather
than the CS group, possibly to give \([\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})\text{C}(\text{O})\text{Me}]^-\). However, subsequent alkylation fails to give a neutral carbene derivative,\(^{110}\) and thus the identity of the initial product remains unclear.

The thiocarbonyl also reacts with KCN in refluxing CH\(_3\)CN, apparently to give a ionic cleavage product. This product was not identified, but could be a thiocarbonyl analog of the known complex K\([\text{CpFe(CO)(CN)}]_2\),\(^{148}\) which was obtained from the carbonyl analog \([\text{CpFe(CC)}]_2\) in a similar manner. With other electrophiles

Numerous attempts to form a protonated or acetylated derivative of \([\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}]\) failed to give isolable products. The desired compounds could be detected by IR in solution, but appeared to be very labile. Additionally, the S-acetyl compound seems to be unstable toward decarbonylation to the S-methyl complex, \([\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-Me}]^+\). Acetyl derivatives of electron-rich terminal CS groups can be isolated,\(^{61}\) and it is not clear why this is not also true of the thiocarbonyl-bridged complex.

It was hoped that reactive small-ring compounds such as thiirane\(^{149}\) would add to the CS group of \([\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}]\) to give bridged carbene-like derivatives. However, no such reaction is observed, presumably because the thiocarbonyl sulfur is insufficiently nucleophilic to cause ring-opening.
Reaction of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$ with an equimolar amount of $\text{ICH}_2\text{COOH}$ in $\text{CH}_2\text{Cl}_2$ gives the interesting $S$-alkyl compound $'[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}=\text{CH}_2\text{COOH}]^+$'. The compound normally is soluble only in the most polar organic solvents, but dissolves in $\text{CH}_2\text{Cl}_2$ in the presence of excess $\text{ICH}_2\text{COOH}$ or other carboxylic acid. Apparently the compound exists as a hydrogen-bonded dimeric di-cation, which dissociates by interaction with either a very polar solvent or another organic acid. A somewhat

\[
\text{ICH}_2\text{COOH} + \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \rightarrow [\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}=\text{CH}_2\text{COOH}]^+.
\]

similar compound, $[\text{Cp}_2\text{Fe}(\text{CO})_2\text{CH}_2\text{COOH}]_2$, has been reported.\textsuperscript{150} Reaction of the $S$-carboxymethyl compound with $\text{Et}_2\text{N}$ in $\text{CH}_3\text{CN}$ in an attempt to form a deprotonated, dipolar species gave instead a product that was identified by its IR spectrum as $[\text{CpFe(}\text{CO})_2\text{]}_2$. Apparently a carboxylate oxygen is transferred to the bridging group, possibly via a cyclic carbene-like intermediate similar to that proposed in reaction 48. The organic products of this reaction were not identified.
Conclusion

The research described above is the first thorough investigation of the chemistry of a thiocarbonyl-bridged complex. As with almost any research project, some of the results obtained were anticipated, while others were unexpected and leave some unanswered questions. In any case, it is evident that introduction of the CS ligand into a bridge position has a pronounced effect on the chemical behavior of a metal thiocarbonyl compound, as well as on the characteristic reactivity of the thiocarbonyl ligand itself.

Certain aspects of the chemistry of Cp₂Fe₂(CO)₃CS — such as reactions of the S-alkyl derivatives with nucleophiles, and reactions of the anion CpFe(CO)(CS)⁻ — probably deserve more thorough investigation. But beyond this, it is hoped that the present research will stimulate further efforts toward the preparation of new types of thiocarbonyl complexes. In particular, it would be
interesting to determine if other, presently unknown, bi-nuclear metal thiocarbonyls, such as \( \text{Mn}_2(\text{CO})_9\text{CS} \) or \([\text{CpW(CO)}_2\text{CS}]_2\), would be isostructural with their CO analogs or, as the results of the present research would suggest, CS-bridged. It is likely that the information obtained in the study of \( \text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS} \) will prove useful in the investigation of such compounds.
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