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Thiocarbonyl complexes of iron

Jan Wallace Dunker
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THIOCARBONYL COMPLEXES OF IRON

Iowa State University

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Thiocarbonyl complexes of iron

by

Jan Wallace Dunker

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

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1981

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LIST OF SYMBOLS AND ABBREVIATIONS

acac	acetylacetonato ligand
arene	η^6 -arene ligand
bipy	2,2'-bipyridine
Bu	butyl
Cp	η^5 -cyclopentadienyl ligand
diphos	1,2-bis(diphenylphosphine)ethane
Et	ethyl
L	a donor ligand
L-L	a bidentate donor ligand
M	a metal atom
Me	methyl
phen	1,10-phenanthroline
ϕ	phenyl
py	pyridine
R	an organic substituent group
S	a coordinating solvent molecule
THF	tetrahydrofuran
TMS	tetramethylsilane
X	a halogen or a uninegative anion

I. INTRODUCTION

The first thiocarbonyl complex was reported by Baird and Wilkinson in 1966 (1). In the intervening years, the area of thiocarbonyl chemistry has blossomed, and indeed now over 100 compounds containing the thiocarbonyl, CS, ligand have been prepared. The first carbonyl complex, $[\text{Pt}(\text{CO})\text{Cl}_2]_2$, was reported in 1868 (2), almost a full century prior to the discovery of the first thiocarbonyl complex. And the chemistry of carbonyl complexes is extensive.

Why then, was there this disparity in the time of discovery, and also in the number of compounds, between carbonyl, CO, and thiocarbonyl, CS, complexes? The thiocarbonyl ligand is a simple permutation of the carbonyl ligand, and is isoelectronic and isomorphous with it. However, the properties of carbon monoxide and carbon monosulfide, the natural precursors of carbonyl and thiocarbonyl complexes, are strikingly different. Whereas carbon monoxide is a stable gas at ordinary temperatures and pressures, and thus can be readily used in synthetic procedures, carbon monosulfide is unstable under these conditions. And therein lies the crux of the disparity. Thiocarbonyl complexes must be prepared by indirect methods.

II. REVIEW OF THE LITERATURE

This review of the literature is not intended to be comprehensive. There have been several fairly recent reviews of the chemistry of thiocarbonyl complexes (3,4,5) which extensively cover the early work. Therefore, the literature coverage herein is intended to be merely representative, with particular emphasis on the recent literature.

Before the chemistry of thiocarbonyl complexes is discussed, it may be fruitful to examine some of the properties of carbon monosulfide.

A. Carbon Monosulfide

Carbon monosulfide was first discovered in 1910 (6), produced from gaseous CS_2 by high-frequency discharge. In the intervening years, there have been numerous spectroscopic studies of the CS molecule; however, it is only relatively recently that quantities sufficient to study the chemical properties of CS have been generated (7,8).

Carbon monosulfide has been generally generated from CS_2 by 1) pyrolysis, 2) thermal decomposition, or 3) electrical discharge (9). It has also been produced from CS_2 by other methods such as reaction with O(10) or S(11) atoms, or with Ar and Xe metastable atoms (12). It has also been produced from other sources, such as COS and Cl_2CS . Carbon monosulfide has been found in the upper atmosphere (13) and in interstellar space (14).

Carbon monosulfide can be condensed at -190°C (along with CS_2 and C_3S_2) from the product of the high-frequency discharge of CS_2 . It is

relatively stable at this temperature; however, upon warming it "polymerizes" (sometimes explosively). The product of this "polymerization" is not a simple $(CS)_n$ polymer -- CS can disproportionate to C_3S_2 and S -- but appears to be carbon rich. The stability of carbon monosulfide is quite variable, depending among other things on the partial pressure, temperature, dimensions of the vessel, and the surface condition of the vessel (15). Lifetimes of a few minutes are attained in clean vessels, but once a wall coating forms, the lifetime is reduced drastically.

Although carbon monosulfide is unstable, spectroscopic studies have determined a few of its molecular properties, some of which are given in Table 1 (along with the corresponding values for carbon monoxide).

Table 1. Selected molecular properties of CS and CO

Property	CS	Reference	CO	Reference
Dipole Moment, μ , (D, -CS +)	1.958	(15, 17)	0.112	(16)
Internuclear Distance, (\AA)	1.535	(18)	1.128	(19)
$\nu(CX)$, (cm^{-1})	1274	($^{12}\text{C}^{32}\text{S}$) (7)	2143	(19)
Force Constant (mdyne/\AA)	8.4	(7)	19.0	(19)
Dissociation Energy, D (kcal/mole)	166	(11)	256	(20)
Ionization Potential, (eV)	11.34	(21)	14.01	(19)
Bond Order	2.2	(7)	3	

The chemical reactions of carbon monosulfide have been studied somewhat, since methods to isolate macroscopic quantities of CS have been developed. Carbon monosulfide reacts with halogens in stoichiometric amounts to form SCX_2 ($X = Cl, Br, I$) (7). With excess halogen, X_3CSX ($X = Cl, Br$) is formed (8). Carbon monosulfide will also react with Se and Te to form $SCSe$ and $SCTe$ (22), respectively, and with HCl and HBr to form $HXCS$, which rapidly trimerizes (8). The reaction between atomic oxygen and CS produces vibrationally excited CO (23), which is the basis for the CO chemical laser.

The chemical behavior of carbon monosulfide has been described as that of a weak Lewis base (8), which seems to fit better than its previous description as an electrophilic carbene (7).

B. Thiocarbonyl Complexes

1. Metal-thiocarbonyl bonding

Molecular orbital calculations on the CS molecule (24) have indicated that CS is both a better π -acceptor, because of the lower energy of the CS π^* orbitals, and a better σ donor than CO. Molecular orbital calculations have also been performed on the thiocarbonyl complexes $Cr(CO)_5CS$ and $CpMn(CO)_2CS$, and compared to their photoelectron spectra (25). The studies indicate that in addition to serving as a σ -donor and π -acceptor CS may also serve as a π -donor.

Spectroscopic studies have been conducted to investigate the nature and strength of the metal-thiocarbonyl bond. A Mössbauer study of the $[CpFe(CO)_2(L)]^+$ complexes (26) has indicated that CS is a better

π -acceptor than CO. The integrated infrared intensities of $\text{CpMn(CO)}_2(\text{CS})$ (27) also indicate that CS is a better π -acceptor. A comparison of the infrared stretching frequencies and force constants for numerous metal thiocarbonyl complexes and their carbonyl analogs suggests that the π -acceptor to $(\sigma+\pi)$ -donor ratio varies more for CS than for CO (28).

Carbon-13 NMR resonances of the CS ligand in metal thiocarbonyl complexes (29,30,31) occur at extremely low field, -288 to -337 ppm downfield from TMS. This low chemical shift has been explained in terms of a $\delta^+ \text{-C}=\text{S}^{\delta-}$ resonance structure stabilized by metal-thiocarbonyl π back-bonding (29). Another feature of the carbon-13 NMR spectra is the upfield shift of the CO resonances in metal-thiocarbonyl (carbonyl) complexes. This contrasts with the normal downfield shift which occurs when CO is substituted by other ligands, *i.e.*, PR_3 and P(OR)_3 , and offers further evidence that CS is a better π -acceptor than CO.

Mass spectra of metal-thiocarbonyl complexes offer further evidence that the M-CS bond is stronger than the M-CO bond (32,33). The CS ligand is among the last fragments to be cleaved from the metal atom, and it occurs only after cleavage of the CO ligands.

The X-ray crystal structures of a few metal-thiocarbonyl complexes containing terminal (34) and ketonic-bridging (35,36) thiocarbonyl ligands here have been determined. In general, the M-CX distances in terminal thiocarbonyl ligands are shorter than M-CO distances, indicative of a stronger metal-ligand bond. In the case of the bridging-thiocarbonyl complexes, the shortening of the metal-metal

distance compared to that in the analogous carbonyl complex argues for increased metal-CS interaction.

Thus, all the evidence indicates that CS does form stronger M-CX bonds than CO.

2. Synthesis of thiocarbonyl complexes

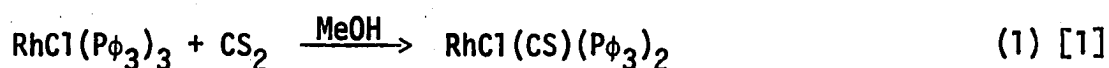
a. Thiocarbonyl complexes from free carbon monosulfide, CS

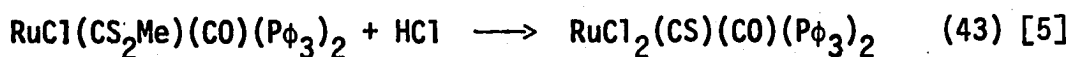
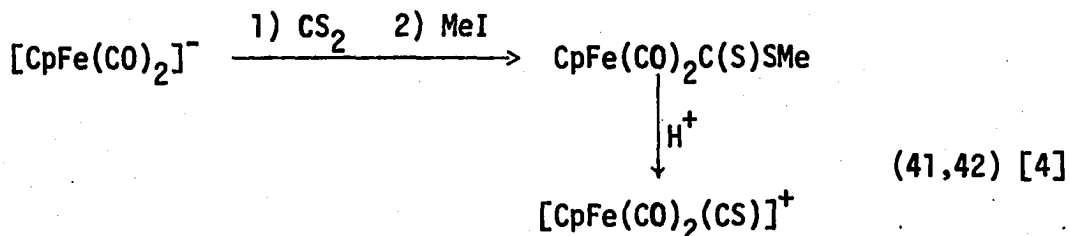
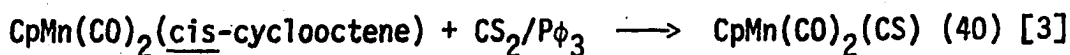
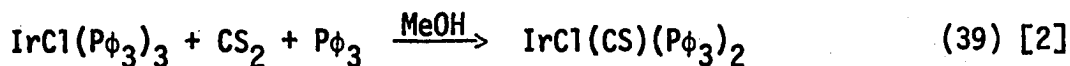
There has been little success in the attempts to prepare thiocarbonyl complexes from carbon monosulfide. Attempts to displace CO from $\text{Fe}(\text{CO})_5$ (8, 37), $\text{Ni}(\text{CO})_4$ (8), and $\text{Cr}(\text{CO})_6$ (37) or $\text{P}\phi_3$ from $\text{RhCl}(\text{P}\phi_3)_3$ (8) have been unsuccessful. One thiocarbonyl complex, $\text{Ni}(\text{CS})_4$, prepared by the cocondensation of Ni atoms and CS in an argon matrix, has been reported (38).

b. Thiocarbonyl complexes prepared from coordinated CS_2 by

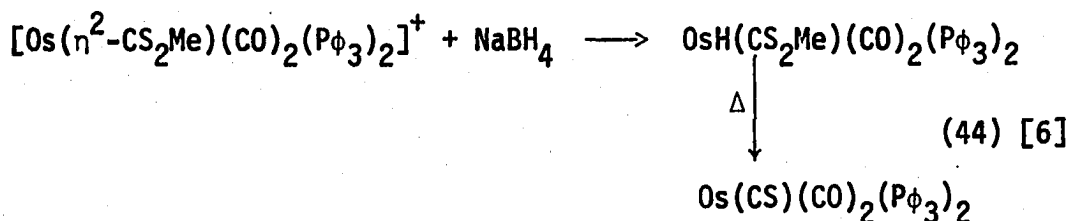
cleavage of a C-S bond The majority of thiocarbonyl complexes have been prepared by cleavage of a C-S bond from a coordinated CS_2 ligand. Usually, the C-S bond cleavage has to be assisted, typically with $\text{P}\phi_3$ -- which may already be present in the molecule or as an added reagent. The C-S bond cleavage may also be effected by first methylating the complexed CS_2 to form a coordinated $\text{C}(\text{S})\text{SMe}^+$ ligand, which can then be converted to the CS ligand by removal of methanethiol, MeSH, upon reaction with H^+ .

A few reactions illustrating these methods of generating the CS ligand are:

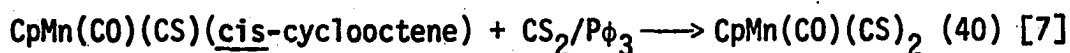




A reaction of this latter mode of CS generation is the attack on a cationic $\text{M}(\text{CS}_2\text{Me})$ complex with NaBH_4 , which forms a thiocarbonyl complex upon heating by 1,2-elimination of MeSH :



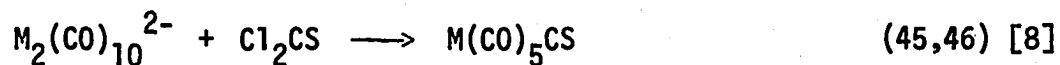
Application of the reaction in equation 3 to $\text{CpMn}(\text{CO})(\text{CS})(\text{cis-cyclooctene})$ gives $\text{CpMn}(\text{CO})(\text{CS})_2$, until the present work one of two known dithiocarbonyl complexes:



Further application of this reaction to $\text{CpMn}(\text{CS})_2(\text{cis-cyclooctene})$ gives spectroscopic evidence for the formation of $\text{CpMn}(\text{CS})_3$ (40).

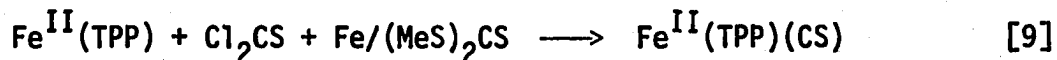
c. Thiocarbonyl complexes prepared by reaction with thiophosgene,

Cl₂CS The Group VIB thiocarbonyls, M(CO)₅CS (M = Cr, Mo and W) have been obtained by reaction of the dimeric carbonyl anions, M₂(CO)₁₀²⁻ (produced by sodium amalgam reduction of M(CO)₆) with thiophosgene:



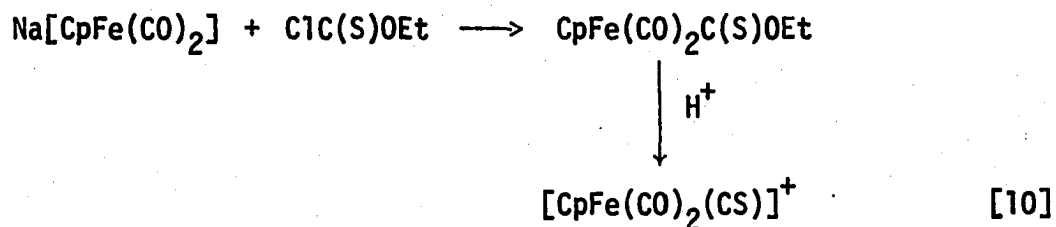
This reaction gives low yields of M(CO)₅CS (usually <10%) contaminated with large amounts of M(CO)₆. Only the tungsten thiocarbonyl, W(CO)₅CS, could be obtained in significant amounts (10-15%).

Recently, the first thiocarbonyl complex of metaloporphyrin was obtained by reaction of thiophosgene with a reducing agent and Fe^{II}(TPP) (TPP is the dianion of meso-tetraphenylporphyrin) (47):



Thiophosgene has also been used to prepare IrCl₃(CS)(Pφ₃)₂, IrCl(CO)(CS)(Pφ₃)₂, and RhCl₃(CS)(Pφ₃)₃ by three-fragment oxidative addition to Ir(Pφ₃)₂(N₂)Cl, [Ir(Pφ₃)₂(CO)(CH₃CN)]PF₆ and Rh(Pφ₃)₃Cl, respectively (48).

d. Thiocarbonyl complexes prepared by reaction with alkoxy derivatives of thiophosgene The cyclopentadienyldicarbonylthiocarbonyliron(II) cation, [CpFe(CO)₂(CS)]⁺, was first prepared by the reaction of Na[CpFe(CO)₂] with ClC(S)OEt followed by acid cleavage (49):



However, a later method (vide ante) gives a greater yield of the product (41,42). Methyl chlorothioformate has also been used to produce [trans-PtCl(Pφ₃)₂CS]⁺ from Pt(Pφ₃)₄ (50).

The first direct insertion of CS into a M-C(S)-M bridging position has recently been achieved by use of the reagent, diphenyl thionocarbonate (51):

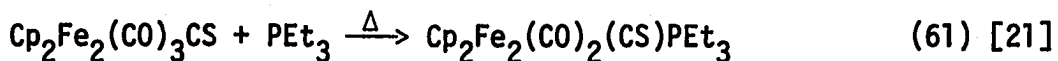
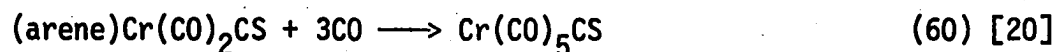
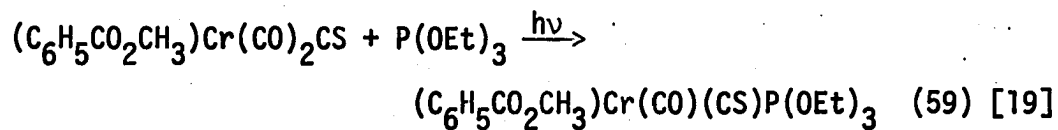
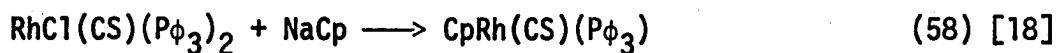
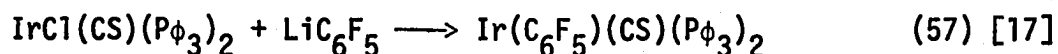
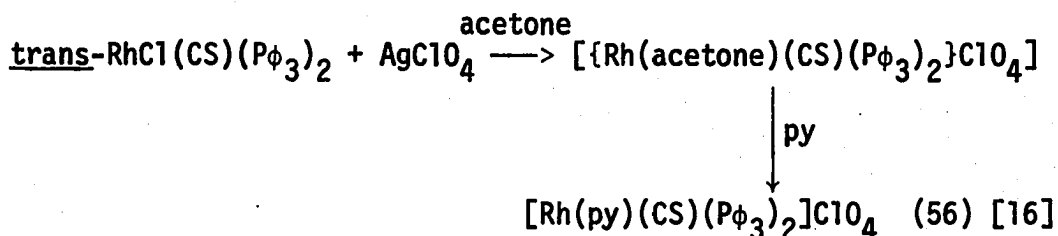
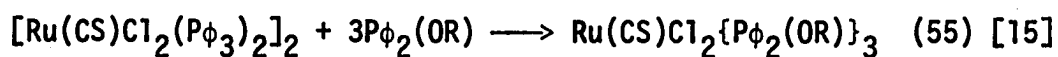
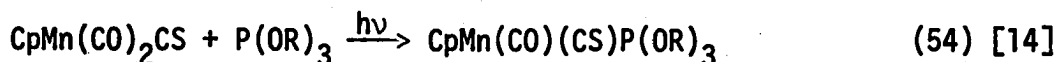
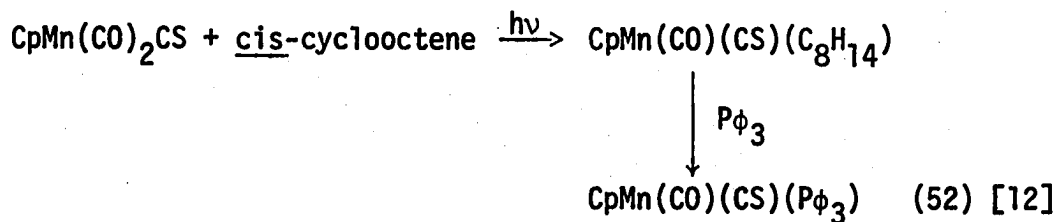


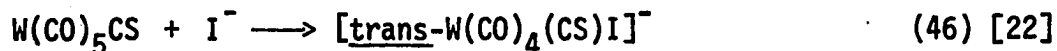
3. Reactions of thiocarbonyl complexes

a. Reactions at the metal center Since the carbonyl and thiocarbonyl ligands are isoelectronic and their analogous compounds are isostructural, it would seem that thiocarbonyl complexes should react similarly to their carbonyl analogs. To a certain extent, this is true. Reactions at the metal center differ more by degree than type.

Thus, metal thiocarbonyl complexes undergo ligand substitution reactions similar to their carbonyl analogs. Inasmuch as most thiocarbonyl complexes also contain carbonyl ligands, and in view of the stronger M-CX bond of the thiocarbonyl ligand, it is not surprising that the carbonyl ligand is preferentially displaced in these reactions. Both thermal and photochemical loss of the CO ligand have been

demonstrated. Ligand substitution by halide abstraction has also been shown. A few reactions illustrating these modes of ligand substitution follow:



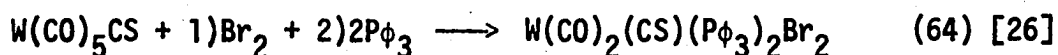
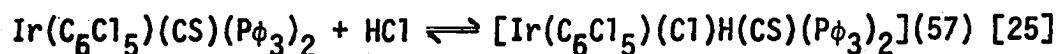
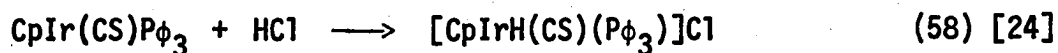
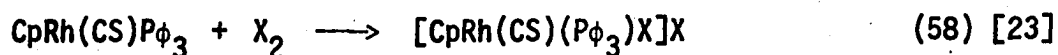


The reaction shown in equation [20] is a better method for the preparation of $\text{Cr(CO)}_5\text{CS}$ than the method in equation [8]. Reaction [22] is unusual in its stereospecificity; only the trans isomer is obtained due to the labilizing effect of the CS ligand (or it may be the more stable isomer due to π -bonding). The reaction shown in equation [21] is the first substitution reaction of a bridging thiocarbonyl complex, and the first where substitution occurs slower than in the analogous carbonyl complex.

Substitution reactions of cyclopentadienyl and arene thiocarbonyl complexes (e.g., [12], [14] and [19]) produce an asymmetric center at the metal atom. Indeed, the enantiomers of $(\text{C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr(CO)(CS)P(O}\phi)_3$ have been resolved (62).

Kinetic studies on substitution reactions of thiocarbonyl complexes (16,63) confirm that they undergo CO replacement easier than their thiocarbonyl analogs.

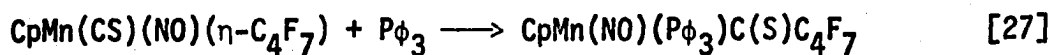
In oxidative-addition reactions, thiocarbonyl complexes also behave similar to their carbonyl analogs:



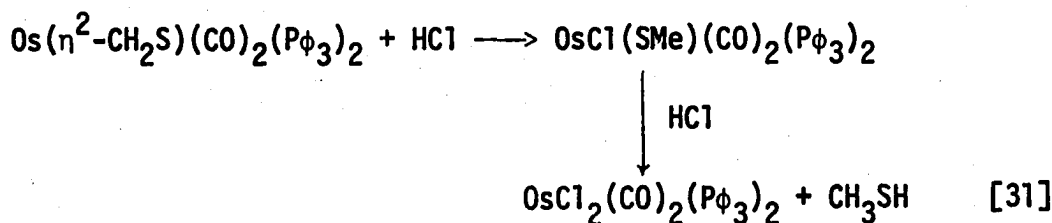
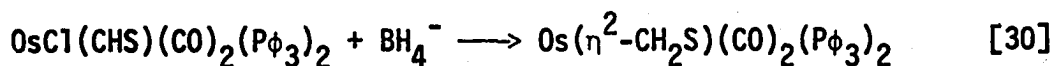
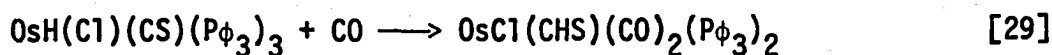
The $W(CO)_2(CS)(P\phi_3)_2Br_2$ produced in the last reaction does not undergo loss of CO upon heating as does the analogous $W(CO)_3(P\phi_3)_2Br_2$. The authors suggest that this may be due to structural factors. If CO is lost in the carbonyl analog from the face capping position, then if the CS ligand occupies this site in the thiocarbonyl complex, its stronger M-CX bond might preclude thermal loss.

The oxidative-addition of MeI to the thiocarbonyl complexes $[Ir(C_6F_5)(CS)(P\phi_3)_2]$ and $[CpM(CS)(P\phi_3)]$ (M = Rh or Ir) produces the unusual thiocarbene ligand, M-CMe(SMe) (57,58). The authors suggest that the mechanism involves (1) oxidative-addition of one MeI molecule to the complex, (2) methyl migration to form a thioacetyl complex, and (3) electrophilic attack at the sulfur atom by a second molecule of MeI. In support of this mechanism, they have isolated the complex, $[CpIr(CH_2CN)(CS)(P\phi_3)]^+$, from the reaction of $ClCH_2CN$ with $[CpIr(CS)(P\phi_3)]$ and the complex, $[IrMe(Cl)I(CS)(P\phi_3)_2]$, from the reaction of MeI with $[IrCl(CS)(P\phi_3)_2]$. Also, addition of the Lewis base $HgCl_2$ to these complexes, $[Ir(C_6F_5)(CS)(P\phi_3)_2]$ and $[CpM(CS)(P\phi_3)]$ (M = Rh or Ir), occurs at the metal, not at the sulfur, to produce the complexes, $[Ir(C_6F_5)Cl(CS)(HgCl)(P\phi_3)_2]$ and $[CpM(CS)(HgCl_2)(P\phi_3)]$ (M = Rh or Ir). Thus, only metal thiocarbonyl complexes with $\nu(CS)$ values less than 1200 cm^{-1} have been observed to undergo electrophilic attack at the sulfur atom (vide infra).

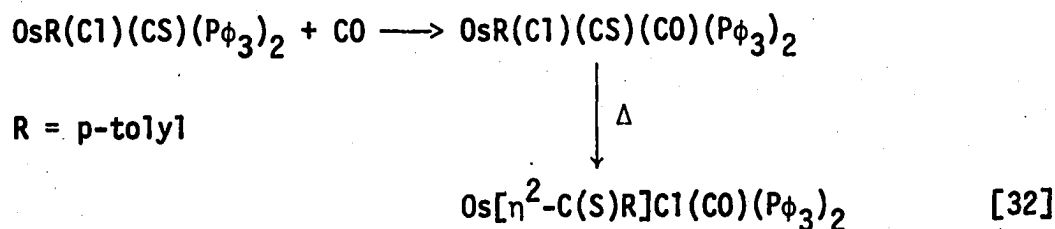
Recently, there have appeared in the literature a few examples of intramolecular thiocarbonyl insertion reactions. Efraty et al. (65) have presented evidence for the reactions:



Collins and Roper [66] have demonstrated the stepwise reduction of the thiocarbonyl ligand:



In that paper, synthetic routes to formyl (Os-CHO), iminoformyl (Os-CHNMe₂), and secondary carbene (Os-CHSMe, Os-CHNMe₂, and Os-CHOMe) complexes were also demonstrated. Intramolecular insertion of σ -aryl-thiocarbonyl complexes to η^2 -thioacyl complexes has been shown (67):

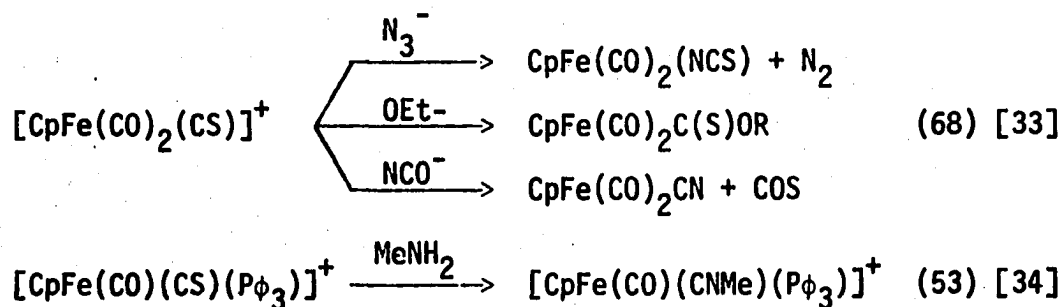


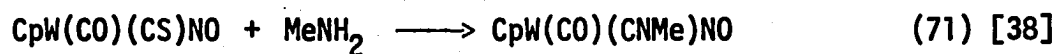
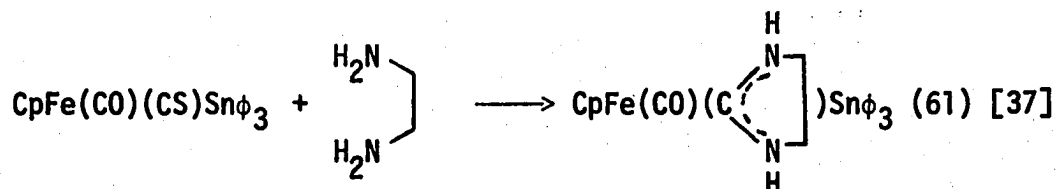
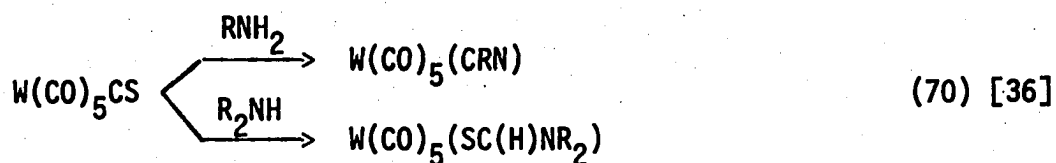
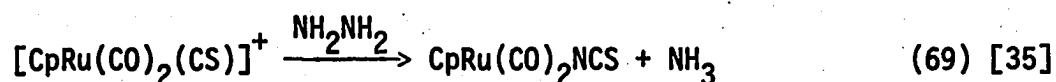
The dihapto-thioformyl and -thioacyl ligands are similar to the η^2 -dithiomethyl ester complexes of osmium and ruthenium, $\{\text{M}[\eta^2\text{-C(S)SMe}](\text{CO})_2(\text{P}\phi_3)_2\}^+$ (M = Ru or Os), which have been prepared previously by Grundy *et al.* (43).

The synthesis and reactions of these new thiocarbonyl containing alkyl, aryl, and hydrido complexes may portend a new expansion in the area of thiocarbonyl catalysis. The complexes obtained from the stepwise reduction of the thiocarbonyl ligand may serve as models for intermediates in the Fischer-Tropsch reaction. Also, the development and resolution of enantiomeric thiocarbonyl complexes may provide complexes for the catalysis of asymmetric organic reactions.

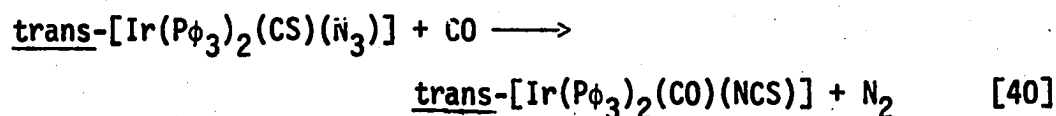
b. Nucleophilic attack at the thiocarbonyl carbon atom A few metal thiocarbonyl complexes have been observed to be susceptible to attack by nucleophiles at the carbon atom of the CS ligand. The attack on the thiocarbonyl carbon atom may be rationalized on the basis of a $\delta^+ \text{-C}=\text{S}^{\delta-}$ resonance structure as postulated by Bodner (29), or the reaction may be frontier controlled as postulated by Lichtenberger and Fenske (25).

The thiocarbonyl complexes that have been shown to undergo nucleophilic attack at the thiocarbonyl carbon atom are $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ (68), $[\text{CpFe}(\text{CO})(\text{CS})(\text{L})]^+$ (53), $[\text{CpRu}(\text{CO})_2(\text{CS})]^+$ (69), $\text{W}(\text{CO})_5\text{CS}$ (70), $\text{CpFe}(\text{CO})(\text{CS})\text{Sn}\phi_3$ (61), $\text{CpW}(\text{CO})(\text{CS})\text{NO}$ and $\text{CpW}(\text{CO})_2(\text{CS})\text{M}\phi_3$ (71), and $\text{PtCl}(\text{P}\phi_3)_2(\text{CS})^+$ (50). A few representative examples of these reactions are listed below:





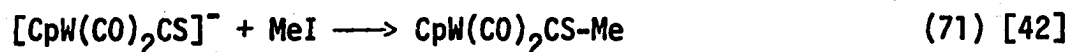
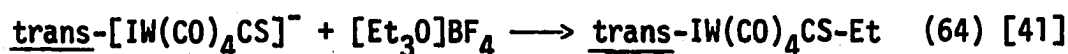
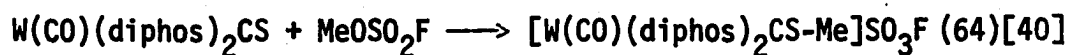
Recently, another example of nucleophilic attack on the thiocarbonyl carbon atom has appeared in the literature (72):



while this reaction might also be included with the ligand substitution reactions (vide ante), it is included here because of the nature of the final products.

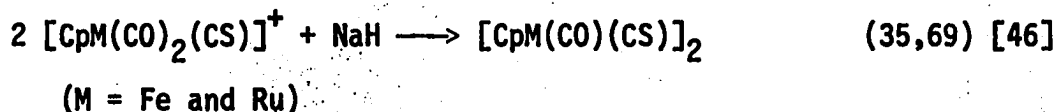
Although nucleophilic attack at the thiocarbonyl carbon atom has been demonstrated with these complexes, it remains to be seen if this reaction is general and occurs with all thiocarbonyl complexes.

c. Electrophilic attack at the thiocarbonyl sulfur atom Thio-
carbonyl ligands in metal thiocarbonyl complexes which are sufficiently
electron-rich to give $\nu(\text{CS})$ values lower than 1200 cm^{-1} have been shown
to be susceptible to electrophilic attack at the thiocarbonyl sulfur
atom. Although there is spectral evidence for the complex
 $\text{CpMn}(\text{CO})_2\text{CSMn}(\text{CO})_2\text{Cp}$ (73), whose "parent" compound, $\text{CpMn}(\text{CO})_2(\text{CS})$, has
a $\nu(\text{CS})$ of 1267 cm^{-1} . Both terminal-thiocarbonyl complexes --
 $\text{W}(\text{CO})_2(\text{diphos})_2\text{CS}$ (64), trans- $[\text{IW}(\text{CO})_4\text{CS}]^-$ (64), and $[\text{CpW}(\text{CO})_2\text{CS}]^-$
(71) -- and bridging-thiocarbonyl complexes -- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ (35)
and $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$ (51,74) -- have been shown to undergo electrophilic
addition by alkylating agents:



These reactions of terminal-thiocarbonyl complexes with organic
electrophiles give products which are examples of complexes containing
the mercaptocarbyne ligand, CS-R^+ . In addition to these reactions with
organic electrophiles, electron-rich thiocarbonyl complexes also form
addition compounds with Lewis acids -- as in $[\text{W}(\text{CO})(\text{diphos})_2\text{CS-W}(\text{CO})_5]$
(64), $\text{W}(\text{CO})(\text{diphos})_2\text{CS-HgCl}_2$ (64), and $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS-HgCl}_2$ (61).

d. Reactions forming bridging thiocarbonyl complexes The first reported bridging thiocarbonyl complex was $W(CO)(diphos)_2CS-W(CO)_5$ (64) (vide ante), an example of an "end-to-end" bridging thiocarbonyl ligand. "Ketonic" bridging thiocarbonyl complexes -- $[CpMn(NO)(CS)]_2$ (65,75), $[CpM(CO)(CS)]_2$ (M = Fe and Ru) (35,69) -- have been prepared by the following methods:



These complexes along with the aforementioned $Cp_2Fe_2(CO)_3CS$ are the only known examples of ketonic-bridging thiocarbonyl complexes. In all cases, the thiocarbonyl ligand seems to prefer the bridging position; this has been confirmed by the X-ray crystal structure determinations of $[CpFe(CO)(CS)]_2$ (35) and $Cp_2Fe_2(CO)_3CS$ (36).

C. Cyclopentadienyliron Carbonyl Complexes

Since this thesis concerns the preparation and properties of cyclopentadienyliron thiocarbonyl complexes, it is fitting that a short review of the literature on the chemistry of cyclopentadienyliron carbonyl complexes should be included.

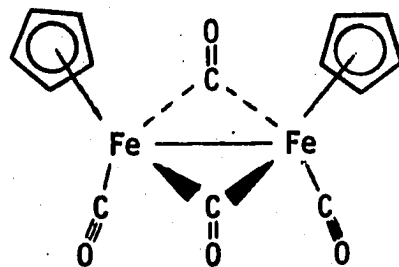
1. The cyclopentadienyliron dicarbonyl dimer, $[CpFe(CO)_2]_2$

The starting material for cyclopentadienyliron carbonyl complexes is the cyclopentadienyliron dicarbonyl dimer, $[CpFe(CO)_2]_2$, as it is

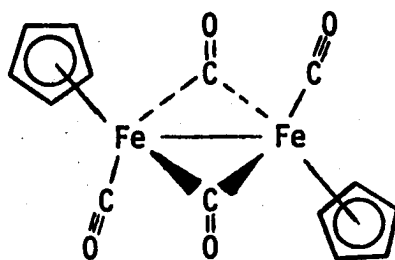
readily available from commercial sources and is fairly inexpensive. The dimer can also be easily prepared by refluxing iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, and dicyclopentadiene, $\text{C}_{10}\text{H}_{12}$ (76).

The cyclopentadienyliron dicarbonyl dimer exists in solution as a mixture of the cis and trans isomers (see Figure 1). The ratio of the isomer concentrations in solution is dependent on the solvent, with the trans isomer being more prevalent in nonpolar solvent, and the cis isomer more prevalent in polar solvents. Adams and Cotton (77) have proposed a mechanism involving simultaneous carbonyl bridge breaking, rotation about the metal-metal bond, and carbonyl bridge reformation to account for this rapid cis-trans isomerization (this mechanism will be discussed in more detail in conjunction with the isomerization of cis,trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ under Results and Discussion). The X-ray crystal structures of both the cis (78) and the trans (79) isomers of $[\text{CpFe}(\text{CO})_2]_2$ have been determined.

There are several reactions such as ligand substitution in which the dimeric form of the complex is retained. The cyclopentadienyliron dicarbonyl dimer, $[\text{CpFe}(\text{CO})_2]_2$, reacts with phosphites (80), phosphines (80), and amines (81) to give the monosubstituted complexes $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{L}$. The dimer also reacts with diphosphines (82), diarsines (82), and disulfides (83) to give the dimeric complexes $[\text{CpFe}(\text{CO})(\text{L})]_2$, where L is a three electron bridging group, $-\text{PR}_2$, $-\text{AsR}_2$ or $-\text{SR}$. The latter reactions can be viewed as homolytic cleavages of both reactants which then combine to form $\text{CpFe}(\text{CO})_2\text{PR}_2$, for example. This monomeric complex then loses CO to give the dimeric product, $[\text{CpFe}(\text{CO})\text{PR}_2]_2$. It



cis-[CpFe(CO)₂]₂



trans-[CpFe(CO)₂]₂

Figure 1. The cis and trans isomers of [CpFe(CO)₂]₂

is worthwhile to note that the $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{L}$ complexes have bridging carbonyl ligands and a formal metal-metal bond, while the $[\text{CpFe}(\text{CO})\text{MR}_n]_2$ complexes have no metal-metal bond and are bridged by the P, As or S ligands.

Another type of reaction of $[\text{CpFe}(\text{CO})_2]_2$ is that involving oxygen-bonded adduct formation by the bridging carbonyl ligand with Lewis acids. One-to-one adducts, $[\text{CpFe}(\text{CO})_2]_2 \cdot \text{MX}_3$, are formed with BX_3 (84), while both 1:1 and 1:2 adducts are formed with AlX_3 and AlR_3 (85).

An interesting reaction of $[\text{CpFe}(\text{CO})_2]_2$ which deserves to be mentioned is the formation of the cyclopentadienyliron carbonyl tetramer, $[\text{CpFe}(\text{CO})]_4$. When $[\text{CpFe}(\text{CO})_2]_2$ is refluxed in xylene (86), or refluxed and irradiated with ultra-violet light (87), the tetrameric species $[\text{CpFe}(\text{CO})]_4$ is formed. The structure of the tetramer consists of a tetrahedron of iron atoms which are capped on the faces of the tetrahedron by triply-bridging carbonyl ligands and on the vertices by the cyclopentadienyl ligands.

The cyclopentadienyliron carbonyl tetramer is a very stable structure. It can undergo oxidation by bromine to the +3 oxidation state, forming $[\text{CpFe}(\text{CO})]_4\text{Br}_3$ (86), or reduction to $[\text{CpFe}(\text{CO})]_4^-$ (88) without cleaving the tetrameric structure. Lewis acid adducts with the triply-bridging carbonyl ligands -- analogous to those of the dimer, $[\text{CpFe}(\text{CO})_2]_2$ -- can also be formed (87).

2. Cleavage reactions of $[\text{CpFe}(\text{CO})_2]_2$

a. Oxidative cleavage of $[\text{CpFe}(\text{CO})_2]_2$ One of the principle routes to cyclopentadienyliron carbonyl complexes is through oxidative cleavage of the dimer, $[\text{CpFe}(\text{CO})_2]_2$. Numerous oxidants -- such as Cl_2 (89), Br_2 (76), I_2 (76,90), O_2 (76,91,92), $\phi_3\text{CBF}_4$ (93), Fe^{+3} (94,95), Hg^{+2} (87) and Ag^{+1} (96) -- have been used to produce monomeric $\text{CpFe}(\text{CO})_2\text{X}$ and $[\text{CpFe}(\text{CO})_2(\text{L})]^+$ complexes. Electrolytic oxidation (97) of $[\text{CpFe}(\text{CO})_2]_2$ has also been used to produce $\text{CpFe}(\text{CO})_2\text{X}$ and $[\text{CpFe}(\text{CO})_2(\text{L})]^+$.

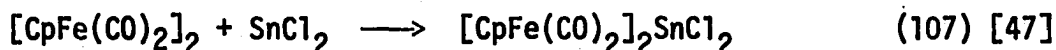
The mechanism of the oxidation of $[\text{CpFe}(\text{CO})_2]_2$ by halogens has been studied (98) and is believed to occur by initial electrophilic attack by the halogen on the dimer forming the halide-bridged intermediate, $\{[\text{CpFe}(\text{CO})_2]_2\text{X}\}^+$. This intermediate then can undergo nucleophilic attack by halide ions to give $\text{CpFe}(\text{CO})_2\text{X}$, or undergo asymmetric cleavage to give $[\text{CpFe}(\text{CO})_3]\text{X}$ (another of the observed products). Support for this mechanism is found in the isolation of $\{[\text{CpFe}(\text{CO})_2]_2\text{X}\}\text{B}\phi_4$ from the low temperature halogenation of $[\text{CpFe}(\text{CO})_2]_2$ in the presence of $\text{NaB}\phi_4$.

b. Reductive cleavage of $[\text{CpFe}(\text{CO})_2]_2$ The second principle route to monomeric cyclopentadienyliron carbonyl complexes is reductive cleavage of the dimer. The classic method is to use sodium-amalgam to reduce the dimer to the sodium salt of the cyclopentadienyliron dicarbonyl anion, $\text{Na}[\text{CpFe}(\text{CO})_2]$ (76). However, there has been a report that contamination with mercury derivatives, such as $[\text{CpFe}(\text{CO})_2]_2\text{Hg}$,

may occur using this method (99). Other reductants such as $\text{NaK}_{2,8}$ (100), C_8K (101), $\text{Mg}/\text{BrCH}_2\text{CH}_2\text{Br}$ (102), and $\text{Mg}/\text{Hg}/\text{py}$ (103) have been used to produce this anion, $[\text{CpFe}(\text{CO})_2]^-$, or other reduced species, $\text{CpFe}(\text{CO})_2\text{MgBr}$ and $[\text{CpFe}(\text{CO})_2]_2\text{Mg}(\text{py})_2$, in the later two cases.

c. Other cleavage reactions of $[\text{CpFe}(\text{CO})_2]_2$ In other reactions, what might be termed homolytic cleavage of the dimer seems to occur. For instance, photolysis of $[\text{CpFe}(\text{CO})_2]_2$ in chlorinated solvents gives $\text{CpFe}(\text{CO})_2\text{Cl}$ (104). The product appears to result from the homolytic cleavage of $[\text{CpFe}(\text{CO})_2]_2$ and RCl to form $\text{CpFe}(\text{CO})_2\cdot$ and $\text{Cl}\cdot$ radicals, which then combine. Indeed, the $\text{CpFe}(\text{CO})_2\cdot$ radical has been identified in a spin-trapping experiment (105). Also, homolytic cleavage may occur in the reaction of $[\text{CpFe}(\text{CO})_2]_2$ with HSiCl_3 , producing $\text{CpFe}(\text{CO})_2\text{SiCl}_3$ among other products (106).

The "insertion" of $\text{Sn}(\text{II})$ compounds in the metal-metal bond of $[\text{CpFe}(\text{CO})_2]_2$, i.e.,



may be viewed as another type of cleavage reaction.

3. Reactions of monomeric cyclopentadienyliron carbonyl complexes

a. Reactions of $\text{CpFe}(\text{CO})_2\text{X}$ The reactions of $\text{CpFe}(\text{CO})_2\text{X}$ fall into two basic types: (1) reactions involving loss of a carbonyl ligand and (2) reactions involving loss of the X ligand (usually a halide ion).

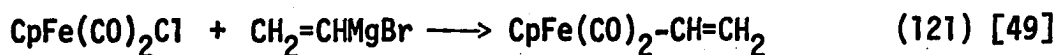
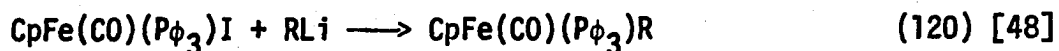
The cyclopentadienyliron dicarbonyl halides, $\text{CpFe}(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$ or I), react with neutral phosphines, PR_3 , or phosphites, $\text{P}(\text{OR})_3$, by either thermal or photochemical routes to yield the neutral substituted cyclopentadienyliron carbonyl halides, $\text{CpFe}(\text{CO})(\text{L})\text{X}$, or the substituted cyclopentadienyliron carbonyl cations, $[\text{CpFe}(\text{CO})_2(\text{L})]\text{X}$ (108,109). The tendency to form the cationic product increases with increasing basicity of the ligand, and also with changes of the halide ($\text{I} < \text{Br} < \text{Cl}$). The kinetics of the reaction of the $\text{CpFe}(\text{CO})_2\text{X}$ complexes with phosphites, $\text{P}(\text{OR})_3$, have been studied, and suggest that this reaction, forming $\text{CpFe}(\text{CO})(\text{L})\text{X}$, proceeds by a dissociative $\text{S}_{\text{N}}1$ type mechanism (110). Reaction of other $\text{CpFe}(\text{CO})_2\text{X}$ complexes ($\text{X} = \text{SnR}_3$ and SiR_3) with phosphines has also been shown to give $\text{CpFe}(\text{CO})(\text{L})\text{X}$ complexes -- and in some cases $\text{CpFe}(\text{L})_2\text{X}$ complexes (111,112).

The second major set of $\text{CpFe}(\text{CO})_2\text{X}$ reactions involve the loss of the X^- ligand. In addition to the above reactions where the halide ion is displaced by a neutral ligand, the halide ion can be removed by a halogen acceptor such as AlCl_3 or by a metathesis reaction where the halogen is lost as a salt, typically NaX . For instance, $\text{CpFe}(\text{CO})_2\text{Br}$ reacts with NaSR to yield the monomeric cyclopentadienyliron dicarbonyl mercaptide complexes, $\text{CpFe}(\text{CO})_2\text{SR}$ (113). With the halogen acceptor AlX_3 , $\text{CpFe}(\text{CO})_2\text{X}$ reacts in the presence of neutral ligands such as ethylene (114), other olefins (115,116), and pyridine (117) to form $[\text{CpFe}(\text{CO})_2(\text{L})]^+$ complexes. The $[\text{CpFe}(\text{CO})_2(\text{olefin})]^+$ complexes recently have been shown to be readily prepared from $[\text{CpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$, a

reagent prepared by reaction of $\text{CpFe}(\text{CO})_2\text{I}$ with AgBF_4 in tetrahydrofuran (118).

In the metathesis reaction of $\text{CpFe}(\text{CO})_2\text{Br}$ with KCN , a carbonyl ligand is displaced in addition to the bromide ligand to yield the anionic complex, $\text{K}[\text{CpFe}(\text{CO})(\text{CN})_2]$ (119).

Some of the more interesting metathesis reactions of $\text{CpFe}(\text{CO})_2\text{X}$, or $\text{CpFe}(\text{CO})(\text{L})\text{X}$, involve displacement of the halide ion through use of a Grignard reagent or organolithium compound to form a metal-carbon σ -bond.



Also, mixed metal carbonyl complexes can be obtained from reactions of $\text{CpFe}(\text{CO})_2\text{X}$ with metal carbonyl anions.



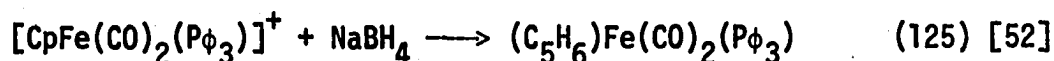
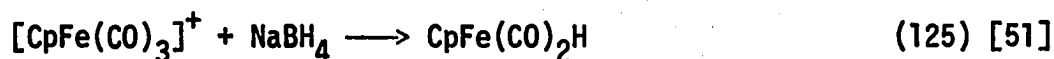
b. Reactions of $[\text{CpFe}(\text{CO})_3]^+$ The tricarbonylcyclopentadienyl-iron cation, $[\text{CpFe}(\text{CO})_3]^+$, and its substituted analogs, $[\text{CpFe}(\text{CO})_2(\text{L})]^+$, undergo three basic types of reactions: (1) ligand displacement, (2) nucleophilic attack at the carbonyl ligand, and (3) nucleophilic attack at the cyclopentadienyl ring.

In the ligand displacement reactions, $[\text{CpFe}(\text{CO})_3]^+$ can react with neutral ligands such as pyridine to form substituted cations, $[\text{CpFe}(\text{CO})_2(\text{L})]^+$ (108), or with halide ions, X^- ($\text{X} = \text{Cl}, \text{Br}$ or I) to

form the neutral cyclopentadienyliron dicarbonyl halides, $\text{CpFe(CO)}_2\text{X}$ (123).

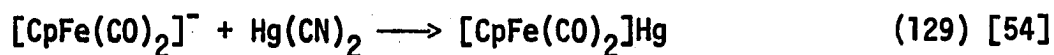
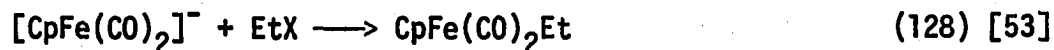
With nucleophiles such as N_3^- or NH_2NH_2 , $[\text{CpFe(CO)}_3]^+$ has been shown to undergo nucleophilic attack at the carbonyl ligand giving $\text{CpFe(CO)}_2\text{NCO}$ and $\text{CpFe(CO)}_2\text{C(O)NHNH}_2$, respectively (124).

Sodium borohydride (125,126) and organolithium reagents (126,127) give products which suggest attack at the metal atom with $[\text{CpFe(CO)}_3]^+$ and attack at the cyclopentadienyl ring with the substituted cation, $[\text{CpFe(CO)}_2(\text{P}\phi_3)]^+$:



With the organolithium reagent, LiC_6F_5 , $\text{CpFe(CO)}_2\text{C}_6\text{F}_5$ and $\text{CpFe(CO)}_2\text{C(O)C}_6\text{F}_5$ are the products of its reaction with $[\text{CpFe(CO)}_3]^+$, while $(\text{C}_6\text{H}_5\text{C}_6\text{F}_5)\text{Fe(CO)}_2(\text{P}\phi_3)$ is the product from its reaction with $[\text{CpFe(CO)}_2(\text{P}\phi_3)]^+$ (126,127).

c. Reactions of $[\text{CpFe(CO)}_2]^-$ The reactions that $\text{Na}[\text{CpFe(CO)}_2]$ undergo can all be described as metathesis reactions. Reaction with an organic or inorganic halide, E-X , causes displacement of the halide ion as NaX and formation of the new complex, $\text{CpFe(CO)}_2\text{E}$. A few illustrative reactions follow:





III. EXPERIMENTAL

A. General

Unless stated otherwise, all reactions were performed under an atmosphere of prepurified nitrogen that was passed through indicating Drierite prior to use. Tetrahydrofuran was distilled from LiAlH_4 or $\text{NaK}_{2.8}$ (under nitrogen) prior to use. All solvents were reagent grade. Acetone and anhydrous ethyl ether were used as received, while all other solvents were stored over 4A molecular sieves.

Elemental analyses were performed by either Chemalytics, Inc. or Galbraith Laboratories, Inc.

B. Spectra

Infrared spectra were recorded on a Perkin-Elmer 337 or 237B grating spectrophotometer using either 1.0 mm or 0.1 mm pathlength cells. In general, the spectra of neutral complexes, or those run in nonpolar solvents (*i.e.*, hexanes, CCl_4 , CS_2 , CHCl_3 or CH_2Cl_2) were recorded with the 1.0 mm pathlength cells. The spectra of ionic complexes, or those run in polar solvents (*i.e.*, CH_2Cl_2 , acetone or acetonitrile) were recorded with the 0.1 mm pathlength cells. Positions of the infrared absorption peaks were determined by expansion with an external recorder, and were calibrated in the carbonyl region with CO gas and in the thiocarbonyl region with polystyrene. The peak positions are believed accurate to within 2 cm^{-1} .

In the infrared spectra of cationic complexes, the absorption due to the anions, either CF_3SO_3^- (1269 vs; 1224 m; 1160 br, m, and 1033 vs cm^{-1}) or PF_6^- (880 w and 845 vs cm^{-1}), are omitted for clarity.

Proton NMR spectra were recorded with Varian A-60, Varian EM-360, or Perkin-Elmer Hitachi R-20B instruments.

The C^{13} NMR spectra were obtained on a Bruker HX-90 Fourier transform spectrometer. The shiftless, paramagnetic relaxing agent, $\text{Cr}(\text{acad})_3$ (132), was added to reduce data collection time. Deuteriochloroform ($\delta = -77.09$) or TMS was used as the internal standard.

The NMR spectral assignments were based in part upon the integrated intensities of the absorptions.

C. Reagents

Triphenylphosphine, triphenylarsine, and triphenylantimony were recrystallized from hexanes. Trimethylphosphite and triethylphosphine were fractionally distilled. Triphenylphosphite was recrystallized from the neat liquid. The cyclopentadienyliron dicarbonyl dimer, $[\text{CpFe}(\text{CO})_2]_2$, was recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexanes}$.

D. Photolysis

Small scale (~ 1 mmole) photolysis reactions were conducted in quartz Schlenk tubes using a photolysis reactor (Bradford Scientific, Inc.) modified with a Plexiglas bottom to enable magnetic stirring.

Large scale photolysis reactions were conducted in a cylindrical 400 ml 3-necked flask -- with two female 24/40 joints and a central 55/50 male joint -- which accepted a water-cooled quartz photolysis

well in which a Hanovia photochemical immersion lamp (Ace Glass, Inc.) was placed.

E. Preparation and Reactions of Complexes

1. Preparation of $\text{CpFe}(\text{CO})_2\text{CS}_2\text{CH}_3$, $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$, and $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$

Although adequate methods for the preparation of $\text{CpFe}(\text{CO})_2\text{CS}_2\text{CH}_3$ and $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ are in the literature (42), syntheses of these complexes are included here because the improvements in yield cited by M. H. Quick (61) were joint developments of M. H. Quick and myself. Also, an improvement in the purity of $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ is obtained with this procedure.

This procedure is basically a modification of Dombek and Angelici's method (42).

Cyclopentadienyliron dicarbonyl dimer, $[\text{CpFe}(\text{CO})_2]_2$, (10.0 g, 28.3 mmol) in 200 ml THF was reduced to $\text{Na}[\text{CpFe}(\text{CO})_2]$ by stirring for one-half hour with ~1% sodium amalgam (2.0 g, 87 mmol Na in 35 ml Hg). After draining the amalgam, carbon disulfide (5 ml, 83 mmol) was added to the well-stirred solution. Methyl iodide (5 ml, 80 mmol) was added 15-20 seconds later, and the solution was stirred for 10 minutes. After evaporation to dryness, the residue was extracted with ethyl ether (~300 ml) and filtered through Celite until all the brown color had been extracted.

If the dithioester, $\text{CpFe}(\text{CO})_2\text{CS}_2\text{CH}_3$, was desired, the volume was reduced to ~ 50 ml. Hexane was added and crystallization at -20°C gave the yellow-brown $\text{CpFe}(\text{CO})_2\text{CS}_2\text{CH}_3$ (60 %).

IR (Hexane): 2035 vs, 1988 vs cm^{-1} .

To prepare the thiocarbonyl cation, $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$, $\text{CF}_3\text{SO}_3\text{H}$ (5.6 ml, 63 mmol in 60 ml of Et_2O) was slowly added dropwise to the Et_2O solution of $\text{CpFe}(\text{CO})_2\text{CS}_2\text{CH}_3$, which was then stirred an additional 2 hours. The precipitated $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ was filtered off and washed with Et_2O . The crude product was then dissolved in 150 ml of acetone, and 350 ml of hexane was added to reprecipitate the product. Filtration gave a yellow-brown powder (the brown color is due to impurities). Washing with (1) Et_2O , (2) THF, (3) Et_2O , (4) THF and (5) Et_2O (care had to be taken not to use too much THF, as the product is slightly soluble in THF. Approximately 30 ml of THF and 50 ml of Et_2O were used for the respective washings) removed the brown color and yielded a bright yellow powder, $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ (79%).

IR (CH_3CN): 2105 s, 2071 s, 1353 s cm^{-1} .

^1H NMR (d^6 -acetone): τ 3.95.

If $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$ was the desired product, hydrogen chloride gas was bubbled through the Et_2O solution of the dithioester for 1 hour. The solution was then concentrated on a rotary evaporator to ~ 50 ml. Addition of a solution of NH_4PF_6 (10.0 g, 61.3 mmol) in 150 ml of acetone was followed by filtration to remove the insoluble NH_4Cl . The product was then precipitated by the addition of 350 ml of hexanes.

Filtration and subsequent washing with Et₂O and THF, as above, yielded a pale yellow powder, [CpFe(CO)₂(CS)]PF₆, (71%).

IR (Nujol Mull): 2093 s, 2064 S, 1348 s cm⁻¹.

¹H NMR (d⁶-acetone): τ 3.82.

The thiocarbonyl cation is somewhat sensitive to moisture, therefore it was stored in a desiccator over Drierite with a small open bottle of Pb(OAc)₂ present to absorb any H₂S given off.

2. Preparation of [CpFe(CO)(CS)]₂

A slurry of [CpFe(CO)₂(CS)]CF₃SO₃ (10.1 g, 27.3 mmoles) and excess sodium hydride (1.43 g of a 57% mineral oil dispersion, 34.0 mmoles) in 200 ml of THF was stirred at room temperature for 2 hours. The mixture was then evaporated to dryness under reduced pressure. The residue was extracted with hot benzene and filtered through Celite until the extractant was a light brown color, i.e., all the green color had been extracted. The solution was then chromatographed on a Florisil column (41 x 390 mm) eluting with benzene. A dark brown band with a blue leading edge developed that eventually colored the entire column. The eluent was collected starting with the first colored material and continuing until all the dark green elutant had been collected. (The initial eluent was a grey or green, but the band rapidly changed to an intense dark green and then tailed into an olive green color.) The eluent was evaporated under reduced pressure to a black solid. This solid contained a mixture of cis- and trans-[CpFe(CO)(CS)]₂, with small amounts of [CpFe(CO)₂]₂ and Cp₂Fe₂(CO)₃(CS) occasionally present.

The $[\text{CpFe}(\text{CO})(\text{CS})]_2$ could be isolated at this stage by crystallization from CH_2Cl_2 /hexane; however, the next purification step removed remaining impurities.

The black solid was dissolved in ~ 75 ml of CHCl_3 , then 50 ml of 95% EtOH and 10 ml of concentrated aqueous HCl (120 mmol) were added, and O_2 gas was slowly bubbled through the solution for 1 hour. (This oxidized the $[\text{CpFe}(\text{CO})_2]_2$ and $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$ to $\text{CpFe}(\text{CO})_2\text{Cl}$ and $\text{CpFe}(\text{CO})(\text{CS})\text{Cl}$, while the $[\text{CpFe}(\text{CO})(\text{CS})]_2$ remained unreacted [*vide post*].) The solution was then placed on a rotary evaporator where the volume was reduced to ~ 50 ml. Addition of ~ 200 ml of H_2O caused the $[\text{CpFe}(\text{CO})(\text{CS})]_2$ to precipitate. The mixture was then filtered and washed with H_2O to remove the water soluble $\text{CpFe}(\text{CO})_2\text{Cl}$ and $\text{CpFe}(\text{CO})(\text{CS})\text{Cl}$. The black residue was dissolved in ~ 50 ml of acetone and again precipitated by addition of ~ 200 ml of H_2O . The mixture was again filtered and washed with H_2O . This second precipitation removed any $\text{CpFe}(\text{CO})_2\text{Cl}$ or $\text{CpFe}(\text{CO})(\text{CS})\text{Cl}$ entrapped in the first precipitation. The residue was dissolved in CH_2Cl_2 and dried over anhydrous MgSO_4 overnight. After filtration through Celite, the green solution was reduced in volume to ~ 40 ml, and ~ 30 ml of heptanes was added. Crystallization at -20°C yielded red to black crystals of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ (thick crystals appeared black, while thin crystals appeared dark red). A second crop of crystals was obtained by concentrating and cooling the filtrate for a total of 1.85 g (35% yield) of a mixture of cis- and trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$. The yields were variable, ranging from 21% to 47%.

IR (CS_2): 2011, 1978, 1124 cm^{-1} .

The relative intensities of the bands varied with the ratio of cis- to trans-[CpFe(CO)(CS)]₂. The 2011 cm⁻¹ band is due to cis-[CpFe(CO)(CS)]₂, the 1978 cm⁻¹ is predominantly due to trans-[CpFe(CO)(CS)]₂, while the 1124 cm⁻¹ band is due to both isomers (vide post).

3. Separation and isolation of cis-[CpFe(CO)(CS)]₂ and trans-[CpFe(CO)(CS)]₂

A mixture of purified cis- and trans-[CpFe(CO)(CS)]₂ was dissolved in benzene and placed on top of a 41 mm x 400 mm Florisil/hexane column. Elution with 1:1 benzene:hexane gave a single band, mostly green, but with a blue leading edge. Elution had to be fairly rapid, approximately 50 ml/minute, as isomerization occurred if the rate was too slow.

The initial grey eluent was collected until the first appearance of a green color, and then evaporated to dryness under reduced pressure. An infrared spectrum in CS₂ of this solid indicated it was enriched in trans-[CpFe(CO)(CS)]₂. Crystallization from CS₂ at -20°C was repeated 3 times until an infrared spectrum of the product indicated that the 2011 cm⁻¹ absorption (cis-[CpFe(CO)(CS)]₂) was absent. Black crystals of trans-[CpFe(CO)(CS)]₂ were obtained.

IR (CS₂): 1979 vs, 1131 s cm⁻¹.

¹H NMR (CS₂): τ 5.32.

¹³C NMR (CDCl₃): δ -374.5 (CS), -210.0 (CO), -96.7 (Cp).

The remaining material was eluted from the column and evaporated to dryness under reduced pressure. An infrared spectrum of this fraction

in CS₂ indicated enrichment in cis-[CpFe(CO)(CS)]₂. Crystallization from CH₂Cl₂/hexane at -20°C was repeated until an infrared spectrum indicated that only cis-[CpFe(CO)(CS)]₂ was present.

IR (CS₂): 2011 vs, 1982 m, 1124 s cm⁻¹.

¹H NMR (CS₂): τ 5.22.

¹³C NMR (CDCl₃): δ -374.5 (CS), -208.9 (CO), -93.8 (Cp).

Mass spectrum parent ion at m/e 385.883.

Anal. Calcd. for [CpFe(CO)(CS)]₂: C, 43.55; H, 2.61; S, 16.61.

Found: C, 43.47; H, 2.69; S, 15.87.

4. Isomerization of [CpFe(CO)(CS)]₂

A solution of trans-[CpFe(CO)(CS)]₂ in xylene was maintained at 50°C. Samples were withdrawn at intervals for analysis by infrared spectroscopy. The isomerization of trans-[CpFe(CO)(CS)]₂ to a cis-trans equilibrium mixture was monitored by the growth in the 2011 cm⁻¹ cis-[CpFe(CO)(CS)]₂ band. A plot of absorbance vs time gave a half-life of approximately 28 minutes for the time required for the 2011 cm⁻¹ absorption to reach maximum intensity. At maximum intensity, an equilibrium mixture of the cis and trans isomers was present. The isomerization of the pure isomers to an equilibrium cis-trans mixture was observed for both isomers in various solvent, e.g., trans-[CpFe(CO)(CS)]₂ in CH₃CN and cis-[CpFe(CO)(CS)]₂ in hexane.

5. Crystal structure of cis-[CpFe(CO)(CS)]₂

Black crystals of cis-[CpFe(CO)(CS)]₂ were obtained by fractional crystallization at -20°C from a CS₂ solution containing a cis-trans

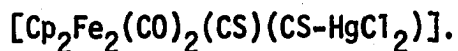
$[\text{CpFe}(\text{CO})(\text{CS})]_2$ mixture. The diffractometer-measured cell constants were found by carefully centering on 12 strong reflections between 35 and 45°C in θ with monochromated Cu- K_α radiation (1.54178 Å). The cell constants for the monoclinic cell are $a = 14.409$ (5), $b = 12.560$ (4), $c = 8.177$ (3) Å, and $\beta = 90.3$ (2)°. The calculated density indicated that four molecules of the complex were in the unit cell. Systematic extinctions indicated the lattice belonged to the common space group $P2_1/c$. The data were collected on a fully-automated Hilger-Watts four-circle diffractometer using Zr-filtered Mo radiation (0.7107 Å). A total of 3080 reflections with $\theta < 25^\circ$ were measured. Of these, 2187 reflections were judged observed after correction for background, Lorentz, and polarization effects. The structure was solved routinely using direct methods [133]. At this time, 187 reflections which were deemed to be subject to systematic errors were eliminated from the data set. Full-matrix, least-squares refinement on the 2000 remaining reflections varying positional and anisotropic thermal parameters for all nonhydrogen atoms reduced the discrepancy index, R_1 , to 0.077 for the observed reflections.

A computer-generated drawing of the molecule is shown in Figure 6. The bond distances and bond angles are given in Tables 3 and 4.

6. Preparation of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS}-\text{HgCl}_2)]$

A solution of a cis,trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ mixture (0.434 g, 1.12 mmol) and HgCl_2 (0.295 g, 1.09 mmol) in 40 ml of Et_2O was stirred for 9 hours. Then, 80 ml of heptane were added and the volume was

reduced to ~25 ml on a rotary evaporator. The mixture was then filtered, and the precipitate washed with pentane. Drying under high vacuum yielded 0.647 g (88% yield) of a black powder,



IR (Nujol Mull): 2028 vs, 2019 sh,s, 1995 s, 1177 sh,s; 1168 s;
1018 s cm^{-1} .

^1H NMR (d^6 -acetone): τ 5.10, 4.87 (relative intensities 11:70).

Anal. Calcd. for $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS}-\text{HgCl}_2)]$: C, 25.57; H, 1.53.

Found: C, 25.36; H, 1.74.

7. Reaction of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ and $\text{CH}_3\text{SO}_3\text{F}$

A solution of cis- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ (0.205 g, 0.532 mmoles) and $\text{CH}_3\text{SO}_3\text{F}$ (2.0 ml, 25 mmoles) in 100 ml CH_2Cl_2 was stirred for 15 min. The solution was then taken to dryness on a rotary evaporator. The residue was dissolved in methanol and the solution was passed through an anion-exchange column (Amberlite IRA-400) in the PF_6^- form. The green eluent was then reduced in volume to ~25 ml, and Et_2O was added until a precipitate began to form. Crystallization at -20°C gave black crystals of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CSMe})]\text{PF}_6$ (0.215 g, 74% yield).

IR (CH_2Cl_2): 2043 s, 2016 m, 1178 s, 1070 w, 1036 m cm^{-1} .

^1H NMR (d^6 -acetone): τ 6.20 (CH_3), 4.17 (Cp), 4.27 (Cp).

Anal. Calcd. for $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CSMe})]\text{PF}_6$: C, 33.00; H, 2.40.

Found: C, 32.85; H, 2.43.

8. Reaction of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ and CH_3I

A solution of cis- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ (0.0513 g, 0.133 mmol) and CH_3I (5 ml, 80 mmol) in 50 ml of CH_2Cl_2 was stirred magnetically, and the progress of the reaction was monitored by infrared spectroscopy. The reaction appeared complete after ~10 hours; however, stirring was continued for a total of 32 hours (some decomposition was evident by the decreased intensity of the 2043 cm^{-1} band of the product). The solution was then reduced on a rotary evaporator to dryness. After dissolving the residue in methanol, the green solution was passed through an anion-exchange resin (Amberlite IRA-400) in the PF_6^- form and then evaporated to dryness under reduced pressure. Crystallization from methanol at -20°C yielded 0.0237 g of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CSMe})]\text{PF}_6$, a 33% yield.

IR (CH_2Cl_2): 2043 s, 2011 m, 1178 s, 1070 w, 1036 m cm^{-1} .

9. Rates of the reactions of cis- and trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ with CH_3I

a. cis- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ Crystals of cis- $[\text{CpFe}(\text{CO})(\text{CS})]_2$

(10.3 mg, 2.67×10^{-5} moles) were dissolved in and diluted with neat CH_3I to 10.0 ml in a volumetric flask. A sample was withdrawn and placed in an unthermostated room-temperature infrared cell. The progress of the reaction of the solution in the infrared cell was periodically monitored by the decrease in intensity of the 2012 cm^{-1} absorption of cis- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ (monitoring the 2043 cm^{-1} absorption of the product was precluded by precipitation of the product toward the

end of the reaction). A plot of absorbance vs time gave an estimate of $t_{1/4} \approx 8$ min.

b. trans-[CpFe(CO)(CS)]₂ Crystals of trans-[CpFe(CO)(CS)]₂ (11.1 g, 2.88×10^{-5} moles) were dissolved in and diluted with neat CH₃I to 10.0 ml as above. The reaction was monitored as above, observing the decrease in intensity of the 1979 cm⁻¹ absorption of trans-[CpFe(CO)(CS)]₂. A plot of absorbance vs time gave an estimate of $t_{1/4} \approx 62$ min. (Unlike the reaction of cis-[CpFe(CO)(CS)]₂, extensive decomposition occurred during the course of the reaction.)

10. Reaction of [CpFe(CO)(CS)]₂ with HCl/O₂

A solution of a cis,trans-[CpFe(CO)(CS)]₂ mixture (2.34 g, 6.06 mmoles) in CHCl₃/EtOH (25 ml/30 ml) was prepared. Concentrated aqueous HCl (10 ml, 120 mmoles) was then added, and O₂(g) was bubbled through the solution for 90 minutes. The volume of the solution was then reduced to ~25 ml on a rotary evaporator. Addition of 200 ml of H₂O produced a black precipitate which was filtered and washed with H₂O. The black precipitate was dissolved in CH₂Cl₂, dried overnight over anhydrous MgSO₄, and filtered through Celite. An infrared spectrum of the solution indicated that only [CpFe(CO)(CS)]₂ was present. Crystallization at -20°C from CH₂Cl₂/hexane yielded 2.07 g of [CpFe(CO)(CS)]₂, an 89% recovery.

A similar reaction of [CpFe(CO)(CS)]₂ with HBF₄/O₂ in acetone also yielded unreacted starting material.

11. Preparation of CpFe(CO)(CS)Br. Method I. Reaction of [CpFe(CO)(CS)]₂ with Br₂

A solution of a cis,trans-[CpFe(CO)(CS)]₂ mixture (0.101 g, 0.261 mmoles) and excess Br₂ (2.0 ml of a solution of 1.0 ml of Br₂ diluted to 100 ml with CCl₄, 0.390 mmoles) in 50 ml of CHCl₃ was refluxed for 20 minutes. The solution was then cooled to room temperature and extracted with aqueous Na₂S₂O₃ (2 x 10 ml portions of 0.42 N Na₂S₂O₃) to destroy the excess Br₂. The organic layer was separated and dried overnight over anhydrous MgSO₄. The orange solution was then filtered through Celite and evaporated to dryness under reduced pressure. Crystallization from CS₂/hexane at -20°C yielded tangerine crystals of CpFe(CO)(CS)Br (0.0992 g, 70% yield).

IR (CS₂): 2033 s, 1309 vs cm⁻¹.

¹H NMR (CS₂): τ 5.00 (Cp).

Anal. Calcd. for CpFe(CO)(CS)Br: C, 30.80; H, 1.85.

Found: C, 30.89; H, 1.95.

12. Reaction of [CpFe(CO)(CS)]₂ with Br₂ at low temperature

A solution of a cis,trans-[CpFe(CO)(CS)]₂ mixture (0.112 g, 0.290 mmoles) in 25 ml of CS₂ was cooled to 0°C in an ice bath. A solution of Br₂ in CS₂ (10 ml of a solution of 1.0 ml of Br₂ diluted to 100 ml with CS₂, 1.95 mmoles) was then added dropwise to the cooled solution. After the addition was complete, the solution was stirred an additional 1/2 hour, then the black precipitate was filtered off and washed with CS₂, which changed the color of the precipitate to

red-orange (the filtrate showed a trace of $\text{CpFe}(\text{CO})(\text{CS})\text{Br}$ after destroying the excess Br_2 by extraction with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and subsequent drying). The red-orange residue dissolved in CH_3CN to give a bright orange solution. An infrared spectrum of this solution suggested a tentative identity for the product as $\{[\text{CpFe}(\text{CO})(\text{CS})]_2\text{Br}\}\text{Br}$.

IR (CH_3CN): 2104 sh,w, 2084 s, 2039 m, 1325 s, 1179 w.

Upon standing, this CH_3CN solution developed infrared bands due to $\text{CpFe}(\text{CO})(\text{CS})\text{Br}$ (2031 s, 1308 vs cm^{-1}).

13. Reaction of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ with Cl_2 at low temperature

After a solution of a cis,trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ mixture (0.382 g, 0.990 mmoles) in 50 ml of CCl_4 was cooled to 0°C in an ice bath, a solution of excess Cl_2 in CCl_4 (15 ml of a Cl_2 -saturated solution, ~ 36 mmoles) was added dropwise to the cooled solution forming an emerald-green precipitate. After removal of the excess Cl_2 and CCl_4 by evaporation under reduced pressure, the residue was dissolved in CH_3CN and filtered through Celite to give a blue-green to emerald-green solution. Evaporation of this blue-green solution resulted in a dark-green to black solid, tentatively identified as $\{[\text{CpFe}(\text{CO})(\text{CS})]_2\text{Cl}\}\text{Cl}$ by analogy to the reaction of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ with Br_2 (vide ante).

Attempts to obtain an infrared spectrum of a solution of this product failed, as invariably the intense blue-green solution decomposed to a light brown solution during the progress of the spectrum. Although the infrared spectrum of this brown solution varied, the expected decomposition product $\text{CpFe}(\text{CO})(\text{CS})\text{Cl}$ was not observed.

IR (Nujol Mull): 2095 w, 2091 w, 2082 w, 2074 m,
2046-2014 br,s, 1984 w, 1220 w, 1119 w cm^{-1} .

14. Reaction of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ with I_2

A solution of cis,trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ (0.333 g, 0.863 mmol) and iodine (0.484 g, 1.91 mmol), in 25 ml of CH_3CN was stirred at room temperature for 30 minutes. An infrared spectrum of the solution at this time indicated that approximately a third of the starting thiocarbonyl dimer had reacted to form what is tentatively identified as $\{[\text{CpFe}(\text{CO})(\text{CS})]_2\text{I}\}\text{I}$.

IR (CH_3CN): 2084 s, 1325 s cm^{-1} .

The flask was then placed in an oil bath and the solution was refluxed for 1 hour and then cooled to room temperature. At this time, an infrared spectrum indicated the presence of $\{[\text{CpFe}(\text{CO})(\text{CS})]_2\text{I}\}\text{I}$ and $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ along with an unidentified band at 2047 cm^{-1} . The excess iodine was then destroyed by extracting with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (2 x 10 ml portions, 0.42 mg/ml) after adding 50 ml of CH_2Cl_2 to ensure a two phase system. The organic layer was dried overnight with anhydrous MgSO_4 , filtered, and evaporated to dryness to yield a black solid. Part of the black solid dissolved (0.105 g) in CS_2 giving a green solution. An infrared spectrum determined that the solution contained predominately $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ (a 19% yield of the crude material) with some $\text{CpFe}(\text{CO})_2\text{I}$ present.

IR (CS_2): 2023 s, 1305 vs cm^{-1} .

By comparison of the intensities of the infrared bands of the two species (2023 cm^{-1} for $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ and 1998 cm^{-1} for $\text{CpFe}(\text{CO})_2\text{I}$), it was determined the product was $\sim 10\%$ $\text{CpFe}(\text{CO})_2\text{I}$ (Beer's Law was proven using pure samples of the two compounds).

Attempts to prepare $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ under milder conditions analogous to those used in the preparation of $\text{CpFe}(\text{CO})_2\text{I}$ from $[\text{CpFe}(\text{CO})_2]_2$ were less successful. The cationic intermediate, $\{[\text{CpFe}(\text{CO})(\text{CS})]_2\text{I}\}^+$, did appear to form slowly in CHCl_3 at room temperature with $[\text{CpFe}(\text{CO})(\text{CS})]_2$ and excess I_2 . However, after refluxing for 40 minutes, only a portion of the thiocarbonyl dimer was converted to $\text{CpFe}(\text{CO})(\text{CS})\text{I}$. There was still an approximate 2:1 ratio of unreacted $[\text{CpFe}(\text{CO})(\text{CS})]_2$ to $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ after refluxing, and also a fair amount of decomposition was evident.

15. Reaction of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ with reducing agents

A THF solution of cis,trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ reacted with an excess of reducing agents such as Na/Hg , C_8K (134), and $\text{NaK}_{2.8}$ (100) to give a grey to dark brown precipitate. This precipitate was insoluble in common solvents, but dissolved in HMPA (hexamethylphosphoramide) to give a dark red solution that decomposed upon exposure to air.

Attempts to characterize this precipitate or a stable derivative thereof were unsuccessful. The precipitate showed no apparent reaction with either MeI or $\phi_3\text{SnCl}$. The dark red HMPA solution also showed no apparent reaction with MeI , and infrared spectra of the products were

ill-defined and showed no strong bands in the thiocarbonyl region (1350 - 1000 cm^{-1}).

However, a THF solution (50 ml) of cis,trans-[CpFe(CO)(CS)]₂ (0.503 g, 1.30 mmol) did react with a slight excess of Na/Hg (~1.5 mmol) to give a red solution within 5-10 minutes. At this time, an infrared spectrum of the solution showed bands at 2007 vs, 1975 m, 1717 m, and 1678 w -- relatively little changed from the starting thiocarbonyl dimer. After stirring for 30 minutes, the Hg was drained from the flask, and 3.0 ml of MeI (48 mmol) was added to the red solution. After stirring a few minutes, the solution was evaporated to dryness, extracted with CS₂, and then filtered through Celite to yield a bright red air-sensitive solution.

IR (CS₂): 2038 w, 2014 vs, 1983 m, 1776 m, 1124 s cm^{-1} .

¹H NMR (CS₂): τ 5.30 (s, 5.0); 5.92 (s, 6.1); 8.42 (s, 6.1); 8.78 (m, 15.2).

While the IR spectrum would suggest the red solution contains [CpFe(CO)(CS)]₂, its color, ¹H NMR, and air-sensitivity suggest otherwise.

With an excess of the homogeneous reducing agent sodium naphthalide (135) (2.0 ml of a 0.37 M solution in THF, 0.74 mmol), the thiocarbonyl dimer, [CpFe(CO)(CS)]₂, (0.101 g 0.261 mmol) reacted in 30 ml of THF to give an olive-green solution. After stirring for 1 hour, $\phi_3\text{SnCl}$ (0.233 g, 0.735 mmol) was added and the solution was allowed to stir overnight. Subsequent treatment and column

chromatography gave a small amount of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ as the only thiocarbonyl-containing product.

No reaction was apparent after stirring a solution of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ in THF with excess sodium hydride for two days.

16. Reaction of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ with MX

In an attempt to find a more direct synthesis for $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ compounds, hopefully with improved overall yields. $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ was reacted with various halide reagents (KI, KCl, NaCl, LiCl, LiBr, LiI, Et_4NI , and NaCN). A typical experiment is described below.

A mixture of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ (0.502 g, 1.36 mmol) and KI (0.104 g, 1.39 mmol) was stirred in 25 ml of THF until all the undissolved solids had disappeared (the solution also changed color from pale yellow to dark green in the case of I^-). The solution was then evaporated to dryness under reduced pressure, the residue was extracted with either CHCl_3 or CS_2 and then filtered through Celite. An infrared spectrum of the green solution showed the presence of both $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ and $\text{CpFe}(\text{CO})_2\text{I}$.

From the intensities of the product absorptions in the IR estimates were made of the ratios, $\text{CpFe}(\text{CO})(\text{CS})\text{X}:\text{CpFe}(\text{CO})_2\text{X}$, using the various reactants (see Table 5).

With KI, KCl, NaCl, LiCl, LiBr, LiI and Et_4NI , the reaction went cleanly to a mixture of $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ and $\text{CpFe}(\text{CO})_2\text{X}$. With NaCN, however, neither $\text{CpFe}(\text{CO})(\text{CS})\text{CN}$ nor $\text{CpFe}(\text{CO})_2\text{CN}$ could be identified from the infrared spectrum of the final solution.

IR (CS₂): 2057 s, 2041 sh,s, 2033 s, 1992 vs, 1950 w,
1280 w, 1250 w, 1208 s cm⁻¹.

17. Photolysis of [CpFe(CO)₂(CS)]CF₃SO₃. Preparation of
CpFe(CO)(CS)CF₃SO₃

Crystals of [CpFe(CO)₂(CS)]CF₃SO₃ (0.437 g, 1.18 mmol) were placed in a quartz Schlenk tube, and the apparatus was degassed by several cycles (4-5) of alternate evacuation and filling with nitrogen. Then, CH₂Cl₂ (35 ml) was added, and the apparatus was fitted with a cooling probe and a mineral oil bubbler, and placed in the small ultraviolet irradiation box. Irradiation at 254 nm was continued until an infrared spectrum of the solution indicated that the production of CpFe(CO)(CS)CF₃SO₃ was at a maximum. With this apparatus and amount of starting material, it was found that the maximum concentration of CpFe(CO)(CS)CF₃SO₃ occurred after 5 hours of irradiation. Further irradiation slowly decreased the amount of CpFe(CO)(CS)CF₃SO₃ present.

After irradiation, the red solution was transferred to a larger N₂-filled Schlenk tube (~150 ml). Ether (~95 ml) or hexane (~65 ml) was added to precipitate remaining starting material and any decomposition products. The solution was then filtered through Celite under nitrogen to give a clear red solution of CpFe(CO)(CS)CF₃SO₃.

IR (CH₂Cl₂): 2051 s, 1322 vs cm⁻¹.

IR (CS₂): 2054 s (νCO), 1333 s, 1318 vs (νCS), 1231 s,
1195 s cm⁻¹.

¹H NMR (CDCl₃): τ 4.76.

^{13}C NMR (CDCl_3): δ -321.7 (CS), -207.8 (CO), -88.0 (Cp).

Solutions of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ were used immediately after preparation for the synthesis of further products, as they decomposed rapidly in air and slowly under nitrogen. Attempts to isolate a crystalline product by evaporation of hexane or other solutions of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ resulted in a red oil which slowly decomposed even at -20°C under nitrogen.

Irradiation of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ in other solvents was not as successful as in CH_2Cl_2 . In THF or acetone, the expected $[\text{CpFe}(\text{CO})(\text{CS})(\text{L})]^+$ (L = THF or acetone) either did not form or low yields (by estimation of the infrared spectra) were obtained.

18. Photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$ in acetone

As in the synthesis of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$, crystals of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$ (0.420 g, 1.15 mmol) were placed in a quartz Schlenk tube and degassed by alternate evacuation and filling with nitrogen. Acetone (35 ml) was added and the apparatus was fitted with a mineral oil bubbler and a cooling probe. Irradiation at 254 nm in a small ultraviolet irradiation box for 5 hours resulted in a dark brown solution. By following the progress of the reaction using infrared spectroscopy, it was determined that the maximum yield of $[\text{CpFe}(\text{CO})(\text{CS})(\text{acetone})]\text{PF}_6$ had formed in 5 hours. Further irradiation resulted in decreased yields.

The brown solution was then transferred under nitrogen to a larger schlenk tube (~ 180 ml). Ether (120 ml) was then added to precipitate

remaining starting material and any decomposition products. Filtration under nitrogen through Celite resulted in a clear brown solution containing $[\text{CpFe}(\text{CO})(\text{CS})(\text{acetone})]\text{PF}_6$.

IR (acetone): 2031 s, 1303 vs cm^{-1} .

Attempts to isolate a solid product by evaporation, or precipitation with ether (or hexane) resulted in a brown oil. Both this oil and the solutions of $[\text{CpFe}(\text{CO})(\text{CS})(\text{acetone})]\text{PF}_6$ are air sensitive and decompose slowly even under nitrogen.

19. Preparation of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$

A large photochemical reactor charged with $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$ (7.81 g, 21.3 mmol) was degassed by several cycles of alternate evacuation and filling with N_2 at atmospheric pressure. De-oxygenated CH_2CN (350 ml) was added, and the solution was irradiated for 8 hours. After 2, 4, and 6 hours, the probe was removed from the reaction vessel and cleaned of accumulated brown residue by wiping with a Kimwipe wetted with acetone. After the 8 hours of irradiation, the yellow-green, air-stable solution of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ was transferred to a 500 ml FB flask and evaporated to dryness. The residue was then dissolved in CH_2Cl_2 and filtered through Celite. The filtrate was reduced in volume until precipitation began (~ 150 ml), then 100 ml of CHCl_3 was added. The volume was again reduced to the point of precipitation while heating in a water bath ($\sim 60^\circ\text{C}$). Cooling to -20°C gave shiny yellow-green crystals of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$. Repetition of this crystallization procedure gave a second batch of crystals for a total of 5.38 g (64% yield).

IR (CH₃CN): 1298 s cm⁻¹.

¹H NMR (d⁶-acetone): τ 4.84 (Cp), 7.48 (CH₃CN).

¹³C NMR (d⁶-acetone): δ -329.4 (CS), -222.6 (-CN), -87.4 (Cp),
4.14 (-CH₃).

Anal. Calcd. for [CpFe(CS)(CH₃CN)₂]PF₆: C, 30.63; H, 2.83;
S, 8.18. Found: C, 30.66; H, 2.94; S, 8.39.

The yield reported was from an early preparation of [CpFe(CS)(CH₃CN)₂]PF₆. Actual yields following this procedure are probably greater.

The irradiation time was determined by following the growth of the 1298 cm⁻¹ band in the IR. For these conditions with this apparatus, 8 hours was found to give the greatest intensity for this band. Further irradiation results in some decomposition and a lessening of the 1298 cm⁻¹ band intensity.

20. Preparation of [CpFe(CS)(Me₂S)₂]PF₆

Crystals of [CpFe(CO)₂(CS)]PF₆ (0.457 g, 1.25 mmoles) were placed in a quartz Schlenk tube, and the apparatus was degassed by several cycles of alternate evacuation and filling with nitrogen. Then deoxygenated acetone (33 ml) and Me₂S (1.0 ml, 13.6 mmoles) were added. The apparatus was fitted with a cooling probe and mineral oil bubbler, and then irradiated for 5 hours at 254 nm. The progress of the reaction was followed in the IR and irradiation was continued until the intensity of the 1287 cm⁻¹ band, due to [CpFe(CS)(Me₂S)₂]PF₆, was at a maximum. Under these conditions, 5 hours of irradiation gave a

maximum yield. The dark green solution was then evaporated to dryness under reduced pressure. The residue was dissolved in CH_2Cl_2 and filtered through Celite. Crystallization from $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ at -20°C gave black crystals of $[\text{CpFe}(\text{CS})(\text{Me}_2\text{S})_2]\text{PF}_6$ (0.322 g, 59% yield).

IR (CH_3CN): 1287 s cm^{-1} .

^1H NMR (d^6 -acetone) (of $[\text{CpFe}(\text{CS})(\text{Me}_2\text{S})_2]\text{CF}_3\text{SO}_3$): τ 4.78 (Cp),
7.60 (Me).

Anal. Calcd. for $[\text{CpFe}(\text{CS})(\text{Me}_2\text{S})_2]\text{PF}_6$: C, 27.66; H, 3.95.

Found: C, 28.34; H, 4.19.

21. Preparation of $\text{CpFe}(\text{CO})(\text{CS})\text{I}$

A solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ was produced by photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ (0.402 g, 1.09 mmol) in 20 ml of CH_2Cl_2 . After isolation of the solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ in ether, KI (0.183 g, 1.10 mmol) and acetone (30 ml) were added, and the mixture was stirred until all the KI had dissolved (typically the mixture was allowed to stir overnight). The solution was then evaporated to dryness, and the residue was extracted with CS_2 until all the green $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ had been extracted. This green solution was filtered, the volume was reduced to ~ 20 ml, then heptane was slowly added while warming the flask until the point of precipitation was reached. Cooling to -20°C gave black crystals of $\text{CpFe}(\text{CO})(\text{CS})\text{I}$. Repetition of the crystallization step gave a second batch of crystals for a total of 0.223 g (64% yield).

IR (CS₂): 2024 s, 1306 vs cm⁻¹.

¹H NMR (CS₂): τ 4.93 (Cp).

¹³C NMR (CDCl₃): δ -322.5 (CS), -212.5 (CO), -87.6 (Cp).

Anal. Calcd. for CpFe(CO)(CS)I: C, 26.28; H, 1.58.

Found: C, 25.91; H, 1.66.

The CpFe(CO)(CS)I produced by this synthesis typically has ~3% CpFe(CO)₂I present. For most purposes, this is sufficiently pure, and unless stated otherwise, the CpFe(CO)(CS)I used in later syntheses was this crude CpFe(CO)(CS)I. However, if a pure product is desired, the CpFe(CO)(CS)I can be separated from the CpFe(CO)₂I by fractional crystallization from CS₂/hexane. The analytical sample was so purified. Pure CpFe(CO)(CS)I was also obtained by liquid chromatography on Florisil eluting with CS₂.

22. Preparation of CpFe(CO)(CS)Br. Method II. Reaction of CpFe(CO)(CS)CF₃SO₃ with KBr

A solution of CpFe(CO)(CS)CF₃SO₃ was prepared by photolysis of [CpFe(CO)₂(CS)]CF₃SO₃ (0.409 g, 1.10 mmoles) in CH₂Cl (20 ml). After isolation of the solution of CpFe(CO)(CS)CF₃SO₃ in ether, KBr (0.17 g, 0.980 mmoles) and acetone (75 ml) were added, and the mixture was stirred until all the KBr had dissolved (typically overnight). The solution was then evaporated to dryness, and the residue was extracted with CS₂ until all the orange CpFe(CO)(CS)Br had been extracted. This orange solution was filtered through Celite, the volume was reduced to ~20 ml, and then heptane was added to the point of precipitation.

Cooling to -20°C gave orange crystals of $\text{CpFe}(\text{CO})(\text{CS})\text{Br}$. Repetition of this crystallization step gave a second batch of crystals for a total of 0.154 g (a 51% yield).

IR (CS_2): 2033 s, 1309 vs cm^{-1} .

The $\text{CpFe}(\text{CO})(\text{CS})\text{Br}$ produced in this synthesis typically had $\sim 11\%$ $\text{CpFe}(\text{CO})_2\text{Br}$ present. As with $\text{CpFe}(\text{CO})(\text{CS})\text{I}$, pure $\text{CpFe}(\text{CO})(\text{CS})\text{Br}$ could be isolated by fractional crystallization or liquid chromatography.

23. Preparation of $\text{CpFe}(\text{CO})(\text{CS})\text{Cl}$

A solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ was prepared by photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ (0.413 g, 1.12 mmol) in CH_2Cl_2 (20 ml). After isolation of the solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ in ether, KCl (0.0829 g, 1.11 mmol) and acetone (50 ml) were added, and the mixture was stirred until all the KCl had dissolved (3 1/2 hours). The solution then was evaporated to dryness, and the residue was extracted with CS_2 until all the red color had been extracted. This red solution was filtered through Celite, the volume was reduced to ~ 10 ml, and ~ 15 ml of heptane was added. Slow evaporation under a stream of nitrogen gave a reddish powder of crude $\text{CpFe}(\text{CO})(\text{CS})\text{Cl}$ (0.0691 g, 31% yield).

IR (CS_2): 2036 s, 1310 vs cm^{-1} .

As with $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ and $\text{CpFe}(\text{CO})(\text{CS})\text{Br}$, the crude $\text{CpFe}(\text{CO})(\text{CS})\text{Cl}$ produced by this method contains some $\text{CpFe}(\text{CO})_2\text{Cl}$ ($\sim 13\%$). Isolation of pure $\text{CpFe}(\text{CO})(\text{CS})\text{Cl}$ was not attempted.

24. Preparation of $[\text{CpFe}(\text{CO})(\text{CS})(\text{P}\phi_3)]\text{CF}_3\text{SO}_3$

A solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ was prepared by photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ (0.402 g, 1.09 mmol) in CH_2Cl_2 (20 ml). The volume of this solution was reduced to ~ 2 ml under a nitrogen stream. Then, 25 ml of Et_2O was added, and the solution filtered through Celite under N_2 to give a clear red solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$. With addition of $\text{P}\phi_3$ (0.288 g, 1.10 mmol), the color of the solution changed to yellow within a minute and a precipitate formed. The solution was stirred for 5 minutes, and then filtered. The precipitate was dissolved in acetone, filtered, and while warming heptane was added to the point of precipitation. Cooling to -20°C gave golden crystals of $[\text{CpFe}(\text{CO})(\text{CS})(\text{P}\phi_3)]\text{CF}_3\text{SO}_3$ (0.399 g, a 61% yield).

IR (CH_3CN): 2034 s, 1323 vs cm^{-1} .

^1H NMR (d^6 -acetone): τ 4.45 (d, $J = 1.0$ Hz, Cp), 2.27-2.72 (m, ϕ).

Anal. Calcd. for $[\text{CpFe}(\text{CO})(\text{CS})(\text{P}\phi_3)]\text{CF}_3\text{SO}_3$: C, 51.67; H, 3.34.

Found: C, 51.61; H, 3.41.

25. Preparation of $[\text{CpFe}(\text{CO})(\text{CS})]\text{CF}_3\text{SO}_3$

A solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ was prepared by photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ (0.432 g, 1.17 mmol) in CH_2Cl_2 (35 ml). After isolation of the solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ in hexane, pyridine (0.4 ml, 6.2 mmol) was added. Within a minute, the color of the solution changed from red to yellow. The solution was stirred for 5 minutes and then evaporated to dryness under reduced pressure. The

greenish residue was dissolved in CH_2Cl_2 (~ 20 ml), filtered through Celite, and hexane (~ 150 ml) was added to precipitate a greenish-brown oil, $[\text{CpFe}(\text{CO})(\text{CS})(\text{py})]\text{CF}_3\text{SO}_3$ (0.347 g, 71% yield). Attempts to obtain a crystalline product by crystallization from acetone/ Et_2O , CH_2Cl_2 /hexane, or acetone/hexanes were unsuccessful.

IR (CH_3CN): 2045 s, 1321 vs cm^{-1} .

^1H NMR (d^6 -acetone): τ 4.32 (Cp), 1.07-2.43 (py).

26. Preparation of $[\text{CpFe}(\text{CO})(\text{CS})(\text{CH}_3\text{CN})]\text{CF}_3\text{SO}_3$

A solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ was prepared by photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ (0.446 g, 1.20 mmoles) in CH_2Cl_2 (35 ml). After isolation of the solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ in hexane, acetonitrile (1.0 ml, 19 mmoles) was added and the solution was refluxed for 30 minutes. After cooling to room temperature, the yellow solution was evaporated to dryness under reduced pressure. The residue was dissolved in CH_2Cl_2 (~ 15 ml), filtered through Celite, and hexane was added to precipitate a yellow-brown oil, $[\text{CpFe}(\text{CO})(\text{CS})(\text{CH}_3\text{CN})]\text{CF}_3\text{SO}_3$ (0.330 g, a 72% yield). Attempts to obtain a crystalline product were unsuccessful.

IR (CH_3CN): 2056 s, 1327 vs cm^{-1} .

^1H NMR (d^6 -acetone): τ 4.33 (Cp), 7.49 (CH_3CN).

27. Reaction of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ with $\text{P}(\text{O}\phi)_3$

A solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ was prepared by photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ (0.453 g, 1.22 mmoles) in CH_2Cl_2 (36 ml). After

isolation of the solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ in hexane, $\text{P}(\text{O}\phi)_3$ (250 μl , 0.95 mmol) was added, and the solution was stirred until the red color disappeared (50 minutes). After evaporating the solution to dryness under reduced pressure, the residue was dissolved in CH_2Cl_2 (~ 20 ml) and filtered through Celite. Addition of hexane (~ 150 ml) gave a yellow-brown oil. Spectroscopic analysis showed the oil to be a mixture of $[\text{CpFe}(\text{CO})(\text{CS})(\text{P}\{\text{O}\phi\}_3)]\text{CF}_3\text{SO}_3$ (the major product) and $[\text{CpFe}(\text{CS})(\text{P}\{\text{O}\phi\}_3)_2]\text{CF}_3\text{SO}_3$. Attempts to separate the two components or to obtain a crystalline product were unsuccessful.

IR (CH_3CN): 2051 s (νCO), 1337 s (νCS , mono-substituted cation), 1323 sh, m cm^{-1} (νCS , bis-substituted cation).

^1H NMR (d^6 -acetone): τ 2.33-2.80 (m, $\text{P}\{\text{O}\phi\}_3$), 4.70 (d, $J = 0.9$ Hz, mono-substituted cation, Cp), 5.16 (t, $J = 1.0$ Hz, bis-substituted cation, Cp), ($\sim 3:1$ ratio of mono:bis-substituted cations).

28. Reaction of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ with $\text{P}(\text{OMe})_3$

A solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ was prepared by photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ (0.454 g, 1.23 mmol) in CH_2Cl_2 (35 ml). After isolation of the solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ in hexane, $\text{P}(\text{OMe})_3$ (130 μl , 1.10 mmol) was added and the solution was stirred for 25 minutes during which time the solution changed color from red to pale yellow, and a brown precipitate formed. The solution was then filtered yielding a pale yellow filtrate, which was evaporated to a yellow-brown oil, and a brown residue.

Spectroscopic analysis of the yellow-brown oil indicated that it was predominantly $[\text{CpFe}(\text{CS})(\text{P}(\text{OMe})_3)_2]\text{CF}_3\text{SO}_3$.

IR (CH_3CN): 1308 s cm^{-1} .

Similarly, the brown precipitate was found to be a mixture of $[\text{CpFe}(\text{CO})(\text{CS})(\text{P}(\text{OMe})_3)]\text{CF}_3\text{SO}_3$ (the major product) and $[\text{CpFe}(\text{CS})(\text{P}(\text{OMe})_3)_2]\text{CF}_3\text{SO}_3$.

IR (CH_3CN): $2043 \text{ s } (\nu\text{CO})$, $1331 \text{ vs } (\nu\text{CS, mono-substituted cation})$, $1308 \text{ s cm}^{-1} (\nu\text{CS, bis-substituted cation})$.

$^1\text{H NMR}$ (d^6 -acetone): τ 4.28 (d, $J = 1.1 \text{ Hz}$, mono-substituted cation, Cp), 4.69 (t, $J = 1.0 \text{ Hz}$, bis-substituted cation, Cp), 5.90-6.27 (m, $\text{P}(\text{OMe})_3$).

Attempts to isolate either product by crystallization, precipitation, or chromatography were unsuccessful. Reducing the amount of $\text{P}(\text{OMe})_3$ initially added to as low as 0.64 mmoles still gave a mixture of products.

29. Reaction of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ with $(n\text{-Bu})_2\text{S}$

A solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ was prepared by photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ (0.440 g, 1.19 mmoles) in CH_2Cl_2 (35 ml). After isolation of the solution of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ in hexane, $(n\text{-Bu})_2\text{S}$ (1.0 ml, 5.7 mmoles) was added. The solution was refluxed for 40 minutes during which time its color changed from red to yellow-brown. After cooling to room temperature, the solution was evaporated to dryness under reduced pressure. The residue was then dissolved in $\sim 10 \text{ ml}$ of CH_2Cl_2 . The solution was filtered through Celite, and hexane

(150 ml) was added to precipitate a brownish oil. This mixture was then filtered, giving a brown residue and a green filtrate. The dissolution of the brown residue and precipitation was repeated two additional times to separate the soluble green $[\text{CpFe}(\text{CS})(\text{Bu}_2\text{S})_2]\text{CF}_3\text{SO}_3$ in the filtrates from the brown insoluble $[\text{CpFe}(\text{CO})(\text{CS})(\text{Bu}_2\text{S})]\text{CF}_3\text{SO}_3$. The separation was not complete as the final greenish-brown powder, $[\text{CpFe}(\text{CO})(\text{CS})(\text{Bu}_2\text{S})]\text{CF}_3\text{SO}_3$, had a small amount of $[\text{CpFe}(\text{CS})(\text{Bu}_2\text{S})_2]\text{CF}_3\text{SO}_3$ present ($\sim 36\%$ yield).

IR (CH_3CN): 2040 s, 1323 vs cm^{-1} .

^1H NMR (d^6 -acetone): τ 4.28 (mono-substituted cation, Cp),
4.70 (bis-substituted cation, Cp), 6.90-7.32 (m, S- CH_2 -),
8.08-9.25 (m, $-\text{CH}_2\text{CH}_2\text{CH}_3$) (the ratio of mono:bis
substituted cation was $\sim 12:1$).

30. Reaction of $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ with PEt_3

Triethylphosphine, PEt_3 , (150 μl , 1.02 mmoles) was added to a solution of crude $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ (0.322 g, 1.01 mmoles) in benzene (50 ml), and the solution was refluxed for one hour under nitrogen. An infrared spectrum of the solution at this time indicated (by absence of the 2024 cm^{-1} band of $\text{CpFe}(\text{CO})(\text{CS})\text{I}$) that the starting material had completely reacted. The solution was cooled to room temperature and filtered to remove the yellow precipitate which had formed within the first 5 minutes of refluxing. The yellow precipitate was washed with benzene and pentane to yield 0.083 g of crude $[\text{CpFe}(\text{CO})(\text{CS})(\text{PEt}_3)]\text{I}$

(~19% yield). The product contained a small percentage of $[\text{CpFe}(\text{CO})_2(\text{PEt}_3)]\text{I}$ {IR (CH_3CN): 2046, 2006 cm^{-1} }.

IR (CH_3CN): 2027 s, 1319 vs cm^{-1} .

The green filtrate from above was evaporated to dryness, and the residue was then dissolved in CS_2 (~15 ml). The solution was filtered and hexane (~15 ml) added. The solution was then slowly evaporated under a stream of nitrogen until a precipitate began to form.

Crystallization at -20°C gave dark green crystals of $\text{CpFe}(\text{CS})(\text{PEt}_3)\text{I}$ (0.134 g, a 33% yield).

IR (CS_2): 1272 cm^{-1} .

^1H NMR (CS_2): τ 5.36 (d, $J = 0.8$ Hz, Cp), 7.68-8.27 (m, $-\text{CH}_2-$), 8.57-9.13 (m, $-\text{CH}_3$).

^{13}C NMR (CDCl_3): δ -324.4 (d, $J = 37.8$ Hz, CS), -85.7 (s, Cp), -21.0 (d, $J = 28.1$ Hz, $-\text{CH}_2-$), -8.4 (s, $-\text{CH}_3$).

Anal. Calcd. for $\text{CpFe}(\text{CS})(\text{PEt}_3)\text{I}$: C, 35.15; H, 4.92.

Found: C, 35.30; H, 5.08.

31. Preparation of $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$. Method I. Reaction of $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ with $\text{P}\phi_3$

A solution of crude $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ (1.51 g, 4.72 mmol) and triphenylphosphine, $\text{P}\phi_3$, (1.24 g, 4.74 mmol) in benzene (80 ml) was refluxed for 3 hours under nitrogen. An infrared spectrum of the solution at this time indicated that the $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ had completely reacted. The solution was then cooled to room temperature and evaporated to dryness under reduced pressure. The residue was dissolved

in CS₂ and chromatographed on a Florisil column (18 x 730 mm). Elution with CS₂ was continued until the initial gray band had been collected. This band contained the unreacted CpFe(CO)₂I impurity. Elution was continued with 1% Et₂O/CS₂. The second, dark green band was then collected in fractions. Essentially all of the CpFe(CS)(Pφ₃)I eluted before the CpFe(CO)(Pφ₃)I; however, as both compounds are dark green, the composition of each fraction had to be monitored by infrared spectroscopy. The fractions containing only CpFe(CS)(Pφ₃)I were then combined and evaporated to dryness. The residue was dissolved in CH₂Cl₂ (~20 ml); the solution was filtered through Celite, and then heptane (20 ml) was added. The solution was slowly evaporated under a nitrogen stream until crystals began to form. Crystallization at -20°C gave green crystals of CpFe(CS)(Pφ₃)I (1.768 g, a 68% yield).

IR (CS₂): 1271 cm⁻¹.

¹H NMR (CS₂): τ 2.22-2.83 (m, φ), 5.58 (d, J = 0.9 Hz, Cp).

¹³C NMR (CDCl₃): δ -325.0 (d, J = 37.2 Hz, CS), -134.9 (s, φ), 132.9 (d, J = 7.4 Hz, φ), -129.5 (s, φ), -127.3 (d, J = 8.9 Hz), -87.1 (s, Cp).

Anal. Calcd. for CpFe(CS)(Pφ₃): C, 52.01; H, 3.64.

Found: C, 51.92; H, 3.68.

The product, CpFe(CS)(Pφ₃)I, can also be isolated by fractional crystallization from CS₂/heptane or CH₂Cl₂/heptane; however, yields of the pure compound are lower.

32. Preparation of CpFe(CS)(As ϕ_3)I

A solution of crude CpFe(CO)(CS)I (0.105 g, 0.329 mmol) and triphenylarsine, As ϕ_3 , (0.155 g, 0.506 mmol) in benzene (25 ml) was refluxed under nitrogen for 22 hours. An infrared spectrum of the solution at this time indicated that almost all the CpFe(CO)(CS)I had reacted. The solution was cooled to room temperature, and then placed on a Florisil chromatography column (12 x 340 mm). Elution with benzene gave two bands. The first band, brown in color, was collected and evaporated to dryness. An infrared spectrum showed this band to contain unreacted CpFe(CO)(CS) and CpFe(CO) $_2$ I. The second, a green band containing the product CpFe(CS)(As ϕ_3)I and some CpFe(CO)(As ϕ_3)I, was collected and evaporated to dryness under reduced pressure. The residue was dissolved in CS $_2$, the solution was filtered, and heptane (~10 ml) was added. The solution was then placed under a slow nitrogen stream until crystals began to form, and then cooled to -20°C. This crystallization procedure was repeated again to yield green crystals of CpFe(CS)(As ϕ_3)I (0.099 g, a 50% yield).

IR (CS $_2$): 1271 cm $^{-1}$.

1 H NMR (CS $_2$): τ 2.33-2.80 (m, ϕ), 5.50 (s, Cp).

33. Preparation of CpFe(CS)(Sb ϕ_3)I

A solution of crude CpFe(CO)(CS)I (0.111 g, 0.346 mmol) and triphenylstilbine, Sb ϕ_3 , (0.231 g, 0.653 mmol) in benzene (25 ml) was refluxed under nitrogen for 37 hours. An infrared spectrum of the solution at this time indicated that essentially all of the CpFe(CO)(CS)I

had reacted. The solution was cooled to room temperature, and placed on a Florisil chromatography column (12 x 340 mm). Elution with 1) benzene and 2) CH_2Cl_2 gave a single green band. The band was collected and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (~10 ml), the solution was filtered, and heptane (~10 ml) was added. The solution was then placed under a slow stream of nitrogen until crystals began to form. Crystallization at -20°C gave green crystals of $\text{CpFe}(\text{CS})(\text{Sb}\phi_3)\text{I}$ (0.153 g, a 68% yield).

IR (CS_2): 1269 cm^{-1} .

^1H NMR (CS_2): τ 2.37-2.83 (m, ϕ), 5.39 (s, Cp).

Anal. Calcd. for $\text{CpFe}(\text{CS})(\text{Sb}\phi_3)\text{I}$: C, 44.69; H, 3.13.

Found: C, 44.56; H, 3.02.

34. Preparation of $\text{CpFe}(\text{CS})(\text{P}\{\text{OMe}\}_3)\text{I}$

A solution of crude $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ (0.335 g, 1.05 mmol) and trimethylphosphite, $\text{P}(\text{OMe})_3$, (1.0 ml, 8.48 mmol) in benzene (50 ml) was refluxed under nitrogen for 11 hours. An infrared spectrum of the solution at this time indicated that the $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ had completely reacted. The solution was then reduced in volume in vacuo to a couple of milliliters and placed on a Florisil chromatography column (12 x 300 mm). Elution with benzene gave a single green band, which was collected and evaporated to dryness. An infrared spectrum of the residue in CS_2 showed this to be a mixture of $\text{CpFe}(\text{CS})(\text{P}\{\text{OMe}\}_3)\text{I}$, the major product, and $\text{CpFe}(\text{CO})(\text{P}\{\text{OMe}\}_3)\text{I}$. Pure $\text{CpFe}(\text{CS})(\text{P}\{\text{OMe}\}_3)\text{I}$ was then isolated by fractional crystallization as indicated below.

The residue was dissolved in a minimum of CH_2Cl_2 (~ 10 ml), filtered, and heptane (~ 15 ml) was added. The solution was placed under a slow nitrogen stream until crystals began to form, and then cooled to -20°C to complete the crystallization. The crystals were recovered by filtration and washed with pentane. After repeating the crystallization 3 additional times, black crystals of pure $\text{CpFe}(\text{CS})(\text{P}\{\text{OMe}\}_3)\text{I}$ (0.190 g, a 44% yield) were obtained.

IR (CS_2): 1278 cm^{-1} .

^1H NMR (CS_2): τ 5.31 (s, Cp), 6.29 (d, $J = 11$ Hz, Me).

^{13}C NMR (CDCl_3): δ -323.1 (d, $J = 55.1$ Hz, CS), -86.5 (s, Cp), -54.0 (d, $J = 4.3$ Hz, Me).

Anal. Calcd. for $\text{CpFe}(\text{CS})(\text{P}\{\text{OMe}\}_3)\text{I}$: C, 25.99; H, 3.39.

Found: C, 26.20; H, 3.44.

35. Preparation of $\text{CpFe}(\text{CS})(\text{P}\{\text{O}\phi\}_3)\text{I}$

A solution of crude $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ (0.322 g, 1.01 mmoles) and triphenylphosphite, $\text{P}(\text{O}\phi)_3$, (1.0 ml, 3.8 mmoles) in benzene (50 ml) was refluxed under nitrogen for 12 hours. An infrared spectrum of the solution indicated that the $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ had completely reacted. The solution was then evaporated to dryness under reduced pressure. The residue was dissolved in CS_2 and placed on top of a Florisil chromatography column (12 x 350 mm). Elution with CS_2 was continued until the single green band extended to almost the entire length of the column. Elution was then continued with 10% $\text{CHCl}_3/\text{CS}_2$, and the green band was collected in fractions. Each fraction was analyzed by infrared

spectroscopy. Most of the band contained pure $\text{CpFe}(\text{CS})(\text{P}\{\text{O}\phi\}_3)\text{I}$, only the last few fractions were contaminated with $\text{CpFe}(\text{CO})(\text{P}\{\text{O}\phi\}_3)\text{I}$. The fractions containing only $\text{CpFe}(\text{CS})(\text{P}\{\text{O}\phi\}_3)\text{I}$ were combined and evaporated to dryness under reduced pressure. The residue was dissolved in CH_2Cl_2 (~ 10 ml), filtered, and heptane (~ 10 ml) was added. The solution was then placed under a slow nitrogen stream until crystals began to form. Cooling to -20°C gave green crystals of $\text{CpFe}(\text{CS})(\text{P}\{\text{O}\phi\}_3)\text{I}$ (0.294 g, a 49% yield).

IR (CS_2): 1289 cm^{-1} .

^1H NMR (CS_2): τ 2.55-2.92 (m, ϕ), 5.88 (s, Cp).

Anal. Calcd. for $\text{CpFe}(\text{CS})(\text{P}\{\text{O}\phi\}_3)\text{I}$: C, 47.87; H, 3.35.

Found: C, 47.63; H, 3.45

36. Preparation of $[\text{CpFe}(\text{CS})(\text{bipy})]\text{PF}_6$

A solution of 2,2'-bipyridine, bipy, (0.171 g, 1.09 mmol) in CH_2Cl_2 (50 ml) was added dropwise very slowly (over ~ 30 minutes) to a solution of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ (0.418 g, 1.07 mmol) in CH_2Cl_2 (40 ml). The solution was stirred an additional 30 minutes and then evaporated to dryness. The residue was extracted with CH_2Cl_2 until all the yellow-orange $[\text{CpFe}(\text{CS})(\text{bipy})]\text{PF}_6$ had been extracted and the red $[\text{Fe}(\text{bipy})_3](\text{PF}_6)_2$ was starting to extract. After filtration, the solution was reduced in volume and chromatographed on alumina (12 x 300 mm column) with CH_2Cl_2 . The initial orange-yellow band was collected and evaporated to dryness. Crystallization from $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ at -20°C gave red crystals of $[\text{CpFe}(\text{CS})(\text{bipy})]\text{PF}_6$ (0.161 g, a 32% yield).

IR (CH₃CN): 1293 s cm⁻¹.

¹H NMR (d⁶-acetone): τ 1.00-2.62 (m, bipy), 4.65 (s, Cp).

Anal. Calcd. for [CpFe(CS)(bipy)]PF₆: C, 41.22; H, 2.81.

Found: C, 41.16; H, 2.94.

The extraction step before chromatography was found necessary, as otherwise the [Fe(bipy)₃](PF₆)₂ flooded the column and separation of the [CpFe(CS)(bipy)]PF₆ was not obtained.

37. Preparation of [CpFe(CS)(phen)]PF₆

A solution of 1,10-phenanthroline, phen, (0.208 g, 1.05 mmoles) in CH₂Cl₂ (50 ml) was added dropwise very slowly (over ~30 minutes) to a solution of [CpFe(CS)(CH₃CN)₂]PF₆ (0.424 g, 1.08 mmoles) in CH₂Cl₂ (25 ml). The solution was stirred an additional 30 minutes and then evaporated to dryness under reduced pressure. The residue was extracted with CH₂Cl₂ until the yellow-brown [CpFe(CS)(phen)]PF₆ had been extracted and the red [Fe(phen)₃](PF₆)₂ was starting to extract. After filtration, the solution was reduced in volume and then chromatographed on alumina (12 x 300 mm column). Elution was initially with CH₂Cl₂, but increasing percentages of CH₃CN (up to 50% CH₃CN) were added as the elution progressed. The initial yellow-brown band was collected and evaporated to dryness. Crystallization from CH₂Cl₂/hexane at -20°C gave brown crystals of [CpFe(CS)(phen)]PF₆ (0.093 g, 18% yield).

IR (CH₃CN); 1290 s, 1299 m, sh cm⁻¹.

¹H NMR (d⁶-acetone): τ 0.65-2.12 (m, phen), 4.58 (s, Cp).

Anal. Calcd. for $[\text{CpFe}(\text{CS})(\text{phen})]\text{PF}_6$: C, 44.11; H, 2.67.

Found: C, 44.32; H, 2.60.

38. Preparation of $[\text{CpFe}(\text{CS})(\text{P}\phi_3)_2]\text{PF}_6$

A solution of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ (0.423 g, 1.08 mmol) and triphenylphosphine, $\text{P}\phi_3$, (0.566 g, 2.16 mmol) in CH_2Cl_2 (50 ml) was stirred for 6 hours. The initial yellow-green solution turned dark green in ~ 15 minutes and then red in ~ 1 hour, and then remained red. Evaporation under reduced pressure gave a red tar. The red tar was then extracted with hot benzene, dissolving a red material and leaving behind orange crystals of $[\text{CpFe}(\text{CS})(\text{P}\phi_3)_2]\text{PF}_6 \cdot \text{C}_6\text{H}_6$ (0.330 g, 34% yield). The analytical sample was crystallized from $\text{CH}_2\text{Cl}_2/\text{benzene}$ at -20°C .

IR (CH_3CN): 1285 s, 1090 m cm^{-1} .

$^1\text{H NMR}$ (d^6 -acetone): τ 2.38-2.92 (m, ϕ), 5.10 (t, $J = 1.3$ Hz, Cp).

Anal. Calcd. for $[\text{CpFe}(\text{CS})(\text{P}\phi_3)_2]\text{PF}_6 \cdot \text{C}_6\text{H}_6$: C, 63.17; H, 4.53.

Found: C, 62.28; H, 4.57.

39. Preparation of $[\text{CpFe}(\text{CS})(\text{P}(\text{OMe})_3)(\text{CH}_3\text{CN})]\text{PF}_6$

Trimethylphosphite, $\text{P}(\text{OMe})_3$, (2.0 ml, 17 mmol) was added to a solution of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ (0.461 g, 1.17 mmol) in CH_2Cl_2 (50 ml). After stirring for 9 hours, the orange solution was evaporated to dryness under reduced pressure. The residue was dissolved in CH_2Cl_2 ; the solution was filtered and hexanes were added to the point of precipitation. Crystallization at -20°C gave orange

crystals of $[\text{CpFe}(\text{CS})(\text{P}\{\text{OMe}\}_3)(\text{CH}_3\text{CN})]\text{PF}_6$ (0.233 g, a 42% yield). The analytical sample was crystallized from acetone/hexane.

IR (CH_3CN): 1304 s cm^{-1} .

$^1\text{H NMR}$ (d^6 -acetone): τ 4.81 (d, $J = 0.8 \text{ Hz}$, Cp), 6.15 (d, $J = 11.7 \text{ Hz}$, $\text{P}\{\text{OMe}\}_3$), 7.55 (d, $J = 0.7 \text{ Hz}$, CH_3CN).

Anal. Calcd. for $[\text{CpFe}(\text{CS})(\text{P}\{\text{OMe}\}_3)(\text{CH}_3\text{CN})]\text{PF}_6$: C, 27.81; H, 3.61.

Found: C, 27.83; H, 3.70.

40. Preparation of $[\text{CpFe}(\text{CS})(\text{P}\{\text{O}\phi\}_3)(\text{CH}_3\text{CN})]\text{PF}_6$

Triphenylphosphite, $\text{P}\{\text{O}\phi\}_3$, (1.0 ml, 3.8 mmol) was added to a solution of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ (0.466 g, 1.19 mmol) in CH_2Cl_2 (50 ml). The solution was stirred overnight, although within 2 hours the initial yellow-green solution had turned orange, and no further color change occurred. The solution was then evaporated to dryness under reduced pressure. The residue was dissolved in a minimum of CH_2Cl_2 ($\sim 15 \text{ ml}$), the solution was filtered and then hexanes ($\sim 100 \text{ ml}$) were added to precipitate the product. After filtering off the hexanes and excess $\text{P}\{\text{O}\phi\}_3$, the orange product was crystallized from CH_2Cl_2 /benzene at -20°C as the mono-benzene solvate, $[\text{CpFe}(\text{CS})(\text{P}\{\text{O}\phi\}_3)(\text{CH}_3\text{CN})]\text{PF}_6 \cdot \text{C}_6\text{H}_6$ (0.634 g, 72% yield).

IR (CH_3CN): 1312 s cm^{-1} .

$^1\text{H NMR}$ (d^6 -acetone): τ 2.40-2.92 (m, ϕ), 5.28 (d, $J = 0.8 \text{ Hz}$, Cp), 7.67 (d, $J = 1.1 \text{ Hz}$, CH_3CN).

Anal. Calcd. for $[\text{CpFe}(\text{CS})(\text{P}\{\text{O}\phi\}_3)(\text{CH}_3\text{CN})]\text{PF}_6 \cdot \text{C}_6\text{H}_6$: C, 51.98; H, 3.95.

Found: C, 51.62; H, 3.91.

41. Reaction of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ with PEt_3

Triethylphosphine PEt_3 , (0.4 ml, 2.7 mmol) was added to a solution of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ (0.424 g, 1.08 mmol) in CH_2Cl_2 (50 ml). The initial yellow-green solution immediately turned blue. After ~30 minutes, the solution had turned red-orange, and remained red-orange until stirring was stopped after 9 hours. After evaporation to dryness, the orange-brown residue was dissolved in a minimum of CH_2Cl_2 (~15 ml). Addition of hexane (~100 ml) caused a red precipitate to form. The mixture was filtered and washed with hexanes to yield a red solid (vide post) and a green filtrate. The green filtrate was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and hexanes were added until the point of precipitation. Crystallization at -20°C gave dark green crystals of $\text{CpFe}(\text{CS})(\text{PEt}_3)\text{Cl}$ (0.041 g, 12% yield).

IR (CS_2): 1274 cm^{-1} .

^1H NMR (CS_2): τ 5.40 (d, $J = 0.8\text{ Hz}$); 7.90-8.37 (m, $-\text{CH}_2-$),
8.58-9.17 (m, $-\text{CH}_3$).

Anal. Calcd. for $\text{CpFe}(\text{CS})(\text{PEt}_3)\text{Cl}$: C, 45.24; H, 6.33.

Found: C, 45.40; H, 6.46.

The red solid from above was dissolved in acetone and placed on a short alumina chromatography column to remove paramagnetic impurities. Elution with acetone gave a yellow to orange band which was collected and found to be a ~1:1 mixture of $[\text{CpFe}(\text{CS})(\text{PEt}_3)(\text{CH}_3\text{CN})]\text{PF}_6$ and $[\text{CpFe}(\text{CS})(\text{PEt}_3)_2]\text{PF}_6$.

The mixture was again dissolved in acetone and placed on a alumina chromatography column (12 x 415 mm). Elution with acetone gave incomplete

resolution of the two bands. The initial yellow band was found to contain $[\text{CpFe}(\text{CS})(\text{PET}_3)_2]\text{PF}_6$, and the trailing orange band was found to contain $[\text{CpFe}(\text{CS})(\text{PET}_3)(\text{CH}_3\text{CN})]\text{PF}_6$.

The leading portion of the yellow band was collected; however, attempts to obtain crystals of $[\text{CpFe}(\text{CS})(\text{PET}_3)_2]\text{PF}_6$ for analysis were unsuccessful.

^1H NMR (d^6 -acetone): τ 4.77 (t, $J = 1.3$ Hz, Cp), 7.67-8.18 (m, $-\text{CH}_2-$), 8.48-9.07 (m, $-\text{CH}_3$).

The trailing portion of the orange band was collected and evaporated to dryness. Crystallization from acetone/hexanes at -20°C gave blood-red crystals of $[\text{CpFe}(\text{CS})(\text{PET}_3)(\text{CH}_3\text{CN})]\text{PF}_6$ (0.062 g, a 12% isolated yield).

IR (CH_3CN): 1292 s cm^{-1} .

^1H NMR (d^6 -acetone): τ 4.84 (d, $J = 1.0$ Hz, Cp), 7.52 (d, $J = 1.0$ Hz, CH_3CN), 7.67-8.18 (m, $-\text{CH}_2-$), 8.48-9.07 (m, $-\text{CH}_3$).

Anal. Calcd. for $[\text{CpFe}(\text{CS})(\text{PET}_3)(\text{CH}_3\text{CN})]\text{PF}_6$: C, 35.84; H, 4.94.

Found: C, 35.11; H, 4.66.

42. Preparation of $\text{CpFe}(\text{CS})_2\text{I}$

Methanol (25 ml) was added to a nitrogen-filled Schlenk tube containing $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ (0.434 g, 1.11 mmol) and KI (0.186 g, 1.12 mmol). The mixture was stirred for 6 hours (if the reaction was conducted in CH_3CN , the progress of the reaction could be followed in the IR, and indicated that the reaction is complete in ~ 90 minutes), to produce an air-stable solution of $\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})\text{I}$.

IR (CH₃CN): 1277 cm⁻¹.

¹H NMR (CD₃CN): τ 5.22 (Cp).

Methylene chloride, CH₂Cl₂, (50 ml) was added to the solution, and then the solution was extracted with aqueous Na₂S₂O₃ (0.42 M, in two 10 ml portions) to destroy the by-product, I₂. The organic phase was collected, dried overnight over anhydrous MgSO₄, and then filtered through Celite to produce a green solution of CpFe(CS)₂I. The volume of the solution was reduced in vacuo to ~10 ml, heptane was added to the point of precipitation, and the product was crystallized at -20°C to yield black crystals of CpFe(CS)₂I (0.105 g, a 57% yield). The analytical sample was crystallized from CS₂/hexane.

IR (CS₂): 1337 s, 1274 vs cm⁻¹.

¹H NMR (CS₂): τ 4.95 (Cp).

¹³C NMR (CDCl₃): δ -323.4 (CS), -90.6 (Cp).

Mass spectrum parent ion at m/e 335.5.

Anal. Calcd. for CpFe(CS)₂I: C, 25.02; H, 1.50.

Found: C, 25.28; H, 1.58.

In an alternate method for the isolation of CpFe(CS)₂I, the CpFe(CS)(CH₃CN)I was evaporated to dryness under reduced pressure. The residue was then extracted with CH₂Cl₂ and filtered through Celite. Again, the by-product, I₂, was removed by extracting with aqueous Na₂S₂O₃. After drying and filtering, the solution of CpFe(CS)₂I was treated as above to yield CpFe(CS)₂I.

Attempts to isolate the intermediate, CpFe(CS)(CH₃CN)I, were unsuccessful. Extraction of a CH₃CN solution of CpFe(CS)(CH₃CN)I with

CS₂ initially showed the presence of CpFe(CS)(CH₃CN)I (by IR), however, this rapidly converted to CpFe(CS)₂I.

43. Preparation of CpFe(CS)₂Br

Methanol (25 ml) was added to a nitrogen-filled Schlenk tube containing [CpFe(CS)(CH₃CN)₂]PF₆ (0.411 g, 1.05 mmoles) and KBr (0.250 g, 2.10 mmoles). The mixture was stirred for 6 hours, after which Et₂O (50 ml) was added. The solution was then extracted with aqueous Na₂S₂O₃ (0.42 M, in two 10 ml portions). The organic phase was collected, dried over anhydrous overnight, and filtered to produce a solution of CpFe(CS)₂Br. Evaporation to dryness yielded impure CpFe(CS)₂Br (0.006 g, 4% yield). The CpFe(CS)₂Br contained ~10% impurities, CpFe(CO)₂Br and CpFe(CO)(CS)Br, and was not further isolated.

IR (CS₂): 1341 s, 1276 vs cm⁻¹.

44. Preparation of CpFe(CS)(Pφ₃)I. Method II. Reaction of

[CpFe(CS)(CH₃CN)₂]PF₆ with 1) KI and 2) Pφ₃

A solution of [CpFe(CO)₂(CS)]PF₆ (0.489 g, 1.33 mmoles) in CH₃CN (35 ml) was irradiated in a quartz Schlenk tube for 7 hours to produce [CpFe(CS)(CH₃CN)₂]PF₆ (vide ante). Potassium iodide (0.251 g, 1.51 mmoles) was added and the solution was stirred overnight to produce a solution of CpFe(CS)(CH₃CN)I (vide ante). Then, triphenylphosphine, Pφ₃, (0.324 g, 1.43 mmoles) was added, and the solution was stirred an additional 11 hours. The green solution was then evaporated to dryness. The residue was dissolved in benzene, filtered through Celite, and placed on a Florisil

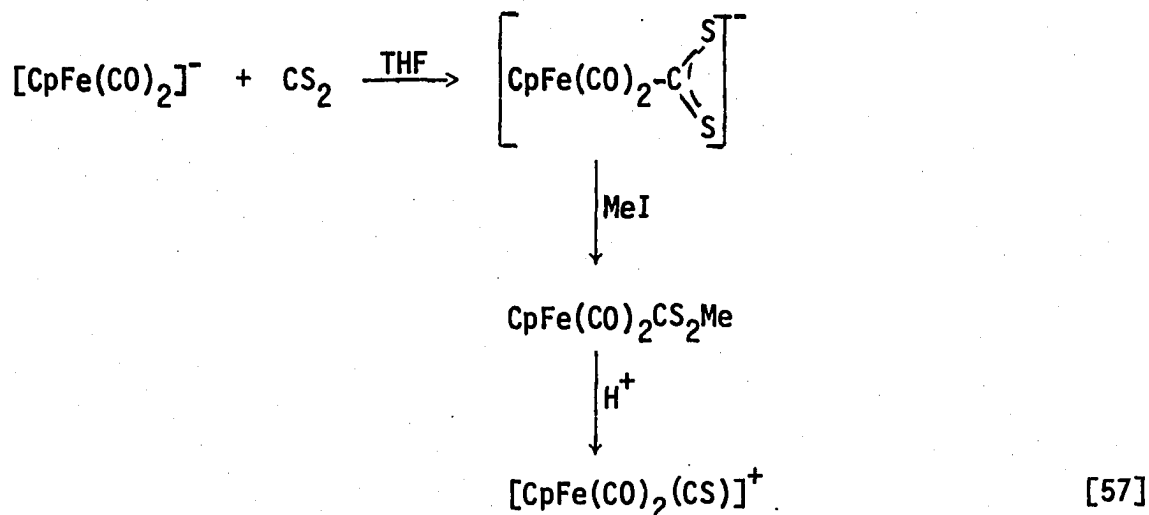
chromatography column (16 x 290 mm). Elution, initially with benzene, and then with 2) CHCl_3 and 3) CH_2Cl_2 , gave a dark green band which was collected and evaporated to dryness. An infrared spectrum of the residue in CS_2 indicated that it was $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$ with traces of $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ and $\text{CpFe}(\text{CO})_2\text{I}$. The residue was then dissolved in CH_2Cl_2 (~ 10 ml), the solution was filtered and heptane (~ 10 ml) was added. The solution was placed under a slow stream of nitrogen until crystals began to form. Cooling to -20°C gave crystals of pure $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$, which were isolated by filtration and washed with pentane (0.433 g, a 59% yield) (vide ante).

IV. RESULTS AND DISCUSSION

Few thiocarbonyl complexes of iron were known before the present work. The one complex that could be easily prepared in good yield was $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$. This work was instigated to find other iron thiocarbonyl complexes that could be obtained from $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$.

A. Preparation of $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$

The $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ cation was prepared according to the following reaction:



Although an adequate method for the preparation of $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ exists in the literature (42), improvements in this method cited herein give greater yields and increase the purity of the product.

The use of diethyl ether rather than benzene to extract $\text{CpFe}(\text{CO})_2\text{CS}_2\text{CH}_3$ from the solid remaining after evaporation of the THF in the first step greatly speeds up this extraction. Then dropwise addition of a diethyl ether solution of trifluoromethanesulfonic acid,

$\text{CF}_3\text{SO}_3\text{H}$, to this solution of $\text{CpFe}(\text{CO})_2\text{CS}_2\text{CH}_3$ results in the precipitation of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$. This crude product is then dissolved in acetone, and amber crystals of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ are obtained by precipitation with hexanes or diethyl ether.

The color of the product is an indication of its purity. Pure $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ is bright yellow. It was found that the brown impurity (unidentified) is fairly soluble in THF, while $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ is only sparingly soluble. Thus, pure $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ could be obtained by washing the amber crystals with small amounts of THF.

The brown impurity is soluble in CH_2Cl_2 and displays IR bands of 2126 (m), 2107 (m), 2074 (sh,s), 2058 (s), 2014 (s), 1160 (br,m), 1060 (m) and 1030 (s) cm^{-1} . When this impurity was chromatographed on Florisil with CH_2Cl_2 , three bands developed. The first was orange (IR: 2035 (w), 1970 (sh,w) and 1945 (w) cm^{-1}); the second was brownish-orange (IR: 2040 (m), 1990 (m), 1975 (sh,m) and 1955 (sh,w)); and the third was brown and remained on the column. Further characterization of these materials was not attempted.

In some instances, it was more advantageous to utilize the PF_6^- salt of $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ as the CF_3SO_3^- anion has IR bands in the thiocarbonyl region and PF_6^- does not. In that case, HCl gas can be bubbled through the diethyl ether solution of $\text{CpFe}(\text{CO})_2\text{CS}_2\text{Me}$ to yield $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{Cl}$ which can be converted to the PF_6^- salt by metathesis with NH_4PF_6 in acetone. The precipitation and purification of

$[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$ is accomplished by the same method used for the CF_3SO_3^- salt.

These modifications of the existing method gave consistently good yields and a pure product.

B. Preparation of $[\text{CpFe}(\text{CO})(\text{CS})]_2$

When $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ is reacted with sodium hydride in THF, a dark green solution is produced which contains $[\text{CpFe}(\text{CO})(\text{CS})]_2$.



Thin layer chromatography of this reaction mixture shows that at least 5 separate products are formed, three of which are trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$, cis- $[\text{CpFe}(\text{CO})(\text{CS})]_2$, and $[\text{CpFe}(\text{CO})_2]_2$.

A cis,trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ mixture can be isolated from this reaction mixture by chromatography on Florisil with benzene. The initial grey-to-dark green band eluting from the column contains the $[\text{CpFe}(\text{CO})(\text{CS})]_2$. However, pure $[\text{CpFe}(\text{CO})(\text{CS})]_2$ is best isolated by chemical methods (vide infra).

Unlike its all-carbonyl analog, $[\text{CpFe}(\text{CO})_2]_2$, and its monothio-carbonyl analog, $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})]$, the cis and trans isomers of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ can be isolated in solution. Chromatography of the cis,trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ mixture on Florisil with 1/1 benzene/hexanes causes the development of a broad band in which the leading fractions are enriched in the trans isomer, while the trailing fractions are enriched in the cis isomer. The trans isomer can be isolated by

fractional crystallization from CS₂/hexanes of the material from the leading fractions. Fractional crystallization from CH₂Cl₂/hexanes of the material in the trailing fractions, or of any cis,trans-[CpFe(CO)(CS)]₂ mixture in which the cis isomer predominates, yields the pure cis isomer.

Structural assignments of the cis and trans isomers of [CpFe(CO)(CS)]₂ were based on the similarities of the positions and intensities of the terminal ν(CO) infrared absorptions of [CpFe(CO)(CS)]₂ (see Table 2) to the terminal ν(CO) infrared absorptions assigned to cis- and trans-[CpFe(CO)₂]₂ (136,137).

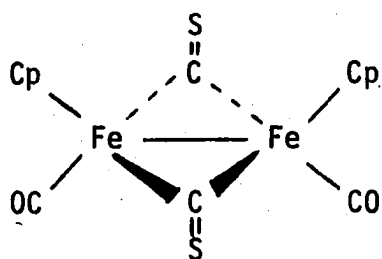
The [CpFe(CO)(CS)]₂ dimer exists in solution as a mixture of the cis and trans isomers (see Figure 2). Although the pure cis and trans isomers can be isolated at room temperature, solutions of either isomer slowly isomerize to an equilibrium cis-trans mixture. The rate of the cis-trans isomerization of [CpFe(CO)(CS)]₂ is markedly slower than that of [CpFe(CO)₂]₂ or [Cp₂Fe₂(CO)₃(CS)], which attain equilibrium immediately at room temperature in solution. The isomerization of trans-[CpFe(CO)(CS)]₂ to a cis-trans equilibrium mixture has been investigated at 50°C in xylene. At that temperature, the half-time to reach an equilibrium cis-trans mixture is approximately 28 minutes. Isomerization of either the pure cis or pure trans isomer to an equilibrium mixture has also been observed in other solvents and at room temperature. In fact, during the separation of cis- and trans-[CpFe(CO)(CS)]₂ by column chromatography, if the elution rate is too slow -- taking one-to-two hours for the entire band to elute --

Table 2. Infrared, ^1H NMR, and ^{13}C NMR spectral data for cis- and trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$

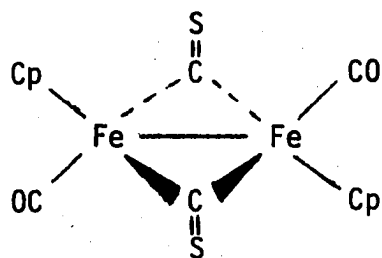
	cis- $[\text{CpFe}(\text{CO})(\text{CS})]_2$	trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$
IR (CS_2)		
$\nu(\text{CO})$	2011 vs cm^{-1} 1982 m	1979 vs cm^{-1}
$\nu(\text{CS})$	1124 s	1131 s
^1H NMR (CS_2)		
Cp	5.22 τ	5.32 τ
^{13}C NMR (CDCl_3) ^a		
CS	-374.5 ^b ppm	-374.5 ppm
CO	-208.9	-210.0
Cp	-93.8	-96.7

^aWith ~ 0.1 M $\text{Cr}(\text{acac})_3$ added.

^bThe previously reported value of -287.6 ppm for the CS ligand (35) is in error.



cis-[CpFe(CO)(CS)]₂



trans-[CpFe(CO)(CS)]₂

Figure 2. The cis and trans isomers of [CpFe(CO)(CS)]₂

enrichment of the leading fractions in trans-[CpFe(CO)(CS)]₂ is not observed. Thus, isomerization on the column occurred nearly as fast as the separation.

The mechanism of the isomerization of [CpFe(CO)₂]₂ has been studied extensively and is now well understood. The proposed Adams-Cotton mechanism (Figure 3) involves the symmetrical opening of the carbonyl bridges, followed by rotation about the metal-metal bond, and then reformation of the carbonyl bridges to give the other isomer. Indeed, weak bands assigned to the intermediate nonbridged isomer have been observed in infrared spectra of [CpFe(CO)₂]₂ in some solvents (136). This mechanism also accounts for the isomerization of [Cp₂Fe₂(CO)₃(CS)] in which one of the bridging CO's is replaced by CS. However, if both bridging CO's are replaced by CS groups, the Adams-Cotton mechanism invariably leads to a structure containing a terminal CS ligand. As no terminal CS absorptions are observed during the isomerization of [CpFe(CO)(CS)]₂, this mechanism can be eliminated as explaining the isomerization of [CpFe(CO)(CS)]₂.

Wnuk and Angelici (69) have proposed two possible mechanisms for the isomerization of [CpRu(CO)(CS)]₂, which is isostructural with [CpFe(CO)(CS)]₂. One (Scheme A) involves the direct exchange of CO and CS sites and subsequent rearrangement via the Adams-Cotton mechanism to produce the other isomer.

The other proposed mechanism (Scheme B) involves cleavage of one bridging CS bond and the metal-metal bond to give a planar three-coordinate intermediate. Rotation about the remaining bridging CS bond gives the trans isomer after closure of the remaining CS bridge.

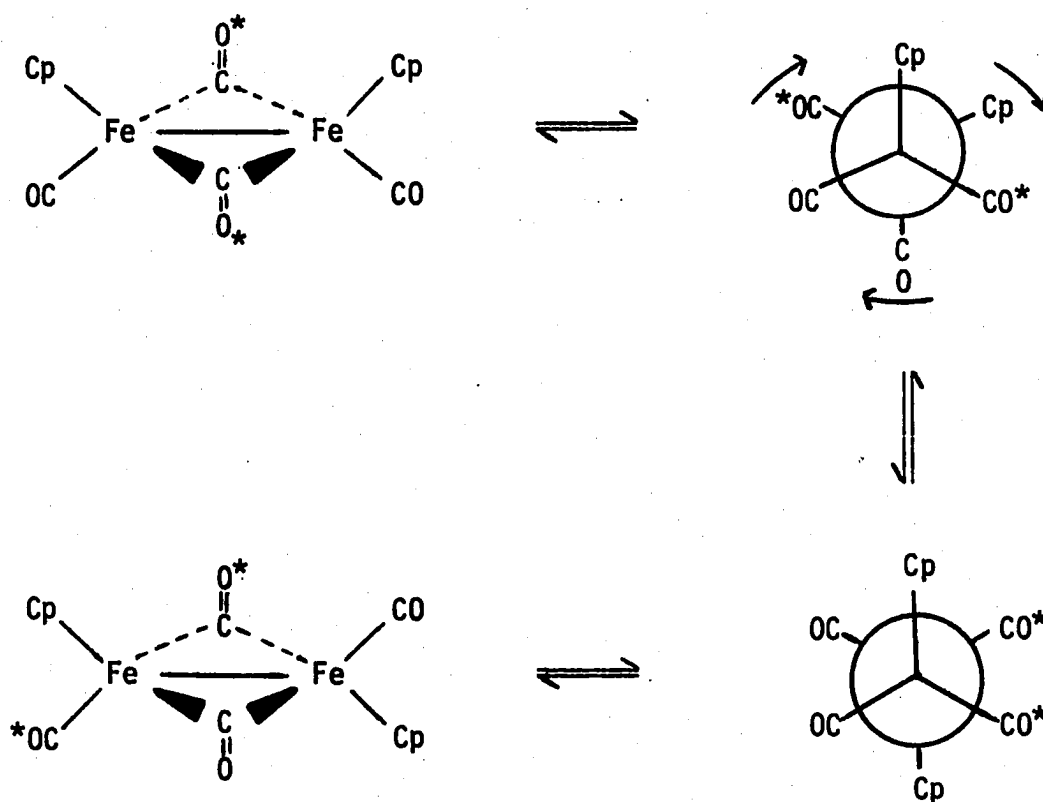


Figure 3. Isomerization of $[\text{CpFe}(\text{CO})_2]_2$ by the Adams-Cotton mechanism

A third proposed mechanism (Scheme C) would involve the unsymmetric cleavage of the $[\text{CpM}(\text{CO})(\text{CS})]_2$ dimer, again giving a planar, three-coordinate intermediate. Then rotation about the M-M bond and subsequent reformation of the CS bridges would give the trans isomer. While it might be argued that the intermediate in this scheme would be of high energy, having formally 20 electrons around one Fe and 16 around the other, this does not preclude consideration of this mechanism. In fact, the utilization of a high energy intermediate may help explain the slower isomerization of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ compared to $[\text{CpFe}(\text{CO})_2]_2$.

All the experimental evidence at present for both the $[\text{CpFe}(\text{CO})(\text{CS})]_2$ and $[\text{CpRu}(\text{CO})(\text{CS})]_2$ dimers is consistent with any of the mechanisms given in Schemes A, B, or C (Figures 4, 5 and 6).

An x-ray crystal structure determination was performed on cis- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ for the purpose of comparing it with the known structure of cis- $[\text{CpFe}(\text{CO})_2]_2$ (138). A computer generated drawing of the molecule is shown in Figure 7. Selected interatomic distances are given in Table 3, and selected interatomic angles are given in Table 4. This structure has been previously reported (35).

With the exception of the Fe(1)-Fe(2) and the C-S bond distances, the distances and angles of cis- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ and cis- $[\text{CpFe}(\text{CO})_2]_2$ are the same. These similarities also exist in the recently reported structure of cis- $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})]$ (36). The Fe(1)-Fe(2) bond distance of 2.482(1) Å is significantly shorter than the 2.531(2) Å in cis- $[\text{CpFe}(\text{CO})_2]_2$ and the 2.505(2) Å in cis- $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})]$. This suggests

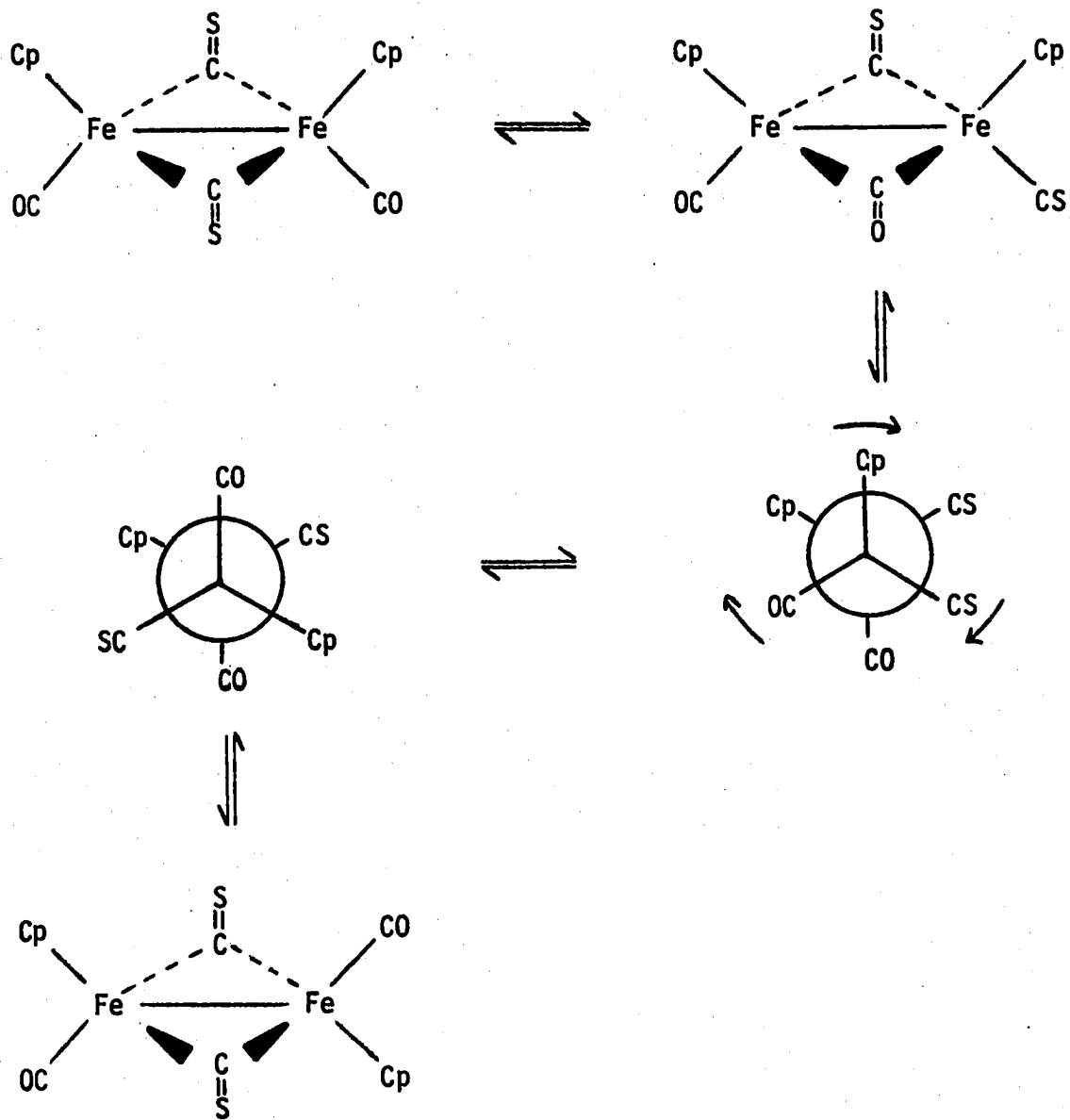


Figure 4. Isomerization of $[\text{CpFe}(\text{CO})(\text{CS})]_2$. Scheme A

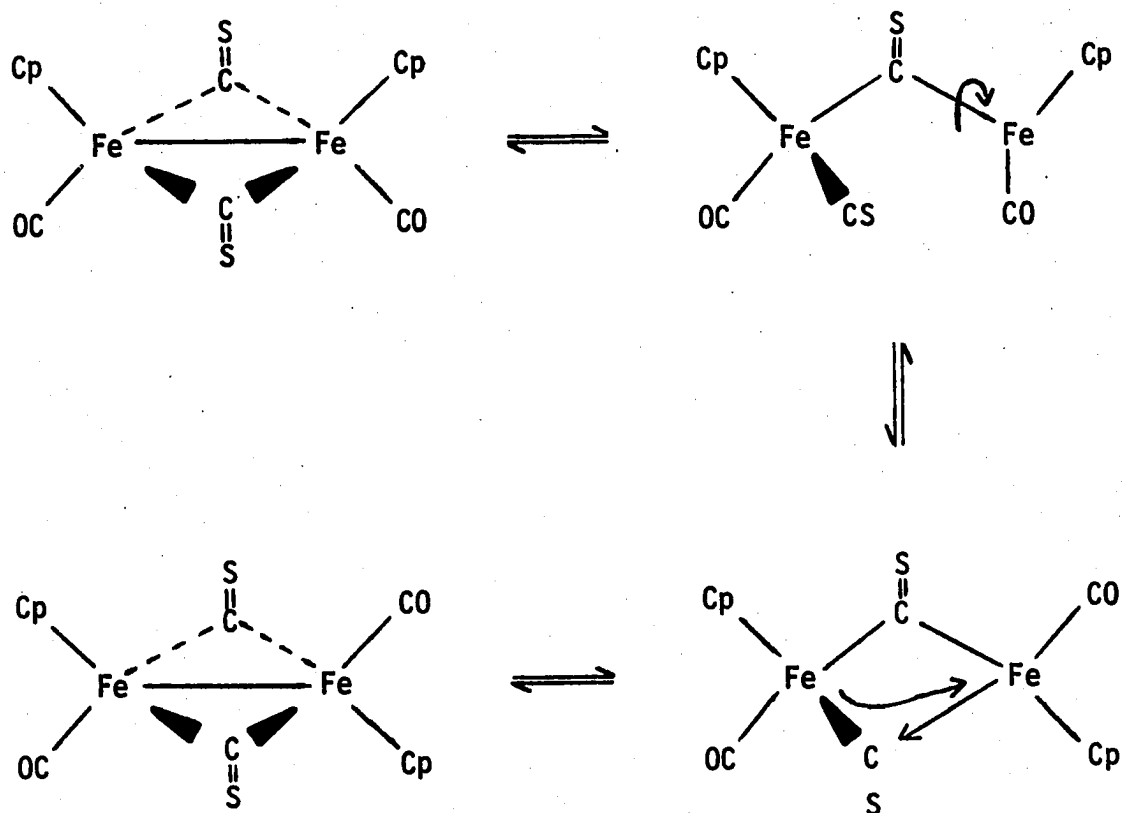


Figure 5. Isomerization of $[\text{CpFe}(\text{CO})(\text{CS})]_2$. Scheme B

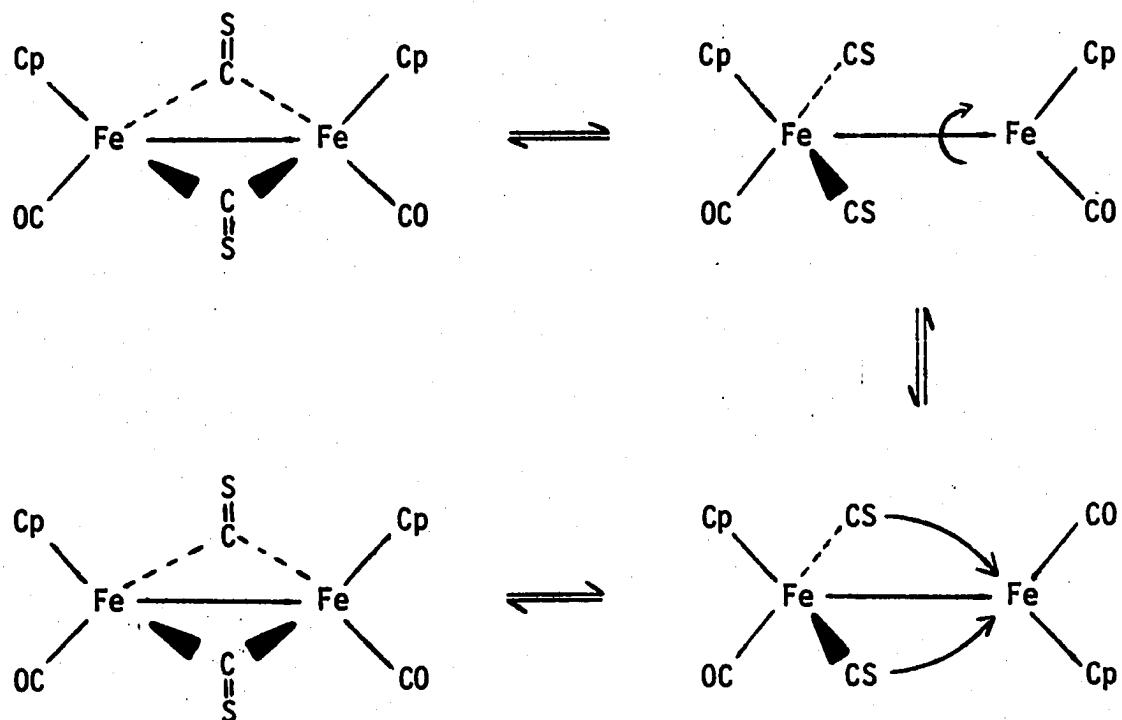


Figure 6. Isomerization of $[\text{CpFe}(\text{CO})(\text{CS})]_2$. Scheme C

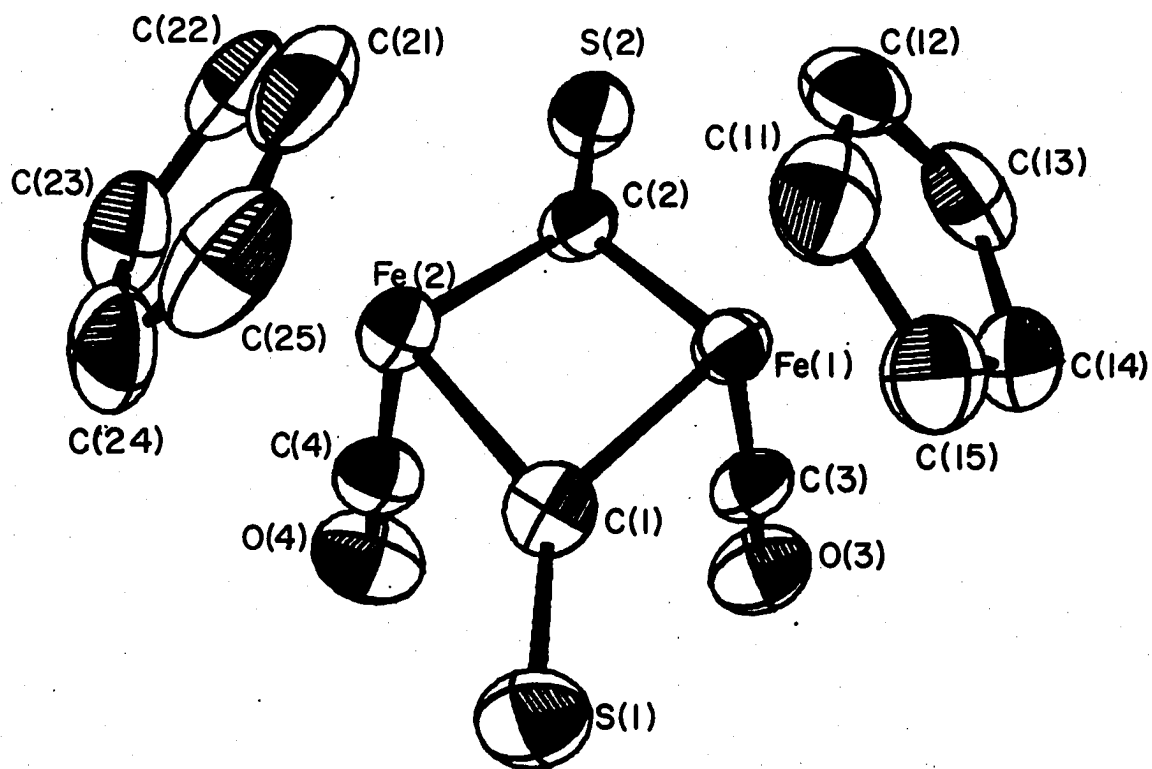


Figure 7. A computer-generated drawing of the *cis*-[CpFe(CO)(CS)]₂ molecule

Table 3. Selected interatomic distances (Å) for *cis*-[CpFe(CO)(CS)]₂

Fe(1)-Fe(2)	2.482(1)		
Fe(1)-C(1)	1.912(8)	Fe(2)-C(1)	1.901(8)
Fe(1)-C(2)	1.910(7)	Fe(2)-C(2)	1.902(7)
Fe(1)-C(3)	1.723(7)	Fe(2)-C(4)	1.756(8)
Fe(1)-CG1 ^a	1.765(1)	Fe(2)-CG2 ^a	1.752(1)
Fe(1)-C(11)	2.104(8)	Fe(2)-C(21)	2.101(9)
-C(12)	2.120(8)	-C(22)	2.148(9)
-C(13)	2.100(9)	-C(23)	2.100(11)
-C(14)	2.110(10)	-C(24)	2.102(9)
-C(15)	2.131(8)	-C(25)	2.122(9)
C(1)-S(1)	1.592(8)	C(2)-S(2)	1.587(7)
C(3)-O(3)	1.166(8)	C(4)-O(4)	1.139(9)
C(11)-C(12)	1.410(16)	C(21)-C(22)	1.354(15)
C(12)-C(13)	1.398(15)	C(22)-C(23)	1.369(15)
C(13)-C(14)	1.396(14)	C(23)-C(24)	1.361(14)
C(14)-C(15)	1.361(15)	C(24)-C(25)	1.369(15)
C(15)-C(11)	1.379(15)	C(25)-C(21)	1.422(18)

^aCG1 and CG2 are the centers of gravity for cyclopentadienyl ring 1 (C(11)-C(15)) and 2 (C(21)-C(25)), respectively.

Table 4. Selected interatomic angles ($^{\circ}$) for *cis*-[CpFe(CO)(CS)]₂

Fe(1)-C(1)-Fe(2)	81.2(3)	Fe(1)-C(1)-S(1)	138.5(5)
Fe(1)-C(2)-Fe(2)	81.2(3)	Fe(1)-C(2)-S(2)	139.2(5)
C(1)-Fe(1)-C(2)	96.8(3)	Fe(2)-C(1)-S(1)	140.3(5)
C(1)-Fe(2)-C(2)	97.5(3)	Fe(2)-C(2)-S(2)	139.5(5)
C(1)-Fe(1)-C(3)	89.5(3)	C(1)-Fe(2)-C(4)	88.2(3)
C(2)-Fe(1)-C(3)	87.9(3)	C(2)-Fe(2)-C(4)	89.8(3)
C(1)-Fe(1)-CG1 ^a	122.6(2)	C(1)-Fe(2)-CG2 ^a	124.4(2)
C(2)-Fe(1)-CG1	125.2(2)	C(2)-Fe(2)-CG2	123.1(2)
C(3)-Fe(1)-CG1	124.9(3)	C(4)-Fe(2)-CG2	124.2(3)
Fe(1)-C(3)-O(3)	178.5(7)	Fe(2)-C(4)-O(4)	177.8(8)
C(11)-C(12)-C(13)	105.6(9)	C(21)-C(22)-C(23)	104.7(11)
C(12)-C(13)-C(14)	107.7(9)	C(22)-C(23)-C(24)	111.5(11)
C(13)-C(14)-C(15)	109.7(10)	C(23)-C(24)-C(25)	108.1(11)
C(14)-C(15)-C(11)	107.1(11)	C(24)-C(25)-C(21)	104.8(10)
C(15)-C(11)-C(12)	109.8(10)	C(25)-C(21)-C(22)	110.9(12)
Fe(1)-CG1-C(11)	89.2(4)	Fe(2)-CG2-C(21)	90.7(5)
Fe(1)-CG1-C(12)	88.5(4)	Fe(2)-CG2-C(22)	91.2(4)
Fe(1)-CG1-C(13)	88.4(4)	Fe(2)-CG2-C(23)	90.4(5)
Fe(1)-CG1-C(14)	90.2(5)	Fe(2)-CG2-C(24)	89.6(5)
Fe(1)-CG1-C(15)	90.5(4)	Fe(2)-CG2-C(25)	90.4(4)
Fe(1)-Fe(2)-C(4)	98.8(3)	Fe(2)-Fe(1)-C(3)	98.3(3)
Fe(1)-Fe(2)-CG2	137.0(1)	Fe(2)-Fe(1)-CG1	136.8(1)

^aCG1 and CG2 are the centers of gravity for cyclopentadienyl ring 1 (C(11)-C(15)) and 2 (C(21)-C(25)), respectively.

Table 4. (Continued)

Torsional Angles

C(3)-Fe(1)-Fe(2)-C(4)	2.1(3)
C(3)-Fe(1)-Fe(2)-CG2	177.8(3)
CG1-Fe(1)-Fe(2)-CG2	3.2(2)
CG1-Fe(1)-Fe(2)-C(4)	176.8(3)

Dihedral Angle

Fe(1)Fe(2)C(2)-Fe(1)Fe(2)C(1)	163.4
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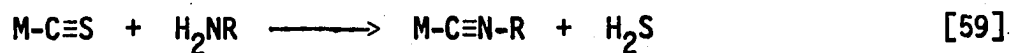
stronger bonding between the two halves of the dimer as the number of bridging CS ligands increases in the molecule. The C-S bond distances of 1.592(8) Å and 1.587(7) Å are longer than the 1.51-1.54 Å distances observed for terminal C≡S ligands (3).

The bridging CS groups are bent away from the cis-cyclopentadienyl ligands at a dihedral angle of 163.4°.

C. Reactions of [CpFe(CO)(CS)]₂

1. Reaction of [CpFe(CO)(CS)]₂ with nucleophiles and electrophiles

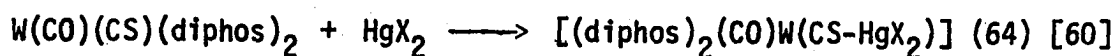
Terminal thiocarbonyl ligands have been shown to react with amines to form coordinated isocyanide ligands as shown in equation 59.



The mechanism is believed to proceed by nucleophilic attack at the thiocarbonyl C atom forming an aminothiocabene intermediate, M-C(SH)NHR, which then decomposes to the observed products (70).

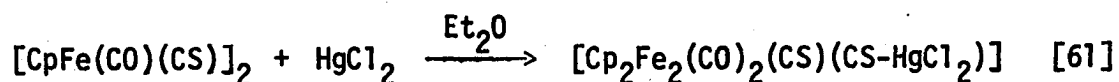
A bridging thiocarbonyl ligand can be envisioned to react by a similar mechanism to give a bridging isocyanide complex. However, [CpFe(CO)(CS)]₂ is not observed to react with the primary amines, methyl amine and cyclohexyl amine, at room temperature in solution. Nucleophilic attack by water is also not observed.

Electron-rich metal terminal thiocarbonyl complexes have been shown to form Lewis acid adducts at the sulfur atom, a behavior rarely observed in electron-rich metal carbonyl complexes.



Metal carbonyl complexes containing bridging carbonyl ligands form Lewis acid adducts at the oxygen of the bridging carbonyl ligand (139). Thus, it was expected that $[CpFe(CO)(CS)]_2$ would react with Lewis acids to form sulfur-bonded adducts. This is indeed the case.

With the Lewis acid $HgCl_2$, a cis,trans- $[CpFe(CO)(CS)]_2$ mixture reacts in solution to form the adduct $[Cp_2Fe_2(CO)_2(CS)(CS-HgCl_2)]$:



The characterized product is a black air-stable powder; however, if the reaction is conducted in CH_2Cl_2 , a red-orange product is formed. There appears to be no difference in the solid-state infrared spectra of the two products; however, they may not be identical. Only the one-to-one adduct appears to form, even with excess $HgCl_2$.

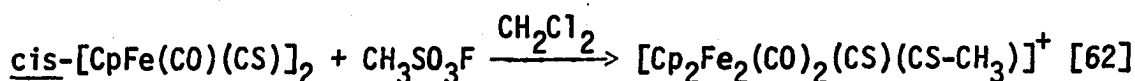
The carbonyl stretching frequencies of the $HgCl_2$ adduct (2028 vs; 2019 sh,s; and 1995 s cm^{-1}) are $\sim 15 \text{ cm}^{-1}$ higher than in the starting $[CpFe(CO)(CS)]_2$ dimer. The $\nu(CS)$ absorption of $[CpFe(CO)(CS)]_2$ is split by the adduct formation, with the uncomplexed CS ligand of the adduct absorbing 55 cm^{-1} higher and the complexed CS ligand absorbing 6 cm^{-1} lower than the 1124 cm^{-1} of the parent $[CpFe(CO)(CS)]_2$.

The $[Cp_2Fe_2(CO)_2(CS)(CS-HgCl_2)]$ adduct appears to exist in both the cis and trans isomers, as the intensities of the $\nu(CO)$ frequencies are characteristic of a cis-trans mixture. (The cis isomer should have terminal $\nu(CO)$ intensities similar to those in cis- $[CpFe(CO)(CS)]_2$

(see Table 2); the same reasoning can be applied to the trans isomer (see Table 2.) As the two major terminal $\nu(\text{CO})$ intensities of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS}-\text{HgCl}_2)]$ are roughly equal, a cis-trans mixture appears to be present. Whether the presence of both cis and trans isomers of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS}-\text{HgCl}_2)]$ is due to isomerization of the adduct, or due to formation of adducts with both isomers of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ is not evident, although the latter seems more probable.

The starting material, $[\text{CpFe}(\text{CO})(\text{CS})]_2$, can be regenerated from $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS}-\text{HgCl}_2)]$ in solution by addition of NH_3 to remove the HgCl_2 .

Organic electrophiles also react with $[\text{CpFe}(\text{CO})(\text{CS})]_2$ at the sulfur atom. As reported in a previous paper (35), $\text{CH}_3\text{SO}_3\text{F}$ reacts with cis- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ to give $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS}-\text{CH}_3)]^+$, an air-stable black solid which was isolated as its PF_6^- salt.



Alkylation of the sulfur atom of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ also occurs using neat methyl iodide, a weaker electrophile. The product is the same, after PF_6^- anion exchange, as that obtained with methyl fluorosulfonate.

The similarities in the intensities of the $\nu(\text{CO})$ absorptions of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS}-\text{CH}_3)]^+$ (Table 5) to those in cis- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ (Table 2) suggest that the cyclopentadienyl rings are cis to each other as in the starting material. Alkylation of the sulfur atom in $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS}-\text{CH}_3)]^+$ causes the $\nu(\text{CO})$ frequencies to increase by $\sim 30 \text{ cm}^{-1}$, the $\nu(\text{CS})$ frequency of the unalkylated CS to increase by

Table 5. Infrared and ^1H NMR spectra of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS}-\text{CH}_3)]\text{PF}_6$

IR (CH_2Cl_2)	2043 s, 2011 m, 1178 s, 1070 w, and 1036 m cm^{-1}
^1H NMR (d^6 -acetone)	τ 6.20 (CH_3)
	4.17 (Cp)
	4.27 (Cp)

$\sim 55 \text{ cm}^{-1}$, and the $\nu(\text{CS})$ of the alkylated CS to decrease by $\sim 90 \text{ cm}^{-1}$ from the starting material, cis- $[\text{CpFe}(\text{CO})(\text{CS})]_2$. The alkylated CS infrared absorption also decreases in intensity and broadens.

The ^1H NMR spectrum of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS}-\text{CH}_3)]^+$ indicates that the $\text{C}=\text{S}-\text{CH}_3$ bond is bent producing inequivalent cyclopentadienyl rings.

The cis arrangement of the cyclopentadienyl rings and the bent $\text{C}=\text{S}-\text{CH}_3$ bond of $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS}-\text{CH}_3)]^+$ is supported by the recent crystal structure of $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS}-\text{Et})]^+$ which displays similar infrared terminal $\nu(\text{CO})$ absorption intensities (51,61).

The rate of reaction of neat methyl iodide with both cis- and trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ is sufficiently slow at room temperature to permit monitoring the reaction. The rate of reaction of

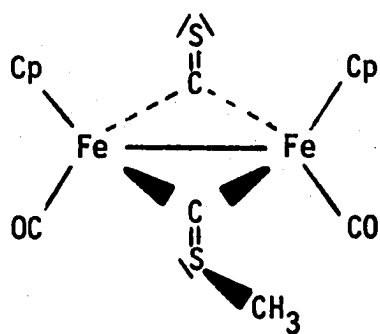


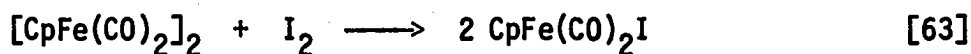
Figure 8. cis-[Cp₂Fe₂(CO)(CS)(CS-CH₃)]⁺

trans-[CpFe(CO)(CS)]₂ with the neat CH₃I is much slower than that of cis-[CpFe(CO)(CS)]₂. (The t_{1/4} is ~60 minutes for trans-[CpFe(CO)(CS)]₂ vs. a t_{1/4} of 8 minutes for cis-[CpFe(CO)(CS)]₂ at room temperature in neat CH₃I.) The same cis product is observed for both isomers, although there is extensive decomposition in the reaction of the trans isomer. The growth of an infrared band at 2004 cm⁻¹, characteristic of cis-[CpFe(CO)(CS)]₂, before observation of IR bands due to the product, [Cp₂Fe₂(CO)₂(CS)(CS-CH₃)]⁺, in the reaction of CH₃I with trans-[CpFe(CO)(CS)]₂ would suggest that trans-[CpFe(CO)(CS)]₂ isomerizes to cis-[CpFe(CO)(CS)]₂ which then reacts to form the product. This also accounts for the slower reaction of trans-[CpFe(CO)(CS)]₂ with CH₃I, and supports the supposition that the cis isomer is somehow more nucleophilic than the trans isomer. (This has been proposed by Quick (61) to account for the observation that only cis-[Cp₂Fe₂(CO)₃(CS-R)]⁺ is formed in the reaction of the monothiocarbonyl dimer, [Cp₂Fe₂(CO)₃(CS)], with alkyl halides.) There is no obvious steric preference for the cis isomer of [Cp₂Fe₂(CO)₂(CS)(CS-CH₃)]⁺.

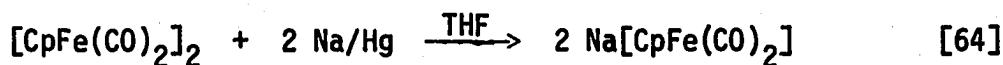
Electrophilic attack at the sulfur atom also appears to occur in the reaction of cis-[CpFe(CO)(CS)]₂ with Ag⁺. A red-violet precipitate forms upon reaction of cis-[CpFe(CO)(CS)]₂ with AgPF₆ in benzene at room temperature. The infrared spectrum of the solid (IR (Nujol mull): 2040 vs, 2007 s, 1993 s, 1090 br, s and 1020 br, s cm⁻¹) would suggest its formulation as [Cp₂Fe₂(CO)₂(CS)(CS-Ag)]PF₆. However, the product was not further characterized.

2. Cleavage reactions of [CpFe(CO)(CS)]₂

The all carbonyl complex, [CpFe(CO)₂]₂, undergoes both oxidative and reductive cleavage to yield monomeric cyclopentadienyliron carbonyl complexes. As noted in the Introduction, oxidative cleavage of [CpFe(CO)₂]₂ can occur using halogens (76,89,90) and HCl/O₂ (76).



Reductive cleavage is typically conducted with sodium amalgam (76).



It was of interest to ascertain whether the reactivity of [CpFe(CO)(CS)]₂ would parallel that of [CpFe(CO)₂]₂.

In contrast to the cleavage of [CpFe(CO)₂]₂ by HCl/O₂ (76) and HBF₄/O₂ (91), the bithiocarbonyl analog, [CpFe(CO)(CS)]₂, remains intact upon attack by HCl/O₂ in EtOH/CHCl₃ at room temperature. Indeed this contrast in reactivity can be used in the isolation and purification of [CpFe(CO)(CS)]₂.

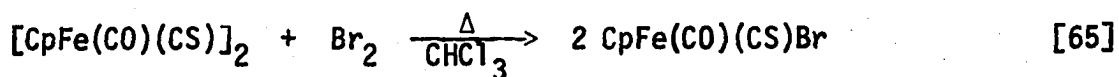
In the preparation of [CpFe(CO)(CS)]₂, after the reaction of [CpFe(CO)₂(CS)]CF₃SO₃ with NaH, the solution is evaporated to dryness. The residue is extracted with benzene, and this solution is filtered through Celite to yield a dark brownish-green solution. This filtrate contains [CpFe(CO)(CS)]₂, small amounts of [CpFe(CO)₂]₂, possibly [Cp₂Fe₂(CO)₃(CS)], and some unknown by-products. As previously discussed, the [CpFe(CO)(CS)]₂ can be isolated by column chromatography; however, as all three dimers color the column dark brown, the band

separations are difficult to ascertain. Invariably, the $[\text{CpFe}(\text{CO})(\text{CS})]_2$ product contains small amounts of the other two dimers, and must be purified by fractional crystallization.

Alternately, the benzene extract containing $[\text{CpFe}(\text{CO})(\text{CS})]_2$ can be filtered through Florisil and evaporated to dryness. The residue is then reacted with HCl/O_2 in $\text{CHCl}_3/\text{EtOH}$, which converts the $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})]$ to $\text{CpFe}(\text{CO})_2\text{Cl}$ and $\text{CpFe}(\text{CO})(\text{CS})\text{Cl}$. Separation of the unreacted $[\text{CpFe}(\text{CO})(\text{CS})]_2$ from $\text{CpFe}(\text{CO})_2\text{Cl}$ and $\text{CpFe}(\text{CO})(\text{CS})\text{Cl}$ is then easy as the later compounds are somewhat water soluble.

Although this method may seem more complicated than chromatography for the isolation of $[\text{CpFe}(\text{CO})(\text{CS})]_2$, it is preferable as it is 1) faster, 2) easier to scale up, and 3) gives pure $[\text{CpFe}(\text{CO})(\text{CS})]_2$ without resorting to fractional crystallization.

Bromine can cleave $[\text{CpFe}(\text{CO})(\text{CS})]_2$ in refluxing CHCl_3 in approximately 20 minutes to yield $\text{CpFe}(\text{CO})(\text{CS})\text{Br}$, a tangerine air-stable solid.



The infrared spectrum of $\text{CpFe}(\text{CO})(\text{CS})\text{Br}$ (see Table 7) shows one terminal carbonyl absorption (2033 cm^{-1}) and one terminal thiocarbonyl absorption (1309 cm^{-1}) as expected. The cyclopentadienyl resonance at 4.90τ in the ^1H NMR is a singlet, also as expected.

At low temperature (0°C) addition of Br_2 to $[\text{CpFe}(\text{CO})(\text{CS})]_2$ results in a black precipitate which dries to a red-orange solid. The infrared spectrum of this orange solid in CH_3CN ($2104 \text{ sh, w; } 2084 \text{ s,}$

2039 m , 1325 s , and 1179 m cm^{-1}) suggests its tentative identification as $\{[\text{CpFe}(\text{CO})(\text{CS})]_2\text{Br}\}\text{X}$. The assignment of a structure to this product is by analogy to the formation of $\{[\text{CpFe}(\text{CO})_2]_2\text{X}\}\text{X}$ upon addition of X_2 to $[\text{CpFe}(\text{CO})_2]_2$ at low temperature (98). The presence of one terminal $\nu(\text{CO})$ absorption (2084 cm^{-1}) and one terminal $\nu(\text{CS})$ absorption (1325 cm^{-1}) in the infrared spectrum of the product suggests a structure with no bridging thiocarbonyl ligands as shown in Figure 9.

Haines and DuPreez (98) have studied the oxidation of $[\text{CpFe}(\text{CO})_2]_2$ by halogens and have concluded that the oxidation proceeds through a $\{[\text{CpFe}(\text{CO})_2]_2\text{X}\}\text{X}$ intermediate to the $\text{CpFe}(\text{CO})_2\text{X}$ product. Indeed, these intermediates have been isolated and characterized. Similarly, the proposed $\{[\text{CpFe}(\text{CO})(\text{CS})]_2\text{Br}\}\text{X}$ product slowly converts upon standing in solution to $\text{CpFe}(\text{CO})(\text{CS})\text{Br}$.

Addition of Cl_2 to $[\text{CpFe}(\text{CO})(\text{CS})]_2$ at low temperature in CCl_4 also results in a precipitate. By analogy with the bromine reaction (vide supra) and with the all carbonyl system, this emerald-green product is tentatively identified as $\{[\text{CpFe}(\text{CO})(\text{CS})]_2\text{Cl}\}\text{X}$. The product dissolves in CH_3CN to give an intense blue-green solution; however, decomposition to a light brown solution occurs during attempts to obtain an infrared spectrum. It also reacts with acetone to give a light brown solution. Neither of these light brown solutions displays the infrared spectrum of the expected decomposition product, $\text{CpFe}(\text{CO})(\text{CS})\text{Cl}$. Infrared spectra of both light brown solutions show only weak bands in the carbonyl region. Further characterization of this product was not attempted.

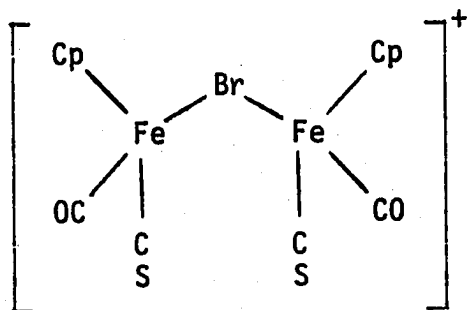


Figure 9. Proposed structure of $\{[\text{CpFe}(\text{CO})(\text{CS})]_2\text{Br}\}^+$

Iodine cleaves $[\text{CpFe}(\text{CO})(\text{CS})]_2$ in refluxing CH_3CH ; however, the yield of $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ is poor (19%). From the infrared spectrum of the reaction mixture taken before refluxing was started, it appears that approximately 1/3 of the $[\text{CpFe}(\text{CO})(\text{CS})]_2$ had reacted at room temperature in 30 minutes to form the proposed intermediate, $\{[\text{CpFe}(\text{CO})(\text{CS})]_2\text{I}\}^+$. As was the case with the bromine analog, $\{[\text{CpFe}(\text{CO})(\text{CS})]_2\text{I}\}^+$ displays one terminal $\nu(\text{CO})$ absorption (2084 cm^{-1}) and one terminal $\nu(\text{CS})$ absorption (1325 cm^{-1}) in this infrared spectrum.

In refluxing CHCl_3 with I_2 , where $[\text{CpFe}(\text{CO})_2]_2$ is completely converted to $\text{CpFe}(\text{CO})_2\text{I}$ in 30 minutes (76), after 40 minutes approximately two-thirds of the starting $[\text{CpFe}(\text{CO})(\text{CS})]_2$ is still unreacted.

It has, therefore, been shown that halogens can cleave $[\text{CpFe}(\text{CO})(\text{CS})]_2$ to form $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ ($\text{X} = \text{Br}, \text{I}$); however, there are better routes to these complexes (vide post).

Although $[\text{CpFe}(\text{CO})_2]_2$ can be cleaved by reduction with Na/Hg (76) and other reducing agents (see II. Review of Literature, p. 21), this does not appear to be the case with $[\text{CpFe}(\text{CO})(\text{CS})]_2$. With an excess (>2:1) of the reducing agents Na/Hg , C_8K , or $\text{NaK}_{2.8}$, $[\text{CpFe}(\text{CO})(\text{CS})]_2$ reacts to form a gray to dark brown precipitate which is insoluble in common solvents. The identity of this reduction product is open to speculation. It shows no apparent reaction with MeI or $\phi_3\text{SnCl}$. It does dissolve in hexamethylphosphortriamide to give a deep red solution, however, again no apparent reactions occur with MeI or $\phi_3\text{SnCl}$, and its infrared spectrum is ill-defined.

With a slight one-to-one excess of Na/Hg in THF, $[\text{CpFe}(\text{CO})(\text{CS})]_2$ reacts to give a red solution whose infrared spectrum is relatively unchanged from that of the starting $[\text{CpFe}(\text{CO})(\text{CS})]_2$. Addition of CH_3I to this solution in hopes of obtaining a stable derivative gave no color change, which would suggest that no reaction occurred. Evaporation of this solution to dryness and extraction of the residue with CS_2 gave an air-sensitive red solution. The infrared spectrum of this solution (2038 w, 2014 vs, 1983 m, 1776 m and 1124 s cm^{-1}) would suggest that it contains $[\text{CpFe}(\text{CO})(\text{CS})]_2$. However, the color, air-sensitivity, and ^1H NMR spectrum (τ 5.30 s, 5.92 s, 8.42 s and 8.78 m) would argue against this.

Reduction of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ with an excess of the homogeneous reducing agent sodium naphthalide (135) in THF gave an olive-green solution. Again, a stable derivative was sought by addition of $\phi_3\text{SnCl}$. No reaction was apparent, and after exposure to air only a small amount of the starting $[\text{CpFe}(\text{CO})(\text{CS})]_2$ was recovered.

As stated above, the reduction of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ does not appear to result in the cleavage of the $[\text{CpFe}(\text{CO})(\text{CS})]_2$ dimer, unlike the reduction of $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})]$ (61). Apparently, three different reduction products can be obtained depending upon the choice of reductants and the stoichiometry of the reaction. All products are air-sensitive and do not oxidize back to the dimer as does $[\text{CpFe}(\text{CO})_2]^-$. Speculation as to the identity of these products is unwarranted until further study offers more clues. Reaction of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ with sodium hydride does not occur.

To summarize the oxidation and reduction reactions of $[\text{CpFe}(\text{CO})(\text{CS})]_2$:

1) Oxidation of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ with halogens does result in cleavage of the dimer similar to $[\text{CpFe}(\text{CO})_2]_2$, and indications are that the cleavage proceeds similar to that of $[\text{CpFe}(\text{CO})_2]_2$. However, the reaction conditions for the cleavage are harsher than those for $[\text{CpFe}(\text{CO})_2]_2$ supporting the postulation that the two halves of the $[\text{CpFe}(\text{CO})(\text{CS})]_2$ dimer are bound more tightly together than in $[\text{CpFe}(\text{CO})_2]_2$.

2) Reduction of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ does not cleave the dimer as does reduction of $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})]$; and the reduction products are as yet unidentified.

3. Other reactions of $[\text{CpFe}(\text{CO})(\text{CS})]_2$

As the tetrahedral iron cluster compound, $[\text{CpFe}(\text{CO})]_4$, can be produced by photolysis of $[\text{CpFe}(\text{CO})_2]_2$, it was of interest to see if the thiocarbonyl analog, $[\text{CpFe}(\text{CS})]_4$, could be produced in a similar manner. This is not the case, however. Photolysis of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ in CHCl_3 given a black residue which is soluble in CH_3CN . The infrared spectrum of the material (2049 vs, 2024 sh, m; 1181 s and 1004 m cm^{-1}) would suggest a tentative identification as $[\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CS})_2]_2$ (see Figure 10). The frequencies and intensities of the thiocarbonyl absorptions (1181 s and 1004 m cm^{-1}) are similar to those of the Lewis acid adducts of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ at the sulfur atom (vide ante). Also, photolysis of carbonyl complexes is known to typically result in CO.

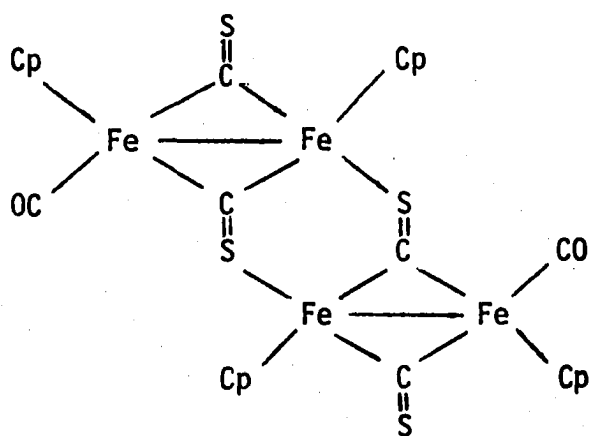


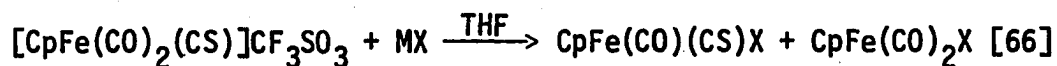
Figure 10. Proposed structure of cis,cis- $[\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CS})_2]_2$

ligand displacement (140), and has been shown to occur with $[\text{CpFe}(\text{CO})_2]_2$ in the presence of a neutral ligand (80). Thus, CO displacement in two $[\text{CpFe}(\text{CO})(\text{CS})]_2$ units, followed by reciprocal adduct formation to form $[\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CS})_2]_2$ is reasonable. However, the product was not further characterized.

In view of the above, it is not surprising that attempts to prepare $[\text{CpFe}(\text{CS})]_4$ under conditions similar to those used in the preparation of $[\text{CpFe}(\text{CO})]_4$ were unsuccessful.

D. Reactions of $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$

Reaction of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ with an equimolar amount of an alkali metal halide, MX, in THF at room temperature gives a mixture of $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ and $\text{CpFe}(\text{CO})_2\text{X}$. The ratio of the two products appears



to be dependent upon both the cation and the anion of MX; however, the relationship between the alkali metal halide and the $[\text{CpFe}(\text{CO})(\text{CS})\text{X}]/[\text{CpFe}(\text{CO})_2\text{X}]$ ratio is not obvious (see Table 6). The physical properties of $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ and $\text{CpFe}(\text{CO})_2\text{X}$ are quite similar, and separation of the two complexes by fractional crystallization, chromatography, or sublimation is difficult. Hence, other methods for preparing the $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ complexes were investigated.

While the reaction of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ with alkali metal halides gives a mixture of $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ and $\text{CpFe}(\text{CO})_2\text{X}$, its reaction

Table 6. The effect of MX upon the $[\text{CpFe}(\text{CO})(\text{CS})\text{X}]/[\text{CpFe}(\text{CO})_2\text{X}]$ ratio for the reaction:

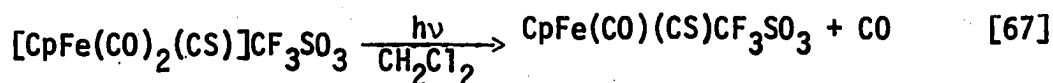


MX	[CpFe(CO)(CS)X]/[CpFe(CO) ₂ X] ^a
KI	2.9
KCl	0.64
NaCl	1.4
LiCl	4.4
LiBr	0.19
LiI	3.3
Et ₄ NI	0.55

^aEstimated from the infrared spectra, assuming equal molar absorptivities for the $\nu(\text{CO})$ absorption in $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ and $\text{CpFe}(\text{CO})_2\text{X}$.

with the pseudohalide, NaCN, does not appear to yield either CpFe(CO)(CS)CN or $\text{CpFe(CO)}_2\text{CN}$. The infrared spectrum of the CS_2 -soluble product (IR (CS_2): 2057 s; 2041 sh, s; 2033 s; 1992 vs; 1950 w; 1280 w; 1250 w; and 1208 s cm^{-1}) does display absorptions in the thiocarbonyl region ($1350\text{-}1000 \text{ cm}^{-1}$); however, the identity of the product(s) is not clear. Further characterization of the product(s) was not attempted.

Photolysis of $[\text{CpFe(CO)}_2(\text{CS})]\text{CF}_3\text{SO}_3$ in CH_2Cl_2 gives the red air-sensitive complex $\text{CpFe(CO)(CS)CF}_3\text{SO}_3$:



From its infrared spectrum in CH_2Cl_2 , the complex appears to exist as an ion pair, $[\text{CpFe(CO)(CS)(S)}]\text{CF}_3\text{SO}_3$ ($\text{S} = \text{CH}_2\text{Cl}_2$), as the absorptions due to the anion, CF_3SO_3^- (1269 vs ; 1224 m ; 1160 br, m ; and 1033 vs cm^{-1}) are relatively unchanged from those in $[\text{CpFe(CO)}_2(\text{CS})]\text{CF}_3\text{SO}_3$. However, the red oil is soluble in nonpolar solvents such as hexene and CS_2 . In CS_2 , the infrared spectrum show a shift in anion absorptions to 1333 s , 1231 vs and 1195 s cm^{-1} which suggests that the CF_3SO_3^- is coordinated to the metal through an oxygen atom (a similar shift in the infrared absorptions of SO_3F^- occurs upon coordination to a metal atom (141)).

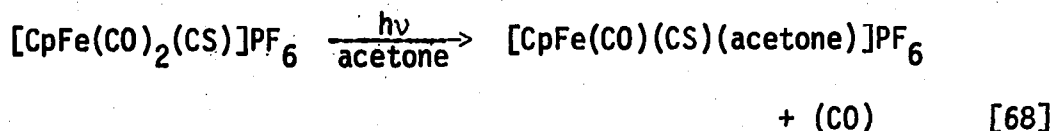
Otherwise, the spectral data are as expected for $\text{CpFe(CO)(CS)CF}_3\text{SO}_3$ displaying a single terminal $\nu(\text{CO})$ absorption (2051 s cm^{-1}) and a single terminal $\nu(\text{CS})$ absorption (1322 vs cm^{-1}) in the infrared spectrum in

CH_2Cl_2 ; a singlet in the ^1H NMR spectrum (4.76 τ) in CS_2 ; and absorptions for CS (-321.7 δ), CO (-207.8 δ), and Cp (-88.0 δ) in the ^{13}C NMR in CDCl_3 .

The utility of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ for the synthesis of other cyclopentadienyliron thiocarbonyl complexes will be discussed later.

In other solvents such as THF or acetone, photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ did not yield the expected $[\text{CpFe}(\text{CO})(\text{CS})(\text{L})]^+$ (L = THF or acetone) cation. Small amounts of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ may be formed in these solvents as evidenced by a slight reddish color and weak bands in the infrared spectrum. However, prolonged irradiation does not increase the yield; instead, decomposition products fog the walls of the irradiation vessel and prevent further photolysis of the solution.

If the PF_6^- salt of $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ is used, photolysis in acetone gives an air-sensitive product which appears to be $[\text{CpFe}(\text{CO})(\text{CS})(\text{acetone})]\text{PF}_6$ (see Table 8 for its IR spectrum)



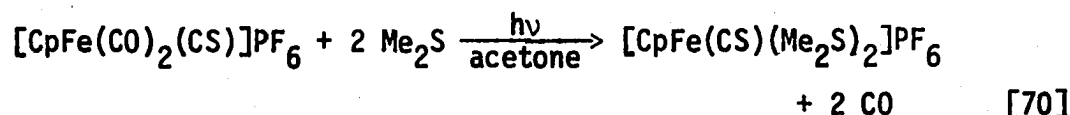
This brown oil decomposes slowly even under nitrogen, and is of little synthetic utility. Irradiation of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$ in other solvents, such as THF or CH_2Cl_2 , is unsuccessful in producing $[\text{CpFe}(\text{CO})(\text{CS})(\text{THF})]\text{PF}_6$ or $[\text{CpFe}(\text{CO})(\text{CS})(\text{S})]\text{PF}_6$. Again, decomposition products quickly fog the walls of the irradiation vessel precluding further reaction.

Photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{X}$ ($\text{X} = \text{PF}_6^-$ or CF_3SO_3^-) in acetonitrile does not stop with the ejection of one carbonyl ligand, but goes fully to $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]^+$ (for spectral data see Table 11).



The yellow-green air-stable solid is isolated in good yield. It dissolves in polar organic solvents, and decomposes in water.

Irradiation of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$ with Me_2S in acetone will also cause both carbonyl ligands to be displaced forming $[\text{CpFe}(\text{CS})(\text{Me}_2\text{S})_2]\text{PF}_6$ (see Table 12 for spectral data). Photolysis



of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$ with di-n-butyl sulfide also appears to give the disubstituted product. The $[\text{CpFe}(\text{CS})(\text{Me}_2\text{S})_2]^+$ complex can be obtained as black crystals by crystallization from its dark green solution in $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$. The $(n\text{-Bu})_2\text{S}$ complex does not crystallize but forms a dark green oil.

Irradiation of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$ with $\text{P}\phi_3$ in acetone does not go completely to $[\text{CpFe}(\text{CS})(\text{P}\phi_3)_2]\text{PF}_6$, but to a mixture of the mono- and bis-substituted cations, even upon prolonged irradiation.

In all the photolysis reactions, prolonged irradiation results in some decomposition products, which deposit on the walls of the photolysis vessel and decrease the light transmitted to the solution, thus preventing further reaction.

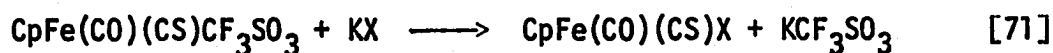
Photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ has thus been shown to be an effective method of removing one or two of the carbonyl ligands. Two of the resulting compounds, $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ and $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$, are useful intermediates in producing other thiocarbonyl complexes of iron (vide post).

E. Reactions of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$

Using $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$, facile routes to the complexes $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ ($\text{X} = \text{I}, \text{Br}$ and Cl) and $[\text{CpFe}(\text{CO})(\text{CS})(\text{L})]\text{CF}_3\text{SO}_3$ have been developed.

1. $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ complexes

Reactions of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ with halide ions give the $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ ($\text{X} = \text{I}, \text{Br}$ and Cl) complexes. The yields of



$\text{CpFe}(\text{CO})(\text{CS})\text{X}$ depend upon the halide ion, being greatest for iodide and lowest for chloride. The formation of a $\text{CpFe}(\text{CO})_2\text{X}$ impurity is also dependent upon the halide ion, but decreases in the order: $\text{Cl} > \text{Br} > \text{I}$. The $\text{CpFe}(\text{CO})_2\text{X}$ impurity probably forms as a result of the decomposition of some of the $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ providing free CO in solution. The yield of $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ (a maximum of 64% for $\text{CpFe}(\text{CO})(\text{CS})\text{I}$) is less than the estimated yield of $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ so some decomposition does occur.

As stated earlier, the physical properties of the $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ and $\text{CpFe}(\text{CO})_2\text{X}$ complexes are very similar. Separation can be

accomplished by fractional crystallization or liquid chromatography; however, the separation is not easy. Thus, for utilization in further syntheses, it is desirable to use the halide that gives the greatest yield and least impurity, CpFe(CO)(CS)I .

The spectra (Table 7) of the CpFe(CO)(CS)X complexes are as expected, each displaying a single $\nu(\text{CO})$ absorption and a single $\nu(\text{CS})$ absorption in the infrared, and a singlet for the cyclopentadienyl ring in the ^1H NMR.

Table 7. Infrared and ^1H NMR spectra of CpFe(CO)(CS)X complexes

X	IR		^1H NMR Cp, τ
	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{CS}), \text{cm}^{-1}$	
I	2024 s ^a	1306 vs ^a	4.93 ^a
Br	2033 s ^a	1309 vs ^a	5.00 ^a
Cl	2036 s ^a	1310 vs ^a	
OSO_2CF_3	2051 s ^b	1322 vs ^b	4.76 ^c
	2054 s ^a	1318 vs ^a	

^a CS_2 solvent.

^b CH_2Cl_2 solvent.

^c CDCl_3 solvent.

2. [CpFe(CO)(CS)(L)]CF₃SO₃ complexes

The monosubstituted [CpFe(CO)(CS)(L)]CF₃SO₃ complexes are produced by action of a neutral ligand, L, on CpFe(CO)(CS)CF₃SO₃. For the



ligands triphenylphosphine, pyridine, and acetonitrile, the reaction proceeds smoothly to a single product, [CpFe(CO)(CS)(L)]CF₃SO₃, which precipitates out of the relatively nonpolar solution (Et₂O or CH₂Cl₂/hexanes). The products are pure and easily isolated.

However, with the ligands, triphenylphosphite, trimethylphosphite and di-n-butyl sulfide, the reaction gives a mixture of the mono-substituted, [CpFe(CO)(CS)(L)]⁺, and bis-substituted, [CpFe(CS)(L)₂]⁺, cations. The products are all tars or oils, and were not isolated, although they were identified spectroscopically.

The formation of both [CpFe(CO)(CS)(L)]⁺ and [CpFe(CS)(L)₂]⁺ with P(Oφ)₃, P(OMe)₃, and (n-Bu)₂S is probably due to the increased solubility of their monosubstituted cations. With these ligands, the [CpFe(CO)(CS)(L)]CF₃SO₃ precipitate does not form as rapidly as with Pφ₃; hence, further substitution can occur.

The Pφ₃-substituted cation, [CpFe(CO)(CS)(Pφ₃)]⁺, has been prepared previously by thermal substitution of [CpFe(CO)₂(CS)]⁺ (53). However, the photochemical method is faster, gives a higher yield, and does not have the [CpFe(CO)₂(Pφ₃)]⁺ contaminant.

Attempts to prepare olefin-substituted cations, [CpFe(CO)(CS)(olefin)]CF₃SO₃, by reaction of CpFe(CO)(CS)CF₃SO₃ with

Table 8. Infrared spectra of $[\text{CpFe}(\text{CO})(\text{CS})(\text{L})]\text{CF}_3\text{SO}_3$ complexes

L	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{CS}), \text{cm}^{-1}$
$\text{P}\phi_3$	2034 s ^a	1323 vs ^a
py	2045 s ^a	1321 vs ^a
CH_3CN	2056 s ^a	1327 vs ^a
$\text{P}(\text{O}\phi)_3$ ^b	2051 s ^a	1337 vs ^a
$\text{P}(\text{OMe})_3$ ^b	2043 s ^a	1331 vs ^a
Bu_2S ^b	2040 s ^a	1323 vs ^a
Acetone ^b	2031 s ^c	1303 vs ^c

^a CH_3CN solvent.

^bComplexes were not isolated.

^cAcetone solvent.

Table 9. ^1H NMR spectra of $[\text{CpFe}(\text{CO})(\text{CS})(\text{L})]\text{CF}_3\text{SO}_3$ complexes

L	Cp, τ	Other resonances, τ
$\text{P}\phi_3$	4.45 (d, $J = 1.0$ Hz) ^a	2.27-2.72 (ϕ) ^a
py	4.32 ^a	1.07-2.43 (m, py) ^a
CH_3CN	4.33 ^a	7.49 (CH_3CN) ^a
$\text{P}(\text{O}\phi)_3$ ^b	4.70 (d, $J = 0.9$ Hz) ^a	2.33-2.80 (m, ϕ) ^{a,c}
$\text{P}(\text{OMe})_3$ ^b	4.28 (d, $J = 1.1$ Hz) ^a	5.90-6.27 (m, Me) ^{a,c}
Bu_2S ^b	4.28 ^a	6.90-7.32 (m, S- CH_2 -), 8.08-9.25 (m, $-\text{CH}_2\text{CH}_2\text{CH}_3$) ^{a,c}

^a d^6 -Acetone solvent.

^bComplexes were not isolated.

^cResonances are mixed with those of the bis-substituted cation, $[\text{CpFe}(\text{CS})(\text{L})_2]^+$.

the olefins cyclopentene or norbornadiene were unsuccessful. No reaction was apparent and the $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ slowly decomposed during the reaction. This would suggest that CF_3SO_3^- is a stronger ligand than an olefin. Also, attempts to prepare $[\text{CpFe}(\text{CO})(\text{CS})(\text{olefin})]^+$ by direct photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$ in CH_2Cl_2 with cyclohexene present were unsuccessful.

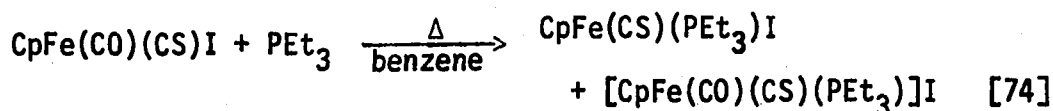
F. Reactions of $\text{CpFe}(\text{CO})(\text{CS})\text{I}$

The $\text{CpFe}(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$ and I) complexes react thermally with phosphines to form $\text{CpFe}(\text{CO})(\text{L})\text{X}$ and $[\text{CpFe}(\text{CO})_2(\text{L})]\text{X}$ (108,109). With the phosphites, only the neutral substituted halides, $\text{CpFe}(\text{CO})(\text{L})\text{X}$, are formed (109,110).

Thermal substitution occurs in the thiocarbonyl analog, $\text{CpFe}(\text{CO})(\text{CS})\text{I}$, according to the following equation:



The neutral substituted halide, $\text{CpFe}(\text{CS})(\text{L})\text{I}$, is the only product when $\text{L} = \text{P}\phi_3, \text{As}\phi_3, \text{Sb}\phi_3, \text{P}(\text{OMe})_3$ and $\text{P}(\text{O}\phi)_3$. With the stronger nucleophile, PEt_3 , both $\text{CpFe}(\text{CO})(\text{PEt}_3)\text{I}$ and $[\text{CpFe}(\text{CO})(\text{CS})(\text{PEt}_3)]\text{I}$ appear to form.



The $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ starting material used for the preparation of these $\text{CpFe}(\text{CS})(\text{L})\text{I}$ complexes contained a small amount of $\text{CpFe}(\text{CO})_2\text{I}$

Table 10. Infrared and ^1H NMR spectra of the $\text{CpFe}(\text{CS})(\text{L})\text{I}$ complexes

L	IR		^1H NMR	
	$\nu(\text{CS}), \text{cm}^{-1}$	Cp, τ	Other resonances, τ	
PEt_3	1272 ^a	5.36 (d, $J = 0.8 \text{ Hz}$) ^a	7.68-8.27 (m, $-\text{CH}_2-$), 8.57-8.13 (m, $-\text{CH}_3$) ^a	
$\text{P}\phi_3$	1271 ^a	5.58 (d, $J = 0.9 \text{ Hz}$) ^a	2.22-2.83 (m, ϕ) ^a	
$\text{As}\phi_3$	1271 ^a	5.50 ^a (s)	2.33-2.80 (m, ϕ) ^a	
$\text{Sb}\phi_3$	1278 ^a	5.39 ^a (s)	2.37-2.83 (m, ϕ) ^a	
$\text{P}(\text{OMe})_3$	1278 ^a	5.31 ^a (s)	6.29 (d, $J = 11 \text{ Hz}$, Me) ^a	
$\text{P}(\text{O}\phi)_3$	1289 ^a	5.88 ^a (s)	2.55-2.92 (m, ϕ) ^a	
$\text{CH}_3\text{CN}^{\text{b}}$	1277 ^c	5.22 ^d (s)		

^a CS_2 solvent.^bComplex was not isolated.^c CH_3CN solvent.^d CD_3CN solvent.

impurity. As a result, some CpFe(CO)(L)I and/or $[\text{CpFe(CO)}_2(\text{PEt}_3)]\text{I}$ was also formed during these reactions. It is, therefore, impossible to state that no CS substitution occurred when CpFe(CO)(CS)I was reacted with the neutral ligands. However, if CS substitution did occur, its extent was certainly small.

The rate of CO substitution in CpFe(CO)(CS)I is markedly faster than in $\text{CpFe(CO)}_2\text{I}$. Formation of the triphenylphosphite substituted halide, $\text{CpFe(CS)(P}\{\text{O}\phi\}_3\text{)I}$, is complete in 12 hours versus 24 hours for $\text{CpFe(CO)(P}\{\text{O}\phi\}_3\text{)I}$ (110). Also, the reaction of CpFe(CO)(CS)I with $\text{P}\phi_3$ to form $\text{CpFe(CS)(P}\phi_3\text{)I}$ is complete in 3 hours, while $\text{CpFe(CO)}_2\text{I}$ takes 18 hours to form $[\text{CpFe(CO)}_2(\text{P}\phi_3)]\text{I}$ and $\text{CpFe(CO)(P}\phi_3\text{)I}$ (108). These reactions were all conducted in refluxing benzene.

Both the preference for CO substitution over CS substitution in CpFe(CO)(CS)I and the increased rate of CO substitution in CpFe(CO)(CS)I vs. $\text{CpFe(CO)}_2\text{I}$ suggest that the Fe-CS bond is stronger than the Fe-CO bond.

Inasmuch as the reduction of $[\text{CpFe(CO)(CS)}]_2$ failed to give any easily characterized reduced thiocarbonyl species (vide ante), several attempts at reducing CpFe(CO)(CS)I were tried.

Attempted reduction of CpFe(CO)(CS)I with Mg or Mg/Hg gave no apparent reaction. Reduction of CpFe(CO)(CS)I with either Zr/Hg or methyllithium gave $[\text{CpFe(CO)(CS)}]_2$ as the major product. An attempt to produce $\text{CpFe(CO)(CS)Co(CO)}_4$ by reaction of CpFe(CO)(CS)I with $\text{Na[Co(CO)}_4]$ gave no identifiable thiocarbonyl-containing products (as

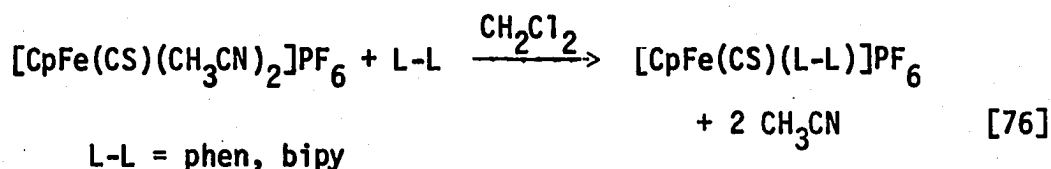
the product apparently did not contain the CS ligand, it was not characterized).

G. Reactions of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$

A general characteristic of organonitrile transition metal complexes is the ease with which the organonitrile ligand can be replaced by other ligands (142). Thus, it was expected that the acetonitrile ligands in $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ could be replaced by Group VA ligands to form new iron thiocarbonyl complexes as shown in equation [75]:



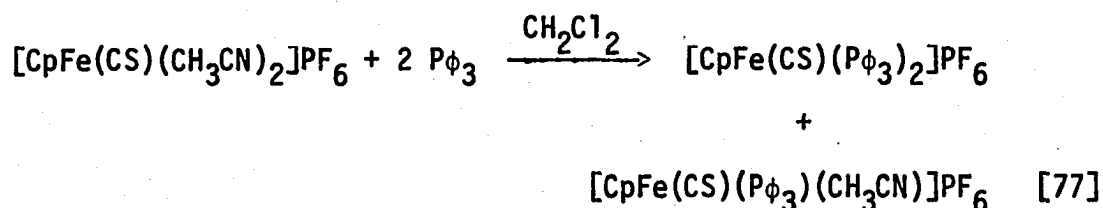
The bidentate ligands o-phenanthroline and 2,2'-bipyridine do displace both acetonitrile ligands to form $[\text{CpFe}(\text{CS})(\text{phen})]\text{PF}_6$ and $[\text{CpFe}(\text{CS})(\text{bipy})]\text{PF}_6$, respectively. The yields are low, with the



major by-product apparently being $[\text{Fe}(\text{phen})_3](\text{PF}_6)_2$ and $[\text{Fe}(\text{bipy})_3](\text{PF}_6)_2$, respectively. These $[\text{Fe}(\text{L-L})_3]^{2+}$ complexes appear to be the major products of these reactions even when stoichiometric amounts of each ligand were slowly added to the solution of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$. There was no evidence of other thiocarbonyl-containing products in these reactions.

The infrared spectrum of $[\text{CpFe}(\text{CS})(\text{phen})]\text{PF}_6$ (see Table 12) is somewhat anomalous as it apparently has two $\nu(\text{CS})$ absorptions (1290 vs and 1299 m, sh cm^{-1}). However, the shoulder at 1299 cm^{-1} occurs at the same position as the $\nu(\text{CS})$ absorption of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$. So it appears that the o-phenanthroline ligand dissociates somewhat in the acetonitrile IR solvent.

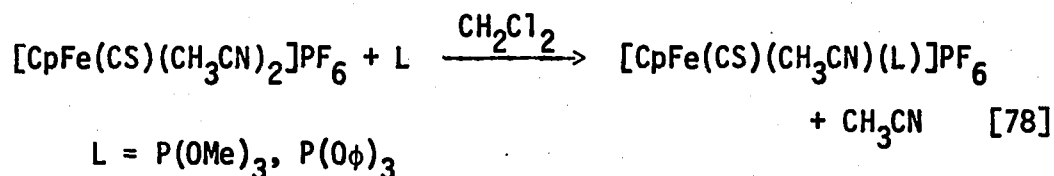
Triphenylphosphine, $\text{P}\phi_3$, also will displace two CH_3CN ligands from $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ to form $[\text{CpFe}(\text{CS})(\text{P}\phi_3)_2]\text{PF}_6$. With stoichiometric



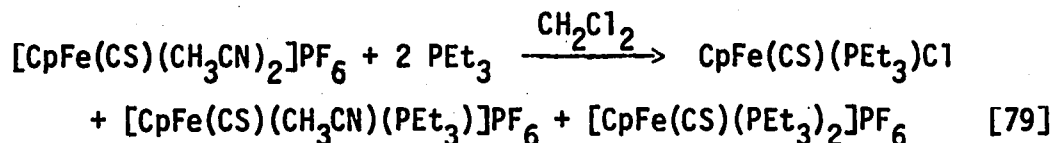
amounts of reactants, only 34% of the theoretical yield of $[\text{CpFe}(\text{CS})(\text{P}\phi_3)_2]\text{PF}_6$ is obtained. The bright orange air-stable complex crystallizes from CH_2Cl_2 /benzene as the benzene monosolvate, $[\text{CpFe}(\text{CS})(\text{P}\phi_3)_2]\text{PF}_6 \cdot \text{C}_6\text{H}_6$. Without the benzene present, the complex does not crystallize but forms a thick oil. A red oil is the other product of the reaction, and from spectral evidence appears to be $[\text{CpFe}(\text{CS})(\text{P}\phi_3)(\text{CH}_3\text{CN})]\text{PF}_6$ (IR (CH_3CN): 1292 vs, 1193 m, 1121 m, and 1095 m cm^{-1} ; ^1H NMR (acetone): τ 7.92 (br, s, CH_3CN), 5.02 (s, Cp), 2.08-3.00 (m, $\text{P}\phi_3$). The ^1H NMR spectrum was not clean and the assignments are only tentative).

The ligands trimethylphosphite and triphenylphosphite only displace one acetonitrile ligand from $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ to form $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})(\text{P}(\text{OMe})_3)]\text{PF}_6$ and $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})(\text{P}(\text{O}\phi)_3)]\text{PF}_6$.

respectively (see Table 12 for spectral data). Both complexes form air-stable orange crystals, with $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})(\text{P}\{\text{O}\phi\}_3)]\text{PF}_6$ crystallizing as the mono-benzene solvate.



Triethylphosphine reacts with $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ in CH_2Cl_2 to form three compounds -- $\text{CpFe}(\text{CS})(\text{PET}_3)\text{Cl}$, $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})(\text{PET}_3)]\text{PF}_6$ and $[\text{CpFe}(\text{CS})(\text{PET}_3)_2]\text{PF}_6$. The presence of the unexpected



$\text{CpFe}(\text{CS})(\text{PET}_3)\text{Cl}$ can be explained by PET_3 reacting with the CH_2Cl_2 solvent to form a phosphonium salt, $[\text{Et}_3\text{PCH}_2\text{Cl}]^+\text{Cl}^-$. The free chloride ion then can react with either $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})(\text{PET}_3)]\text{PF}_6$ or $[\text{CpFe}(\text{CS})(\text{PET}_3)_2]\text{PF}_6$ to form the $\text{CpFe}(\text{CS})(\text{PET}_3)\text{Cl}$. Alternatively, the chloride ion can attack the starting material giving $\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})\text{Cl}$ which subsequently undergoes ligand replacement to give $\text{CpFe}(\text{CS})(\text{PET}_3)\text{Cl}$.

The number of acetonitrile ligands displaced in $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ increases with the nucleophilicity of the Group VA ligand. The phosphites react to replace one CH_3CN ligand, while the more nucleophilic phosphines are able to replace the second acetonitrile ligand to a certain extent.

Table 11. Infrared and ^1H NMR spectra of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})(\text{L})]\text{PF}_6$ complexes

L	IR ^a		^1H NMR ^b	
	$\nu(\text{CS}), \text{cm}^{-1}$	Cp, τ	Other resonances, τ	
CH_3CN	1298	4.84	7.48 (CH_3CN)	
PEt_3	1292	4.84 (d, $J = 1.0$ Hz)	7.52 (d, $J = 1.0$ Hz, CH_3CH), 7.67-8.18 (m, $-\text{CH}_2-$), 8.48-9.07 (m, $-\text{CH}_3$)	
$\text{P}(\text{OMe})_3$	1304	4.81 (d, $J = 0.8$ Hz)	6.15 (d, $J = 11.7$ Hz, $\text{P}(\text{OMe})_3$), 7.55 (d, $J = 0.7$ Hz, CH_3CN)	
$\text{P}(\text{O}\phi)_3$	1312	5.28 (d, $J = 0.8$ Hz)	2.40-2.92 (m, $\text{P}(\text{O}\phi)_3$), 7.67 (d, $J = 1.1$ Hz, CH_3CN)	

^a CH_3CN solvent.^b d^6 -Acetone solvent.

Table 12. Infrared and ^1H NMR spectra of $[\text{CpFe}(\text{CS})(\text{L})_2]\text{X}$ complexes

$(\text{L})_2$	IR^{a}		$^1\text{H NMR}^{\text{b}}$	
	$\nu(\text{CS}), \text{cm}^{-1}$	Cp, τ	Other resonances, τ	
$(\text{P}\phi_3)_2^{\text{c}}$	1298	5.10 (t, $J = 1.3$ Hz)	2.38-2.93 (m, ϕ)	
bipy $^{\text{c}}$	1293	4.65	1.00-2.62 (m, bipy)	
phen $^{\text{c}}$	1290 vs; 1299 m, sh	4.58	0.65-2.12 (m, phen)	
$(\text{PEt}_3)_2^{\text{c,d}}$	1299	4.77 (t, $J = 1.3$ Hz)	7.67-8.18 (m, $-\text{CH}_2-$), 8.48-9.09 (m, $-\text{CH}_3$)	
$(\text{P}(\text{O}\phi)_3)_2^{\text{d,e}}$	1323	5.16 (t, $J = 1.0$ Hz)	2.33-2.80 (m, ϕ) $^{\text{f}}$	
$(\text{P}(\text{OMe})_3)_2^{\text{d,e}}$	1308	4.69 (t, $J = 1.0$ Hz)	5.90-6.27 (m, Me) $^{\text{f}}$	
$(\text{Me}_2\text{S})_2^{\text{c}}$	1287	4.78	7.60 (Me)	
$\text{Bu}_2\text{S}^{\text{d,e}}$	1287	4.70	6.90-7.32 (m, $\text{S}-\text{CH}_2-$) $^{\text{f}}$, 8.08-9.25 (m, $-\text{CH}_2\text{CH}_2\text{CH}_3$) $^{\text{f}}$	

$^{\text{a}}\text{CH}_3\text{CN}$ solvent.

$^{\text{b}}\text{d}^6$ -Acetone solvent.

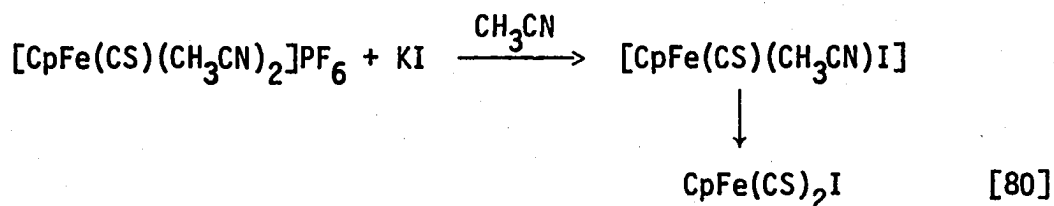
$^{\text{c}}\text{X} = \text{PF}_6$.

$^{\text{d}}$ Complex was not isolated.

$^{\text{e}}\text{X} = \text{CF}_3\text{SO}_3$.

$^{\text{f}}$ Resonances are mixed with those of the monosubstituted cation, $[\text{CpFe}(\text{CS})(\text{CO})(\text{L})]^+$.

When $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ is reacted with KI in CH_3CN , spectral evidence suggests that $\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})\text{I}$ (IR (CH_3CN): 1277 cm^{-1} ; $^1\text{H NMR}$ (CD_3CN): τ 5.22 (Cp)) is formed. The complex is air-stable in solution; however, attempts to isolate it were unsuccessful, and resulted in the unexpected product, $\text{CpFe}(\text{CS})_2\text{I}$. Even extraction of



the CH_3CN solution of $\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})\text{I}$ with CS_2 results in rapid formation of $\text{CpFe}(\text{CS})_2\text{I}$ rather than transfer of $\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})\text{I}$ to the nonpolar solvent. It appears that a decrease in the CH_3CN concentration either by extraction into CS_2 or evaporation to dryness results in the formation of $\text{CpFe}(\text{CS})_2\text{I}$. The $\text{CpFe}(\text{CS})_2\text{I}$ complex can also be prepared by reaction of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ with KI in other solvents (acetone and methanol); however, the existence of $\text{CpFe}(\text{CS})(\text{S})\text{I}$ intermediates in these solvents has not been confirmed due to the opaqueness of the thiocarbonyl region in infrared spectra taken in these solvents.

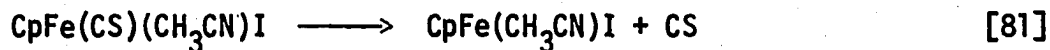
Reaction of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ with KBr in CH_3CN gives $\text{CpFe}(\text{CS})_2\text{Br}$ in an analogous manner; however, the yields are poor.

The mechanism of the formation of $\text{CpFe}(\text{CS})_2\text{I}$ from $\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})\text{I}$ is unclear. One possibility would involve CS dissociation from $\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})\text{I}$; then the free CS ligand would displace the CH_3CN ligand from a second $\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})\text{I}$ molecule to give $\text{CpFe}(\text{CS})_2\text{I}$

Table 13. Infrared and ^1H NMR spectra of the $\text{CpFe}(\text{CS})_2\text{X}$ complexes in CS_2

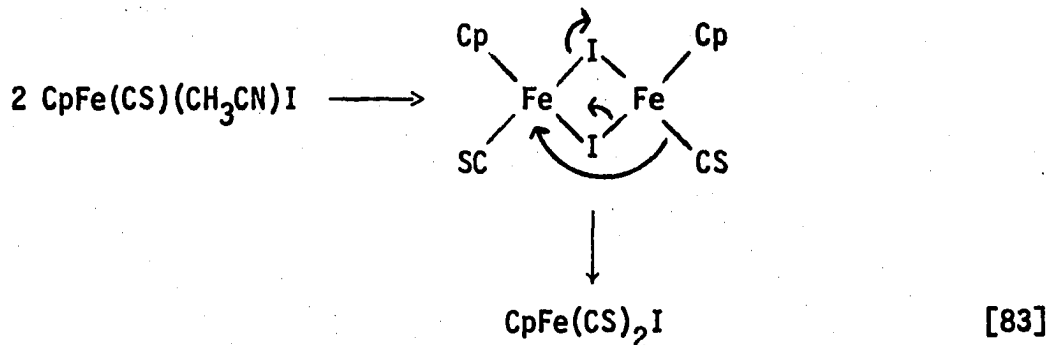
X	IR	^1H NMR
	$\nu(\text{CS}), \text{cm}^{-1}$	Cp, τ
I	1337 s, 1274 vs	4.95
Br	1341 s, 1276 vs	---

(as in the following equations):



However, this sequence is unlikely in view of the apparent stability of $\text{CpFe(CS)(CH}_3\text{CN)I}$ in solution. The instability of free CS would also argue against this mechanism.

Another mechanism would involve formation of a binuclear complex from $\text{CpFe(CS)(CH}_3\text{CN)I}$, which subsequently decomposes to $\text{CpFe(CS)}_2\text{I}$:

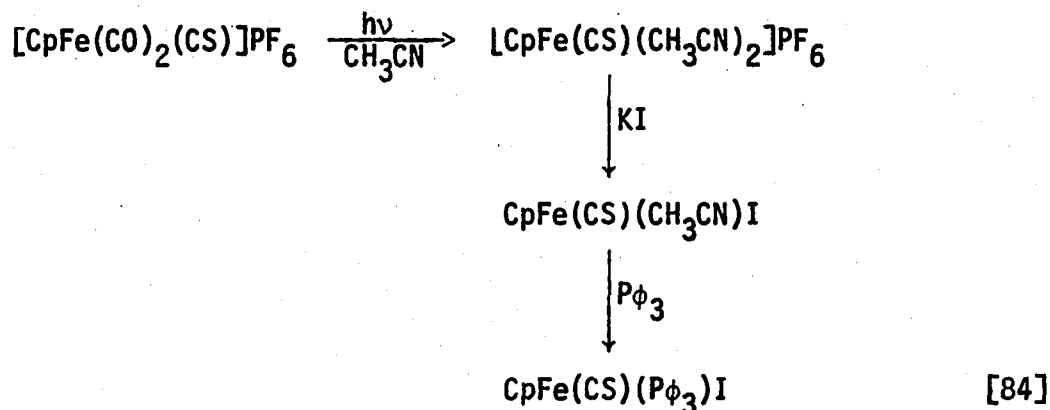


However, any discussion of a mechanism for the formation of $\text{CpFe(CS)}_2\text{I}$ at this point is speculative and must await further evidence.

Confirmation of $\text{CpFe(CS)(CH}_3\text{CN)I}$ as the intermediate in the formation of $\text{CpFe(CS)}_2\text{I}$ comes from the reaction of the intermediate with $\text{P}\phi_3$ to form $\text{CpFe(CS)(P}\phi_3\text{)I}$. This is the best method of preparing $\text{CpFe(CS)(P}\phi_3\text{)I}$, and probably other CpFe(CS)(L)I complexes, although only the triphenylphosphine complex has been prepared by this procedure.

The preparation of $\text{CpFe(CS)(P}\phi_3\text{)I}$ from $[\text{CpFe(CO)}_2\text{(CS)]PF}_6$ can be conducted in a single flask by 1) irradiating to produce

[CpFe(CS)(CH₃CN)₂]PF₆, 2) adding KI to form CpFe(CS)(CH₃CN)I, and 3) finally adding the neutral ligand, Pφ₃, to form CpFe(CS)(Pφ₃)I:



The only contaminants in the product are CpFe(CO)(CS)I and CpFe(CO)₂I, probably formed by the attack of I⁻ on what [CpFe(CO)₂(CS)]PF₆ remains after irradiation. These are easily separated from CpFe(CS)(Pφ₃)I by crystallization or column chromatography.

Reaction of KCN with [CpFe(CS)(CH₃CN)₂]PF₆ in methanol gives a brown solution. The residue resulting from evaporating the solution to dryness dissolves in CH₃CN giving a yellow solution whose infrared spectrum suggests the presence of an unknown thiocarbonyl species (IR (CH₃CN): 2097 s, 2057 w, 1954 w and 1278 vs cm⁻¹). The same substance is obtained from the reaction of KCN with CpFe(CO)(CS)Br. By analogy to the carbonyl system, where CpFe(CO)₂Br reacts with KCN to yield K[CpFe(CO)(CN)₂] (119), one would expect the unknown thiocarbonyl species to be K[CpFe(CS)(CN)₂]. Attempts to crystallize the compound were unsuccessful, and it was not characterized further.

Several attempts were made to prepare thiocarbonyl complexes by reaction of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ with reducing agents. With NaH, no reaction was apparent. With Na/Hg and sodium naphthalide, a reaction occurred; however, no thiocarbonyl-containing products were apparent. With Zn/Hg, partial reaction occurred, and after subsequent treatment with MeI the only thiocarbonyl-containing products were $\text{CpFe}(\text{CO})(\text{CS})\text{I}$, $\text{CpFe}(\text{CS})_2\text{I}$ and unreacted $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$. Reaction with Mg/Hg (prepared from HgI_2 and Mg), on the other hand, gave a yellow product whose infrared spectrum strongly suggests a new thiocarbonyl species (IR (CS_2): 1320 s and 1259 vs cm^{-1}). The infrared band positions and intensities indicate the species is of the form $\text{CpFe}(\text{CS})_2\text{X}$, possibly $\text{CpFe}(\text{CS})_2\text{MgI}$ or $[\text{CpFe}(\text{CS})_2]\text{M}$ (M = Mg or Hg), although the product was not further characterized.

H. Miscellaneous Reactions

The substituted thiocarbonyl cations, $[\text{CpFe}(\text{CS})(\text{P}\phi_3)_2]\text{PF}_6$ and $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})(\text{P}\phi_3)]\text{PF}_6$, like $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$ undergo nucleophilic substitution with the iodide ligand, in these cases producing $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$.

Reaction of MeLi with $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$ in THF at -78°C gives a burgundy solution. The residue resulting from evaporation of this solution to dryness dissolves in CS_2 giving an air-sensitive burgundy solution whose infrared spectrum suggests the presence of a thiocarbonyl species (IR (CS_2): 1271 s, 1184 w, 1121 w, 1091 m and 1070 m cm^{-1}). The $\nu(\text{CS})$ absorption at 1271 cm^{-1} coincides with the

Table 14. ^{13}C NMR spectra of some cyclopentadienylthiocarbonyl complexes of iron^a

Complex	CS	CO	Cp	Other resonances
$\text{CpFe}(\text{CO})(\text{CS})\text{I}$	-322.5	-212.5	-87.6	
$\text{CpFe}(\text{CO})(\text{CS})\text{OSO}_2\text{CF}_3$	-321.7	-207.8	-88.0	
$[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]\text{PF}_6$	-329.4	---	-87.4	-222.6 (CN), 4.1 (Me)
$\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$	-325.0 (d, J = 37.2 Hz)	---	-87.1	-134.9, -132.9 (d, J = 7.4 Hz), -129.5, -127.3 (d, J = 8.9 Hz) (ϕ)
$\text{CpFe}(\text{CS})(\text{P}(\text{OMe})_3)\text{I}$	-323.1 (d, J = 55.1 Hz)	---	-86.5	-54.0 (d, J = 4.3 Hz, Me)
$\text{CpFe}(\text{CS})(\text{PET}_3)\text{I}$	-324.4 (d, J = 37.8 Hz)	---	-85.7	21.0 (d, J = 2.1 Hz, $-\text{CH}_2-$), 8.4 ($-\text{CH}_3$)
$\text{CpFe}(\text{CS})_2\text{I}$	-323.4	---	-90.6	---

^aChemical shifts in ppm downfield from TMS, CDCl_3 solvent and internal standard.

$\nu(\text{CS})$ absorption of the starting material, $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$. The product of the reaction was expected to be $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{Me}$, by analogy to the reaction of $\text{CpFe}(\text{CO})(\text{P}\phi_3)\text{I}$ with MeLi to give $\text{CpFe}(\text{CO})(\text{P}\phi_3)\text{Me}$ (120). However, the physical evidence (color and air-sensitivity) and infrared spectrum agree with neither $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$ or $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{Me}$ (the $\nu(\text{CS})$ absorption of $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{Me}$ should be lower than that of $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$). The product was not further characterized.

Reaction of $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$ with AgNO_3 in CH_2Cl_2 appears to produce $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{NO}_3$ (IR (CS_2): 1290 vs, 1260 s, 1252 vs cm^{-1} ; ^1H NMR (CS_2): τ 5.45 (d, $J = 1$ Hz, Cp), 2.28-2.92 (m, ϕ); the assignment of a $\nu(\text{CS})$ absorption in the IR spectrum was not possible due to the presumed presence of $\nu(\text{NO})$ absorptions of the NO_3^- ligand). Attempts to separate the $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{NO}_3$ from unreacted $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$ by fractional crystallization were unsuccessful, and the complex was not further characterized.

V. CONCLUSIONS

The cyclopentadienylthiocarbonyl complexes of iron described herein, along with those described by Quick (61), greatly expand the number and kind of known iron thiocarbonyl complexes. As with the chemistry of other thiocarbonyl complexes, some of the results were expected and paralleled known reactions of analogous carbonyl complexes or known reactions of thiocarbonyl complexes. In other cases, the results were unexpected.

One interesting product, $[\text{CpFe}(\text{CO})(\text{CS})]_2$, came from the reaction of $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ with NaH. The thiocarbonyl ligand in this dimer shows a strong preference for the bridging position, as recently found in other binuclear thiocarbonyl complexes. The bridging thiocarbonyl ligands appear to bind the two halves of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ stronger than in $[\text{CpFe}(\text{CO})_2]_2$. This is evident in its shorter Fe-Fe distance and in its rate of cis-trans isomerization which is markedly slower than found in the all-carbonyl analog, $[\text{CpFe}(\text{CO})_2]_2$.

Like electron-rich terminal thiocarbonyl ligands, bridging thiocarbonyl groups form Lewis acid adducts at the sulfur atom. The $[\text{CpFe}(\text{CO})(\text{CS})]_2$ dimer forms Lewis acid adducts at one of its sulfur atoms with both inorganic (HgCl_2) and alkyl (CH_3^+) Lewis acids. The formation of other Lewis acid adducts involving a bridging thiocarbonyl ligand has been studied by Quick (61) using $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})]$.

Oxidative cleavage of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ has been shown to be more difficult than for $[\text{CpFe}(\text{CO})_2]_2$, testifying to the stronger binding of

the two halves of the molecule by the bridging thiocarbonyl ligands. The mechanism of the reaction with halogens to give $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ appears to proceed in a similar manner to that of the reaction of halogens with $[\text{CpFe}(\text{CO})_2]_2$.

Reduction of $[\text{CpFe}(\text{CO})(\text{CS})]_2$, unlike the reduction of $[\text{CpFe}(\text{CO})_2]_2$, appears not to cleave the dimer. However, the identity of the reduction product is not clear, and appears to depend upon the reducing agent and the stoichiometry of the reagents.

Photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ has been shown to be an effective method for selectively removing one or two carbonyl ligands. Photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{CF}_3\text{SO}_3$ in CH_2Cl_2 gives $\text{CpFe}(\text{CO})(\text{CS})\text{CF}_3\text{SO}_3$ which is useful in preparing $\text{CpFe}(\text{CO})(\text{CS})\text{X}$ and $[\text{CpFe}(\text{CO})(\text{CS})(\text{L})]^+$ complexes. And, photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ in CH_3CN yields $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]^+$ from which $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})(\text{L})]^+$ and $[\text{CpFe}(\text{CS})(\text{L})_2]^+$ complexes can be prepared. Also, the $[\text{CpFe}(\text{CS})(\text{Me}_2\text{S})_2]^+$ complex has been prepared by the photolysis of $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$ in the presence of Me_2S in acetone.

The $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ complex has been shown to undergo thermal CO substitution to give $\text{CpFe}(\text{CS})(\text{L})\text{I}$ complexes. The preference for CO substitution in $\text{CpFe}(\text{CO})(\text{CS})\text{I}$ indicates that the M-CS bond is stronger than the M-CO bond in this system.

The novel complex $\text{CpFe}(\text{CS})_2\text{I}$ is the end product of the reaction of $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]^+$ with KI. The reaction apparently proceeds through a $\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})\text{I}$ intermediate, which has been confirmed by spectral evidence and its reaction with $\text{P}\phi_3$ to give $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$. However,

the mechanism by which $\text{CpFe}(\text{CS})_2\text{I}$ is formed is open to question. The synthetic route through $\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})\text{I}$ is the best method of preparing $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$.

The preparation and properties of these thiocarbonyl complexes offers further insight into the chemistry of metal thiocarbonyl complexes. In particular, the synthesis and properties of $[\text{CpFe}(\text{CO})(\text{CS})]_2$, and the crystal structure of cis- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ have demonstrated the stability of the bridging CS ligand. Also, photolysis has been shown to be an effective method for selectively removing carbonyl ligands from metal carbonyl-thiocarbonyl complexes.

VI. SUGGESTIONS FOR FURTHER STUDY

There are many areas uncovered by this research which warrant investigation. Some of these have undergone preliminary investigation while others became apparent in retrospect.

A study of the cis-trans isomerization of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ would shed light on the mechanism of this isomerization. Also, it may help explain the stability that bridging thiocarbonyl ligands impart to binding the two halves of the molecule together.

A detailed study of the kinetics of the reaction of CH_3I with cis- and trans- $[\text{CpFe}(\text{CO})(\text{CS})]_2$ may indicate why only cis- $[\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS-Me})]^+$ is formed. There is no apparent steric preference for the cis isomer.

The reduction of $[\text{CpFe}(\text{CO})(\text{CS})]_2$ also poses questions. The identity of the reaction products is not apparent. The fact that something unexpected is occurring in these reactions would make their study worthwhile.

The substituted cyclopentadienyliron thiocarbonyl cations, $[\text{CpFe}(\text{CS})(\text{CO})(\text{L})]^+$ and $[\text{CpFe}(\text{CS})(\text{L})_2]^+$, offer new starting materials for other iron thiocarbonyl complexes. For example, reaction with NaH may give the substituted dimers, $[\text{CpFe}(\text{CS})(\text{L})]_2$, or attack the cyclopentadienyl ring to give $(\text{C}_5\text{H}_6)\text{Fe}(\text{CS})(\text{L})_2$.

Preliminary reactions indicate that it may be possible to abstract I^- from $\text{CpFe}(\text{CS})(\text{P}\phi_3)\text{I}$. Thus, the $\text{CpFe}(\text{CS})(\text{L})\text{I}$ complexes may form starting materials for $\text{CpFe}(\text{CS})(\text{L})\text{R}$ complexes,

$[\text{CpFe}(\text{CS})(\text{L})(\text{olefin})]^+$ complexes, and mixed-metal thiocarbonyl dimers (i.e., $\text{CpFe}(\text{CS})(\text{L})\text{Co}(\text{CO})_4$).

Finally, the formation of $\text{CpFe}(\text{CS})_2\text{I}$ from $[\text{CpFe}(\text{CS})(\text{CH}_3\text{CN})_2]^+$ and KI raises questions as to the mechanism of its formation. And it also offers potential routes to other dithiocarbonyl complexes of iron.

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