

1980

Synthesis and reactivity of iron carbene complexes

Fred Boyle McCormick
Iowa State University

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SYNTHESIS AND REACTIVITY OF IRON CARBENE COMPLEXES

Iowa State University

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Synthesis and reactivity of iron carbene complexes

by

Fred Boyle McCormick

A Dissertation Submitted to the
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Requirements for the Degree of
DOCTOR OF PHILOSOPHY

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Iowa State University
Ames, Iowa

1980

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GENERAL INTRODUCTION

The first transition metal carbene complex was prepared in 1915 by Chugaev, but was not recognized as such until 1970-1971 (Figure 1).^{1,2}

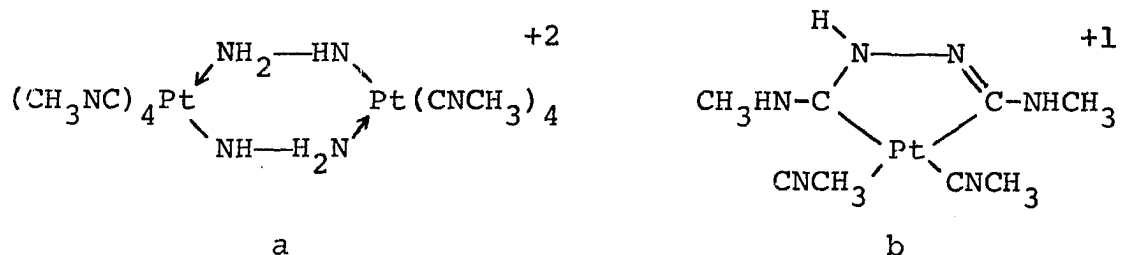
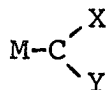


Figure 1. The structure of a Chugaev salt, a) original formulation by Chugaev, and b) current formulation as a carbene complex

The first complex to be formulated as a transition metal carbene complex, $(\text{CO})_5\text{WC}(\text{OCH}_3)\text{Ph}$, was reported in 1964 by Fischer and Maasböl.³ Since that time, the study of transition metal carbene complexes has been an actively researched area of organometallic chemistry and several excellent reviews are available.^{1,2,4-8}

Transition metal carbene complexes are of the general formula



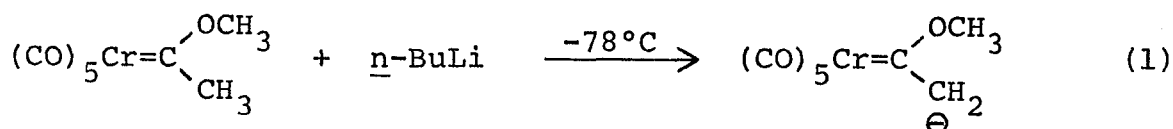
where a carbene, $:CXY$, acts as a two-electron donor to a metal atom. In most stable carbene complexes, either X or Y (or both) are heteroatomic groups, usually OR, SR, or amino groups. These groups are able to stabilize the sp^2 -hybridized carbene carbon by donating π -electron density into its p_z orbital. The carbene carbon may also be stabilized by $d_{\pi}-p_{\pi}$ backbonding from the metal atom. Although it is generally believed that $M \rightarrow C(\text{carbene}) \pi$ -donation is much less significant than heteroatom $\rightarrow C(\text{carbene}) \pi$ -donation,^{1,2,4-6} a formal double bond is often depicted between the metal and the carbene carbon, $M=CXY$.

In a majority of the known carbene complexes, the carbene carbon is an electrophilic center.^{1,2,4-6} Exceptions to this are the carbene complexes of Ta and Nb, such as $Cp_2(CH_3)Ta=CH_2$ ($Cp = \eta^5-C_5H_5$), where the carbene carbon is a nucleophilic center.⁹ These complexes behave like the related Wittig reagents (phosphorus ylides, $R_3P=CR'_2$) and are referred to as alkylidene complexes to differentiate them from the electrophilic carbene complexes.⁹

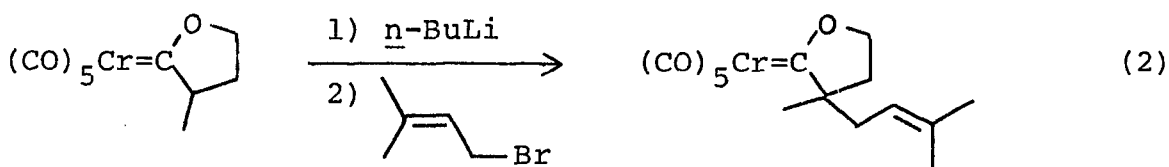
Initial interest in carbene complexes was centered on their synthesis and structural characterization.² Subsequently, much was learned about the chemistry of coordinated carbene ligands.² The potential use of carbene complexes

in organic synthesis is a subject of much current interest.^{1,2,4-8,10-13}

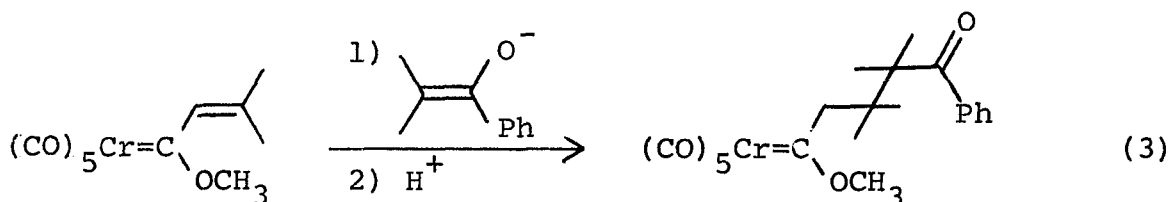
Casey has shown that carbene anions may be generated from neutral carbene complexes and organolithium reagents (eq. 1).^{10,11}



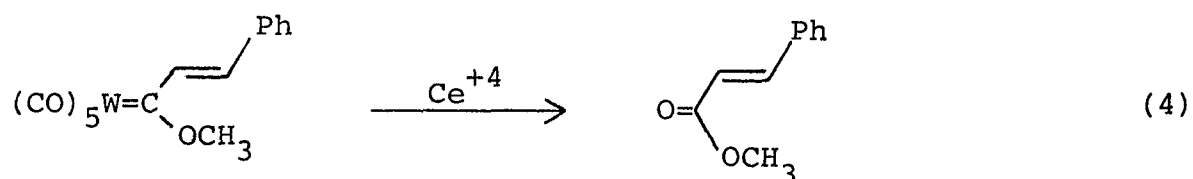
These carbene anions may then be alkylated by highly reactive alkylating agents such as $\text{CH}_3\text{SO}_3\text{F}$, allyl and benzyl halides, and α -bromoesters (eq. 2).^{10,11}



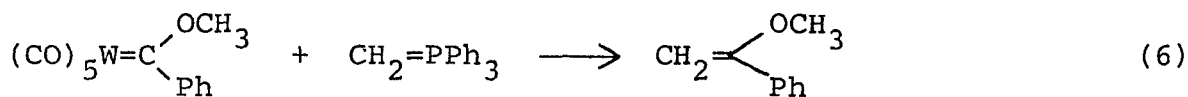
Enolate anions will conjugately add to vinyl carbene complexes via a stable carbene anion (eq. 3).^{10,11}

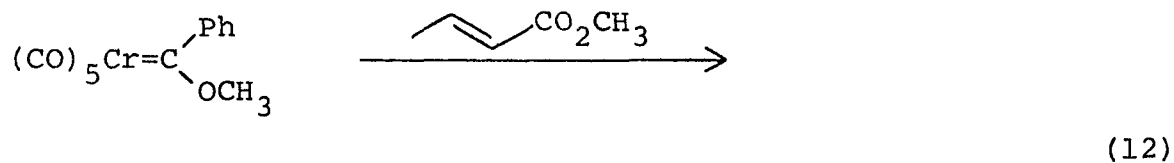


These methods (eq. 1-3) could be useful in organic synthesis if the resulting carbene ligands can be effectively cleaved from the metal center. There are several possibly useful methods for removing the carbene ligand: by oxidation (eq. 4),^{10,11} reaction with elemental sulfur or selenium (eq. 5),^{10,12} reaction with phosphorous ylides (eq. 6),^{10,11} reaction with diazoalkanes (eq. 7),¹⁰⁻¹² base catalyzed decomposition (eq. 8),¹⁰⁻¹² thermal decomposition (eq. 9),^{4,11,12} reduction (eq. 10),¹⁰ reaction with carboxylic acids (eq. 11),¹² and cyclopropanation (eq. 12).^{2,4,5,10-13}



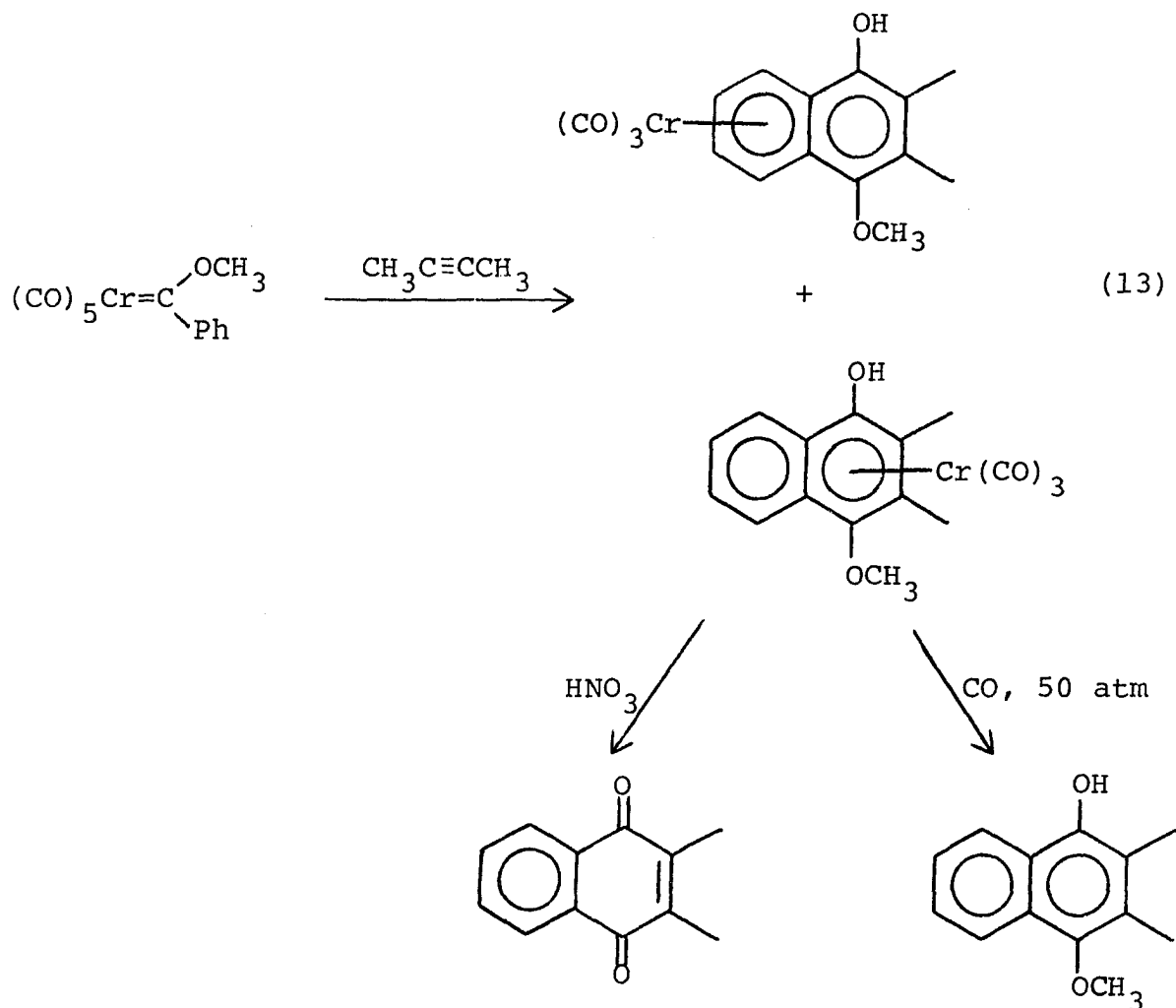
Y = S, Se





Quite recently, Dötz has demonstrated that the reactions of $(\text{CO})_5\text{Cr}(\text{carbene})$ complexes with alkynes lead to the formation of condensed aromatic ligands, such as indenenes, naphthalenes, phenanthrenes, benzofurans, and benzothio-phenes.¹⁴⁻²¹ In many cases, the free ligands may be obtained by reaction of the resulting complexes with CO under pressure. Oxidation of the resulting complexes with HNO_3 often leads to the formation of free quinone derivatives. An example of the reactions of $(\text{CO})_5\text{Cr}(\text{carbene})$ complexes with alkynes is shown in eq. 13.¹⁷

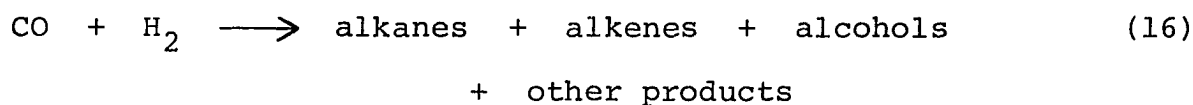
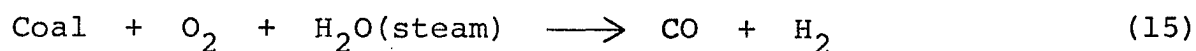
Of more significance than the use of carbene complexes as reagents in stoichiometric organic synthesis, is their role in the commercially important olefin metathesis^{22,23}



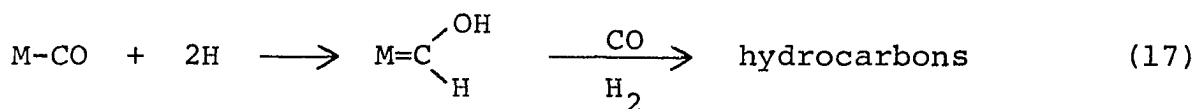
and Fischer-Tropsch²⁴ reactions. For both of these processes, metal-carbene species are thought to be key intermediates.

The olefin metathesis reaction has been extensively studied and the generally accepted mechanism involves carbene complexes and metallocyclobutanes (eq. 14).²²

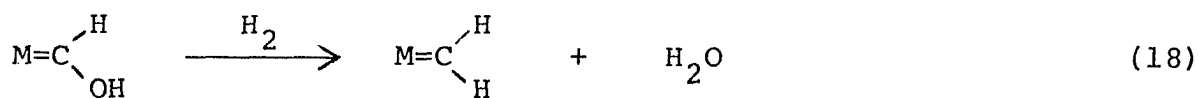
1902.²⁴ Recent economic factors and the growing awareness of the limited nature of the world's crude oil reserves has rekindled interest in this reaction. Coal, a presently abundant resource, may be converted to petrochemicals by the reactions in eq. 15 and 16.



Metal-carbene species were first proposed as catalytic intermediates in the Fischer-Tropsch reaction in 1951 (eq. 17).²⁶



Since then, several mechanisms which involve metal-carbene species have been proposed for the Fischer-Tropsch reaction,^{24,27} one of which is shown in Scheme 1.²⁷ Hydroxycarbene complexes are not involved in the recently proposed mechanisms,^{24,27} but they are still possible intermediates by virtue of their postulated reaction with H₂ (eq. 18).²⁴



There is also evidence that more than one metal center may be required to effect catalysis of the Fischer-Tropsch reaction and, thus, metal-cluster complexes containing carbene ligands may be important intermediates.²⁴

Because of the interesting possible applications of carbene complexes in organic synthesis and their postulation as catalytic intermediates in the commercially important olefin metathesis and Fischer-Tropsch reactions, we decided to undertake this investigation of iron carbene complexes. Our studies are mainly concerned with di(heteroatom)carbene ligands, especially dithiocarbene ligands, for several reasons. First of all, starting materials are readily available. Secondly, carbene ligands with two heteroatomic substituents have the potential for more varied chemistry than the extensively studied^{1,2,4-8} carbene complexes with only one heteroatomic substituent, M-C(heteroatom)R. Thirdly, relatively few complexes containing dithiocarbene ligands have been described in the literature²⁸⁻³⁷ (Table I) and there have been no reports concerning the reactivity of these ligands. A complex containing two di(methylthio)carbene ligands, cis-(CO)₄Cr[C(SCH₃)₂]₂, has been reported without

Table I. Previously reported dithiocarbene complexes

Complex	Reference
$(\text{CO})_5\text{Cr}-\text{C} \begin{array}{l} \diagup \text{SPh} \\ \diagdown \text{SPh} \end{array}$	28, 29
$(\text{CO})_5\text{Cr}-\text{C} \begin{array}{l} \diagup \text{SCH}_2\text{CH}_3 \\ \diagdown \text{SCH}_2\text{CH}_3 \end{array}$	30
$(\text{CO})_5\text{W}-\text{C} \begin{array}{l} \diagup \text{SPh} \\ \diagdown \text{SPh} \end{array}$	29
$(\text{CO})_5\text{W}-\text{C} \begin{array}{l} \diagup \text{SCH}_2\text{CH}_3 \\ \diagdown \text{SCH}_2\text{CH}_3 \end{array}$	30
$(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2\text{Fe}-\text{C} \begin{array}{l} \diagup \text{S} \\ \diagdown \text{S} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \begin{array}{l} \text{CO}_2\text{CH}_2\text{CH}_3 \\ \text{CO}_2\text{CH}_2\text{CH}_3 \end{array}$	31
$(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2\text{Fe}-\text{C} \begin{array}{l} \diagup \text{S} \\ \diagdown \text{S} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \begin{array}{l} \text{p-C}_6\text{H}_4\text{Cl} \\ \text{CHO} \end{array}$	31
$(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2\text{Fe}-\text{C} \begin{array}{l} \diagup \text{S} \\ \diagdown \text{S} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \begin{array}{l} \text{CO}_2\text{CH}_3 \\ \text{CO}_2\text{CH}_3 \end{array}$	31
$\text{Br}(\text{CO})(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})(\text{PPh}_3)_2\text{Ru}-\text{C} \begin{array}{l} \diagup \text{S} \\ \diagdown \text{S} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{+}$	32

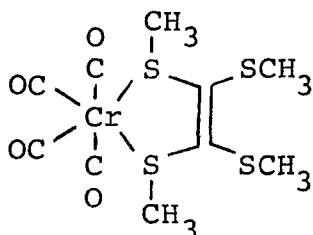
Table I. (Continued)

Complex	Reference
$\text{Br}(\text{CO})(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})(\text{PPh}_3)_2\text{Ru}-\text{C} \begin{array}{l} \diagup \text{S} \\ \diagdown \text{S} \end{array} +$	32
$(\text{CO})(\text{PPh}_3)_2 [(\text{CH}_3\text{CH}_2)_2\text{NCS}_2]\text{Ru}-\text{C} \begin{array}{l} \diagup \text{SCH}_3 \\ \diagdown \text{SCH}_3 \end{array} +$	33
$\text{H}(\text{CO})(\text{PPh}_3)_2\text{Os} \begin{array}{l} \diagup \text{SCH}_3 \\ \diagdown \text{S} \\ \diagup \text{C} \\ \diagdown \text{N}(\text{CH}_3)(\text{p-C}_6\text{H}_4\text{CH}_3) \end{array}$	34
$\text{Br}(\text{CO})_2(\text{PPh}_3)_2\text{Os}-\text{C} \begin{array}{l} \diagup \text{S} \\ \diagdown \text{S} \end{array} +$	32
$\text{Br}(\text{CO})_2(\text{PPh}_3)_2\text{Os}-\text{C} \begin{array}{l} \diagup \text{S} \\ \diagdown \text{S} \end{array} +$	32
$\text{Br}(\text{CO})(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})(\text{PPh}_3)_2\text{Os}-\text{C} \begin{array}{l} \diagup \text{S} \\ \diagdown \text{S} \end{array} +$	32
$\text{Br}(\text{CO})(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})(\text{PPh}_3)_2\text{Os}-\text{C} \begin{array}{l} \diagup \text{S} \\ \diagdown \text{S} \end{array} +$	32
$\text{I}(\text{CO})_2(\text{PPh}_3)_2\text{Os}-\text{C} \begin{array}{l} \diagup \text{SCH}_3 \\ \diagdown \text{SCH}_3 \end{array} +$	35

Table I. (Continued)

Complex	Reference
$\text{Br}_2(\text{CO})(\text{PPh}_3)_2\text{Os}-\text{C} \begin{array}{l} \diagup \text{S} \\ \diagdown \text{S} \end{array}$	32
$\text{Br}_2(\text{CO})(\text{PPh}_3)_2\text{Os}-\text{C} \begin{array}{l} \diagup \text{S} \\ \diagdown \text{S} \end{array}$	32
$\text{Cl}(\text{PPh}_3)_2\text{Pt}-\text{C} \begin{array}{l} \diagup \text{SCH}_2\text{CH}_3^+ \\ \diagdown \text{SCH}_2\text{CH}_3 \end{array}$	36
$\text{Cl}(\text{PPh}_3)_2\text{Pt}-\text{C} \begin{array}{l} \diagup \text{SCH}_2\text{CH}_3^+ \\ \diagdown \text{SCH}_3 \end{array}$	36
$\text{I}(\text{PPh}_3)_2\text{Pt}-\text{C} \begin{array}{l} \diagup \text{SCH}_3^+ \\ \diagdown \text{SCH}_3 \end{array}$	37
$\text{I}(\text{PPh}_3)_2\text{Pt}-\text{C} \begin{array}{l} \diagup \text{SCH}_2\text{CH}_3^+ \\ \diagdown \text{SCH}_2\text{CH}_3 \end{array}$	37
$\text{I}_2(\text{PPh}_3)\text{Pt}-\text{C} \begin{array}{l} \diagup \text{SCH}_3 \\ \diagdown \text{SCH}_3 \end{array}$	37
$\text{I}_2(\text{PPh}_3)\text{Pt}-\text{C} \begin{array}{l} \diagup \text{SCH}_2\text{CH}_3 \\ \diagdown \text{SCH}_2\text{CH}_3 \end{array}$	37

experimental detail.³⁸ A later report,³⁹ has described a complex of the same molecular formula which, by X-ray diffraction, has the following structure:



As these two complexes are reported to have identical ¹³C-NMR spectra,^{38,39} the earlier³⁸ carbene complex formulation is probably incorrect. Di(heteroatom)carbene complexes have not been proposed as intermediates in the Fischer-Tropsch reaction,²⁴ nor have they been found to be effective olefin metathesis catalysts.²² Nevertheless, the study of di(heteroatom)carbene complexes could lead to a better understanding of these catalytic processes.

Our purpose was to prepare a variety of carbene complexes with two heteroatomic carbene substituents, Cp(CO)₂Fe-[C(XR)YR]⁺, and study their reactivity towards nucleophilic reagents, especially amines. It was hoped that the reactivity patterns of these complexes could be correlated with the electronic environment of the carbene carbon and, thus, lead to a comprehensive understanding of their chemistry. Valuable

techniques for probing the electronic environment of the carbene carbon were IR, ^1H -NMR, and ^{13}C -NMR spectroscopy.

In the present work, the basic reactivity patterns for the iron carbene complexes were established by the study of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$. These results were then applied to the $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ complexes, where X and Y are O, S, Se, and/or NR, to determine the effects of these various heteroatomic groups on the reactivity of the carbene carbon. Photochemical procedures led to a series of $\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ derivatives. By varying the ligand, L, we were able to study how the reactivity of the carbene carbon was affected by changes in the electron density at the metal center. The spectroscopic data for the iron carbene complexes were found to be significantly dependent on the nature of the ligands, L, and the heteroatomic carbene substituents, XR and YR.

Explanation of Dissertation Format

The material in this dissertation was arranged so that a minimum of rewriting was required for preparation of a manuscript for publication. Each section constitutes an article which has been submitted for journal publication. References to figures apply only to those contained within that section. The literature cited in the General Introduction and Summary appear in the final list of references.

SECTION I. SYNTHESIS OF CYCLOPENTADIENYLDICARBONYL-
[DITHIOCARBENE]IRON CATIONS AND THEIR
REACTIONS WITH AMINES

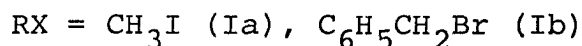
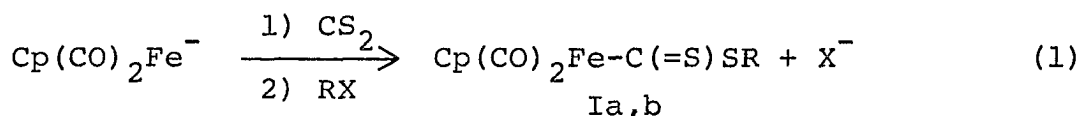
INTRODUCTION

Transition metal carbene complexes have become a well known class of organometallic compounds.¹⁻⁴ Only recently, however, have complexes with dithiocarbene ligands, $M-C(SR)_2$, been isolated. Such complexes have been reported for iron,⁵ chromium,⁶⁻⁸ tungsten,^{7,8} osmium,⁹ and platinum.^{10,11} One route used to prepare dithiocarbene complexes has been alkylation of the thione sulfur atom in dithioester complexes, $M-C(=S)SR$, by CH_3SO_3F or $[Et_3O]BF_4$.¹⁰ In the present paper, we extend this route to the preparation of $Cp(CO)_2Fe-C(SR)_2^+$ ($Cp = \eta^5-C_5H_5$) starting with the iron dithioester complexes $Cp(CO)_2Fe-C(=S)SR$ ($R = CH_3$,¹² $CH_2C_6H_5$).

Since there are no reports describing reactions of the dithiocarbene ligand itself, it was of interest to examine its reactions for the purpose of preparing novel ligands, as well as establishing general patterns of reactivity of this ligand.

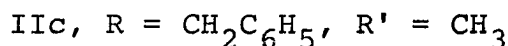
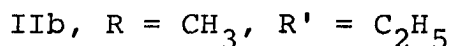
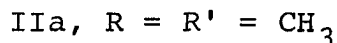
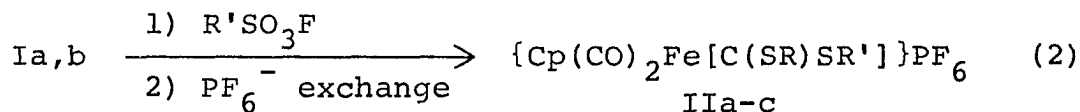
RESULTS AND DISCUSSION

Preparation and characterization of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SR})\text{SR}']^+$ carbene complexes Iron dithioester complexes are readily available through the reaction of $\text{Cp}(\text{CO})_2\text{Fe}^-$ with carbon disulfide and a suitable alkyl halide (eq. 1).¹² Short reaction times are important since other products have been observed by using longer reaction times.¹³



A ruthenium analog of Ia has been prepared by the same route.¹⁴ The dithioester complexes Ia,b are stable towards air in the solid state, but they decompose slowly when exposed to light.

Alkyl fluorosulfonates readily alkylate the thio-carbonyl sulfur atom of the dithioester ligand to give the corresponding cationic dithiocarbene complexes (eq. 2).

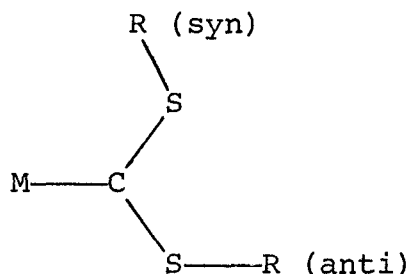


The yields are generally in the range of 60-70%. Anion exchange is performed as the SO_3F^- salts of IIa-c are less stable and less readily crystallized than the PF_6^- salts. In the solid state the yellow crystalline carbene complexes IIa-c show no noticeable decomposition after several months of exposure to air. Complex IIa is slightly soluble in water; it is also stable towards water at room temperature and can be recovered almost quantitatively from aqueous solutions. The carbenes are soluble in polar solvents such as CH_2Cl_2 , CH_3CN , and acetone, slightly soluble in CHCl_3 and THF, and insoluble in nonpolar solvents such as hexanes or Et_2O . Solutions of IIa exposed to air at room temperature are stable for several days. This stability differs markedly from that of a related carbene complex with no stabilizing heteroatomic groups, $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{C}_6\text{H}_5)\text{H}]\text{PF}_6$, solutions of which decompose completely within one hour under similar conditions.¹⁵

The IR spectrum of IIa in CH_2Cl_2 shows two $\nu(\text{CO})$ absorptions at 2058 and 2017 cm^{-1} with a calculated $\nu(\text{CO})$ force constant^{16a} of 16.8 $\text{mdyn}/\text{\AA}$. Comparison of this value with the $\nu(\text{CO})$ force constants of 17.6 and 17.1 $\text{mdyn}/\text{\AA}$ found for $\{\text{CpFe}(\text{CO})_3\}\text{PF}_6$ ^{16b} and $\{\text{Cp}(\text{CO})_2\text{FeCNCH}_3\}\text{PF}_6$ ^{16b} respectively, indicates that the dithiocarbene ligand has a lower π -acceptor/ σ -donor ratio than either the carbonyl or

isocyanide ligand, which is consistent with conclusions drawn for other transition metal carbene complexes.³ The position of the carbene carbon resonance in the ^{13}C -NMR (acetone- d_6) spectrum of IIa occurs at 303 ppm downfield relative to TMS, which is also consistent with previous reports.³

A single line at $\tau 6.73$ is observed for the two methyl groups of the carbene ligand in the ^1H -NMR (acetone- d_6) spectrum of IIa. This is in contrast with spectra reported for $\{\text{PtCl}[\text{C}(\text{SEt})_2](\text{PPh}_3)_2\}\text{BF}_4$,¹⁰ $\{\text{PtI}[\text{C}(\text{SMe})_2](\text{PPh}_3)_2\}\text{I}$,¹¹ and $\{\text{PtI}[\text{C}(\text{SEt})_2](\text{PPh}_3)_2\}\text{I}$ ¹¹ which show different resonances for the two alkyl groups of the carbene ligands. The inequivalence of the alkyl groups is explained by the presence of syn and anti R groups



caused by restricted rotation around the C(carbene)-S bonds.^{10,11} Upon cooling an acetone- d_6 solution of IIa to -55°C , the methyl groups become nonequivalent, and two sharp singlets at $\tau 6.87$ and 6.53 are observed. When the solution is warmed, the two singlets broaden, become less

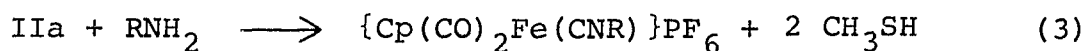
intense, and finally coalesce at -2.5° C. As the sample is warmed further, the signal sharpens to the previously observed singlet at $\tau 6.73$. The equivalence of the methyl groups of IIa is presumably due to rapid rotation around the C(carbene)-S bonds. Single resonances for the R and R' groups in the room temperature $^1\text{H-NMR}$ spectra of IIb and IIc suggest that there is rapid rotation in these complexes as well.

Since the coalescence temperature of IIa is lower (-2.5° C) than that of $\text{Cl}(\text{PPh}_3)_2\text{Pt}[\text{C}(\text{SR})_2]^+$ ($>30^{\circ}$ C), the rate of rotation around the C(carbene)-S bonds is presumably greater in IIa. This rate difference may be rationalized by suggesting that the $\text{Cl}(\text{PPh}_3)_2\text{Pt}^+$ moiety is more electron withdrawing than $\text{Cp}(\text{CO})_2\text{Fe}^+$. This would promote more $\text{S}\rightarrow\text{C}(\text{carbene})$ π -bonding in the Pt complexes, which would restrict rotation around the C(carbene)-S bonds. That the $\text{Cl}(\text{PPh}_3)_2\text{Pt}^+$ group is indeed more electron withdrawing than $\text{Cp}(\text{CO})_2\text{Fe}^+$ is supported by the higher $\nu(\text{CO})$ force constant for $\{\text{Cl}(\text{PPh}_3)_2\text{Pt}(\text{CO})\}\text{BF}_4$ ($18.2 \text{ m dyn}/\text{\AA}^{\circ}$)¹⁷ than for $\{\text{CpFe}(\text{CO})_3\}\text{PF}_6$ ($17.6 \text{ m dyn}/\text{\AA}^{\circ}$).^{16b} The steric bulk of the two triphenylphosphine ligands in $\text{Cl}(\text{PPh}_3)_2\text{Pt}[\text{C}(\text{SR})_2]^+$ may also be a factor in restricting rotation around the C(carbene)-S bonds in the platinum complexes.

Reactions of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ with primary amines

Except for reactions with methylamine and aniline, two products are identified in reactions of IIa with amines. The minor product, usually too little to isolate, is a neutral complex that has been characterized as cyclopentadienyldicarbonyltri(methylthio)methyliron, $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_3]$; it is formed in reactions of IIa with certain bases. This neutral complex, with $\nu(\text{CO})$ values of 2013 and 1964 cm^{-1} in CH_2Cl_2 , is presently under investigation, and an X-ray analysis is in progress, the details of which will be presented in a later report.¹⁸

In all cases, the major product (55-88%) of the reaction of IIa with a primary amine at room temperature in CH_2Cl_2 is a cationic isocyanide derivative (eq. 3).



IIIa-i

R = CH_3 (IIIa), n-Pr (IIIb), i-Pr (IIIc),
 cyclohexyl (IIId), benzyl (IIIe), C_6H_5 (IIIf),
 $\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ (IIIg), $\text{CH}(\text{CH}_3)\text{C}(=\text{O})\text{OCH}_3$ (IIIh),
 $\text{CH}_2(\text{CH}_2)_2\text{OH}$ (IIIi).

With the exception of aniline, all of the reactions are usually complete within one hour. Aniline, a considerably

weaker nucleophile, reacts much slower and gives the lowest yield (25%) of the corresponding isocyanide complex. Although no kinetic studies have been carried out on these reactions, the slowness of the aniline reaction suggests that an important step is attack of the amine on the carbene carbon to give an intermediate which subsequently collapses to the product.

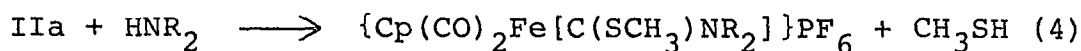
In the reaction solutions, these type III complexes undergo further reaction with excess amine to form carbamoyl complexes, $\text{Cp}(\text{CO})\text{Fe}(\text{CNR})[\text{C}(=\text{O})\text{NHR}]$, characterized by their $\nu(\text{CO})$ absorptions at approximately 2160 and 1950 cm^{-1} .^{16b} Upon evaporating the amine, they revert to III, as described previously.^{16b}

The spectral characteristics of IIIa-i are generally very similar. Their IR spectra show three bands: 2192-2242(m) cm^{-1} , $\nu(\text{CN})$; 2079-2085(s) cm^{-1} , $\nu(\text{CO})$; 2037-2046(s) cm^{-1} , $\nu(\text{CO})$. The Cp resonance in their $^1\text{H-NMR}$ spectra appears at approximately $\tau 4.25$. Exceptions to this are IIIe ($\tau 4.34$), possibly due to shielding effects of the phenyl ring, and IIIf ($\tau 4.10$), most likely due to the weaker donor ability of the isocyanide ligand. Resonances arising from the isocyanide ligands, while consistent

with the proposed products, are sometimes broadened or of unexpected multiplicities due to possible coupling with the nitrogen of the ligand.

Reactions of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ with secondary amines

The reaction of IIa with secondary amines is very similar to the aminolysis of $(\text{CO})_5\text{Cr}[\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5]$.¹⁹ One thiomethoxy group is readily replaced to produce amino-thiocarbene complexes (eq. 4).



IVa-c

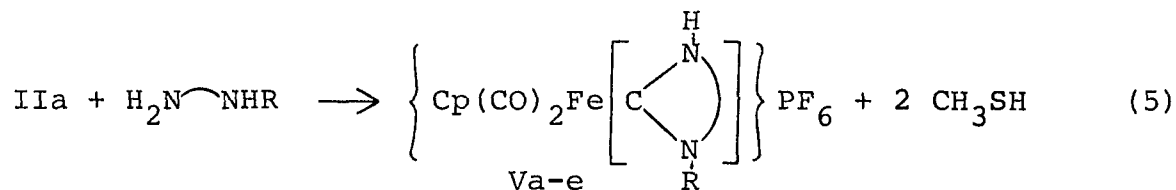
$\text{HNR}_2 = \text{HNMe}_2$ (IVa), piperidine (IVb),
morpholine (IVc)

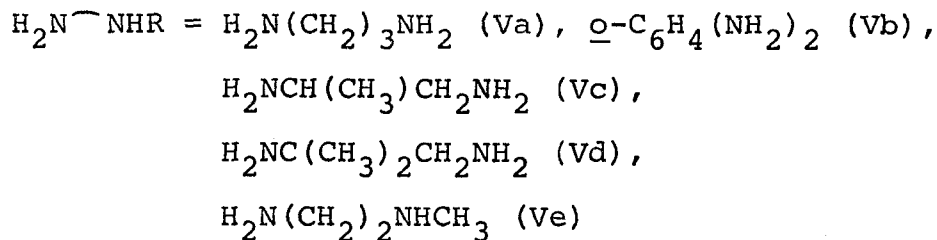
When the reaction is run at room temperature in CH_2Cl_2 , even with a large excess of secondary amine, the second thiomethoxy group is not replaced. Only sterically small amines such as dimethyl or heterocyclic amines will react in this manner to give carbenes of type IV. Diethyl and higher amines are too bulky and give $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_3]$ ¹⁸ as the only identified organometallic product. Infrared spectral studies indicate that, when reacted with IIa, piperazine, pyrrolidine and aziridine also form amino-thiocarbene complexes of type IV, but these products were

not isolated. A large amount of intractable tar with an IR spectrum characteristic of isocyanide complexes of type III is also formed in the aziridine reaction.

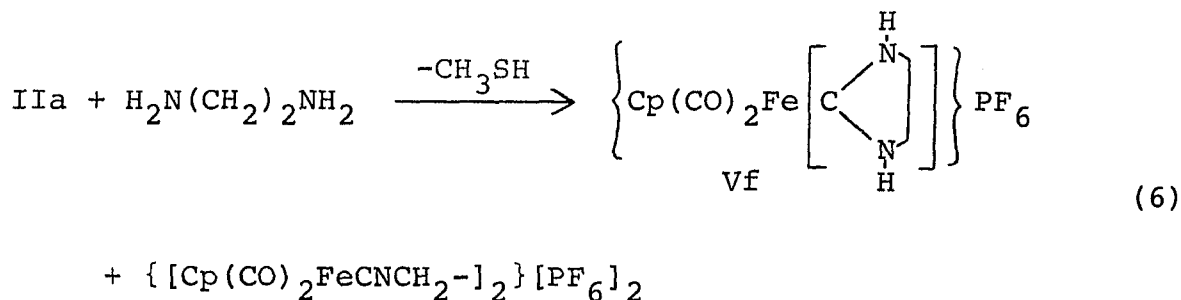
The IR spectra of complexes IVa-c contain strong $\nu(\text{CO})$ absorptions at 2046-2047 cm^{-1} and 2001-2002 cm^{-1} . These low frequencies, as compared to those of IIa (2058 and 2017 cm^{-1}), reflect the greater ability of nitrogen to donate π -electron density into the carbene carbon atom.^{3,20} In the $^1\text{H-NMR}$ spectra of the complexes, singlets are found at τ 4.40-4.45 and τ 7.04-7.09 for the Cp and SCH_3 groups, respectively. Complex IVa shows nonequivalent amine methyl groups in its room temperature $^1\text{H-NMR}$ which is consistent with a large $\text{N}\rightarrow\text{C}(\text{carbene})$ π -interaction.

Reactions of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ with diamines The reaction of IIa with appropriate diamines at room temperature in CH_2Cl_2 provides a general, high yield synthesis of cyclic diaminocarbene complexes (eq. 5).



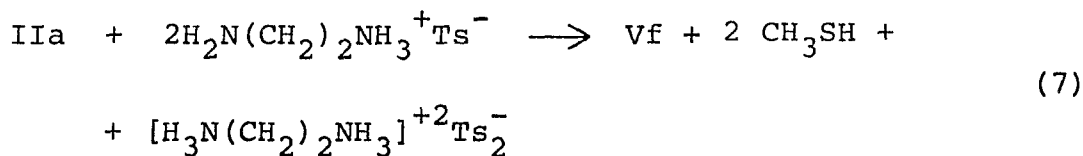


When IIa is allowed to react with an equimolar amount of ethylenediamine, approximately equal amounts of carbene and isocyanide products are always obtained (eq. 6).



VI

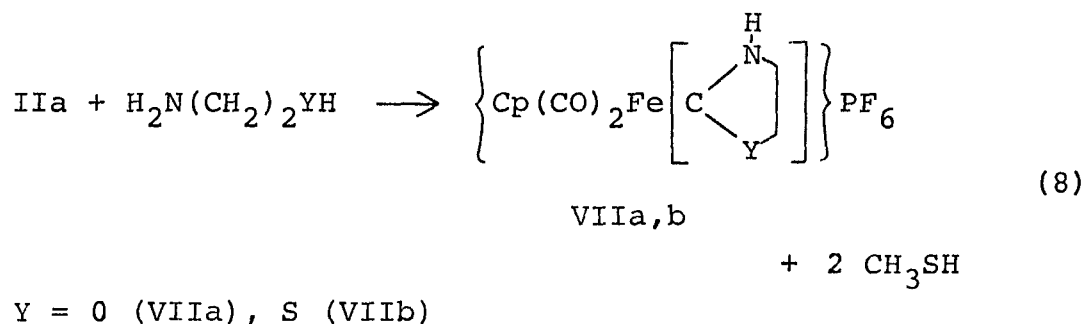
Analytically pure samples of the binuclear isocyanide complex VI are obtained by fractional crystallization, but Vf obtained in this manner is always contaminated with traces of VI. However, when IIa is allowed to react with two equivalents of the monotosylate salt of ethylenediamine, pure samples of Vf are obtained (eq. 7).



It was hoped that $\text{Cp}(\text{CO})_2\text{Fe}[\text{CN}(\text{CH}_2)_2\text{NH}_3^+]^+$ could be isolated as a possible intermediate in this reaction. But when IIa is reacted with one equivalent of $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_3^+\text{Ts}^-$ only equal amounts of IIa and Vf are obtained; thus, there is no evidence for the isocyanide intermediate.

Infrared spectra of the cyclic diaminocarbene complexes Va-f are quite similar to those of the amino-thiocarbene complexes IVa-c, displaying strong $\nu(\text{CO})$ absorptions at 2050-2056 cm^{-1} and 2000-2006 cm^{-1} . In their $^1\text{H-NMR}$ spectra, protons attached to the nitrogens cannot be observed in any of these complexes; presumably this is due to quadrupolar interactions with the nitrogen atoms.

Reactions of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ with amino alcohols and amino thiols Both ethanolamine and β -mercaptoethylamine react with IIa at room temperature in a manner similar to diamines to give cyclic carbene complexes (eq. 8).

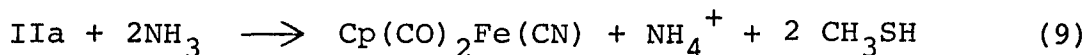


However, 3-aminopropanol seems to behave simply as a primary amine to give IIIi, $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{CN}(\text{CH}_2)_3\text{OH}]\}\text{PF}_6$, as indicated in eq. 3. When IIIi is stirred in CH_2Cl_2 at room temperature for several days, bands at 2058 and 2011 cm^{-1} slowly develop while those of IIIi slowly diminish. This indicates that IIIi may slowly cyclize to give a carbene complex of type VII, but this cyclic carbene has not been isolated. Infrared data (very weak $\nu(\text{CN})$ absorptions in spectra of the reaction mixtures) also indicate that the reactions shown in eq. 8 may proceed through an isocyanide intermediate analogous to IIIi, but these intermediates have not been isolated.

The availability of VIIa,b as well as the diaminocarbene Vf allows us to compare the effect of the heteroatoms on the CO groups. The $\nu(\text{CO})$ frequencies and force constants^{16a} of $\{\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CNHCH}_2\text{CH}_2\text{NH}}]\}\text{PF}_6$ (Vf: $2053, 2003\text{ cm}^{-1}$; $16.61\text{ m dyn}/\text{\AA}$), $\{\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CNHCH}_2\text{CH}_2\text{S}}]\}\text{PF}_6$ (VIIb: $2059, 2014\text{ cm}^{-1}$; $16.75\text{ m dyn}/\text{\AA}$), and $\{\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CNHCH}_2\text{CH}_2\text{O}}]\}\text{PF}_6$ (VIIa: $2063, 2017\text{ cm}^{-1}$; $16.81\text{ m dyn}/\text{\AA}$) increase as the heteroatom is changed from nitrogen to sulfur to oxygen. The same trend is found in comparing carbene complexes where both heteroatoms are changed. This is seen in the

series: $\{\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CNHCH}_2\text{CH}_2\text{NH}}]\text{PF}_6$ (vf: 2053, 2003 cm^{-1} ; 16.61 $\text{mdyn}/\text{\AA}$), $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\text{PF}_6$ (2058, 2017 cm^{-1} ; 16.77 $\text{mdyn}/\text{\AA}$), $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)_2]\text{PF}_6$ (2068, 2020 cm^{-1} ; 16.87 $\text{mdyn}/\text{\AA}$).²¹ These results suggest that the carbene ligand becomes a weaker donor ligand as the heteroatoms are changed in the following order: $\text{N} > \text{S} > \text{O}$.

Reactions of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ with miscellaneous reagents Ammonia reacts readily with IIa in CH_2Cl_2 at room temperature to give the neutral cyanide complex in fair (34%) yield (eq. 9).



VIII

Its spectral characteristics are identical to those reported for the complex obtained by a different route.²² Infrared studies indicate that NaN_3 also reacts very rapidly with IIa in CH_3CN at room temperature to give $\text{Cp}(\text{CO})_2\text{Fe}(\text{CN})$, $\text{Cp}(\text{CO})_2\text{FeC}(\text{SCH}_3)_3$, and other unidentified products.

When cyclohexylphosphine, $\text{C}_6\text{H}_{11}\text{PH}_2$, is allowed to react with IIa in hopes of preparing a complex with the unknown $\text{C}\equiv\text{P}-\text{R}$ ligand, no such product is obtained. No reaction is observed between IIa and I^- , Cl^- , I_2 , HCl , HF , or PPh_3 at room temperature.

EXPERIMENTAL SECTION

General information $\text{Cp}(\text{CO})_2\text{FeC}(=\text{S})\text{SCH}_3$ was prepared as reported previously.¹² Reagent grade chemicals were used without further purification. Tetrahydrofuran (THF) was distilled from $\text{NaK}_{2.8}$ ²³ under N_2 immediately prior to use. Unless otherwise noted, the following procedures did not require the use of an inert atmosphere.

Infrared spectra were recorded on a Perkin-Elmer 237B or 337 spectrophotometer equipped with an expanded-scale recorder calibrated with gaseous CO. Routine ^1H -NMR spectra were recorded on Perkin-Elmer Hitachi R-20B or Varian A-60 spectrometers; temperature dependent ^1H -NMR spectra were recorded on a Varian HA-100 spectrometer. Carbon-13 spectra were run on a Bruker HX-90 FT-NMR spectrometer; $\text{Cr}(\text{acac})_3$ (~ 0.1 M) was added to the solutions to reduce data collection time.²⁴ Tetramethylsilane (TMS) was employed as the internal standard for all NMR spectra.

Synthesis of complexes. $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(=\text{S})\text{SCH}_2\text{C}_6\text{H}_5]$ (Ib)
This complex was prepared from $\text{BrCH}_2\text{C}_6\text{H}_5$ (6.80 mL, 57.2 mmol) and 10.0 g (28.3 mmol) of $[\text{CpFe}(\text{CO})_2]_2$ following the procedure¹² used for $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(=\text{S})\text{SCH}_3]$ (Ia). The evaporated reaction mixture was extracted with Et_2O until

the extracts were only a faint yellow. The extracts were filtered through Celite and then evaporated to a dark, viscous oil. Repeated fractional crystallization of this oil from hexanes and/or Et₂O at -20° C afforded 7.2 g (37%) of Ib as dark orange crystals. IR(CH₂Cl₂): 2031(s), 1982(s) cm⁻¹. ¹H-NMR(CDCl₃): τ2.61(s, C₆H₅), 5.03(s, C₅H₅), 5.39(s, CH₂). Mp 73-75° C. Anal. calcd. for C₁₅H₁₂FeO₂S₂: C, 52.34; H, 3.51. Found: C, 52.38; H, 3.58.

{Cp(CO)₂Fe[C(SCH₃)₂]}PF₆ (IIa) The methyl dithio-ester, Ia, (0.500 g, 1.87 mmol) in 20 mL of CH₂Cl₂ was stirred with CH₃SO₃F (200 μL, 2.48 mmol) for 1 h. The resulting dark solution was evaporated to a dark oil which was washed with Et₂O. The oil was dissolved in a minimum amount of acetone, placed on an anion exchange column (Amberlite IRA-400, 35 x 1 cm) in the PF₆⁻ form, and eluted slowly with acetone. The yellow acetone fraction was collected, concentrated to ~10 mL, filtered, and hexanes carefully added such that two layers formed. When the solution was cooled to -20° C, yellow crystals of IIa precipitated as the hexanes slowly diffused into the acetone solution. After the crystals were washed with Et₂O and

dried under high vacuum, 0.55 g (69%) of IIa was isolated. IR(CH₂Cl₂): 2058(s), 2017(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.43(s, C₅H₅), 6.73(s, 2 CH₃). Mp 163-165° C. Anal. calcd. for C₁₀H₁₁F₆FeO₂PS₂: C, 28.05; H, 2.59. Found: C, 28.04; H, 2.57.

{Cp(CO)₂Fe[C(SCH₃)SC₂H₅] }PF₆ (IIb) This complex was prepared by the same method as IIa. Starting with Ia (0.500 g, 1.87 mmol) and C₂H₅SO₃F (250 μL, 2.47 mmol), 0.50 g (60%) of IIb was obtained as fine yellow crystals. IR(CH₂Cl₂): 2060(s), 2017(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.37(s, C₅H₅), 6.16(q, CH₂), 6.69(s, SCH₃), 8.44(t, CH₃). Mp 117-119° C. Anal. calcd. for C₁₁H₁₃F₆FeO₂PS₂: C, 29.88; H, 2.96. Found: C, 29.85; H, 2.97.

{Cp(CO)₂Fe[C(SCH₃)SCH₂C₆H₅] }PF₆ (IIc) The method used to prepare IIa was also employed for this complex. Starting with Ib (1.00 g, 2.90 mmol) and CH₃SO₃F (300 μL, 3.70 mmol) in 40 mL of CH₂Cl₂, 0.93 g (64%) of IIc was obtained as bright yellow crystals. IR(CH₂Cl₂): 2056(s), 2017(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ2.54(s, C₆H₅), 4.34(s, C₅H₅), 4.99(s, CH₂), 6.63(s, CH₃). Mp 150° C dec. Anal. calcd. for C₁₆H₁₅F₆FeO₂PS₂: C, 38.11; H, 3.00. Found: C, 37.98; H, 2.90.

{Cp(CO)₂Fe[CNCH₃] }PF₆ (IIIa) Methylamine was bubbled through 50 mL of CH₂Cl₂ containing IIa (0.21 g,

0.49 mmol) for 1 h. The bright yellow solution was concentrated to 10 mL, and the product was precipitated by addition of hexanes and cooling to -20° C. After recrystallization from acetone with hexanes at -20° C, 0.11 g (63%) of IIIa was isolated as a pale yellow powder. The complex displayed the same physical characteristics as observed for a sample prepared by a different route.^{16b}

$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{CNCH}_2\text{CH}_2\text{CH}_3]\}\text{PF}_6$ (IIIb) An 80 mL solution of CH_2Cl_2 containing IIa (0.640 g, 1.49 mmol) and n-propylamine (125 μL , 1.52 mmol) was stirred for 1 h and then evaporated to a dark oil. The oil was washed with Et_2O to remove any neutral species. The residue was crystallized from CH_2Cl_2 with Et_2O at -20° C to give 0.51 g (87%) of IIIb as light orange-yellow crystals. IR(CH_2Cl_2): 2226(s), 2081(vs), 2041(vs) cm^{-1} . $^1\text{H-NMR}$ (acetone- d_6): τ 4.26(s, C_5H_5), 6.04(t, CN- CH_2), 8.22-(m, CH_2CH_3), 8.96(t, CH_3). Mp 118-120 $^{\circ}$ C. Anal. calcd. for $\text{C}_{11}\text{H}_{12}\text{F}_6\text{FeNO}_2\text{P}$: C, 33.79; H, 3.09. Found: C, 33.68; H, 3.28.

$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{CNCH}(\text{CH}_3)_2]\}\text{PF}_6$ (IIIc) This complex was prepared in the same manner as IIIb. Starting with 0.10 g (0.23 mmol) of IIa and 20 μL (0.23 mmol) of isopropylamine in 20 mL of CH_2Cl_2 , 0.64 g (70%) of IIIc was isolated as

cream-yellow needles. IR(CH₂Cl₂): 2215(s), 2082(vs), 2042(vs) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.24(s, C₅H₅), 5.61(m, CH), 8.51(doublet of triplets, 2 CH₃). Mp 98-99° C. Anal. calcd. for C₁₁H₁₂F₆FeNO₂P: C, 33.79; H, 3.09; N, 3.58. Found: C, 33.67; H, 3.03; N, 3.61.

{Cp(CO)₂Fe[CNC₆H₁₁]}PF₆ (IIIId) This derivative was prepared in the same manner as IIIb. From the reaction of IIa (0.25 g, 0.58 mmol) and cyclohexylamine (75 μL, 0.66 mmol) in 50 mL of CH₂Cl₂ for 35 min, 0.18 g (72%) of IIIId was isolated as tan needles. IR(CH₂Cl₂): 2212(s), 2081(vs), 2042(vs) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.20(s, C₅H₅), 5.80(m, CN-CH), 8.06 and 8.46(m, 5 CH₂). Mp 135-137° C. Anal. calcd. for C₁₄H₁₆F₆FeNO₂P: C, 39.01; H, 3.74; N, 3.25. Found: C, 38.79; H, 3.72; N, 3.19.

{Cp(CO)₂Fe[CNCH₂C₆H₅]}PF₆ (IIIe) This complex was prepared by a route analogous to that used for IIIb. Starting with 0.10 g (0.23 mmol) of IIa and 52 μL (0.47 mmol) of benzylamine in 20 mL of CH₂Cl₂, 0.091 g (88%) of IIIe was obtained as yellow-orange needles. IR(CH₂Cl₂): 2225(s), 2082(vs), 2042(vs) cm⁻¹. ¹H-NMR(acetone-d₆): τ2.66(s, C₆H₅), 4.34(s, C₅H₅), 4.83(s, CH₂). Mp 168-170° C. Anal. calcd. for C₁₅H₁₂F₆FeNO₂P: C, 41.03; H, 2.75; N, 3.19. Found: C, 41.26; H, 2.80; N, 3.16.

{Cp(CO)₂Fe[CNC₆H₅]}PF₆ (III f) A large excess of aniline (1.00 mL, 11.0 mmol) was stirred with IIa (0.20 g, 0.47 mmol) in 40 mL of CH₂Cl₂ for 4 days. The reaction mixture was then evaporated to an oil and washed with Et₂O. The resulting tar was dissolved in a small volume of CH₂Cl₂ and treated with decolorizing carbon. After filtration, the addition of Et₂O to the yellow solution and cooling the mixture to -20° C afforded 0.050 g (25%) of III f as pale yellow needles. IR(CH₂Cl₂): 2192(s), 2085(s), 2046(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ 2.40(m, C₆H₅), 4.10(s, C₅H₅). Mp 153-155° C. Anal. calcd. for C₁₄H₁₀F₆FeNO₂P: C, 39.56; H, 2.37; N, 3.30. Found: C, 39.50; H, 2.38; N, 3.30.

{Cp(CO)₂Fe[CNCH₂CH₂N(CH₃)₂]}PF₆ (III g) This complex was prepared in the same manner as III b. Starting with 0.10 g (0.23 mmol) of IIa and 30 μL (0.27 mmol) of N,N-dimethylethylenediamine in 20 mL of CH₂Cl₂, 0.050 g (51%) of III g was isolated as cream-yellow needles. IR(CH₂Cl₂): 2228(s), 2082(vs), 2042(vs) cm⁻¹. ¹H-NMR(acetone-d₆): τ 4.27(s, C₅H₅), 5.96(t, CN-CH₂), 7.27(t, CH₂), 7.68(s, 2 CH₃). Mp 75-76° C. Anal. calcd. for C₁₂H₁₅F₆FeN₂O₂P: C, 34.31; H, 3.60; N, 6.67. Found: C, 34.16; H, 3.60; N, 6.60.

$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{CNCH}(\text{CH}_3)\text{C}(=\text{O})\text{OCH}_3]\}\text{PF}_6$ (IIIh) The hydrochloride salt of alanine methyl ester (0.065 g, 0.47 mmol) was suspended as a fine powder in 50 mL of CH_2Cl_2 . Ammonia gas was bubbled through the solution for 45 min to generate the soluble amino acid ester and insoluble NH_4Cl . Nitrogen was then bubbled through the solution to purge it of ammonia. After filtration and concentration of the solution to ~20 mL, IIa (0.10 g, 0.23 mmol) was added and stirred for 4 h. The reaction mixture was then evaporated to an oil and washed with Et_2O . Crystallization of the residue from acetone with Et_2O at -20°C gave 0.063 g (62%) of IIIh as large, bright-orange crystals. IR(CH_2Cl_2): 2223(s), 2083(vs), 2043(vs), 1759(s) cm^{-1} . $^1\text{H-NMR}$ (acetone- d_6): τ 4.20(s, C_5H_5), 4.86(q, CH), 6.19(s, OCH_3), 8.26(d, CH_3). Mp $68-70^\circ\text{C}$. Anal. calcd. for $\text{C}_{12}\text{H}_{12}\text{F}_6\text{FeNO}_4\text{P}$: C, 33.13; H, 2.78; N, 3.22. Found: C, 33.15; H, 2.79; N, 3.21.

$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{CN}(\text{CH}_2)_3\text{OH}]\}\text{PF}_6$ (IIIi) This complex was prepared in the same manner as IIIb. Starting with 0.10 g (0.23 mmol) of IIa and 20 μL (0.26 mmol) of 3-aminopropanol in 20 mL of CH_2Cl_2 and stirring the mixture for 15 min, we isolated 0.064 g (67%) of IIIi as orange-yellow needles.

IR(CH₂Cl₂): 2226(vs), 2081(vs), 2040(s) cm⁻¹. ¹H-NMR-(acetone-d₆): τ4.24(s, C₅H₅), 5.92(t, CNCH₂), 6.26(t, CH₂O), 8.00(m, CH₂). Mp 99-101° C. Anal. calcd. for C₁₁H₁₂F₆FeNO₃P: C, 32.46; H, 2.97; N, 3.44. Found: C, 32.65; H, 3.02; N, 3.43.

{Cp(CO)₂Fe[C(SCH₃)N(CH₃)₂]}PF₆ (IVa) Dimethylamine was bubbled through 20 mL of CH₂Cl₂ containing IIa (0.10 g, 0.23 mmol) for 10 min, and the solution was stirred for an additional 30 min. After evaporation to dryness and washing of the solid with Et₂O, the residue was crystallized from acetone with Et₂O at -20° C to give 0.044 g (44%) of IVa as fine yellow crystals. IR(CH₂Cl₂): 2046(s), 2001(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.40(s, C₅H₅), 5.98-(s, NCH₃), 6.24(s, NCH₃), 7.04(s, SCH₃). Mp 190° C dec. Anal. calcd. for C₁₁H₁₄F₆FeNO₂PS: C, 31.08; H, 3.32; N, 3.29. Found: C, 31.26; H, 3.42; N, 3.44

{Cp(CO)₂Fe[C(SCH₃)N(CH₂)₄CH₂]}PF₆ (IVb) This complex was prepared in a manner analogous to that used for IIIb. From 0.20 g (0.47 mmol) of IIa and 93 μL (0.94 mmol) of piperidine in 40 mL of CH₂Cl₂ with stirring for 2 h, 0.15 g (69%) of IVb was obtained as a yellow powder. IR(CH₂Cl₂): 2047(s), 2002(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.45(s, C₅H₅), 5.63(m, 2 NCH₂), 8.13(m, 3 CH₂),

7.09(s, CH₃). Mp 153-155° C. Anal. calcd. for C₁₄H₁₈F₆FeNO₂PS: C, 36.15; H, 3.90; N, 3.01. Found: C, 36.26; H, 4.47; N, 3.24.

{Cp(CO)₂Fe[C(SCH₃)N(CH₂CH₂)₂O]}PF₆ (IVc) This derivative was prepared in the same manner as IIIb. The reaction of IIa (0.10 g, 0.23 mmol) and morpholine (50 μL, 0.58 mmol) in 20 mL of CH₂Cl₂ for 3 h yielded 0.069 g (64%) of IVc as yellow needles. IR(CH₂Cl₂): 2047(s), 2001(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.42(s, C₅H₅), 5.54 and 6.06 (m, N(CH₂CH₂)₂O), 7.06(s, CH₃). Mp 185-187° C dec. Anal. calcd. for C₁₃H₁₆F₆FeNO₃PS: C, 33.42; H, 3.45; N, 3.00. Found: C, 33.51; H, 3.47; N, 2.92.

{Cp(CO)₂Fe[$\overline{\text{CNH(CH}_2\text{)}_3\text{NH}}$]}PF₆ (Va) A solution of 30 mL of CH₂Cl₂ containing IIa (0.500 g, 1.17 mmol) was added dropwise with stirring to 50 mL of CH₂Cl₂ containing 1,3-diaminopropane (100 μL, 1.20 mmol) over a period of 30 min. The reaction mixture was stirred for an additional 40 min, evaporated to an oil, and washed with Et₂O. The residue was crystallized from CH₂Cl₂ with Et₂O at -20° C to give 0.31 g (66%) of Va as cream yellow needles. IR(CH₂Cl₂): 2051(s), 2000(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.62(s, C₅H₅), 6.60(t, 2 CH₂), 8.00(m, CH₂). Mp 204° C. Anal. calcd.

for $C_{11}H_{13}F_6FeN_2O_2P$: C, 32.54; H, 3.23; N, 6.90. Found: C, 32.03; H, 3.21; N, 6.80.

$\{Cp(CO)_2Fe[\overline{CNH(o-C_6H_4)NH}]\}PF_6$ (Vb) An inert (N_2) atmosphere and N_2 -saturated solvents were used in this synthesis. A solution of 20 mL of CH_2Cl_2 containing IIa (0.10 g, 0.23 mmol) and *o*-diaminobenzene (0.050 g, 0.46 mmol) was stirred in a Schlenk tube for 3 days. The dark reaction mixture was evaporated to an oil and chromatographed on a Celite/ CH_2Cl_2 column (50 x 2 cm). A pink band separated from extensive bright blue trailings of unknown composition. The pink band was collected and treated with decolorizing carbon to give a pale yellow solution after filtration. The addition of hexanes to the filtrate (after concentration) and cooling of the solution to $-20^\circ C$ gave 0.022 g (21%) of Vb as pale yellow needles. IR(CH_2Cl_2): 2056(s), 2006(s) cm^{-1} . 1H -NMR(acetone- d_6): τ 2.50(AA'BB', C_6H_4), 4.51(s, C_5H_5). Mp $230-233^\circ C$. Anal. calcd. for $C_{14}H_{11}F_6FeN_2O_2P$: C, 38.21; H, 2.52. Found: C, 38.21; H, 2.51.

$\{Cp(CO)_2Fe[\overline{CNHCH(CH_3)CH_2NH}]\}PF_6$ (Vc) This complex was prepared in the same manner as Va. The reaction of 0.10 g (0.23 mmol) of IIa and 21 μ L (0.25 mmol) of 1,2-diaminopropane gave 0.081 g (85%) of Vc as yellow crystals.

IR(CH₂Cl₂): 2055(s), 2004(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.58(s, C₅H₅), 5.60 and 6.70(m, CH₂CH), 8.69(d, CH₃). Mp 177-179° C. Anal. calcd. for C₁₁H₁₃F₆FeN₂O₂P: C, 32.54; H, 3.23; N, 6.90. Found: C, 32.70; H, 3.29; N, 6.86.

{Cp(CO)₂Fe[C⁺NHC(CH₃)₂CH₂NH]}PF₆ (Vd) By use of the method for the preparation of IIIb, 0.20 g (0.47 mmol) of IIB and 60 μL (0.48 mmol) of 2-methyl-1,2-diaminopropane were reacted in 40 mL of CH₂Cl₂ while stirring for 40 min. Yellow needles (0.17 g, 88%) of Vd were isolated. IR-(CH₂Cl₂): 2050(s), 2001(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.59(s, C₅H₅), 6.44(s, CH₂), 8.61(s, 2 CH₃). Mp 246° C dec. Anal. calcd. for C₁₂H₁₅F₆FeN₂O₂P: C, 34.31; H, 3.60; N, 6.67. Found: C, 33.98; H, 3.58; N, 6.59.

{Cp(CO)₂Fe[C⁺NH(CH₂)₂NCH₃]}PF₆ (Ve) This complex was prepared in the same manner as IIIb. Starting with 0.10 g (0.23 mmol) of IIA and 21 μL (0.24 mmol) of N-methylethylenediamine in 20 mL of CH₂Cl₂ and stirring the mixture for 20 min, we isolated 0.063 g (66%) of Ve as yellow crystals. IR(CH₂Cl₂): 2052(s), 2004(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.52(s, C₅H₅), 6.19(s, 2 CH₂), 6.68-(s, CH₃). Mp 178-180° C. Anal. calcd. for C₁₁H₁₃F₆FeN₂O₂P: C, 32.54; H, 3.23; N, 6.90. Found: C, 32.81; H, 3.30; N, 6.80.

$$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{CNH}(\text{CH}_2)_2\text{NH}]\}\text{PF}_6 \text{ (Vf)}$$
 The mono-tosylate salt of ethylenediamine was prepared by dissolving ethylenediamine (36 μL , 0.54 mmol) and p-toluenesulfonic acid monohydrate (0.103 g, 0.541 mmol) in 20 mL of CH_3CN containing enough CH_3OH to give a clear solution. Complex IIa (0.10 g, 0.23 mmol) was then added and the solution stirred for 2 h. The cloudy reaction mixture was evaporated to dryness, washed with Et_2O , and extracted with CH_2Cl_2 . Addition of Et_2O to the CH_2Cl_2 extracts followed by cooling of the mixture to -20°C gave 0.049 g (54%) of Vf as pale yellow crystals. IR(CH_2Cl_2): 2053(s), 2003(s) cm^{-1} . $^1\text{H-NMR}$ (acetone- d_6): τ 4.56(s, C_5H_5), 6.22(s, 2 CH_2). Mp 183-185 $^\circ\text{C}$. Anal. calcd. for $\text{C}_{10}\text{H}_{11}\text{F}_6\text{FeN}_2\text{O}_2\text{P}$: C, 30.64; H, 2.83; N, 7.15. Found: C, 30.89; H, 2.86; N, 7.08.

$$\{[\text{Cp}(\text{CO})_2\text{FeCNCH}_2\text{-}]_2\}[\text{PF}_6]_2 \text{ (VI)}$$
 A solution of 10 mL of CH_2Cl_2 containing ethylenediamine (16 μL , 0.24 mmol) was added dropwise with stirring to 10 mL of CH_2Cl_2 containing IIa (0.20 g, 0.47 mmol) over a period of 30 min. A precipitate slowly formed, and the reaction mixture was allowed to stir for an additional 45 min. The precipitate was collected by filtration and recrystallized from

acetone with Et₂O at -20° C to give 0.070 g (41%) of VI as a tan powder. IR(CH₃CN): 2211(m), 2084(s), 2037(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.21(s, 2 C₅H₅), 5.49(s, 2 CH₂). Mp 254° C dec. Anal. calcd. for C₁₈H₁₄F₁₂Fe₂N₂O₄P₂: C, 29.86; H, 1.95; N, 3.87. Found: C, 29.95; H, 2.01; N, 3.92.

{Cp(CO)₂Fe[CNH(CH₂)₂O]}PF₆ (VIIa) This was prepared in the same manner as IIIb. Starting with 0.20 g (0.47 mmol) of IIa and 29 μL (0.48 mmol) of β-aminoethanol in 40 mL of CH₂Cl₂ and stirring the mixture for 15 min, we obtained 0.13 g (71%) of VIIa as cream-yellow needles. IR(CH₂Cl₂): 2063(s), 2017(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.52(s, C₅H₅), 5.20 and 6.10(AA'BB', 2 CH₂). Mp 154-157° C. Anal. calcd. for C₁₀H₁₀F₆FeNO₃P: C, 30.56; H, 2.56; N, 3.56. Found: C, 30.61; H, 2.58; N, 3.56.

{Cp(CO)₂Fe[CNH(CH₂)₂S]}PF₆ (VIIb) This was prepared by the same method as used for IIIh. The free aminothiols was generated from β-aminoethanethiol hydrochloride (0.080 g, 0.70 mmol) and stirred with IIa (0.10 g, 0.23 mmol) for 50 min to give 0.046 g (48%) of VIIb as yellow crystals. IR(CH₂Cl₂): 2059(s), 2014(s) cm⁻¹. ¹H-NMR(acetone-d₆): τ4.52(s, C₅H₅), 5.64 and 6.50(AA'BB', 2 CH₂). Mp

168-170° C. Anal. calcd. for $C_{10}H_{10}F_6FeNO_2PS$: C, 29.36; H, 2.46; N, 3.42. Found: C, 29.36; H, 2.49; N, 3.37.

{Cp(CO)₂Fe(CN)} (VIII) Ammonia gas was bubbled through 15 mL of CH₂Cl₂ containing IIa (0.21 g, 0.49 mmol) for 1 h. The solution was filtered and concentrated to 5 mL. Upon addition of 10 mL of a 50:50 pentane/Et₂O mixture and cooling of the solution to -20° C, 0.034 g (34%) of VIII was isolated as yellow needles. Its physical properties were identical to those reported previously.²¹

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SECTION II. PREPARATION OF η^5 -CYCLOPENTADIENYLDICARBONYLTRI-
(ORGANOTHIO)METHYLIRON COMPLEXES AND THE
STRUCTURE OF η^5 -CYCLOPENTADIENYLDICARBONYLTRI-
(METHYLTHIO)METHYLIRON

INTRODUCTION

The chemistry of sulfur-stabilized organic anions has been extensively studied as they are very versatile organic synthons.¹⁻³ The best known examples are lithiated 1,3-dithiane derivatives, $\text{Li}(\text{R})\overline{\text{CS}(\text{CH}_2)_3\text{S}}$, but lithiated orthothioformates, $\text{LiC}(\text{SR})_3$, have also received much attention.¹⁻⁶ We have recently extended the scope of metallated orthothioformate chemistry to include transition metal derivatives by the fortuitous preparation of η^5 -cyclopentadienyldicarbonyltri(methylthio)methyliron, $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_3]^-$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$).⁷ Further work now has revealed a general route to tri(organothio)methyliron derivatives from $\text{Cp}(\text{CO})_2\text{Fe}[\text{dithiocarbene}]^+$ complexes. Direct preparation of these complexes from $\text{CpFe}(\text{CO})_2\text{X}$ species and lithiated orthothioformates has not been successful. However, lithiated 1,3-dithiane does react with $\text{CpFe}(\text{CO})_2\text{I}$ to give the corresponding iron(1,3-dithiane) derivative and this has been evaluated as a possible route to cationic iron(dithiocarbene) complexes. Some chemical and physical characteristics, as well as the results of an X-ray diffraction study on $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_3]^+$, are reported herein.

EXPERIMENTAL SECTION

General information Reagent grade chemicals were used without further purification, and $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$, I, was prepared as reported previously.⁷ Tetrahydrofuran (THF) was distilled from $\text{NaK}_{2.8}$ ⁸ under N_2 immediately prior to use. Infrared spectra were recorded on a Perkin-Elmer 281 spectrophotometer. Routine ^1H -NMR spectra were recorded on a Perkin-Elmer Hitachi R-20B spectrometer; temperature dependent ^1H -NMR spectra were recorded on a Varian HA-100 spectrometer. Carbon-13 spectra were recorded on a Jeol FX-90Q spectrometer; $\text{Cr}(\text{acac})_3$ (~ 0.1 M) was added to the solutions to reduce data collection time.⁹ Tetramethylsilane (TMS) was employed as the internal standard for all NMR spectra. All reactions were carried out in N_2 saturated solvents under an N_2 atmosphere.

Preparation of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_3]$ (IIa) Sodium hydride (57% mineral oil dispersion, 0.025 g, 0.59 mmol) was dissolved in 40 mL of THF and CH_3SH was slowly bubbled through the solution until H_2 production ceased (~ 0.5 h). To this, $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$ (I) (0.20 g, 0.47 mmol) was added, and the reaction was stirred for 20 min at room temperature. After evaporation to dryness, the residue was extracted with Et_2O until the extracts were colorless.

These were filtered and evaporated to dryness under an N_2 stream. The resulting crude product was crystallized from hexanes at $-20^\circ C$ to give 0.12 g (77%) of IIa as large yellow-orange needles. IR(CH_2Cl_2): 2013(s), 1964(s) cm^{-1} . IR(hexanes): 2023(s), 2013(m), 1977(s), 1968(m) cm^{-1} . 1H -NMR(CS_2): τ 5.17(s, C_5H_5), 7.89(s, 3 SCH_3). ^{13}C -NMR(acetone- d_6): 217.0 ppm(s, 2 CO), 90.9(s, C_5H_5), 60.7(s, $C(SCH_3)_3$), 19.6(s, 3 SCH_3). Mp $98-101^\circ C$. Anal. calcd. for $C_{11}H_{14}FeO_2S_3$: C, 40.00; H, 4.27; S, 29.12. Found: C, 40.00; H, 4.42; S, 28.76.

Preparation of $Cp(CO)_2Fe[C(SCH_3)_2SPh]$ (IIb) Sodium hydride (57% mineral oil dispersion, 0.0205 g, 0.487 mmol) was dissolved in 40 mL of THF and PhSH (50.0 μL , 0.487 mmol) was added. This mixture was stirred until H_2 production ceased (~ 20 min); then I (0.20 g, 0.47 mmol) was added. The reaction mixture immediately became dark green and then rapidly turned yellow-orange in color. After 15 min of stirring, the solution was evaporated to dryness and extracted with CS_2 until the extracts were colorless. These extracts were filtered and evaporated to dryness. The crude product was crystallized by dissolving in a minimum amount of an 80:20 mixture of hexanes/ Et_2O and cooling to $-20^\circ C$ to give 0.13 g (70%) of IIb as dark yellow-orange

crystals. IR(CH₂Cl₂): 2017(s), 1966(s) cm⁻¹. IR(hexanes): 2024(s), 1978(s) cm⁻¹. ¹H-NMR(CS₂): τ2.83(m, C₆H₅), 5.21(s, C₅H₅), 8.31(s, 2 CH₃). Mp 99-101° C dec. Anal. calcd. for C₁₆H₁₆FeO₂S₃: C, 48.98; H, 4.11. Found: C, 48.89; H, 4.09.

Preparation of Cp(CO)₂Fe[C(H)S(CH₂)₃S] (V) Lithiated 1,3-dithiane was generated in 75 mL of THF at -78° C from 0.395 g (3.28 mmol) of 1,3-dithiane and 2.00 mL (3.20 mmol) of butyllithium (1.6 M THF solution) by stirring the solution for 20 min. A solution of 75 mL of THF containing Cp(CO)₂FeI¹⁰ (0.999 g, 3.27 mmol) was added, and the mixture was stirred at -78° C for 15 min. Stirring continued as the mixture was allowed to come to room temperature (≈2 h). After evaporation, the reaction residue was chromatographed on Florisil (38 x 2 cm) using CS₂/Et₂O (98:2) as the elutant. A yellow product band was followed by a maroon [CpFe(CO)₂]₂ band and a blue-green band which could not be eluted. The yellow band was collected, evaporated, and crystallized from hexanes at -20° C to give 0.53 g (55%) of V as yellow crystals. IR(hexanes): 2026(s), 1979(s) cm⁻¹. ¹H-NMR(CS₂): τ5.09(s, C₅H₅), 5.99(s, CH), 7.00-8.00(m, 3 CH₂). Mp 104-107° C. Anal. calcd. for C₁₁H₁₂FeO₂S₂: C, 44.61; H, 4.08. Found: C, 44.89; H, 4.19.

Reaction of IIa with acid Trifluoromethanesulfonic acid (13 μL , 0.15 mmol) was added to 10 mL of Et_2O containing IIa (0.050 g, 0.15 mmol); a yellow precipitate formed instantaneously. After stirring the reaction for 15 min, the precipitate was collected and washed with Et_2O . The precipitate was crystallized from acetone with Et_2O at -20°C to give 0.063 g (96%) of $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{CF}_3\text{SO}_3$ (VI) as yellow crystals. IR(CH_2Cl_2): 2055(s), 2014(s) cm^{-1} . $^1\text{H-NMR}$ (acetone- d_6): τ 4.34(s, C_5H_5), 6.69(s, 2 CH_3). Mp $73-76^\circ\text{C}$. Anal. calcd. for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{FeO}_5\text{S}_3$: C, 30.57; H, 2.57. Found: C, 30.80; H, 2.61.

Reaction of IIb with acid Trifluoromethanesulfonic acid (17 μL , 0.20 mmol) was added to 15 mL of Et_2O containing IIb (0.072 g, 0.18 mmol). A yellow precipitate formed immediately and changed to a yellow oil on further stirring. After 20 min of stirring, the oil was collected and washed with Et_2O , but it could not be made to crystallize. The yield was 0.081 g (96%) of a mixture of $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{CF}_3\text{SO}_3$ (VI) and $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{SPh}]\}\text{CF}_3\text{SO}_3$ (VII) (56 and 40% respectively, from $^1\text{H-NMR}$). IR(CH_2Cl_2): 2055(s), 2014(s) cm^{-1} . $^1\text{H-NMR}$ (acetone- d_6): τ 2.24(s, C_6H_5), 4.36(s, C_5H_5 VI), 4.44(s, C_5H_5 VII), 6.72(s, CH_3).

Structural details for IIa A single crystal of approximately rectangular shape with dimensions of

0.1 x 0.1 x 0.15 mm was chosen for X-ray diffraction studies. The observed Laue symmetry (2/m) indicated the monoclinic crystal system. The cell dimensions at 25° C were $a = 8.319(2)$, $b = 12.575(5)$, $c = 6.886(2)$ Å, $\beta = 101.41(3)^\circ$, with $Z = 2$. Two octants of data ($2\theta < 45^\circ$) were collected on a four-circle diffractometer designed and built in the Ames Laboratory¹¹ using graphite-monochromated Mo K_α X-rays ($\lambda = 0.70954$ Å). Of the 837 measured intensities, 637 were considered observed ($I > 3\sigma_i$). Data were corrected for Lorentz-polarization effects; no absorption corrections were made. The only extinction observed was for $0k0$: $k = 2n + 1$ implying either $P2_1$ or $P2_1/m$ as possible space groups. An HPR plot¹² indicated that the structure was centrosymmetric. A disordered arrangement seemed to be a distinct possibility since there are only two molecules per cell and the molecule could not possess a center of symmetry nor was mirror symmetry likely.

Patterson superposition techniques were utilized in order not to bias space group selection; indeed these results also indicated a disordered centrosymmetric cell with, for example, four half-iron atoms per cell. One sulfur (S1) and two carbon atoms of the cyclopentadienyl ring (C7 and C9) lay almost on the pseudo-mirror plane. As might be

expected, the presence of this pseudo-symmetry complicated refinement of the structure, but full-matrix refinement with the cyclopentadienyl ring isotropic and the remaining non-hydrogen atoms anisotropic yielded a final crystallographic residual index of 13.2% and a corresponding weighting residual of 12.9%. The positional parameters thus obtained are given in Table I, and selected interatomic distances and angles are given in Table II.

Table I. Atomic positional parameters with (Esd's) for
 $(C_5H_5)Fe(CO)_2C(SCH_3)_3$

Atom	x	y	z
Fe	0.1117(5)	0.1892(3)	0.1694(6)
S1	0.4547(7)	0.2510(12)	0.4257(8)
S2	0.3367(13)	0.3983(8)	0.1102(14)
S3	0.1698(10)	0.3840(6)	0.4349(13)
O1	0.3434(36)	0.0461(25)	0.0518(42)
O2	0.1376(39)	0.0874(19)	0.5495(37)
C1	0.2838(26)	0.3057(20)	0.2858(34)
C2	0.1116(45)	0.1289(24)	0.4163(47)
C3	0.2576(42)	0.1021(24)	0.0976(41)
C4	0.4354(30)	0.3114(21)	-0.0439(40)
C5	0.6098(42)	0.3325(27)	0.5426(52)
C6	0.2943(42)	0.4991(24)	0.5355(53)
C7	-0.1278(25)	0.2430(61)	0.1426(30)
C8	-0.0429(32)	0.3056(24)	0.0129(47)
C9	0.0068(27)	0.2322(17)	-0.1162(32)
C10	-0.0584(38)	0.1290(25)	-0.0825(45)
C11	-0.1284(44)	0.1422(33)	0.0883(56)

Table II. Selected Interatomic Distances and Angles
with (Esd's) for $(C_5H_5)Fe(CO)_2C(SCH_3)_3$

(a) Distances

Fe-C1	2.09(2) (Å)	Fe-C7	2.08(3) (Å)
Fe-C2	1.86(3)	Fe-C8	2.10(3)
Fe-C3	1.78(3)	Fe-C9	2.06(2)
C2-O2	1.04(4)	Fe-C10	2.15(3)
C3-O1	1.09(5)	Fe-C11	2.05(4)
C1-S1	1.70(2)	C7-C8	1.47(5)
C1-S2	1.79(3)	C8-C9	1.40(4)
C1-S3	1.82(3)	C9-C10	1.44(5)
S1-C5	1.72(3)	C10-C11	1.42(5)
S2-C4	1.83(3)	C11-C7	1.32(8)
S3-C6	1.83(3)		

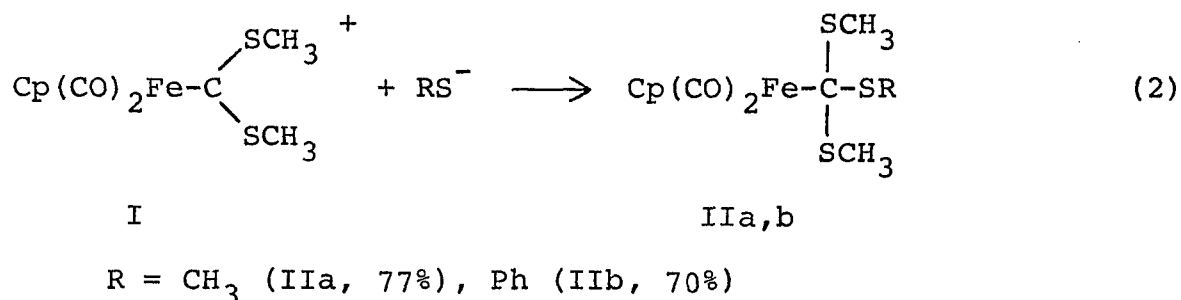
(b) Angles

C1-Fe-C2	93.4(1.2) °	C1-S1-C5	119.4(1.7) °
C1-Fe-C3	94.9(1.2)	C1-S2-C4	101.7(1.3)
C2-Fe-C3	97.3(1.4)	C1-S3-C6	108.7(1.5)
Fe-C3-O1	177.8(3.2)	C7-C8-C9	105.7(3.4)
Fe-C2-O2	166.4(3.7)	C8-C9-C10	108.9(2.5)
Fe-C1-S1	111.5(1.4)	C9-C10-C11	104.9(2.8)
Fe-C1-S2	115.9(1.1)	C10-C11-C7	111.5(3.4)
Fe-C1-S3	101.6(1.1)	C11-C7-C8	108.5(3.1)

(M = Cr, W) complexes and certain phosphines and tertiary amines.^{13,14} No physical evidence for the proposed cationic ylide, other than the formation of a transitory bright red color in the reactions of I with amines, has been found in our system. The unstable ylide formed from I and 1° and 2° amines could react intramolecularly by loss of HSCH₃ to give the observed cationic isocyanide and amino-thiocarbene complexes.⁷ This cannot occur with 3° amines and the unstable ylide decomposes, possibly by mercaptide transfer between two ylides or I and an ylide to give IIa in yields not to exceed the theoretical 66% value based on I. The relatively low yields of IIa and the formation of large amounts of insoluble, unidentified decomposition products in these indirect routes support this mechanistic possibility.

General route to tri(organothio)methyliron derivatives

Complex I reacts readily with mercaptides to give the corresponding tri(organothio)methyl complexes (IIa,b) in good yield (eq. 2).

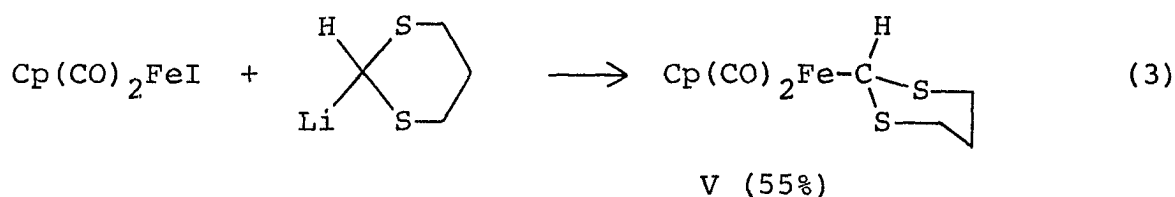


The reaction appears to be a simple nucleophilic addition of mercaptide to the electron deficient carbene carbon.

The crystalline products are stable in the solid state at low temperatures (-20°C) for several months, but at room temperature noticeable decomposition occurs within a few days, even in the absence of air. Solutions of IIa,b are not very stable at room temperature and decomposition is evident within 1 h. Even at low temperatures (-20°C), some decomposition occurs in the solutions after a few days.

The oxygen analog of IIa cannot be obtained from the reaction of $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)_2]\}\text{PF}_6$ (III)¹⁵ and methoxide. Infrared spectra of these reaction solutions give some evidence for the formation of the iron-orthoester complex, $\text{Cp}(\text{CO})_2\text{FeC}(\text{OCH}_3)_3$ (IV), with bands appearing at 2035 and 1979 cm^{-1} (CH_2Cl_2), but attempts to isolate IV yield $\text{Cp}(\text{CO})_2\text{FeC}(=\text{O})\text{OCH}_3$ and $[\text{CpFe}(\text{CO})_2]_2$ as the only identifiable organometallic products. Organic orthoesters are known to undergo hydrolysis (usually acid catalyzed) to give one equivalent of ester and two equivalents of alcohol.^{16,17} Thus, if IV is formed it could hydrolyze to give $\text{Cp}(\text{CO})_2\text{FeC}(=\text{O})\text{OCH}_3$, which is known to decompose to $[\text{CpFe}(\text{CO})_2]_2$.¹⁸

Preparation of $\text{Cp}(\text{CO})_2\text{FeC}(\text{H})\text{S}(\text{CH}_2)_3\text{S}$ (V) In attempts to prepare di- or tri(organothio)methyliron complexes by the direct combination of the iron moiety and sulfur-stabilized anions, we have reacted $\text{Cp}(\text{CO})_2\text{FeI}^{10}$ with $\text{LiC}(\text{SCH}_3)_3$,⁴ $\text{LiCH}(\text{SCH}_3)_2$,¹ and $\text{LiCH}(\text{SPh})_2$,¹ as well as $\text{Cp}(\text{CO})_2\text{FeCl}^{10}$ and $\text{Cp}(\text{CO})_2\text{Fe}(\text{THF})^{+19}$ with $\text{LiC}(\text{SPh})_3$ ⁴ but obtain none of the desired complexes. Lithiated 1,3-dithiane does react with $\text{Cp}(\text{CO})_2\text{FeI}^{10}$ to give the di(organothio)methyliron complex, V, in reasonable yield (eq. 3).



Structure of $\text{Cp}(\text{CO})_2\text{FeC}(\text{SCH}_3)_3$ (IIa) As IIa is an unexpected product of the reaction of I and amines, an X-ray diffraction study was undertaken to confirm its formulation as a η^5 -cyclopentadienyldicarbonyltri-(organothio)methyliron complex. Unfortunately, the presence of pseudo-symmetry in the unit cell prevents refinement of the structure below $R = 12.9\%$. However, the atomic positional parameters (Table I) and selected interatomic distances and angles (Table II) clearly show the complex to be a tri(methylthio)methyl ligand σ -bound to the $\text{Cp}(\text{CO})_2\text{Fe}$ moiety (Figure 1).

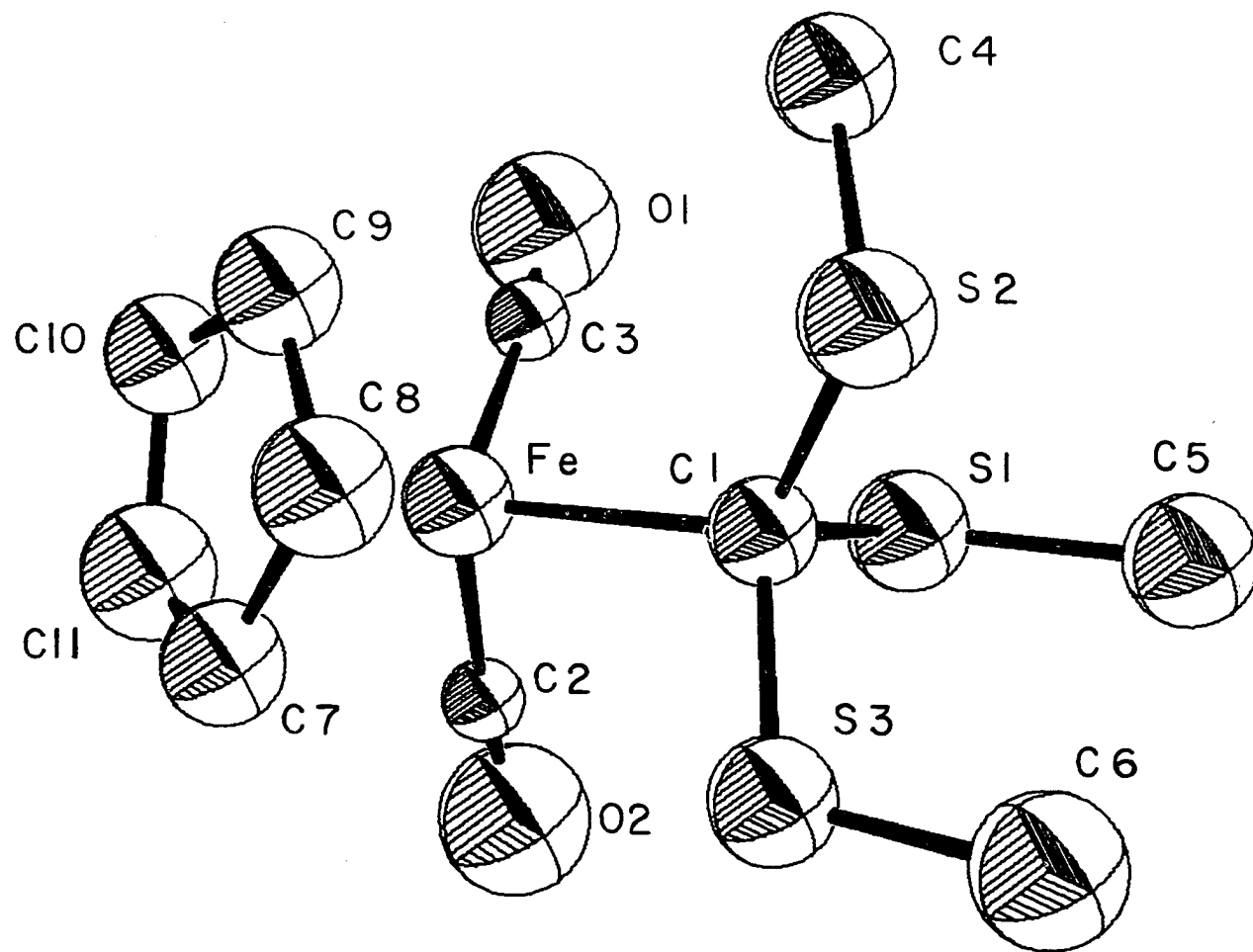


Figure 1. The structure of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_3]$, IIa

The $\text{Cp}(\text{CO})_2\text{Fe}$ moiety adopts the same geometry as observed in several other $\text{Cp}(\text{CO})_2\text{Fe-R}$ systems with all bond lengths and angles being in reasonable agreement with the previously determined structures.²⁰⁻²⁴

The most interesting part of the structure of IIa is the $\text{Fe-C}(\text{SCH}_3)_3$ moiety. The Fe-Cl σ -bond length of 2.09 Å is in good agreement with the Fe-C σ -bond lengths found for $\text{Cp}(\text{CO})_2\text{FeC}_4\text{H}_7\text{C}_2(\text{CN})_4$ (2.0977 Å),²⁴ $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{COOH}$ (2.06 Å),²⁰ and $\text{Cp}(\text{CO})_2\text{FeC}_5\text{H}_5$ (2.11 Å)²¹ and Cl has an approximately tetrahedral geometry (Fe-Cl-S average of 109.7°). The average value of the six C-S distances of 1.78 Å is only slightly shorter than the values obtained from microwave studies of CH_3SH (1.819 Å)²⁵ and $(\text{CH}_3)_2\text{S}$ (1.802 Å)²⁶ and seems reasonable for a C-S σ -bond.

The three CH_3S groups of the $\text{C}(\text{SCH}_3)_3$ ligand are staggered, as expected, with respect to the Cp and CO ligands. The S1-C5 and S3-C6 bonds are nearly parallel while the S2-C4 bond is directed away from the rest of the ligand. The pseudo-parallel nature of the two $\text{CH}_3\text{-S}$ bonds is unexpected as it would not seem to be the most favored steric conformation. This conformation may be mandated by crystal packing forces and/or possible interactions of the sulfur lone pairs with the ligands on iron.

Spectra Complex IIa displays some unusual spectral features. The IR spectrum in hexanes shows four $\nu(\text{CO})$ absorptions at 2023(s), 2013(m), 1977(s), and 1968(m) cm^{-1} rather than the expected two bands. Similar results have been obtained for other $\text{Cp}(\text{CO})(\text{L})\text{Fe}-\text{R}$ systems (L = CO, phosphorus ligands), and this has been interpreted as being the result of the presence of conformational isomers due to restricted Fe-C rotation.²⁷⁻³⁰ However, in all these cases, conformers were detected only when the σ -bound carbon was unsymmetrically substituted (Figure 2).

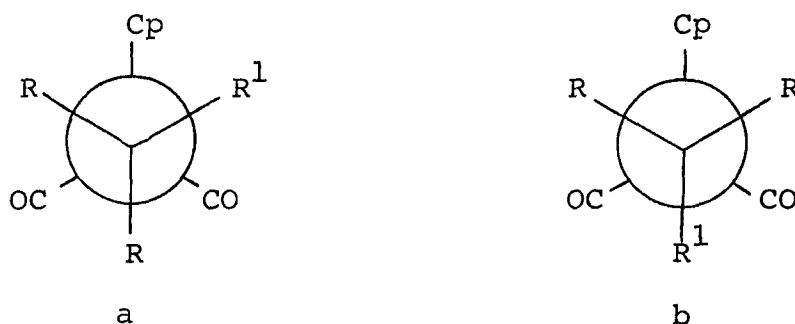


Figure 2. Newman projections of the possible conformational isomers for $\text{Cp}(\text{CO})_2\text{Fe}[\text{CR}_2\text{R}^1]$ systems

In $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_3]$, IIa, the σ -bound carbon is symmetrically substituted and such conformational isomerization is not possible if the three mercapto groups are structurally equivalent. In the unsymmetrically substituted complexes IIb and V, where this isomerization could be expected, only

two $\nu(\text{CO})$ absorptions are observed (2024(s), 1978(s) and 2026(s), 1979(s) cm^{-1} , respectively, hexanes), indicating the presence of only one conformer.

All three methyl groups of IIa are equivalent in the ambient temperature $^1\text{H-NMR}$ spectrum. However, in CS_2 at low temperature (-106°C), two rather broad singlets at $\tau 7.85$ (6H) and $\tau 7.96$ (3H) for the methyls and a sharp singlet at $\tau 4.83$ for the Cp ring appear. Lower temperature spectra could not be obtained because of sample crystallization. As the temperature is raised, the two broad singlets coalesce (-100°C) and eventually a sharp singlet ($\tau 7.89$) is observed for the equivalent methyl groups.

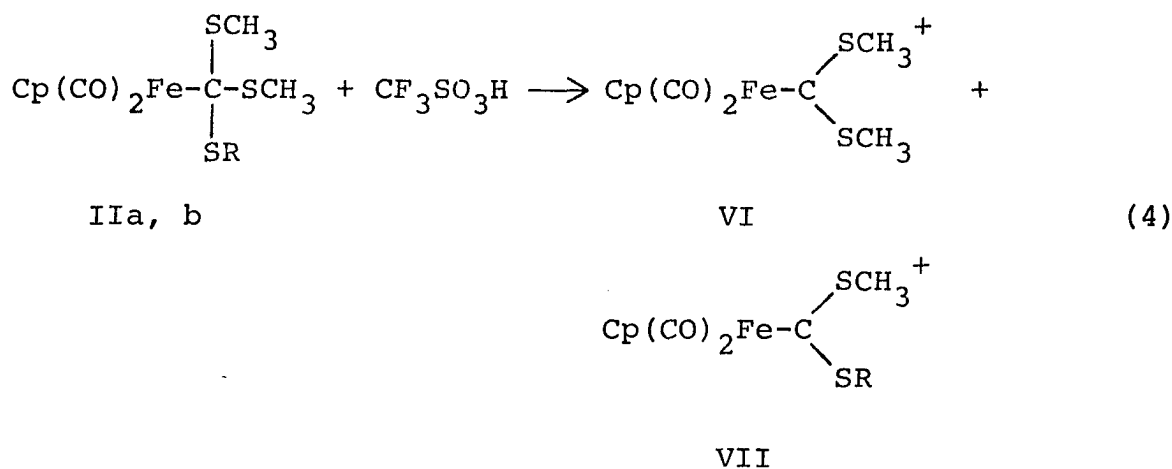
The splitting of the methyl groups at low temperature and coalescence at higher temperature may be due to restricted rotation around the Fe-C bond. The free energy of activation for this process, $\Delta G^\ddagger \approx 8.7 \text{ kcal/mole}$, is calculated from the coalescence temperature and peak width at half height using the Eyring equation.³¹ This agrees reasonably well with previously observed rotational barriers for $\text{Cp}(\text{CO})_2\text{FeCH}_3$ (2.9 kcal/mole calculated, 5.4 kcal/mole observed),³² $\text{Cp}_3\text{U}(\text{CH}_3)_2$ (10.5 kcal/mole),³³ and the suggested range of 5-10 kcal/mole for such barriers.^{29,34} The rotations about the C-S bonds should be less restricted than the Fe-C bond rotation as the

barriers observed for CH_3SH and CH_3SCH_3 are 1.3 kcal/mole²⁵ and 2.1 kcal/mole,²⁶ respectively. Thus, the low temperature $^1\text{H-NMR}$ spectrum of IIa may be described as freezing the rotation about the Fe-C bond into a staggered conformation where there is a unique mercapto group lying between two CO ligands (R^1 in Figure 2b) and two equivalent mercapto groups lying between a CO and a Cp ligand (R in Figure 2b). The resonances observed for the methyl groups in the low temperature spectrum would then be averaged signals of the possible conformations around the C-S bonds as these rotations should be unrestricted in the temperature range studied.

While the low temperature $^1\text{H-NMR}$ spectrum may be explained by restricted Fe-C bond rotation, it is difficult to rationalize the IR spectrum (hexanes) of IIa by the conventional conformational isomerism argument.²⁷⁻³⁰ One possibility is that although the C-S bond rotations should be quite facile at room temperature, they may be correlated such that two of the S- CH_3 bonds are always pseudo-parallel while the other S- CH_3 bond is directed away from the rest of the $-\text{C}(\text{SCH}_3)_3$ ligand as observed in the solid state (Figure 1). Thus, the conformers shown in Figure 2, where R^1 is the non-parallel SCH_3 group, would exist in solution and could be interconverted by either

Fe-C bond rotation or correlated rotations of the C-S bonds. Another possible explanation is that an eclipsed conformation around the Fe-C bond could have a finite lifetime on the IR time scale due to bonding interactions of the sulfur lone pair electrons with the π^* orbitals of the CO ligands.

Reaction of the tri(organothio)methyliron complexes with acid Complexes IIa,b react readily with strong acid, $\text{CF}_3\text{SO}_3\text{H}$, to give the triflate salts of cationic carbene complexes in almost quantitative yield by the elimination of thiol (eq. 4).



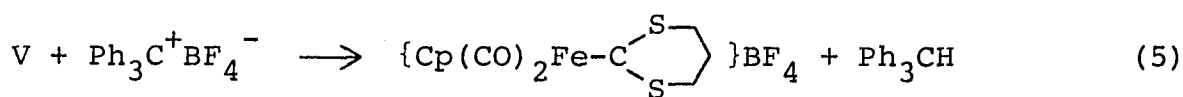
R = CH_3 (VI, 96%)

Ph (VII, 40% and VI, 56%)

Complex IIa gives the di(methylthio)carbene complex VI, (previously prepared as the hexafluorophosphate salt)⁷ very cleanly. Complex IIb, however, gives a mixture of VI and a new phenyl-methyl(dithio)carbene complex, VII.

Hydride abstraction from $\text{Cp}(\text{CO})_2\text{FeC}(\text{H})\text{S}(\text{CH}_2)_3\text{S}$ (V)

Stirring complex V in CH_2Cl_2 under an N_2 atmosphere with an equivalent amount of trityl tetrafluoroborate for 12 h at room temperature leads to the formation of the new carbene complex, VIII (eq. 5).



VIII

This product is initially obtained as an impure oil which cannot be purified or crystallized. That the oil is predominantly VIII with some unidentified contamination may be inferred from its spectral data. The IR spectrum of the oil in CH_2Cl_2 shows two $\nu(\text{CO})$ absorptions at 2058(s) and 2018(s) cm^{-1} , consistent with that observed for similar complexes.⁷ The ^1H -NMR (acetone- d_6) spectrum displays the expected resonances at τ 4.50(s, C_5H_5), 6.57(t, 2 SCH_2), and 7.45(m, CH_2) along with unidentified phenyl, cyclopentadienyl, and aliphatic resonances. Conclusive evidence for the formation of VIII is found in the ^{13}C -NMR (CD_3CN) spectrum of the oil. Major resonances occur at 283.9 ppm (s, carbene), 210.5(s, 2 CO), 89.1(s, C_5H_5), 39.6(s, 2 SCH_2), and 18.9(s, CH_2) along with minor resonances corresponding

to the impurities found in the $^1\text{H-NMR}$ spectrum. In addition, precedent for the reaction in eq. 5 may be found in the related conversions of η^1 -1-benzocyclobutenyl- η^5 -cyclopentadienyldicarbonyliron,³⁵ η^5 -cyclopentadienyldicarbonyl- η^1 -1-naphtho[b]cyclobutenyliron,³⁵ η^5 -cyclopentadienyldicarbonyl- η^1 -methoxymethyliron,³⁶ and η^1 -cycloheptatrienyl- η^5 -cyclopentadienyldicarbonyliron³⁷ to the corresponding cationic carbene complexes by α -hydride abstraction from the σ -bound organic moiety.

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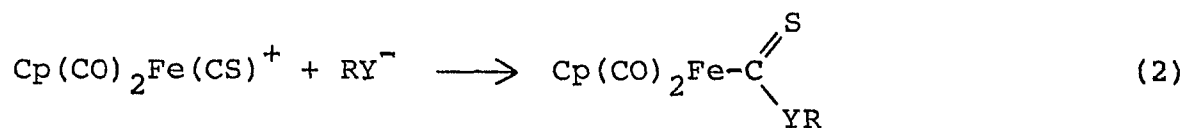
SECTION III. SYNTHESIS AND SPECTROSCOPIC STUDY OF
 $\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ CARBENE COMPLEXES,
WHERE X AND Y ARE O, S, Se, AND/OR NR

INTRODUCTION

Transition metal carbene complexes are of great interest as they are postulated as intermediates in catalytic processes, most notably in the Fischer-Tropsch reaction¹ and in olefin metathesis.² A better understanding of chemical, physical, and electronic factors which influence model carbene systems should lend insight into these catalytic processes. The interesting chemical behavior found for $\text{Cp}(\text{CO})_2\text{Fe}[\text{dithiocarbene}]^+$ complexes³ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) has prompted us to investigate the $\text{Cp}(\text{CO})_2\text{Fe}[\text{carbene}]^+$ system further.

Carbon-13 NMR spectroscopy has proven to be a valuable tool in organometallic chemistry.⁴⁻⁶ Analysis of carbene complexes by ¹³C-NMR spectroscopy is especially interesting because of the high sensitivity of the carbene carbon resonance to changes in the electronic environment.⁷ In this report, we present the synthesis of a variety of iron carbene complexes incorporating O, S, and Se into the carbene ligands. These complexes, and other carbene complexes reported previously,^{3,8} are analyzed by means of IR, ¹H-NMR, and ¹³C-NMR spectroscopy with emphasis on the relative π -stabilization abilities of the heteroatoms in the carbene ligands.

The thiocarbonyl complex, $\text{Cp}(\text{CO})_2\text{Fe}(\text{CS})^+$, may be readily converted to thioester derivatives by reaction with alkoxides,^{12,13} mercaptides, and selenides (eq. 2).



IIa-d

$\text{RY} = \text{CH}_3\text{O}$ (IIa, 70%)¹²

PhO (IIb)¹³

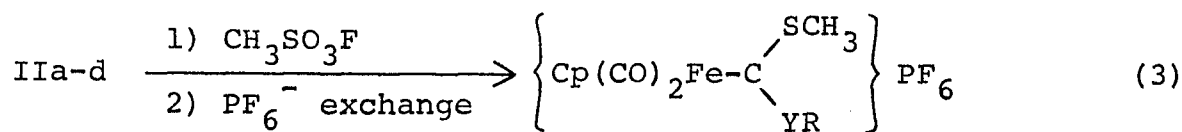
PhS (IIc)

PhSe (IIId, 56%)

When this reaction is attempted with PhTe^- , much gas evolution results, and an unstable, intractable green tar is obtained. Nucleophilic attack by PhTe^- appears to occur with CO ligand displacement to give the unstable green $\text{Cp}(\text{CO})(\text{CS})\text{Fe}-\text{TePh}$ and a very small amount of the desired thioester complex, $\text{Cp}(\text{CO})_2\text{FeC}(=\text{S})\text{TePh}$, as suggested by IR spectra of the reaction solutions.

The thioester complexes, IIa-d, need not be isolated; IIb,c have been characterized only by their IR spectra (IIb(hexanes): 2042(s), 1996(s) cm^{-1} ;¹³ IIc(THF): 2028(s), 1979(s) cm^{-1}). Reaction of the crude thioester complexes

with methyl fluorosulfonate followed by anion exchange affords cationic carbene complexes in reasonable yield (eq. 3).



IIIa-d

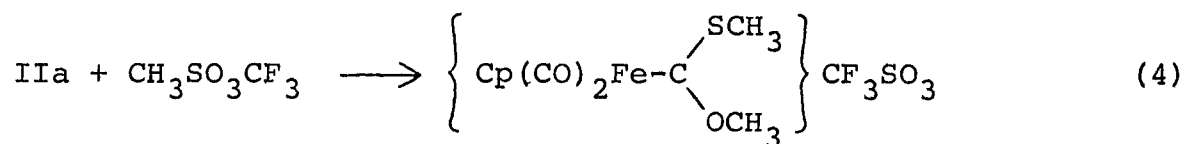
YR = OCH₃ (IIIa, 41%)

OPh (IIIb, 43%)

SPh (IIIc, 75%)

SePh (IIId, 74%)

Methyl triflate, CH₃SO₃CF₃, also alkylates the thioester complexes, but with IIB-d the carbene complexes obtained are difficult to purify as they do not crystallize readily. With IIA, however, the corresponding carbene complex is obtained in excellent yield by alkylation with CH₃SO₃CF₃ (eq. 4).



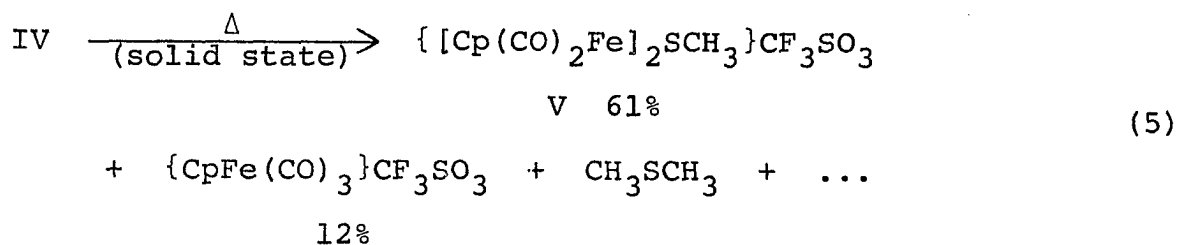
IV, 92%

Entirely satisfactory elemental analyses could not be obtained for IIIc,d on independent samples even after several recrystallizations. However, their spectral data (Tables I-III), especially the characteristic carbene carbon resonance in the ^{13}C -NMR spectra of IIc,d, and their reactivity¹⁴ clearly show their formulation as carbene complexes to be correct.

Complex IIIc is quite stable towards air in the solid state. Complexes IIIb, IIId, and especially IIIa and IV are less stable in this respect and are best stored at low temperatures (-20°C). Samples of IIIa, IIIb, and IV stored in this manner, but handled periodically in air at room temperature, gradually develop small amounts of $\text{CpFe}(\text{CO})_3^+$ as impurities. This may be due to a slight moisture sensitivity. Solutions of IIIa-d and IV, when not protected from the atmosphere, show little or no decomposition after storage for several days at -20°C . Even at room temperature, decomposition of these solutions appears to be slow and is not noticeable for several hours.

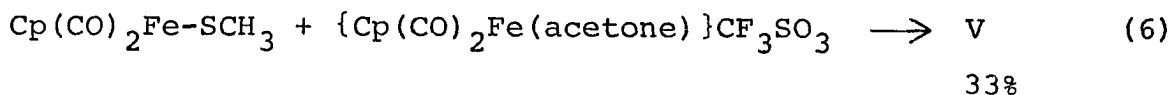
In contrast to Ia,b and IIIb-d, the dimethyl(thio-oxo)carbene complexes (IIIa and IV) display a marked thermal instability. When stored in air or under vacuum at room temperature, the yellow crystals of IIIa and IV

become red-orange after approximately 12 h and eventually become deep red. At elevated temperatures ($\sim 100^\circ \text{C}$), this conversion becomes very rapid and represents the formation of a sulfido-bridged binuclear complex (eq. 5).



The evolution of CH_3SCH_3 is confirmed by its characteristic odor as well as by the mass spectrum and ^1H -NMR spectrum of the volatile products from the reaction in eq. 5, but the mechanism of this reaction is presently not understood as all of the side products have not been identified. In addition, IIIb shows no tendency to form V, even at higher temperatures ($\sim 150^\circ \text{C}$). Refluxing IV in dried, degassed CH_3CN under an N_2 atmosphere for 10 h affords $\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_3\text{CN})^+$ (47%) and a large amount of unstable, unidentified decomposition product. The acetonitrile complex probably results from the conversion of IV to $\text{CpFe}(\text{CO})_3^+$ which is known to lose a CO ligand in refluxing acetonitrile.¹⁵ The decomposition product appears to be the same as that observed when V is refluxed under the same conditions as for IV.

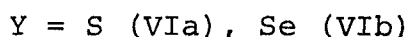
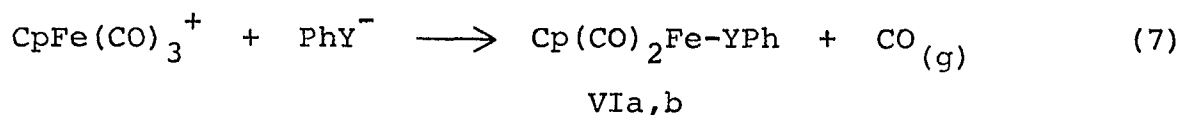
The production (eq. 5) of V and $\text{CpFe}(\text{CO})_3^+$ from IV would appear to be independent processes. The binuclear complex V may also be prepared by another route (eq. 6).



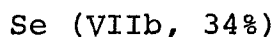
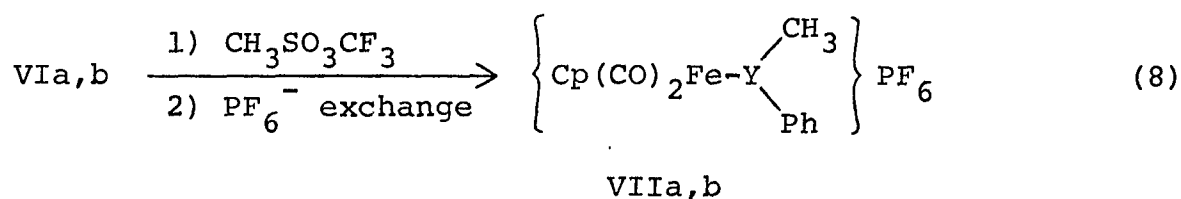
The iron sulfide complex is prepared from $\text{Cp}(\text{CO})_2\text{FeX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)¹⁶ and CH_3S^- ,¹⁷ and $\{\text{Cp}(\text{CO})_2\text{Fe}(\text{acetone})\}\text{X}$ species may be obtained by oxidation of $[\text{CpFe}(\text{CO})_2]_2$ with the appropriate silver(I) salt.¹⁸ Complex V behaves very much like the ethyl derivative, $\{[\text{Cp}(\text{CO})_2\text{Fe}]_2\text{SCH}_2\text{CH}_3\}^+$, which was prepared by a route analogous to that of eq. 6.^{19,20} Complex V shows three $\nu(\text{CO})$ bands in its IR(CH_2Cl_2) spectrum (Table I); the two high energy bands are sharp while the lower energy band is broad. This is due to rotational isomerism about the Fe-S bonds, as observed for $\{[\text{Cp}(\text{CO})_2\text{Fe}]_2\text{SCH}_2\text{CH}_3\}^+$.¹⁹ Three bands are observed, rather than the expected four, because the two asymmetric stretches are not resolved and give rise to one broad band.

The method outlined above (eq. 2 and 3) for the preparation of carbene complexes from $\text{Cp}(\text{CO})_2\text{Fe}(\text{CS})^+$ cannot be extended to the $\text{CpFe}(\text{CO})_3^+$ system. The alkoxy-carbonyl complex, $\text{Cp}(\text{CO})_2\text{Fe-C}(=\text{O})\text{OCH}_3$, is prepared by the

reaction of CpFe(CO)_3^+ and CH_3O^- but decomposes to $[\text{CpFe(CO)}_2]_2$ fairly readily.²¹ In addition, the reaction of $\text{Cp(CO)}_2\text{FeC(=O)OCH}_3$ with $\text{CH}_3\text{SO}_3\text{F}$ or $\text{CH}_3\text{SO}_3\text{CF}_3$ affords CpFe(CO)_3^+ as the only isolable organometallic product by cleavage of the methoxy group. The reactions of CpFe(CO)_3^+ with PhS^- or PhSe^- do not yield ester complexes but rather iron sulfide or selenide complexes by displacement of a CO ligand (eq. 7).

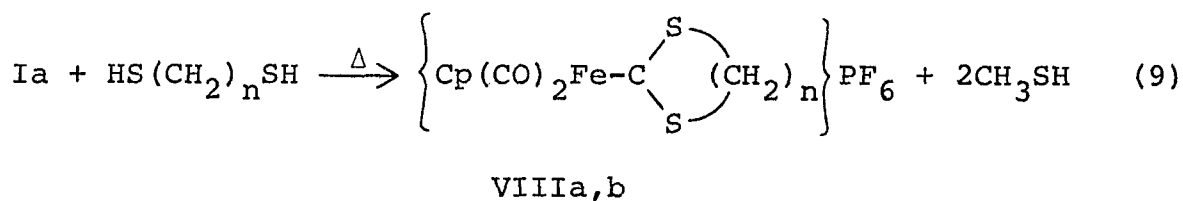


Complex VIa behaves as previously reported¹⁷ and VIb forms an unstable green oil with two $\nu(\text{CO})$ absorptions in its $\text{IR}(\text{CH}_2\text{Cl}_2)$ spectrum at 2025(s) and 1979(s) cm^{-1} . The crude products obtained by the reaction in eq. 7 are reacted with $\text{CH}_3\text{SO}_3\text{CF}_3$ followed by anion exchange to give stable, crystalline iron thio- or selenoether complexes (eq. 8).



The spectroscopic data (Tables I-III) for VIIa are nearly identical to those in a previous report.¹⁸ The lower $\nu(\text{CO})$ approximate force constant, $k(\text{CO})$,²² for VIIb indicates that the PhSeCH_3 ligand has a lower π -acceptor/ σ -donor ratio than the PhSCH_3 ligand.

Preparation of carbene complexes by "heteroatom metathesis" Complex Ia reacts with excess dithiol under reflux conditions by displacement of both CH_3S groups to give carbene complexes with cyclic dithiocarbene ligands (eq. 9).



$n = 2$ (VIIIa, 78%)

3 (VIIIb, 60%)

Enough solvent, CH_2Cl_2 or acetone, is added to the systems so that reflux is obtained at 50-60° C. Both reactions are complete within 3.5 h. The reaction of Ia and PhSH under similar conditions for 6 h produces a mixture of Ia, $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{SPh}]^+$, and $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SPh})_2]^+$. The mixture displays two $\nu(\text{CO})$ bands in its $\text{IR}(\text{CH}_2\text{Cl}_2)$ spectrum

at 2058(s) and 2020(s) cm^{-1} . In the $^1\text{H-NMR}$ (acetone- d_6) spectrum, the di(phenylthio)carbene complex is the major component of the mixture with resonances at τ 2.29(s, 2 C_6H_5) and τ 4.57(s, C_5H_5). The carbene complexes VIIIa,b are yellow crystalline solids displaying the same stability and solubility characteristics as Ia.³ The spectral properties of VIIIb are nearly identical to those reported for an impure sample of $\{\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CS}(\text{CH}_2)_3\text{S}}]\}\text{BF}_4$ prepared by α -hydride abstraction from $\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{C}(\text{H})\text{S}(\text{CH}_2)_3\text{S}}]$.²³

The dioxo analogs of VIIIa,b could not be obtained. Refluxing Ia with ethylene glycol yields $\text{CpFe}(\text{CO})_3^+$ as the only organometallic product, and no organometallic products could be separated from the excess diol after stirring Ia in 1,3-propanediol and a small amount of acetone for 19 h. Refluxing Ia in dried CH_3OH under an N_2 atmosphere for 2.5 h affords no dioxocarbene complexes but rather an 81% yield of $\text{CpFe}(\text{CO})_3^+$. The dimethoxycarbene complex, $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)_2]\}\text{PF}_6$ (IX),¹³ also gives a high yield (88%) of $\text{CpFe}(\text{CO})_3^+$ when refluxed with CH_3OH under similar conditions. Thus, dioxocarbene complexes may form when Ia is refluxed with CH_3OH or ethylene glycol but they are not stable under these conditions and decompose to $\text{CpFe}(\text{CO})_3^+$.

Table I. IR spectra of the new complexes and of other pertinent carbene complexes in CH₂Cl₂

Complex		$\nu(\text{CO}), \text{cm}^{-1}$	$\underline{k}^{\text{a}}(\text{CO}), \text{mdyn}/\text{\AA}^{\circ}$
{Cp(CO) ₂ Fe[C(SCH ₃) ₂]}PF ₆ ^b	Ia	2058(s), 2017(s)	16.77
{Cp(CO) ₂ Fe[C(SCH ₃) ₂]}CF ₃ SO ₃	Ib	2055(s), 2014(s)	16.72
Cp(CO) ₂ FeC(=S)SePh	IIId	2032(s), 1983(s)	16.28
{Cp(CO) ₂ Fe[C(SCH ₃)OCH ₃]}PF ₆	IIIa	2062(s), 2019(s)	16.82
{Cp(CO) ₂ Fe[C(SCH ₃)OPh]}PF ₆	IIIb	2060(s), 2019(s)	16.80
{Cp(CO) ₂ Fe[C(SCH ₃)SPh]}PF ₆	IIIc	2057(s), 2016(s)	16.75
{Cp(CO) ₂ Fe[C(SCH ₃)SePh]}PF ₆	IIId	2058(s), 2019(s)	16.78
{Cp(CO) ₂ Fe[C(SCH ₃)OCH ₃]}CF ₃ SO ₃	IV	2060(s), 2017(s)	16.78
{[Cp(CO) ₂ Fe] ₂ SCH ₃ }CF ₃ SO ₃	V	2056(vs), 2039(s), 2003(vs, br)	
{Cp(CO) ₂ Fe[S(CH ₃)Ph]}PF ₆	VIIa	2064(s), 2022(s)	16.86
{Cp(CO) ₂ Fe[Se(CH ₃)Ph]}PF ₆	VIIb	2057(s), 2017(s)	16.76

^aReference 22.

^bReference 3.

Table I. (continued)

Complex		$\nu(\text{CO}), \text{cm}^{-1}$	$\underline{k}^{\text{a}}(\text{CO}), \text{mdyn/\AA}^{\circ}$
$\{\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CS}(\text{CH}_2)_2\text{S}}]\}\text{PF}_6$	VIIIa	2065(s), 2024(s)	16.88
$\{\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CS}(\text{CH}_2)_3\text{S}}]\}\text{PF}_6$	VIIIb	2057(s), 2015(s)	16.74
$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)_2]\}\text{PF}_6^{\text{c}}$	IX	2068(s), 2020(s)	16.87
$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)_2]\}\text{CF}_3\text{SO}_3$	Xa	2063(s), 2016(s)	16.80
$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)\text{OCH}_2\text{CH}_3]\}\text{CF}_3\text{SO}_3$	Xb	2064(s), 2017(s)	16.82
$\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2\text{H}]^{\text{d}}$	XI	2018(s), 1968(s)	16.04
$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{H}]\}\text{CF}_3\text{SO}_3$	XII	2067(s), 2026(s)	16.91
$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)\text{H}]\}\text{PF}_6^{\text{e}}$	XIII	2085(s), 2043(s)	17.21
$\{\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CNH}(\text{CH}_2)_2\text{NH}}]\}\text{PF}_6^{\text{b}}$		2053(s), 2003(s)	16.61
$\{\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CNH}(\text{CH}_2)_3\text{NH}}]\}\text{PF}_6^{\text{b}}$		2051(s), 2000(s)	16.57
$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{SCH}_2\text{CH}_3]\}\text{PF}_6^{\text{b}}$		2060(s), 2017(s)	16.78

^cReference 13.

^dIn hexanes.

^eReference 24, in CH_3NO_2 .

Table II. $^1\text{H-NMR}$ spectra of the new complexes and other pertinent carbene complexes in acetone- d_6 (τ)^a

Complex	C_6H_5	C_5H_5	OCH_3	SCH_3	Other Resonances
Ia ^b		4.43		6.73	
Ib		4.34		6.69	
IIId ^c	2.73	5.09			
IIIa		4.34	5.09	7.33	
IIIb ^d	2.53 (m)	4.80		7.22	
IIIc ^d	2.33 (br)	4.74 (br)		6.88	
IIId ^d	2.31 (br)	4.69 (br)		6.84	
IV		4.33	5.09	7.33	
V		4.48		7.88	
VIIa	2.41 (m)	4.30		6.99	
VIIb	2.42 (m)	4.32		7.06	
VIIIa		4.36			5.87 (2 CH_2)
VIIIb		4.50			6.57 (t, 2 CH_2), 7.45 (m, CH_2)

^aAll resonances are singlets unless otherwise indicated.

^bReference 3.

^cIn CS_2 .

^dIn CD_3CN .

Table II. (continued)

Complex	C ₆ H ₅	C ₅ H ₅	OCH ₃	SCH ₃	Other Resonances
IX ^e		4.35	5.58		
Xa		4.34	5.59		
Xb		4.36	5.63		5.18(q, OCH ₂), 8.50(t, CH ₃)
XI ^f		5.07		7.80	6.03(CH)

^eReference 13.

^fIn CCl₄.

Table III. ^{13}C -NMR spectra of the new complexes and other pertinent carbene complexes in acetone- d_6 (singlets, ppm)

Complex	C(carbene)	CO	C_5H_5
Ia ^a	303.1	209.5	88.6
Ia ^{a,b}	304.3	210.1	89.2
Ib ^b	304.2	210.5	89.4
IIIb	301.1	209.0	89.4
IIIb ^b	301.2	208.9	89.4
IIIc	308.9	209.6	89.3
IIIc ^c	309.4	209.7	89.6
IIIId ^c	321.0	209.8	90.0
IV	297.9	210.0	89.2
V		212.5	88.6
VIIa		209.6	88.7
VIIb		210.2	87.9
VIIIa	294.7	209.8	89.7
VIIIb	283.7	210.9	89.4
IX ^d	251.9	210.3	88.1
Xa	251.8	210.3	88.2
Xa ^b	251.9	210.2	88.1
Xb	250.4	210.5	88.3
$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{CNH}(\text{CH}_2)_2\text{NH}]\}\text{PF}_6^{\text{a}}$	200.0	212.2	87.6
$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{CNH}(\text{CH}_2)_3\text{NH}]\}\text{PF}_6^{\text{a}}$	192.2	212.7	87.6

^aReference 3.

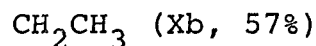
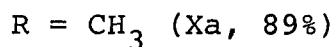
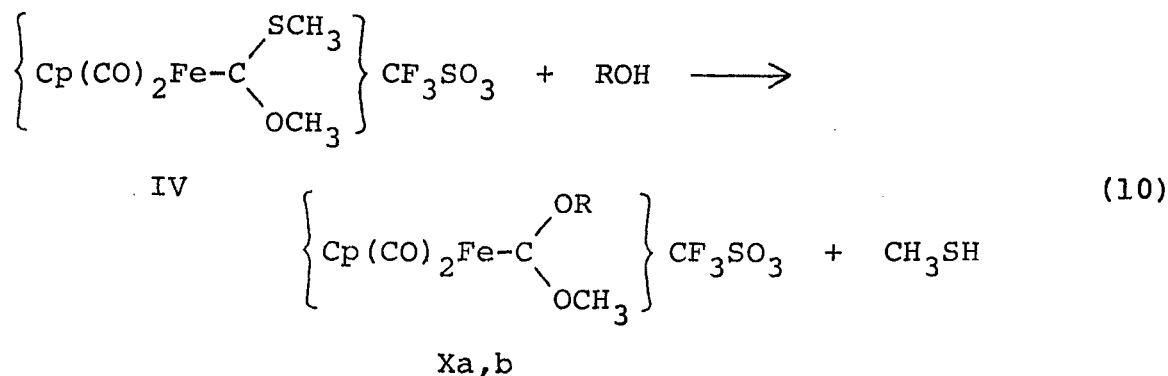
^bIn CD_3CN .

^cIn CD_3CN at 73°C .

^dReference 13.

OCH ₃	SCH ₃	C ₆ H ₅	Other Resonances
	29.6		
	30.3		
	30.3		
	22.5	159.7, 131.6, 129.6, 122.6	
	23.0	159.6, 131.7, 129.7, 122.6	
	30.4	134.4, 133.0, 131.3	
	31.3	135.3, 134.8, 133.6, 131.8	
	34.4	136.4, 134.9, 133.0, 132.1	
71.8	21.5		
	28.9		
	26.6	134.5, 131.5, 131.0, 129.5	
		131.4, 131.2, 130.6, 128.4	17.8(SeCH ₃)
			48.2(2 SCH ₂)
			39.6(2 SCH ₂), 19.1(CH ₂)
63.6			
63.8			
63.9			
63.4			74.9(OCH ₂), 14.3(CH ₃)
			46.4(2 CH ₂)
			42.7(2 CH ₂), 20.1(CH ₂)

The dimethyl(thio-oxo)carbene complex, IV, reacts readily with methanol and ethanol by nucleophilic substitution of the CH_3S group (eq. 10).



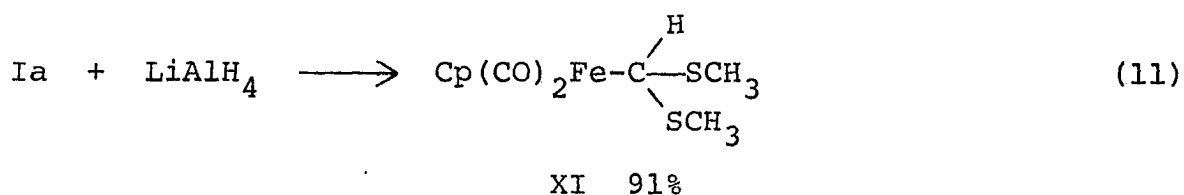
This reaction is very similar to that of IIIb with methanol in which both the CH_3S and the PhO groups are displaced to give IX in 44% yield.¹³ Stirring IV in CH_3SH at room temperature under slight pressure in a sealed tube for 12 h produces approximately equal amounts of Ib and $\text{CpFe}(\text{CO})_3^+$. Complex Ib results from displacement of the CH_3O group of IV, and $\text{CpFe}(\text{CO})_3^+$ may result from thermal decomposition of IV.

The dioxocarbene complexes IX, Xa, and Xb are fairly stable, pale yellow crystalline solids. All show a tendency to slowly decompose to $\text{CpFe}(\text{CO})_3^+$ on prolonged exposure to

the atmosphere at room temperature in solution or in the solid state. Entirely satisfactory elemental analysis for Xb could not be obtained, but its spectral properties (Tables I-III), especially the characteristic carbene resonance in its ^{13}C -NMR spectrum, clearly show its formulation as a carbene complex to be correct.

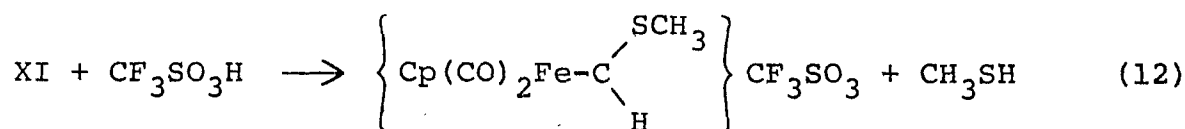
Preparation of an unstable secondary carbene complex

Complex Ia reacts rapidly with LiAlH_4 in THF to produce cyclopentadienyldicarbonyldi(methylthio)methyliron (XI) in nearly quantitative yield (eq. 11).



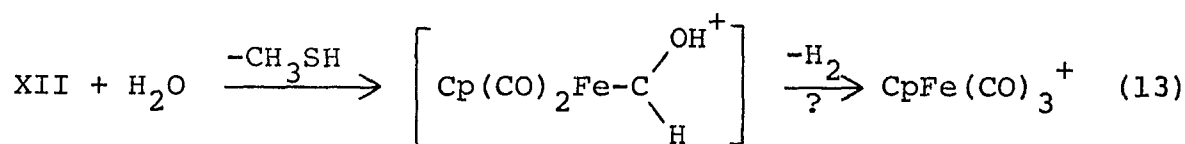
Complex XI is a low melting, yellow, crystalline solid which is very stable in the solid state at low temperatures (-20°C). Its properties are very similar to those of the related di(organothio)methyliron complex, $\text{Cp}(\text{CO})_2\text{Fe}-\overline{[\text{C}(\text{H})\text{S}(\text{CH}_2)_3\text{S}]}$.²³

The reaction of XI with strong acid, $\text{CF}_3\text{SO}_3\text{H}$, in Et_2O causes the immediate precipitation of a new secondary carbene complex (eq. 12).



XII

This reaction has precedent in the related conversion of tri(organothio)methyliron complexes, $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SR})_3]$, to cationic dithiocarbene complexes by reaction with $\text{CF}_3\text{SO}_3\text{H}$.²³ The new secondary carbene complex, XII, has been characterized by its IR spectrum (Table I) only due to its low stability. Exposure of XII to moisture in the atmosphere, solvents, or in the acid reagent employed causes the rapid formation of $\text{CpFe}(\text{CO})_3^+$. This may proceed through a Fischer-Tropsch type intermediate, a secondary hydroxycarbene complex,¹ by nucleophilic attack of H_2O on the carbene carbon followed by loss of CH_3SH and possibly H_2 (eq. 13).



The IR spectrum of XII is consistent with its formulation as a secondary carbene complex. The replacement of one π -donating CH_3S group in Ib with a H atom would

induce more $M \rightarrow C$ π -backbonding and raise the $\nu(\text{CO})$ frequencies. Comparison of Ib and XII show this indeed to be the case with XII having a $\underline{k}(\text{CO})$ value which is 0.19 $\text{mdyn}/\text{\AA}$ larger than that of Ib. The IR spectrum of XII also compares favorably with its oxygen analog, $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)\text{H}]\}\text{PF}_6$ (XIII).²⁴ In going from a dithiocarbene complex (Ia,b, IIIc) to a dioxocarbene (IX, Xa) or a thio-oxo carbene complex (IIIb), an increase in $\nu(\text{CO})$ and $\underline{k}(\text{CO})$ is observed. In accordance with this trend, the $\underline{k}(\text{CO})$ value of XIII is 0.30 $\text{mdyn}/\text{\AA}$ higher than that of XII. Like complex XII, complex XIII is also moisture sensitive,²⁴ but hydrolyzes much slower than does XII. This difference in rate of hydrolysis may be due to the relatively poor leaving group characteristics of the alkoxy group in nucleophilic substitution reactions.²⁵

Spectroscopic analysis The IR, ^1H -NMR, and ^{13}C -NMR spectra of the complexes prepared herein and those discussed below are presented in Tables I, II, and III, respectively. All $\nu(\text{CO})$ force constants, $\underline{k}(\text{CO})$, are calculated by the method of Cotton and Kraihanzel.²²

Previous reports have shown that a linear correlation exists between $\underline{k}(\text{CO})$ and the ^{13}C -NMR chemical shift of the CO ligands, $\delta(\text{CO})$, for $\text{Cp}(\text{CO})_2\text{FeX}^{26}$ and $\text{Cp}(\text{CO})_2\text{FeL}^{+27}$

derivatives; $\delta(\text{CO})$ moves to lower field as M-CO π -backbonding increases.⁴ No such correlation exists among the various $\text{Cp}(\text{CO})_2\text{Fe}[\text{carbene}]^+$ complexes. As a group, however, these complexes come reasonably close to fitting the previously observed correlation,^{26,27} but the CO ligands are all slightly (0.2-2.5 ppm) more shielded in the ^{13}C -NMR spectra than would be predicted from their $\underline{k}(\text{CO})$ values. The correlation between $\underline{k}(\text{CO})$ and $\delta(\text{CO})$ for $\text{Cp}(\text{CO})_2\text{FeX}$ derivatives fails when $X = \text{SiR}_3, \text{GeR}_3, \text{or SnR}_3$, and this was accounted for by possible π -bonding between Fe and the group IV ligands.²⁶ The lack of correlation between $\underline{k}(\text{CO})$ and $\delta(\text{CO})$ for the carbene complexes may also be a consequence of an Fe-C(carbene) π -interaction. It is interesting to note that the diaminocarbene complexes, where Fe-C(carbene) π -bonding should be at a minimum due to the strong nitrogen π -donor ability,^{3,28-31} come the closest to fitting the previously observed correlation.^{26,27}

The ^{13}C -NMR chemical shift of the carbene carbon, $\delta(\text{carbene})$, has been shown to be more sensitive to changes in the electronic environment than $\delta(\text{CO})$ ⁷ and may be a measure of the degree of π -donation from the heteroatomic substituents to the carbene carbon. For complexes

of the type, $(\text{CO})_5\text{CrC}(\text{YR})\text{R}^1$, a large upfield shift was noted in $\delta(\text{carbene})$ on changing the YR group from an alkoxy to the better π -donating NR_2 group.⁷ It was also found that $\delta(\text{carbene})$ moves to higher field with increasing π -donor ability of the aryl carbene substituent for a series of $(\text{CO})_5\text{MC}(\text{p-C}_6\text{H}_4\text{X})\text{OCH}_3$ ($\text{M} = \text{Cr}, \text{W}$) complexes.³² These trends seem logical considering that the low field resonance of the carbene carbon is due, in part, to its presumed electron deficient nature.^{6,7,29} Thus, relieving this electron deficiency by π -donation from the carbene substituents could cause an upfield shift in $\delta(\text{carbene})$.

However, no correlation between $\underline{k}(\text{CO})$ and $\delta(\text{carbene})$ exists for the $\text{Cp}(\text{CO})_2\text{Fe}[\text{carbene}]^+$ complexes. In fact, the use of $\underline{k}(\text{CO})$ and $\delta(\text{carbene})$ data by themselves leads to very different conclusions concerning the π -donation ability of the various heteroatomic carbene substituents. Thus, it appears that $\underline{k}(\text{CO})$ is the most reliable parameter of the bonding in these $\text{Cp}(\text{CO})_2\text{Fe}[\text{carbene}]^+$ complexes.

The $\underline{k}(\text{CO})$ values for the iron carbene complexes are probably related to the π -acceptor/ σ -donor ratio of the carbene ligand which is, in turn, inversely related to the π -donor ability of the carbene substituents. Therefore, higher $\underline{k}(\text{CO})$ values are indicative of a lower degree of carbene π -stabilization by the heteroatomic substituents.

The $\underline{k}(\text{CO})$ values of IIIb-d indicate that Se is slightly better than S and both are better than O in π -donor ability, while the $\delta(\text{carbene})$ values for these complexes and for $(\text{CO})_5\text{WC}(\text{YCH}_3)\text{CH}_3$ (Y = O, 332.9; S, 332.5; Se, 355.5 ppm)⁸ suggest the opposite trend. Infrared data for complexes Ia, Ib, IX, Xa, Xb, and $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{SCH}_2\text{CH}_3]\}\text{PF}_6$ support the trend that S has a greater π -donation ability than O. The $\underline{k}(\text{CO})$ values for the dioxocarbene complexes are all higher than the corresponding dithiocarbene complexes while the thio-oxocarbene complexes have intermediate $\underline{k}(\text{CO})$ values.

The ambient temperature ^1H -NMR spectra of IIIc,d show broad singlets for the Ph and Cp groups while IIIb shows a well resolved multiplet for the Ph group and a sharp singlet for the Cp ligand. In addition, $\delta(\text{carbene})$ cannot be observed for IIIId and is quite broad for IIIc in the ambient temperature ^{13}C -NMR spectra while $\delta(\text{carbene})$ for IIIb is sharp. The $\delta(\text{carbene})$ resonances for IIIc,d become sharp singlets when the ^{13}C -NMR spectra are obtained at elevated temperatures (73° C). This behavior may be due to syn-anti isomerization by restricted rotation about the C(carbene)-YPh (Y = S, Se) bonds with coalescence

occurring near the NMR probe temperature ($\sim 30^\circ \text{C}$). The increased barrier for such a rotation in IIIc,d as compared to Ia (coalescence at -2.5°C)³ is likely due to the steric bulk of the Ph group and/or slightly better π -donation from the PhY groups,³³ compared to the CH_3Y carbene substituents, as indicated by the $\underline{k}(\text{CO})$ values of Ia and IIIa-c. The fact that IIIB does not show this behavior at ambient temperatures may be a consequence of the weaker $\text{O}\rightarrow\text{C}(\text{carbene})$ π -donation.

Comparison of the $\underline{k}(\text{CO})$ values for complexes VIIIa,b and their diamino analogs, $\{\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CNH}(\text{CH}_2)_n\text{NH}}]\}\text{PF}_6$ ($n = 2, 3$), indicate a significantly stronger π -donation from nitrogen to the carbene carbon than from sulfur. For these complexes, $\delta(\text{CO})$ and $\delta(\text{carbene})$ follow the expected trends with $\delta(\text{CO})$ shifted to lower and $\delta(\text{carbene})$ to higher field for the diamino carbene complexes.

There is also a large difference in $\underline{k}(\text{CO})$ values between VIIIa and VIIIb which indicates a significantly poorer $\text{S}\rightarrow\text{C}(\text{carbene})$ π -donation in the five-membered ring carbene ligand of VIIIa. The same trend is seen in the $\underline{k}(\text{CO})$ values for the cyclic diaminocarbene complexes, although the difference between the five and six-membered ring carbene ligands appears to be smaller for these complexes.

Better π -donation from the heteroatoms to the carbene carbon in the six-membered ring complexes may be rationalized by comparing ring conformations in the five and six-membered ring carbene ligands (Figure 1). Models show that the ring strain introduced by the planarity of the carbene linkage (both heteroatoms and the carbene carbon are sp^2 hybridized) may be easily alleviated by the six-membered ring assuming a half-chair conformation (Figure 1a). This leaves the filled p_z orbitals of the heteroatoms coplanar with the p_z of the carbene carbon allowing for good π -overlap. In the five-membered ring, the strain may only be alleviated by a twisting of the ethylene linkage (Figure 1b). This would tend to force the filled p_z orbitals of the heteroatoms out of coplanarity with the p_z orbital of the carbene carbon and, thus, reduce the π -overlap of these orbitals.

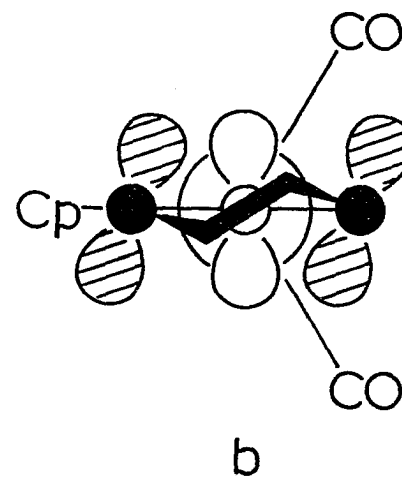
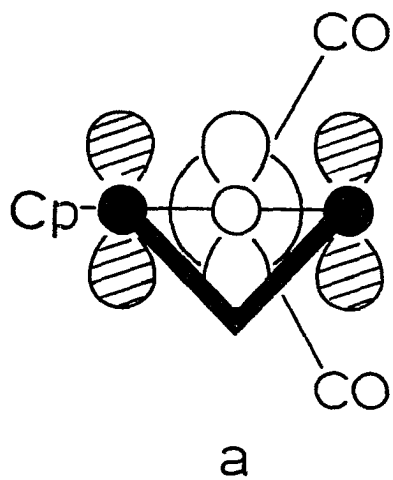


Figure 1. Newman-type projections down the Fe-C(carbene) bond axis for $\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CS}(\text{CH}_2)_3\text{S}}]^+$ (a) and $\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CS}(\text{CH}_2)_2\text{S}}]^+$ (b)

CONCLUSION

Infrared data indicate that the order of decreasing π -donation to the carbene carbon by the heteroatoms in $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ carbene complexes is $\text{N} \gg \text{Se} \geq \text{S} > \text{O}$ and that the differences between Se, S, and O are small. This compares well with previously reported trends.^{3,25,28,34-36} The large range of $\delta(\text{carbene})$ values (~ 130 ppm) and small range of $\delta(\text{CO})$ values (~ 4 ppm) observed for these complexes further confirms the higher sensitivity of $\delta(\text{carbene})$ to changes in the electronic environment.⁷ The lack of correlation with $\underline{k}(\text{CO})$ suggests that $\delta(\text{carbene})$ resonances are best used at this time to confirm the presence of a carbene ligand and not for discussions of bonding within these ligands. Exceptions to this may be when the π -donation differences are large, such as N vs. Se, S, or O, or when the atoms directly bound to the carbene carbon are not changed, such as in the series of complexes, $(\text{CO})_5\text{MC}(\underline{\text{p}}\text{-C}_6\text{H}_4\text{X})\text{OCH}_3$ ($\text{M} = \text{Cr}, \text{W}$).³² Some definite trends in $\delta(\text{carbene})$ are observed as the heteroatoms are changed for the $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ carbene complexes: the seleno-thiocarbene derivative resonates at approximately 320 ppm; dithio and thio-oxocarbene complexes between 280 and 310 ppm; dioxocarbene

complexes at approximately 250 ppm; and diaminocarbene derivatives between 190 and 200 ppm. It is also apparent that ring strain and conformation play an important role in π -stabilization of cyclic carbene ligands.

EXPERIMENTAL SECTION

General information Reagent grade chemicals were used without further purification; $\text{Cp}(\text{CO})_2\text{FeC}(=\text{S})\text{SCH}_3$,⁹ $\text{Cp}(\text{CO})_2\text{FeC}(=\text{S})\text{OCH}_3$,¹² $\{\text{Cp}(\text{CO})_2\text{Fe}(\text{CS})\}\text{CF}_3\text{SO}_3$,¹³ $\{\text{CpFe}(\text{CO})_3\}\text{CF}_3\text{SO}_3$,¹³ $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$ (Ia),³ and $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)_2]\}\text{PF}_6$ (IX)¹³ were prepared as reported previously. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketal under N_2 immediately prior to use. Infrared spectra were recorded on a Perkin-Elmer 281 spectrophotometer. Routine ^1H -NMR spectra were recorded on a Perkin-Elmer Hitachi R-20B spectrometer and ^{13}C -NMR spectra were recorded on a Jeol FX-90Q spectrometer; $\text{Cr}(\text{acac})_3$ (~ 0.1 M) was added to the ^{13}C samples to reduce data collection time.³⁷ Tetramethylsilane (TMS) was employed as the internal standard for all NMR spectra.

Preparation of the complexes. $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{CF}_3\text{SO}_3$ (Ib) A 50 mL solution of CH_2Cl_2 containing $\text{Cp}(\text{CO})_2\text{FeC}(=\text{S})\text{SCH}_3$ (2.50 g, 9.32 mmol) and $\text{CH}_3\text{SO}_3\text{CF}_3$ (1.05 mL, 9.32 mmol) was allowed to stir for 1 h. The brownish solution was then evaporated to dryness and the resulting residue was washed with Et_2O . Crystallization of this residue from CH_2Cl_2 with Et_2O at -20°C afforded

3.5 g (87%) of Ib as large, dark yellow crystals. Mp 76-78° C. Anal. calcd. for $C_{11}H_{11}F_3FeO_5S_3$: C, 30.57; H, 2.57. Found: C, 30.80; H, 2.61.

$Cp(CO)_2FeC(=S)SePh$ (IIId) An N_2 atmosphere was required for this preparation. A solution of 25 mL of THF containing PhSeSePh (0.16 g, 0.51 mmol) was stirred with 5 mL of Na/Hg (0.050 g Na, 2.2 mmol) until the yellow color of the PhSeSePh disappeared (~15 min). The amalgam was removed and $\{Cp(CO)_2Fe(CS)\}CF_3SO_3$ (0.37 g, 1.0 mmol) was added to the cloudy $PhSe^-/THF$ solution. A deep red-brown color developed rapidly. This solution was stirred for 10 min and was then evaporated to a red-brown oil. The N_2 atmosphere was not necessary beyond this point. The oil was extracted with CS_2 until the extracts were colorless (~30 mL). These extracts were filtered and evaporated to give a red-orange solid which was crystallized from a minimum amount of hexanes by cooling the sample to -20° C. Large red crystals of IIId (0.21 g, 56%) were obtained. Mp 76-79° C. Anal. calcd. for $C_{14}H_{10}FeO_2SSe$: C, 44.59; H, 2.67. Found: C, 44.68; H, 2.77.

$\{Cp(CO)_2Fe[C(SCH_3)OCH_3]\}PF_6$ (IIIa) A sample of $Cp(CO)_2FeC(=S)OCH_3$ (0.300 g, 1.19 mmol) was stirred with

$\text{CH}_3\text{SO}_3\text{F}$ (120 μL , 1.48 mmol) in 15 mL of CH_2Cl_2 for 30 min. The yellow-brown solution was then evaporated to a yellowish oil which was washed with Et_2O . This oil was dissolved in a minimum amount of acetone, placed on an anion-exchange column (Amberlite IRA-400, 35 X 1 cm) in the PF_6^- form, and eluted slowly with acetone. The yellow acetone fraction was collected and evaporated to dryness. The resulting yellow residue was crystallized from CH_2Cl_2 with Et_2O at -20°C to give 0.20 g (41%) of IIIa as golden yellow crystals. Mp 105°C (conversion to PF_6^- salt of V). Anal. calcd. for $\text{C}_{10}\text{H}_{11}\text{F}_6\text{FeO}_3\text{PS}$: C, 29.15; H, 2.69. Found: C, 29.21; H, 2.72.

$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{OPh}]\}\text{PF}_6^-$ (IIIb) An N_2 atmosphere was required in this preparation. Phenol (0.060 g, 0.64 mmol) and NaH (50% mineral oil dispersion, 0.026 g, 0.54 mmol) were reacted in 40 mL of THF for 12 h. To this solution, $\{\text{Cp}(\text{CO})_2\text{Fe}(\text{CS})\}\text{CF}_3\text{SO}_3$ (0.20 g, 0.54 mmol) was added and the mixture was stirred for 1 h. The solution was then evaporated to a dark oil. The N_2 atmosphere was no longer required, and the oil was extracted with CS_2 until the extracts were colorless (~ 30 mL). After filtration, these extracts were evaporated to a dark oil. The oil was

dissolved in 20 mL of CH_2Cl_2 and was stirred with $\text{CH}_3\text{SO}_3\text{F}$ (50 μL , 0.62 mmol) for 1.5 h. The resulting dark solution was evaporated to an oil which was washed with Et_2O . This crude SO_3F^- salt was converted to its PF_6^- salt and crystallized by the method used for IIIa. The yield of IIIb, as clear yellow needles, was 0.11 g (43%). Mp 153-154° C. Anal. calcd. for $\text{C}_{15}\text{H}_{13}\text{F}_6\text{FeO}_3\text{PS}$: C, 38.00; H, 2.76. Found: C, 37.64; H, 2.75.

$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{SPh}]\}\text{PF}_6$ (IIIc) This complex was prepared in the same manner as IIIb. Thus, PhSH (60 μL , 0.58 mmol) and $\{\text{Cp}(\text{CO})_2\text{Fe}(\text{CS})\}\text{CF}_3\text{SO}_3$ (0.20 g, 0.54 mmol) yielded 0.20 g (75%) of IIIc as bright yellow crystals. Mp 155-157° C. Anal. calcd. for $\text{C}_{15}\text{H}_{13}\text{F}_6\text{FeO}_2\text{PS}_2$: C, 36.75; H, 2.67. Found: C, 34.75; H, 2.68.

$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{SePh}]\}\text{PF}_6$ (IIId) A solution of 10 mL of CH_2Cl_2 containing IIId (0.095 g, 0.25 mmol) and $\text{CH}_3\text{SO}_3\text{F}$ (25 μL , 0.31 mmol) was stirred for 1.5 h. The resulting orange solution was then evaporated to dryness, and the residue was converted to the PF_6^- salt by the method used for IIIa. Small yellow crystals of IIId (0.10 g, 74%) were obtained. Mp 142-145° C. Anal. calcd. for $\text{C}_{15}\text{H}_{13}\text{F}_6\text{FeO}_2\text{PSSe}$: C, 33.54; H, 2.44. Found: C, 31.23; H, 2.42.

$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{OCH}_3]\}\text{CF}_3\text{SO}_3$ (IV) This complex was prepared by the method used for Ib. Starting with 0.271 g (1.08 mmol) of $\text{Cp}(\text{CO})_2\text{FeC}(=\text{S})\text{OCH}_3$ and 125 μL (1.10 mmol) of $\text{CH}_3\text{SO}_3\text{CF}_3$ in 20 mL of CH_2Cl_2 , 0.41 g (92%) of IV was isolated as yellow crystals. Mp 92-95° C (conversion to V). Anal. calcd. for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{FeO}_6\text{S}_2$: C, 31.75; H, 2.66. Found: C, 31.55; H, 2.61.

$\{[\text{Cp}(\text{CO})_2\text{Fe}]_2\text{SCH}_3\}\text{CF}_3\text{SO}_3$ (V). From $\text{Cp}(\text{CO})_2\text{FeSCH}_3$ and $\{\text{Cp}(\text{CO})_2\text{Fe}(\text{acetone})\}\text{CF}_3\text{SO}_3$ This preparation required an N_2 atmosphere. A 40 mL solution of acetone (dried over CaSO_4 and N_2 saturated) containing $[\text{CpFe}(\text{CO})_2]_2$ (0.416 g, 1.18 mmol) and AgSO_3CF_3 (0.604 g, 2.35 mmol) was stirred for 1 h. The maroon color of $[\text{CpFe}(\text{CO})_2]_2$ was replaced by a red-orange color, and metallic silver was deposited as a silver mirror. This solution was then filtered through Celite to give a clear red solution. To this stirred solution, 20 mL of acetone (dried over CaSO_4 and N_2 saturated) containing crude $\text{Cp}(\text{CO})_2\text{FeSCH}_3$ (generated from $\text{Cp}(\text{CO})_2\text{FeCl}$ (0.500 g, 2.35 mmol) and a slight excess of $\text{CH}_3\text{S}^{-17}$) was added dropwise over a 15 min period. The reaction was allowed to stir for an additional 30 min and was then evaporated to a red oil. The oil was washed

with Et₂O and was crystallized from CH₂Cl₂ with Et₂O at -20° C to give 0.43 g (33%) of V as dark red needles. Mp 110-112° C. Anal. calcd. for C₁₆H₁₃F₃Fe₂O₇S₂: C, 34.94; H, 2.38. Found: C, 34.58; H, 2.37. From IV
 A sample of IV (0.050 g, 0.12 mmol) was placed in a sealed, evacuated tube and the tube was placed in an oil bath at 115° C for 5 min. The yellow crystals rapidly changed to a red oil. After cooling the red oil to room temperature, it was fractionally crystallized from CH₂Cl₂ with Et₂O at -20° C to afford 5.0 mg (12%) of {CpFe(CO)₃}⁻CF₃SO₃ as yellow crystals and 0.020 g (61%) of V as red needles. Anal. calcd. for C₁₆H₁₃F₃Fe₂O₇S₂: C, 34.94; H, 2.38. Found: C, 34.80; H, 2.37.

{Cp(CO)₂Fe[S(CH₃)Ph]}PF₆ (VIIa) An N₂ atmosphere was required for this synthesis. Diphenyldisulfide (0.031 g, 0.14 mmol) and LiAlH₄ (0.012 g, 0.32 mmol) were stirred together in 30 mL of THF until gas evolution ceased (~5 h). To this PhS⁻/THF solution, {CpFe(CO)₃}CF₃SO₃ (0.10 g, 0.28 mmol) was added and the mixture was stirred for an additional 1.5 h. Vigorous gas evolution was noted during this time. The reaction mixture was then filtered and evaporated to a red-brown oil. The use of the N₂ atmosphere

was discontinued, and the oil was extracted with Et₂O until the extracts were colorless (~40 mL). These extracts were then filtered and evaporated to an oil which was dissolved in 10 mL of CH₂Cl₂. This CH₂Cl₂ solution was stirred with CH₃SO₃CF₃ (35 μL, 0.31 mmol) for 2 h. The resulting dark yellow solution was then evaporated to a yellow-brown oil which could not be made to crystallize. The oil was then dissolved in 15 mL of warm H₂O and 15 mL of a saturated NH₄PF₆(aq) solution was added. A yellow powder precipitated immediately and was crystallized from CH₂Cl₂ with Et₂O at -20° C to give VIIa (0.030 g, 24%) as bright yellow flakes. Mp 145-148° C. Anal. calcd. for C₁₄H₁₃F₆FeO₂PS: C, 37.69; H, 2.94. Found: C, 38.01; H, 2.98.

{Cp(CO)₂Fe[Se(CH₃)Ph]}PF₆ (VIIb) This complex was prepared by the method used for VIIa. Thus, PhSeSePh (0.045 g, 0.14 mmol) and the same quantities of other reagents as used for VIIa produced 0.047 g (34%) of VIIb as small yellow crystals. Mp 141-143° C. Anal. calcd. for C₁₄H₁₃F₆FeO₂PSe: C, 34.11; H, 2.66. Found: C, 34.11; H, 2.64.

{Cp(CO)₂Fe[CS(CH₂)₂S]}PF₆ (VIIIa) A solution consisting of 5 mL of acetone (dried over CaSO₄),

1,2-ethanedithiol (3.00 mL, 35.8 mmol), and Ia (1.00 g, 2.34 mmol) was refluxed under an N₂ atmosphere for 3 h. The resulting orange solution was evaporated to an oil (~3 mL). The addition of 40 mL of Et₂O to this oil followed by cooling the solution to -20° C caused the formation of a yellow precipitate. This precipitate was crystallized from CH₂Cl₂ with Et₂O at -20° C to afford 0.78 g (78%) of VIIIa as dark yellow crystals. Mp 109-110° C. Anal. calcd. for C₁₀H₉F₆FeO₂PS₂: C, 28.19; H, 2.13. Found: C, 28.48; H, 2.21.

{Cp(CO)₂Fe[CS(CH₂)₃S]}PF₆ (VIIIb) A 10 mL solution of CH₂Cl₂ (dried over CaSO₄) containing Ia (1.00 g, 2.34 mmol) and 1,3-propanedithiol (3.00 mL, 29.9 mmol) was refluxed under an N₂ atmosphere for 3.5 h. The resulting black solution was evaporated to a yellow-green oil (~3 mL). Diethyl ether (40 mL) was added to the oil, and a greenish-yellow precipitate formed when the solution was cooled to -20° C. Crystallization of this precipitate from CH₂Cl₂, after treatment with decolorizing carbon, with Et₂O at -20° C yielded 0.62 g (60%) of VIIIb as yellow needles. Mp 166-168° C. Anal. calcd. for C₁₁H₁₁F₆FeO₂PS₂: C, 30.02; H, 2.52. Found: C, 30.34; H, 2.65.

$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)_2]\}\text{CF}_3\text{SO}_3$ (Xa) A sample of IV (0.102 g, 0.245 mmol) was dissolved in 10 mL of CH_3OH (dried over CaSO_4), and the solution was stirred for 30 min. The residue obtained after evaporation of this solution was crystallized from CH_2Cl_2 with Et_2O at -20°C , and 0.087 g (89%) of Xa was obtained as small, pale yellow crystals. Mp $128\text{--}131^\circ\text{C}$. Anal. calcd. for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{FeO}_7\text{S}$: C, 33.02; H, 2.77. Found: C, 33.07; H, 2.77.

$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)\text{OCH}_2\text{CH}_3]\}\text{CF}_3\text{SO}_3$ (Xb) A 0.094 g (0.23 mmol) sample of IV was dissolved in 10 mL of $\text{CH}_3\text{CH}_2\text{OH}$ (dried over CaSO_4), and the solution was stirred for 1 h. The yellow oil obtained on evaporation of this solution was crystallized from CH_2Cl_2 with Et_2O at -20°C to give 0.053 g (57%) of Xb as yellow needles. Mp $66\text{--}68^\circ\text{C}$. Anal. calcd. for $\text{C}_{12}\text{H}_{13}\text{F}_3\text{FeO}_7\text{S}$: C, 34.80; H, 3.16. Found: C, 33.89; H, 3.04.

$\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2\text{H}]$ (XI) This procedure required an N_2 atmosphere. A solution of 100 mL of THF containing Ia (0.10 g, 0.23 mmol) and LiAlH_4 (0.018 g, 0.47 mmol) was stirred for 20 min. This solution was then evaporated to a yellow oil which was extracted with hexanes until the extracts were colorless (~ 20 mL). These extracts were

filtered and reduced in volume to 2 mL by evaporation under an N₂ stream. Cooling this hexanes solution to -20° C afforded 0.053 g (91%) of XI as small, bright yellow crystals. Mp 36-38° C. Anal. calcd. for C₁₀H₁₂FeO₂S₂: C, 42.27; H, 4.26. Found: C, 42.29; H, 4.28.

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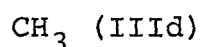
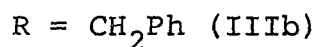
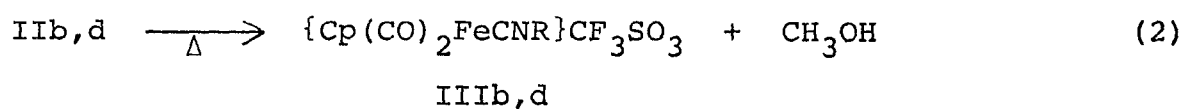
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SECTION IV. REACTIONS OF $\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ CARBENE
COMPLEXES, WHERE X AND Y ARE O, S, Se, AND/OR
NR, WITH AMINES

INTRODUCTION

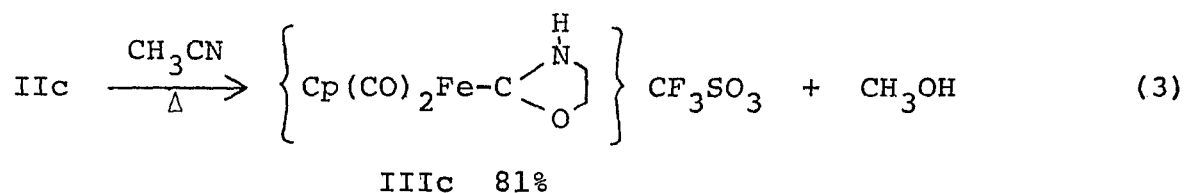
Transition metal carbene complexes are of interest as they may be reactive intermediates in several catalytic¹⁻³ and stoichiometric³⁻⁶ organic reactions. Although there have been numerous reports concerning the preparation of carbene complexes,³⁻⁷ few systematic studies on the reactivity of carbene ligands with two heteroatomic substituents have been reported.⁸ The availability of a variety of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) carbene complexes where X and Y are O, S, Se and/or NR,^{8,9} has allowed us to compare the electronic environment of the carbene carbon in these complexes by the use of IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy. We now report on the effect of these various substituents on the electrophilic reactivity of the carbene ligand towards amines. The electronic effects of the heteroatomic carbene substituents are studied further by spectroscopic analysis of the new carbene complexes reported herein.

Intramolecular extrusion of CH_3OH may be seen when IIb-d are exposed to elevated temperatures. Partial conversions of IIb,d to the corresponding isocyanide complexes, as identified by their IR spectra,⁸ occur when the complexes are heated in the solid state to temperatures (150-165° C) well above their melting points for a few minutes (eq. 2).



Evolution of gas, presumably methanol, is evidenced by slow and continuous bubbling of the melts. Refluxing IIb in CH_3CN , however, produces no isocyanide complex; after 35 h, only starting material is recovered. Complex IIc loses methanol under milder conditions than IIb,d.

Refluxing IIc in acetonitrile for 12 h produces the cyclic amino-oxocarbene complex which had been reported earlier as a PF_6^- salt⁸ (eq. 3).

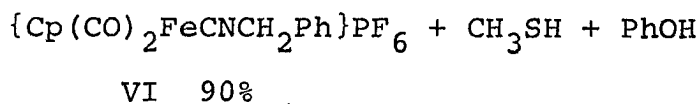
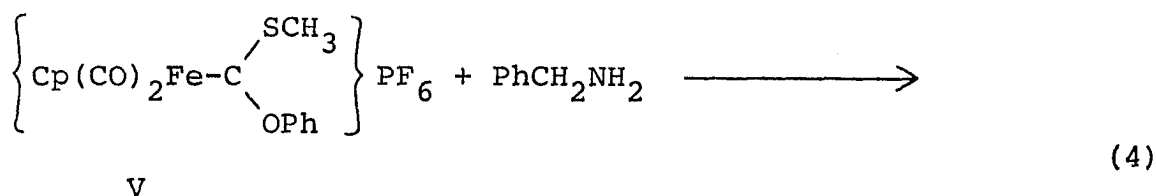


Reactions of $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)_2]\}\text{PF}_6$ (IV) with amines

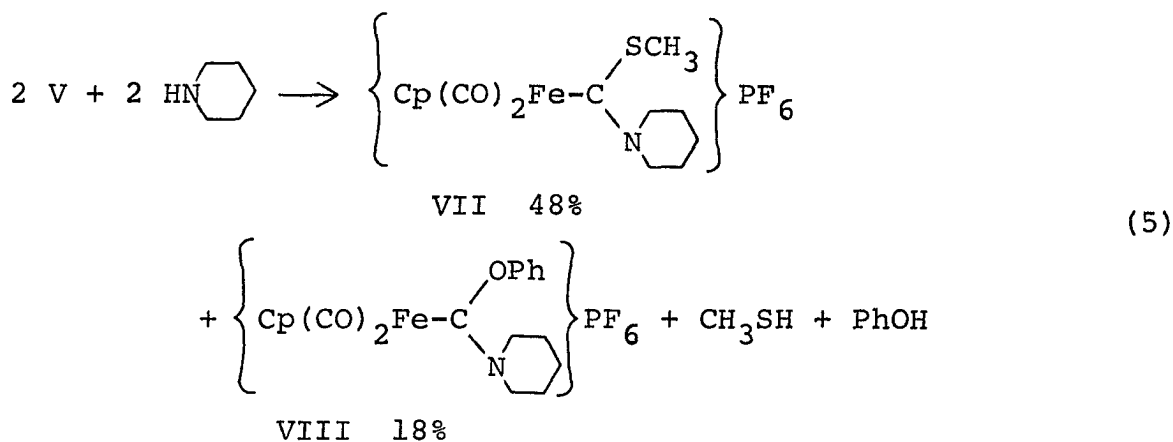
Complex IV seems to react with amines in a manner similar to that of I. However, the yields of amino-oxocarbene products are much lower (less than 20%) and several other uncharacterized products are observed. For example, the reaction of IV with benzylamine produces a 17% yield of the PF_6^- salt of IIb and a large quantity of a complex mixture of neutral organometallic species which includes $[\text{CpFe}(\text{CO})_2]_2$ and $\text{Cp}(\text{CO})_2\text{FeC}(=\text{O})\text{OCH}_3$.¹⁰ The reaction of IV with piperidine forms only trace amounts of the PF_6^- salt of IIc and the same mixture of neutral species. Reacting IV with $(\text{CH}_3)_3\text{N}$ also produces this complex mixture of neutral species. The IR spectra of all of these reaction solutions show two strong bands, one at 2023-2035 cm^{-1} and the other at 1964-1980 cm^{-1} , as the major absorptions, but upon evaporation the complex mixture of products results.

Reactions of $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{OPh}]\}\text{PF}_6$ (V) with amines

Complex V behaves rather differently than I towards amines. With benzylamine at room temperature, complex V yields the isocyanide complex by displacement of both carbene substituents (eq. 4).

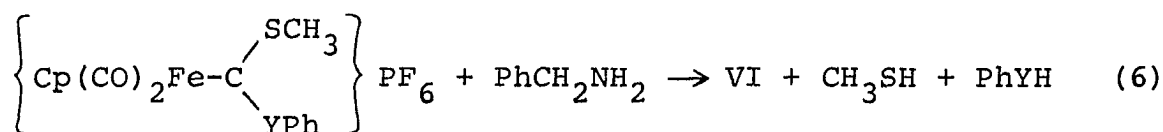


This reaction is similar to that of $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$ with primary amines to give isocyanide complexes.⁸ With piperidine, a mixture of carbene complexes is obtained (eq. 5).



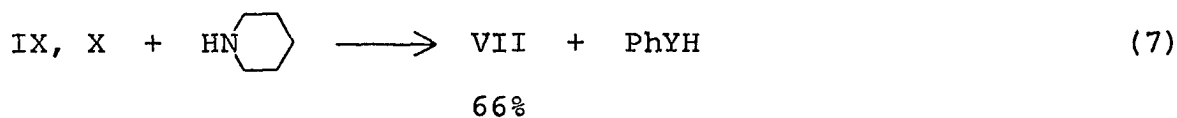
Since this mixture has not been separated, the yields are based on the ^1H -NMR spectrum of the mixture. Complex VII is identified from its previously reported spectra.⁸

Reactions of $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{SPh}]\}\text{PF}_6$ (IX) and $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{SePh}]\}\text{PF}_6$ (X) with amines Complexes IX and X show almost identical behavior towards amines and yield the same products as found in the reactions of $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$.⁸ The reactions of IX and X with benzylamine produce the isocyanide complex, VI, (eq. 6) and with piperidine, the amino-thiocarbene complex, VII, is formed (eq. 7).



IX, X

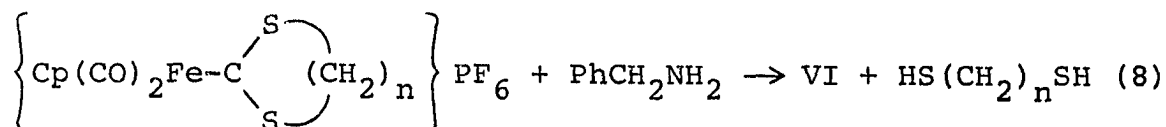
56-58%



Y = S (IX), Se (X)

Both IX and X give VII in identical yields, and there is no evidence for nucleophilic substitution of the CH_3S group by piperidine.

Reactions of $\{\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CS}(\text{CH}_2)_n\text{S}}]\}\text{PF}_6$ ($n = 2$, XIa; $n = 3$, XIb) with amines Both of these complexes react in the same manner as $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$ with benzylamine⁸ to give the isocyanide derivative, VI (eq. 8).

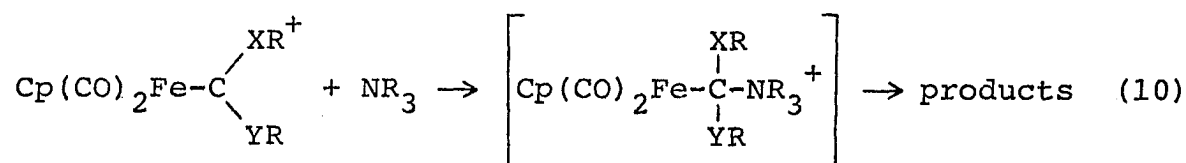


n = 2 (XIa)	85% (from XIa)
3 (XIb)	32% (from XIb)

Complex XIa reacts cleanly to give VI in high yield, while XIb gives a cloudy reaction solution, a low yield of VI, and a large amount of an unstable, neutral species with bands at 2018(s) and 1967(s) cm^{-1} in its IR(CH_2Cl_2) spectrum and a Cp resonance at τ 5.22 in its $^1\text{H-NMR}(\text{CS}_2)$ spectrum. Like $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$, complex XIa reacts with NH_3 to produce the neutral cyano complex, $\text{Cp}(\text{CO})_2\text{FeCN}$.⁸ In contrast to $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$,⁸ no amino-thiocarbene complexes are produced in the reactions of XIa,b with secondary amines. The reactions of XIa with dimethylamine and the reaction of XIb with piperidine both produce new species with $\nu(\text{CO})$ at 2027(s) and 1978(s) cm^{-1} in CH_2Cl_2 ; these species are not characterized further as they decompose to $[\text{CpFe}(\text{CO})_2]_2$ upon attempted isolation. Similar results are obtained in the reaction of XIa and trimethylamine; a new species, with $\nu(\text{CO})$ at 2019(s) and 1968(s) in CH_2Cl_2 forms but decomposes readily to $[\text{CpFe}(\text{CO})_2]_2$.

DISCUSSION

Mechanism The results reported here support the formation of a transitory transition metal-ylide complex as suggested earlier for the reactions of $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$ with amines.¹⁴ The proposed first step of the reaction between the carbene complex, $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ (X, Y = O, S, Se), and an amine is nucleophilic attack at the carbene carbon to form an unstable ylide complex which reacts further to give the observed products (eq. 10).



In the ylide intermediate, the originally sp^2 -hybridized carbene carbon becomes sp^3 -hybridized, and the positive charge is transferred to the nitrogen atom. Support for such an ylide intermediate may be found in the isolation of neutral ylide complexes from the reactions of $(\text{CO})_5\text{M}[\text{carbene}]$ (M = Cr, W) complexes with certain phosphines and tertiary amines.^{15,16} A similar, but more complex, mechanism has also been proposed for the reaction of $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{Ph}$ with primary amines to give aminocarbene complexes, $(\text{CO})_5\text{CrC}(\text{NHR})\text{Ph}$.¹⁷

The ability of a $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ carbene complex to form an ylide intermediate when reacted with amines should be influenced by the amount of heteroatom π -donation into the carbene carbon atom. Thus, in complex VII, the nitrogen atom is sufficiently π -donating⁹ to reduce the electrophilicity of the carbene carbon to the point that amine attack at the carbene carbon does not occur, but rather reaction takes place at a CO ligand to reversibly form carbamoyl complexes (eq. 9).¹¹⁻¹³

The reactivity of the ylide intermediate seems to be controlled largely by the relative leaving group abilities of the carbene substituents, RX^- and RY^- . Although the leaving groups are considered to be anions, the heteroatoms could be protonated before the groups dissociate. In the absence of mechanistic studies, little can be said about the details of the mechanisms of these reactions. The pK_a values of $\text{PhSH}(6.50)$,¹⁸ $\text{PhOH}(9.99)$,¹⁹ $\text{CH}_3\text{SH}(10.3)$,¹⁸ and $\text{CH}_3\text{OH}(15.5)$ ¹⁹ suggest that the order of decreasing leaving group ability of the corresponding anions should be $\text{PhS}^- > \text{PhO}^- > \text{CH}_3\text{S}^- > \text{CH}_3\text{O}^-$. Our results agree with this trend. The reactions of I, V, IX, and X with piperidine (eq. 1, 5, and 7) indicate the order of

decreasing leaving group ability for RX^- and RY^- in the $Cp(CO)_2Fe[C(XR)YR]^+$ carbene complexes to be $PhSe^- \approx PhS^- > PhO^- > CH_3S^- > CH_3O^-$.

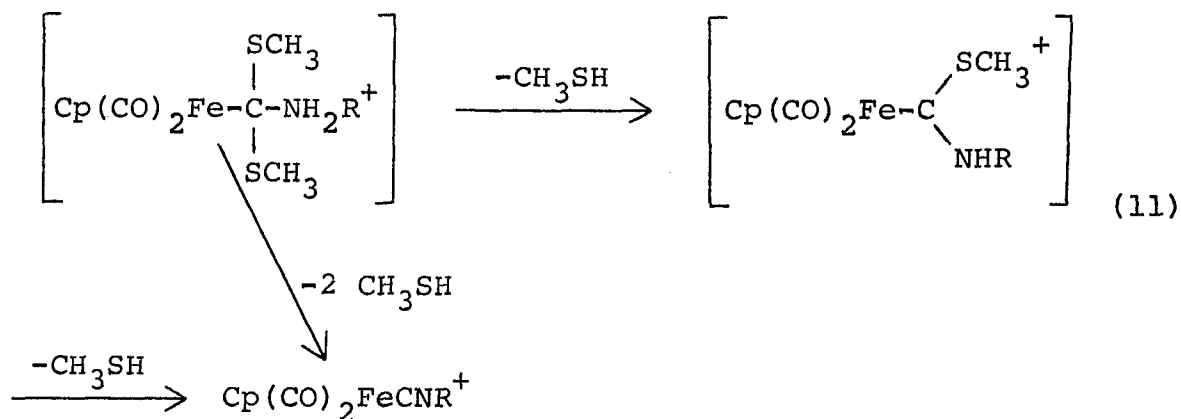
The product distributions observed in the reactions of the various $Cp(CO)_2Fe[C(XR)YR]^+$ carbene complexes with amines are quite logical considering this trend in leaving group ability. Complexes V (eq. 4), IX, X (eq. 6) and $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$,⁸ where both carbene substituents are good leaving groups ($PhSe^-$, PhS^- , PhO^- , or CH_3S^-), all react readily with primary amines to yield isocyanide complexes, $Cp(CO)_2FeCNR^+$. With piperidine, the better leaving groups of IX (PhS^-) and X ($PhSe^-$) (eq. 7) are replaced exclusively giving aminocarbene complexes. Complex V (eq. 5) reacts with piperidine to give a mixture of aminocarbene complexes resulting from the displacement of either substituent. The somewhat higher yield of the PhO^- -displaced product suggests that it is a slightly better leaving group than CH_3S^- . Complex I, in which only one of the carbene substituents (CH_3S^-) is a good leaving group, reacts readily with primary and secondary amines (eq. 1) to give amino-oxocarbene complexes by displacement of the good leaving

group. When both carbene substituents are poor leaving groups (CH_3O^-), as in IV, the reactions with primary and secondary amines give very low yields of amino-oxocarbene complexes and a variety of other species, possibly including unstable ylide intermediates (eq. 10).

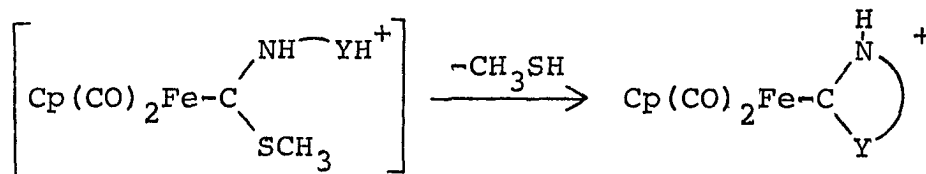
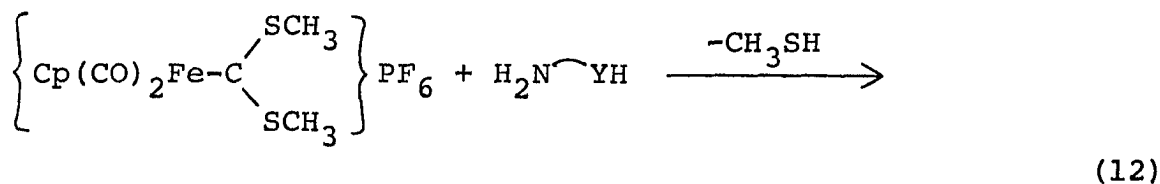
Based on the pK_a values¹⁸ of the parent dithiols of the cyclic dithiocarbene complexes XIa,b, $\{\text{Cp}(\text{CO})_2\text{Fe}-\overline{[\text{CS}(\text{CH}_2)_n\text{S}]}\}\text{PF}_6$ ($n = 2, 3$), these carbenes would be expected to react with amines much like $\{\text{Cp}(\text{CO})_2\text{Fe}-[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$.⁸ However, only the five-membered ring complex, XIa, (eq. 8) reacts well with benzylamine to give the corresponding isocyanide derivative, and neither complex forms amino-thiocarbene complexes when reacted with secondary amines. These results suggest that the dithio groups in the cyclic carbene complexes have a poorer leaving group ability than CH_3S^- . This is probably due to the stability of the five and six-membered ring systems. The higher yield of isocyanide complex from XIa than from XIb (eq. 8) may be a consequence of strain in the five-membered ring allowing for easier cleavage of a C-S bond.

The reactions of $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$ with primary amines to give isocyanide complexes⁸ could go

by either concerted loss of two CH_3SH molecules from the ylide intermediate, or by stepwise loss of CH_3SH via a transitory amino-thiocarbene complex (eq. 11).



The formation of amino-oxocarbene complexes in the reactions of I with primary amines (eq. 1) and their thermal conversion to isocyanide complexes (eq. 2), support the stepwise mechanism but do not exclude the concerted pathway. The relative ease with which IIc is converted to IIIc (eq. 3), as compared to the conversions of IIb,d to IIIb,d (eq. 2), indicates that the ring closure does not proceed through an isocyanide intermediate. These results suggest that the reactions of $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$ with diamines, amino alcohols, and amino thiols⁸ may also proceed through a carbene intermediate (eq. 12) rather than an isocyanide intermediate, $\text{Cp}(\text{CO})_2\text{FeCN}\text{---}\text{YH}^+$, where $\text{Y} = \text{O}, \text{S}, \text{NR}$ or NH .



Y = O, S, NR, or NH

Spectroscopic analysis Spectroscopic data for the new complexes are shown in Tables I-III, and the $\nu(\text{CO})$ force constants, $\underline{k}(\text{CO})$, discussed are calculated by the method of Cotton and Kraihanzel.²⁰

We have shown that no correlation exists between $\underline{k}(\text{CO})$ and the ^{13}C -NMR chemical shift of the CO ligands, $\delta(\text{CO})$, for $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ carbene complexes,⁹ and the amino-oxocarbene complexes reported herein show the same lack of correlation. In fact, their $\delta(\text{CO})$ values are fairly constant, varying over a 0.7 ppm range. As observed for other $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ carbene complexes,⁹ the amino-oxocarbene complexes, as a group, do fit reasonably well the reported correlation between $\underline{k}(\text{CO})$ and $\delta(\text{CO})$ for $\text{Cp}(\text{CO})_2\text{FeX}^{21}$ and $\text{Cp}(\text{CO})_2\text{FeL}^{+22}$ derivatives. According to that correlation, the amino-oxocarbene complexes

Table I. Infrared spectra of the complexes in CH₂Cl₂

Complex		$\nu(\text{CO}), \text{cm}^{-1}$ ^a	$\underline{k}(\text{CO})$ ^b , mdyn/Å ^o
{Cp(CO) ₂ Fe[C(OCH ₃)NH ₂]}CF ₃ SO ₃	IIa	2059, 2012	16.73
{Cp(CO) ₂ Fe[C(OCH ₃)NHCH ₂ Ph]}CF ₃ SO ₃	IIb	2058, 2006	16.68
{Cp(CO) ₂ Fe[C(OCH ₃)NH(CH ₂) ₂ OH]}CF ₃ SO ₃	IIc	2058, 2006	16.68
{Cp(CO) ₂ Fe[C(OCH ₃)NHCH ₃]}CF ₃ SO ₃	II d	2056, 2005	16.65
{Cp(CO) ₂ Fe[C(OCH ₃)N(CH ₃) ₂]}CF ₃ SO ₃	IIe	2048, 2001	16.55
{Cp(CO) ₂ Fe[C(OCH ₃)N(CH ₂) ₄ CH ₂]}CF ₃ SO ₃	II f	2048, 2002	16.56
{Cp(CO) ₂ Fe[CO(CH ₂) ₂ NH]}CF ₃ SO ₃	III c	2062, 2017	16.80
{Cp(CO) ₂ Fe[C(SCH ₃)N(CH ₂) ₄ CH ₂]}PF ₆	VII ^c	2047, 2002	16.55
{Cp(CO) ₂ Fe[C(OPh)N(CH ₂) ₄ CH ₂]}PF ₆	VIII ^d	2048, 2005	16.59

^aAll absorptions are strong.

^bReference 20.

^cReference 8.

^dIn mixture, predominantly VII.

Table II. ^1H -NMR spectra of the complexes in acetone- d_6 (τ)

Complex	NH^{a}	$\text{C}_5\text{H}_5^{\text{b}}$	OCH_3^{b}	Other Resonances
IIa	0.10, 0.82	4.54	5.92	
IIb	-0.23	4.46	5.73	2.64(s, C_6H_5), 5.37(d, CH_2) ^c
IIc	0.37	4.45	5.75	5.97(t, OH), 6.38(m, 2 CH_2)
IId	0.30	4.45	5.74	7.03(d, CH_3) ^d
IIe		4.36	5.75	6.38(s, NCH_3), 6.73(s, NCH_3)
IIf		4.36	5.75	5.87(t, NCH_2), 6.06(t, NCH_2), 8.28(m, 3 CH_2)
IIIc	--- ^e	4.45		5.20 and 6.11(AA'BB', 2 CH_2)
VII ^f		4.45		5.63(m, 2 NCH_2), 7.09(s, SCH_3), 8.13(m, 3 CH_2)
VIII ^g		4.59		2.63(m, C_6H_5), 5.68(m, 2 NCH_2), 8.13(m, 3 CH_2)

^aAll resonances are very broad singlets.

^bAll resonances are singlets.

^c $J_{\text{HNCH}} = 5.9 \text{ Hz.}$

^d $J_{\text{HNCH}} = 4.6 \text{ Hz.}$

^eNH resonance not observed.

^fReference 8, NCH_2 resonances have been re-assigned.

^gIn mixture, predominantly VII.

Table III. ^{13}C -NMR spectra of the complexes in acetone- d_6
(ppm)^a

Complex	C(carbene)	CO	C_5H_5	OCH_3	Other Resonances
IIa	227.2	211.9	87.9	59.5	
IIb	226.1	211.5	88.4	63.9	137.6, 129.4, 128.9, and 128.4(C_6H_5), 49.3(CH_2)
IIc	225.9	211.6	88.3	63.8	60.1(OCH_2), 48.5(NCH_2)
IId	224.6	211.5	88.1	63.7	31.8(NCH_3)
IIe	223.6	211.7	88.9	63.4	46.6(NCH_3), 40.9(NCH_3)
IIIf ^b	221.4	211.6	88.7	63.4	56.6(NCH_2), 50.1(NCH_2), 27.3, 26.7, and 24.7(3 CH_2)
IIIc	220.4	211.2	88.0		73.3(OCH_2), 46.2(NCH_2)
VII ^b	237.6	211.4	89.2		64.9(NCH_2), 59.5(NCH_2), 27.7, 27.3, and 24.0 (3 CH_2), 26.4(SCH_3)

^aAll resonances are singlets.

^bIn CD_3CN .

generally have $\delta(\text{CO})$ values which are slightly (0.0-1.5 ppm) more shielded than would be predicted from their $k(\text{CO})$ values.

In contrast to the wide variety of carbene complexes studied previously,⁹ the more limited group of amino-oxocarbene complexes displays a fairly good correlation between $k(\text{CO})$ and the ^{13}C -NMR chemical shift of the carbene carbon, $\delta(\text{carbene})$, (Figure 1). The amino-oxocarbene derivatives also have a much narrower range of $\delta(\text{carbene})$ values (~ 7 ppm) than found in the previous study (~ 130 ppm).⁹ Complex IIIc is the only exception to this correlation (Figure 1) and its anomalous behavior may be a consequence of the five-membered ring carbene system. We have previously postulated that the strain in five-membered ring carbene ligands may cause less effective heteroatom \rightarrow C(carbene) π -donation than would normally be expected.⁹

For the acyclic amino-oxocarbene complexes, there is also a fair correlation between $\delta(\text{carbene})$ and the solution basicities²³ of the amine substituents. The correlation of $\delta(\text{carbene})$ with the gas-phase basicities²⁴⁻²⁶ of the amine substituents is even better (Figure 2). A similar correlation has been observed for a series of $(\text{CO})_5\text{Cr}-(\text{NR}_2)\text{CH}_3$ ($\text{NR}_2 = \text{NHCH}_3, \text{NH}(i\text{-Pr}), \text{N}(\text{CH}_3)_2$) complexes.²⁷

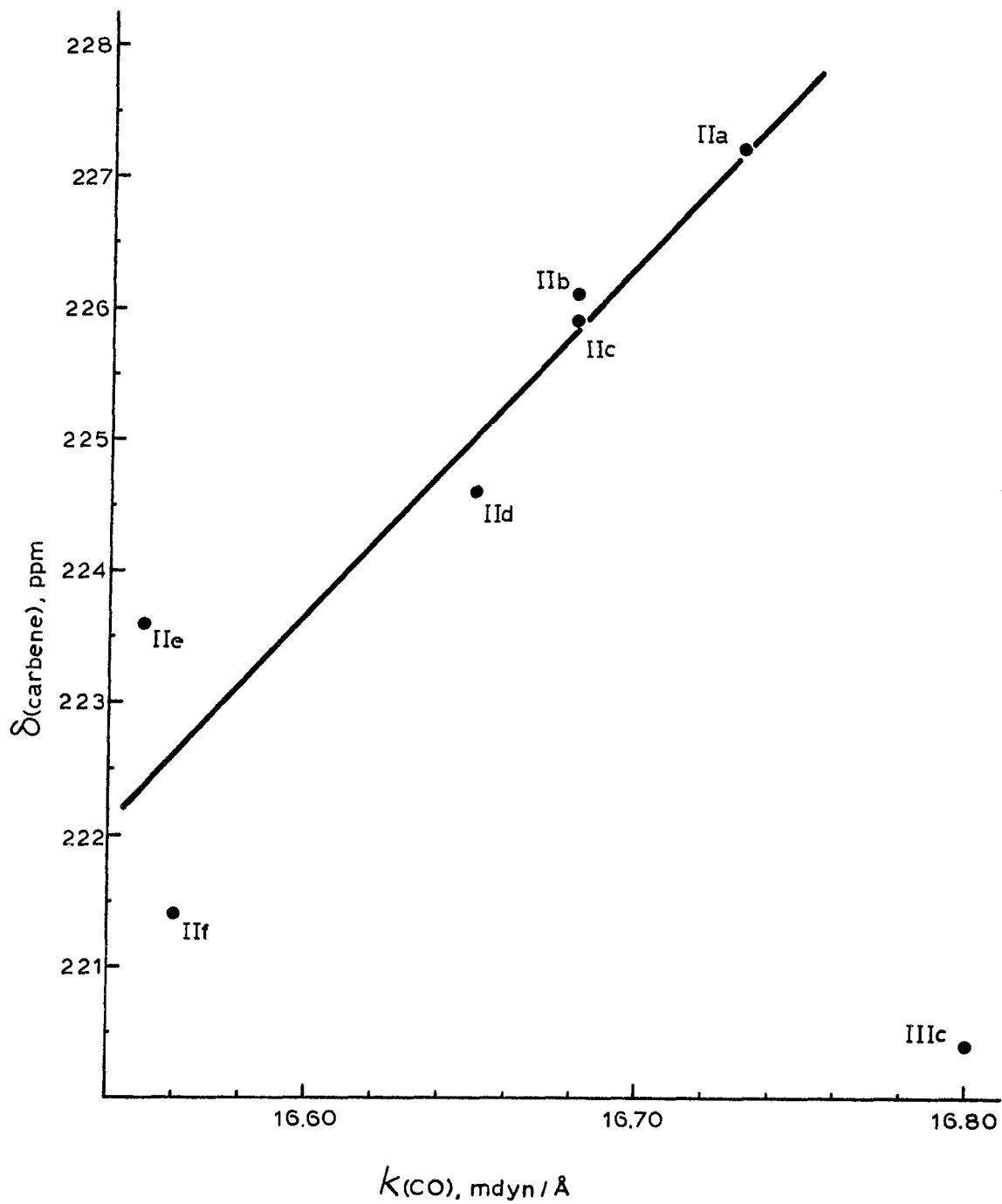


Figure 1. Plot of $\delta(\text{carbene})$ vs. $k(\text{CO})$ for the amino-oxocarbene complexes

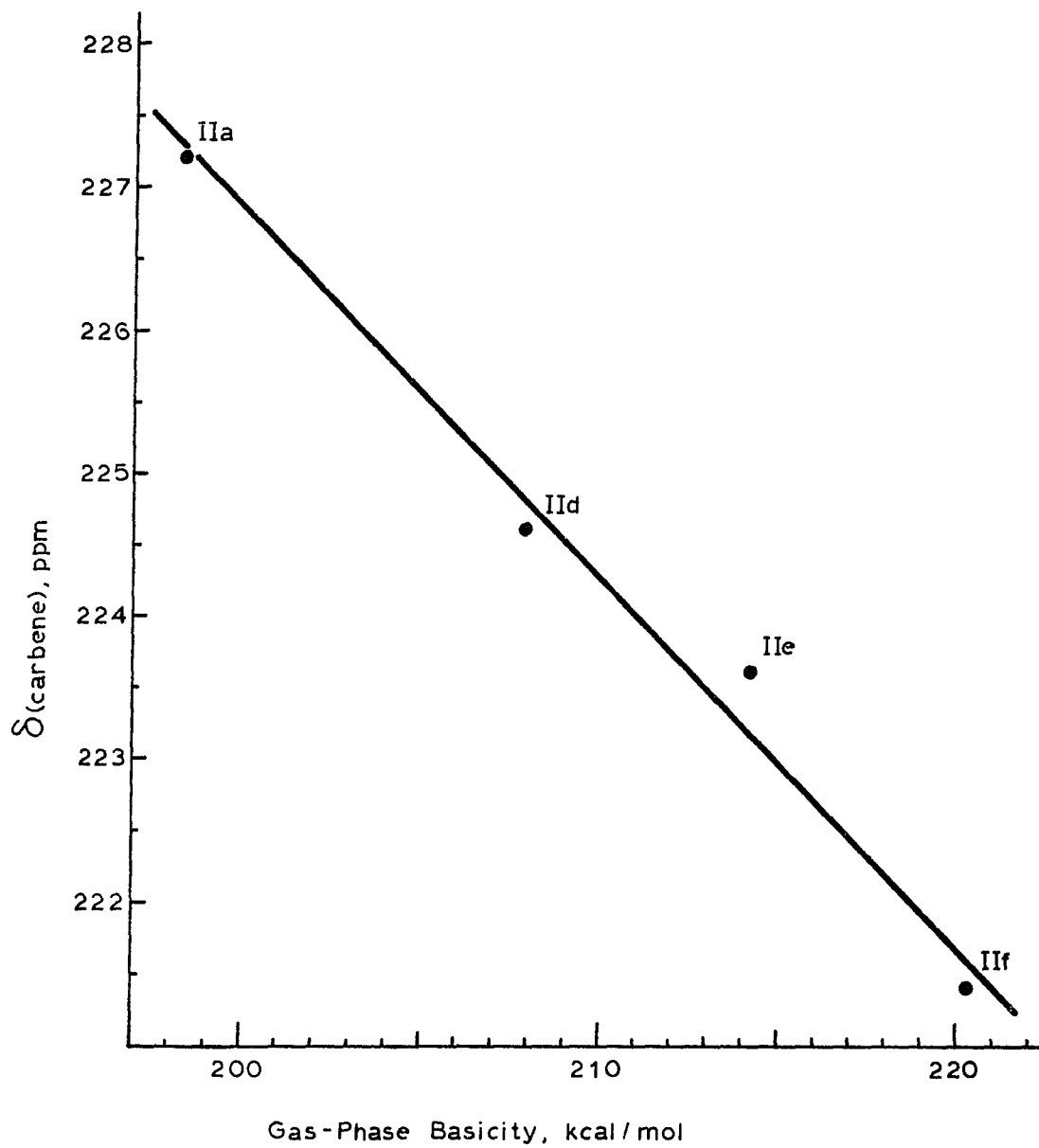


Figure 2. Plot of $\delta(\text{carbene})$ vs. the gas-phase basicity of the amine substituent for the amino-oxocarbene complexes

Thus, as the basicity of the amine substituent increases, the carbene carbon becomes more shielded due to increased N→C(carbene) π-donation. This trend is exactly that which would be predicted.⁹

The trends observed previously in δ(carbene) values for the Cp(CO)₂Fe[C(XR)YR]⁺ carbene complexes, where X and Y are O, S, Se, or NR, as X and Y were varied,⁹ may be extended by the observation that the carbene carbon resonates between 220 and 230 ppm in the ¹³C-NMR spectra of the amino-oxocarbene complexes.

The ¹H-NMR spectra of the new amino-oxocarbene complexes (Table II) are all quite similar. The amine hydrogens may be seen below τ1.00 as very broad resonances. Coupling of the amine protons with the amine alkyl substituents is seen in the splitting of the alkyl protons in IIb,d. That the doublets are not due to syn-anti isomerization of the carbene ligands is shown by the observation of singlets for the alkyl groups and the disappearance of the NH resonances upon addition of D₂O to the ¹H-NMR samples of IIb,d. Restricted rotation about the C(carbene)-N bonds is shown by separate signals for the α-amino substituents of IIe,f. One set of resonances for the amine substituents of IIb,d may be interpreted as indicating one preferred configuration about the N-C(carbene) bond.

EXPERIMENTAL SECTION

General information Reagent grade chemicals were used without further purification and $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{-OCH}_3]\}\text{CF}_3\text{SO}_3$ (I),⁹ $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)_2]\}\text{PF}_6$ (IV),²⁸ $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{OPh}]\}\text{PF}_6$ (V),⁹ $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{SPh}]\}\text{PF}_6$ (IX),⁹ $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{SePh}]\}\text{PF}_6$ (X),⁹ $\{\text{Cp}(\text{CO})_2\text{Fe}-[\text{CS}(\text{CH}_2)_2\text{S}]\}\text{PF}_6$ (XIa),⁹ $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{CS}(\text{CH}_2)_3\text{S}]\}\text{PF}_6$ (XIb),⁹ and $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{N}(\text{CH}_2)_4\text{CH}_2]\}\text{PF}_6$ (VII)⁸ were prepared as reported previously. Routine ^1H - and ^{13}C -NMR spectra were recorded on a Jeol FX-90Q spectrometer; $\text{Cr}(\text{acac})_3$ (~ 0.1 M) was added to the ^{13}C samples to reduce data collection time.²⁹ Tetramethylsilane (TMS) was employed as the internal standard for all NMR spectra. Infrared spectra were recorded on a Perkin-Elmer 281 spectrophotometer.

Preparation of amino-oxocarbene complexes.

$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)\text{NH}_2]\}\text{CF}_3\text{SO}_3$ (IIa) Complex I (0.090 g, 0.21 mmol) was dissolved in 15 mL of CH_3CN and 400 μL of CH_3CN saturated with $\text{NH}_3(\text{g})$ was added in 25 μL increments to the stirred solution over a 2 h period. The reaction was allowed to stir for an additional 30 min and was then evaporated to dryness. The resulting residue was washed

with Et₂O and crystallized from CH₂Cl₂ with Et₂O at -20° C to give 0.068 g (81%) of IIa as large yellow crystals. Mp 119-121° C. Anal. calcd. for C₁₀H₁₀F₃FeNO₆S: C, 31.19; H, 2.62; N, 3.64. Found: C, 30.89; H, 2.47; N, 3.67.

{Cp(CO)₂Fe[C(OCH₃)NHCH₂Ph]}CF₃SO₃ (IIb) A 15 mL solution of CH₂Cl₂ containing I (0.10 g, 0.24 mmol) and PhCH₂NH₂ (56 μL, 0.51 mmol) was stirred for 30 min. The solution was then evaporated to an orange oil which was washed with Et₂O. Crystallization of the oil from CH₂Cl₂ with Et₂O at -20° C afforded 0.061 g (53%) of IIb as yellow crystals. Mp 118-122° C. Anal. calcd. for C₁₇H₁₆F₃FeNO₆S: C, 42.97; H, 3.39; N, 2.95. Found: C, 42.77; H, 3.38; N, 2.97.

{Cp(CO)₂Fe[C(OCH₃)NH(CH₂)₂OH]}CF₃SO₃ (IIc) This complex was prepared by the same method as IIb. From the reaction of I (0.10 g, 0.24 mmol) and β-aminoethanol (15 μL, 0.25 mmol), 0.070 g (68%) of IIc was isolated as yellow needles. Mp 124-128° C. Anal. calcd. for C₁₂H₁₄F₃FeNO₇S: C, 33.59; H, 3.29; N, 3.26. Found: C, 33.29; H, 3.04; N, 3.24.

{Cp(CO)₂Fe[C(OCH₃)NHCH₃₃SO₃ (IIId) Complex I (0.10 g, 0.24 mmol) was dissolved in CH₂Cl₂ and a slow stream of CH₃NH₂(g) was passed through the stirred solution

for 30 min. The solution was then evaporated to dryness, and the yellow residue was washed with Et₂O. Crystallization of this residue from CH₂Cl₂ with Et₂O at -20° C yielded 0.067 g of a mixture of IIId and IIA (50 and 20% respectively, from ¹H-NMR) as small yellow crystals. Mp 128-134° C.

{Cp(CO)₂Fe[C(OCH₃)N(CH₃)₂]CF₃SO₃} (IIe) This complex was prepared in the same manner as IIId. Starting with 0.10 g (0.24 mmol) of I and (CH₃)₂NH(g), 0.067 g (68%) of IIe was obtained as small yellow needles. Mp 174-178° C dec. Anal. calcd. for C₁₂H₁₄F₃FeNO₆S: C, 34.89; H, 3.42; N, 3.39. Found: C, 34.82; H, 3.39; N, 3.41.

{Cp(CO)₂Fe[C(OCH₃)N(CH₂)₄CH₂]CF₃SO₃} (IIIf) This complex was prepared by the method used for IIb. The reaction of I (0.10 g, 0.24 mmol) and piperidine (48 μL, 0.48 mmol) produced 0.065 g (60%) of IIIf as large yellow-orange crystals. Mp 141-143° C. Anal. calcd. for C₁₅H₁₈F₃FeNO₆S: C, 39.75; H, 4.00; N, 3.09. Found: C, 39.58; H, 3.98; N, 3.07.

Thermal behavior of IIc Complex IIc (0.040 g, 0.093 mmol) was dissolved in 25 mL of CH₃CN (dried over CaSO₄ and N₂ saturated), and the solution was refluxed under an N₂ atmosphere for 12 h. The yellow solution

was then evaporated to dryness, and the residue was washed with Et₂O. The yellow residue was crystallized from CH₂Cl₂ with Et₂O at -20° C to give 0.030 g (81%) of {Cp(CO)₂Fe[CO(CH₂)₂NH]}CF₃SO₃ (IIIc) as pale yellow needles. Mp 118° C. Anal. calcd. for C₁₁H₁₀F₃FeNO₆S: C, 33.28; H, 2.54; N, 3.53. Found: C, 33.50; H, 2.34; N, 3.63.

Reaction of {Cp(CO)₂Fe[C(SCH₃)OPh]}PF₆ (V) with benzylamine This reaction was carried out using the procedure used to prepare I Ib. The reaction of V (0.012 g, 0.025 mmol) and PhCH₂NH₂ (6.0 μL, 0.055 mmol) thus yielded 0.010 g (90%) of {Cp(CO)₂FeCNCH₂Ph}PF₆⁸ (VI) as yellow needles.

Reaction of V with piperidine The procedure used was the same as for the preparation of I Ib. Starting with V (0.030 g, 0.063 mmol) and piperidine (13 μL, 0.13 mmol), 0.020 g of a mixture of {Cp(CO)₂Fe[C(SCH₃)-N(CH₂)₄CH₂]}PF₆⁸ VII, and {Cp(CO)₂Fe[C(OPh)N(CH₂)₄CH₂]}PF₆⁸ VIII, (48 and 18% respectively, from ¹H-NMR) was isolated as a yellow powder.

Reaction of {Cp(CO)₂Fe[C(SCH₃)SPh]}PF₆ (IX) with benzylamine The procedure used for the preparation of I Ib was employed here. The reaction of IX (0.030 g, 0.061 mmol) and PhCH₂NH₂ (14 μL, 0.13 mmol) afforded 0.015 g (56%) of VI⁸ as yellow needles.

Reaction of IX with piperidine This reaction was carried out using the method used to prepare I Ib. From the reaction of IX (0.040 g, 0.082 mmol) and piperidine (16 μ L, 0.16 mmol), 0.025 g (66%) of VII⁸ was isolated as small yellow needles.

Reaction of $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{SePh}]\}\text{PF}_6$ (X) with benzylamine The method used to prepare I Ib was also used in this reaction. Starting with X (0.024 g, 0.044 mmol) and PhCH_2NH_2 (10 μ L, 0.092 mmol), 0.011 g (58%) of VI⁸ was obtained as yellow needles.

Reaction of X with piperidine The reaction of X (0.028 g, 0.052 mmol) with piperidine (11 μ L, 0.11 mmol), under the same conditions as used in the preparation of I Ib, yielded 0.016 g (66%) of VII⁸ as small yellow needles.

Reaction of $\{\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CS}(\text{CH}_2)_2\text{S}}]\}\text{PF}_6$ (XIa) with benzylamine This reaction was carried out using the same procedure as used for I Ib. The reaction of XIa (0.025 g, 0.059 mmol) with PhCH_2NH_2 (13 μ L, 0.12 mmol) afforded 0.022 g (85%) of VI⁸ as yellow needles.

Reaction of $\{\text{Cp}(\text{CO})_2\text{Fe}[\overline{\text{CS}(\text{CH}_2)_3\text{S}}]\}\text{PF}_6$ (XIb) with benzylamine A solution of 15 mL of CH_2Cl_2 containing XIb (0.025 g, 0.057 mmol) and PhCH_2NH_2 (13 μ L, 0.12 mmol)

was stirred for 1 h. The resulting cloudy yellow solution was evaporated to dryness and the residue was washed with Et_2O to remove an unidentified, neutral, yellow species. The remaining residue was then crystallized from CH_2Cl_2 with Et_2O at -20°C to give 8.0 mg (32%) of VI^8 as yellow needles.

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SECTION V. SYNTHESIS, REACTIVITY, AND SPECTROSCOPIC
STUDIES OF $\eta^5\text{-C}_5\text{H}_5(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$
CARBENE COMPLEXES

INTRODUCTION

Carbene complexes are of interest because of their importance in stoichiometric¹⁻⁴ as well as catalytic⁴⁻⁶ organic syntheses. In hopes of more fully understanding the chemistry of carbene complexes, we have studied a series of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) carbene derivatives and found the reactivity and electronic environment of the carbene carbon to be strongly influenced by the π -donation ability of the heteroatomic groups, XR and YR.⁷⁻⁹ We now wish to report on the effects of changing L in a series of $\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ carbene complexes on the bonding and reactivity of the carbene ligand.

photolysis appears to be a general reaction for $\text{Cp}(\text{CO})_2\text{Fe}[\text{carbene}]^+$ complexes as Ib-d are also efficiently converted to IIb-d. However, their CF_3SO_3^- salts are reluctant to crystallize; IIb,d form red oils and crystals of IIc are isolated in fairly low yield.

Attempts to prepare complexes with other coordinating solvents have been unsuccessful. The photolysis of Ia in THF leads to slow decomposition of Ia with no evidence for the formation of $\text{Cp}(\text{CO})(\text{THF})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$. The photolysis of Ia in acetone leads to decomposition of Ia and what appears to be very slow formation of $\text{Cp}(\text{CO})(\text{acetone})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ ($\nu(\text{CO}) = \sim 1970 \text{ cm}^{-1}$ in acetone) which could not be isolated.

Synthesis of $\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ complexes

Photolysis of Ia in non-coordinating solvents in the presence of ligand does not appear to produce any of the $\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ complexes. However, preformation of the acetonitrile adduct, IIa, followed by its reaction with various ligands at room temperature in CH_2Cl_2 provides a good route to the ligand substituted carbene complexes, IIIa-g (eq. 2).

The reaction of IIa with $P(CH_2CH_3)_3$ or $P(Ph)_2CH_3$ results in the decomposition of IIa rather than in the formation of the expected ligand substituted carbene complex. These highly nucleophilic phosphines may react with the carbene ligand to form unstable ylide complexes.^{9,10} The reaction of IIa with $N(CH_2CH_2)_3N$ also leads to decomposition, possibly for the same reason.

The reaction of IIb with an excess of $\{(CH_3CH_2)_4N\}I$ in CH_2Cl_2 under an N_2 atmosphere for 30 min produces a low yield of a neutral mono-carbonyl complex with spectra consistent with the expected product, $Cp(CO)(I)Fe[C(SCH_3)_2]$ (IR(CH_2Cl_2): $1958(s) \text{ cm}^{-1}$; 1H -NMR(CS_2): $\tau 5.44(s, C_5H_5)$, $6.85(s, 2 \text{ SCH}_3)$). However, this complex does not appear to be very stable and crystals have not been obtained. The reaction of IIa with stoichiometric amounts of $\{PhCH_2(CH_3CH_2)_3N\}Cl$ or $\{PPN\}Cl$ under similar conditions for 8 h produces $Cp(CO)_2FeCl$ as the only organometallic product.

Spectroscopic studies The IR, 1H -NMR, and ^{13}C -NMR data for the complexes discussed herein are presented in Tables I, II, and III, respectively. All $\nu(CO)$ force constants, $k(CO)$, are calculated by the method of Cotton and Kraihanzel.¹¹

Table I. Infrared spectra of the complexes in CH₂Cl₂

Complex		$\nu(\text{CN}), \text{cm}^{-1}$	$\nu(\text{CO}), \text{cm}^{-1}$	$\frac{k(\text{CO})}{\text{mdyn/\AA}}^{\text{a}}$
{Cp(CO) ₂ Fe[C(SCH ₃) ₂]}PF ₆ ^b	Ia		2058(s), 2017(s)	16.77
{Cp(CO)(CH ₃ CN)Fe[C(SCH ₃) ₂]}PF ₆	IIa	--- ^c	1997(s)	16.10
{Cp(CO)(CH ₃ CN)Fe[C(SCH ₃) ₂]}CF ₃ SO ₃	IIb	--- ^c	1994(s)	16.06
{Cp(CO)(CH ₃ CN)Fe[C(OCH ₃)SCH ₃]}CF ₃ SO ₃	IIc	--- ^c	1999(s)	16.14
{Cp(CO)(CH ₃ CN)Fe[C(OCH ₃)NH ₂]}CF ₃ SO ₃	IId	--- ^c	1983(s)	15.88
{Cp(CO)[P(OPh) ₃]Fe[C(SCH ₃) ₂]}PF ₆	IIIa		1985(s)	15.91
{Cp(CO)[P(OCH ₃) ₃]Fe[C(SCH ₃) ₂]}PF ₆	IIIb		1981(s)	15.85
{Cp(CO)(PPh ₃)Fe[C(SCH ₃) ₂]}PF ₆	IIIc		1970(s)	15.67

^aReference 11.

^bReference 7.

^c $\nu(\text{CN})$ of the CH₃CN ligand not observed.

Table I. (continued)

Complex		$\nu(\text{CN}), \text{cm}^{-1}$	$\nu(\text{CO}), \text{cm}^{-1}$	$\frac{k(\text{CO})}{\text{mdyn/\AA}}$
$\{\text{Cp}(\text{CO})(\text{AsPh}_3)\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$	IIIId		1969(s)	15.66
$\{\text{Cp}(\text{CO})(\text{SbPh}_3)\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$	IIIe		1965(s)	15.59
$\{\text{Cp}(\text{CO})(\text{CH}_3\text{NC})\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$	IIIIf	2203(m)	2001(s)	16.17
$\{\text{Cp}(\text{CO})(\text{C}_5\text{H}_5\text{N})\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$	IIIg		1977(s)	15.78
$\{\text{Cp}(\text{CH}_3\text{NC})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$	IV	2187(s), 2161(s)		
$\{\text{Cp}(\text{CO})_2\text{Fe}(\text{CNCH}_2\text{Ph})\}\text{PF}_6^b$	V	2225(m)	2082(s), 2042(s)	17.17
$\{\text{Cp}(\text{CO})[\text{P}(\text{OPh})_3]\text{Fe}(\text{CNCH}_2\text{Ph})\}\text{PF}_6$	VIa	2196(m)	2023(s)	16.53
$\{\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe}(\text{CNCH}_2\text{Ph})\}\text{PF}_6$	VIc	2180(m)	1998(s)	16.12
$\{\text{Cp}(\text{CO})(\text{AsPh}_3)\text{Fe}(\text{CNCH}_2\text{Ph})\}\text{PF}_6$	VIId	2177(m)	1997(s)	16.10
$\{\text{Cp}(\text{CO})(\text{CH}_3\text{NC})\text{Fe}(\text{CNCH}_2\text{Ph})\}\text{PF}_6$	VIIf	2225(m), 2195(s)	2027(vs)	16.59

Table I. (continued)

Complex		$\nu(\text{CN}), \text{cm}^{-1}$	$\nu(\text{CO}), \text{cm}^{-1}$	$\frac{k(\text{CO})_0}{\text{mdyn/\AA}}$
$\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\overline{\text{N}(\text{CH}_2)_4\text{CH}_2}]\text{PF}_6^b$	VII		2047(s), 2002(s)	16.55
$\{\text{Cp}(\text{CO})(\text{CH}_3\text{NC})\text{Fe}[\text{C}(\text{SCH}_3)\overline{\text{N}(\text{CH}_2)_4\text{CH}_2}]\text{PF}_6$	VIII	2184(m)	1986(s)	15.93
$\{\text{Cp}(\text{CO})(\text{CH}_3\text{CN})\text{Fe}(\text{CNCH}_2\text{Ph})\text{PF}_6^d$	IX	2188(m)	2013(s)	16.36

^dIn CH_3CN .

Table II. $^1\text{H-NMR}$ spectra of the complexes in acetone- d_6 (τ)^a

Complex	C_5H_5	SCH_3	Other Resonances
Ia ^b	4.43	6.73	
IIa	4.97	6.77	7.56 (CH_3CN)
IIc	4.91	7.37	5.11 (OCH_3), 7.54 (CH_3CN)
IId	5.11		5.92 (OCH_3), 7.60 (CH_3CN)
IIIa	4.85 (d) ^c	6.93	2.63 (m, 3 C_6H_5)
IIIb	4.78 (d) ^d	6.81	6.23 (d, 3 OCH_3) ^e
IIIc	4.81 (d) ^f	6.94	2.42 (m, 3 C_6H_5)
IIId	4.76	6.91	2.51 (m, 3 C_6H_5)
IIIe	4.64	6.88	2.47 (m, 3 C_6H_5)
IIIf	4.80	6.80	6.35 (CH_3NC)
IIIg	4.79	7.01	1.47 (dd, <u>o</u> - $\text{C}_5\text{H}_5\text{N}$), 2.05 (tt, <u>p</u> - $\text{C}_5\text{H}_5\text{N}$), 2.63 (tt, <u>m</u> - $\text{C}_5\text{H}_5\text{N}$)

^aAll resonances are singlets unless otherwise indicated.

^bReference 7.

^c $J_{\text{PFeCH}} = 1.1$ Hz.

^d $J_{\text{PFeCH}} = 1.2$ Hz.

^e $J_{\text{POCH}} = 11.5$ Hz.

^f $J_{\text{PFeCH}} = 1.5$ Hz.

Table II. (continued)

Complex	C ₅ H ₅	SCH ₃	Other Resonances
IV ^g	5.35	6.95	6.56 (2 CH ₃ NC)
V ^b	4.34		2.66 (C ₆ H ₅), 4.83 (CH ₂)
VIa	5.07 (d) ^d		2.58 (m, 4 C ₆ H ₅), 4.83 (d, CH ₂) ^f
VIc	4.82 (d) ^h		2.46 (PhCH ₂ NC), 2.64 (m, PPh ₃), 5.05 (d, CH ₂) ⁱ
VI d ^g	4.98		2.68 (m, 4 C ₆ H ₅), 5.23 (CH ₂)
VIf	4.64		2.53 (C ₆ H ₅), 4.80 (CH ₂), 6.39 (CH ₃ NC)
VII ^j	4.45	7.09	5.62 (m, 2 NCH ₂), 8.13 (m, 3 CH ₂)
VIII ^g	5.07	7.22	5.65 (t, NCH ₂), 5.84 (t, NCH ₂), 6.56 (CH ₃ NC), 8.23 (m, 3 CH ₂)
IX	4.79		2.53 (C ₆ H ₅), 4.92 (CH ₂), 7.61 (CH ₃ CN)

^gIn CD₃CN.

^hJ_{PFeCH} = 1.6 Hz.

ⁱJ_{PFeCH} = 1.8 Hz.

^jReference 7, NCH₂ resonances have been re-assigned.

Table III. ^{13}C -NMR spectra of the complexes in CD_3CN (ppm)^a

Complex	C(carbene)	CO	C_5H_5	SCH_3	Other Resonances
Ia ^b	304.3	210.1	89.2	30.3	
IIa ^c	321.2	216.4	85.0	28.1	136.1 (br, CH_3CN), 4.0 (CH_3CN)
IIc ^c	313.0	215.9	84.9	19.9	69.9 (OCH_3), 4.2 (CH_3CN) ^d
IIIa	310.2 (d) ^e	214.9 (d) ^f	87.5	29.9	151.2 (d), ^g 131.0, 127.0, and 122.0 (3 C_6H_5)

^aAll resonances are singlets unless otherwise indicated.

^bReference 8.

^cIn acetone- d_6 .

^d CH_3CN resonance not observed.

^e $J_{\text{PFeC}} = 29.3$ Hz.

^f $J_{\text{PFeC}} = 43.0$ Hz.

^g $J_{\text{POC}} = 9.8$ Hz.

Table III. (continued)

Complex	C(carbene)	CO	C ₅ H ₅	SCH ₃	Other Resonances
IIIb	314.3(d) ^e	215.3(d) ^h	86.9	29.5	54.8(d, 3 OCH ₃) ⁱ
IIIc	317.7(d) ^j	218.0(d) ^e	87.7	29.7	130.8(m, 3 C ₆ H ₅)
IIId	317.5	217.4	86.1	29.9	133.9, 133.3, 131.7, and 130.3(3 C ₆ H ₅)
IIIe	316.1	216.4	84.9	30.2	135.9, 132.1, 130.8, and 130.4(3 C ₆ H ₅)
IIIf	315.8	214.9	86.8	29.6	151.6(br, CH ₃ NC _̄), 31.9(br, <u>CH</u> ₃ NC)
IIIg	319.6	218.6	88.0	28.0	158.9, 139.5, and 127.1 (C ₅ H ₅ N)
IV	325.6		84.3	29.0	159.9(br, 2 CH ₃ NC _̄), 31.7(br, 2 <u>CH</u> ₃ NC)

$$h_{J_{\text{PFeC}}} = 46.9 \text{ Hz.}$$

$$i_{J_{\text{POC}}} = 7.8 \text{ Hz.}$$

$$j_{J_{\text{PFeC}}} = 17.6 \text{ Hz.}$$

Table III. (continued)

Complex	C(carbene)	CO	C ₅ H ₅	SCH ₃	Other Resonances
VII ^k	237.6	211.4	89.2	26.4	64.9 (NCH ₂), 59.5 (NCH ₂), 27.7 (NCH ₂ <u>CH</u> ₂), 27.3 (NCH ₂ <u>CH</u> ₂), 24.6 (CH ₂)
VIII	248.1	216.7	86.2	25.1	154.5 (br, CH ₃ <u>NC</u>), 64.5 (NCH ₂), 58.3 (NCH ₂), 31.9 (br, <u>CH</u> ₃ NC), 28.2 (NCH ₂ <u>CH</u> ₂), 27.4 (NCH ₂ <u>CH</u> ₂), 24.4 (CH ₂)

^kReference 9.

The $\underline{k}(\text{CO})$ values of the $\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ complexes decrease in the order: $\text{CO} > \text{CH}_3\text{NC} > \text{CH}_3\text{CN} > \text{P}(\text{OPh})_3 > \text{P}(\text{OCH}_3)_3 > \text{C}_5\text{H}_5\text{N} > \text{PPh}_3 \approx \text{AsPh}_3 > \text{SbPh}_3$. With the exceptions of CH_3CN and $\text{C}_5\text{H}_5\text{N}$, this is the trend established for the decreasing π -acceptor/ σ -donor ratios of these ligands.¹²⁻¹⁸ The CH_3CN and $\text{C}_5\text{H}_5\text{N}$ ligands are generally regarded as having lower π -acceptor/ σ -donor ratios¹⁶⁻²² than indicated by the $\underline{k}(\text{CO})$ values of the $\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ carbene complexes. As for the $\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ complexes, the $\underline{k}(\text{CO})$ values for the CH_3CN and $\text{C}_5\text{H}_5\text{N}$ derivatives of the related $\text{Cp}(\text{CO})_2\text{FeL}^+$ complexes²³⁻²⁶ are also anomalously high. No unequivocal explanation of the apparently anomalous IR data for these iron CH_3CN and $\text{C}_5\text{H}_5\text{N}$ complexes is evident, but one possibility is coupling of the $\nu(\text{CO})$ mode with CH_3CN and $\text{C}_5\text{H}_5\text{N}$ modes which results in unusually high approximate $\underline{k}(\text{CO})$ values.^{11,16}

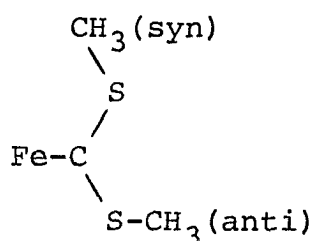
It is also of interest that $\nu(\text{CN})$ for IIIf and IV are $40\text{-}50\text{ cm}^{-1}$ less than the corresponding frequencies of $\text{Cp}(\text{CO})_2\text{Fe}(\text{CNCH}_3)^+$ and $\text{Cp}(\text{CO})\text{Fe}(\text{CNCH}_3)_2^+$.²⁴ This is a reflection of the lower π -acceptor/ σ -donor ratio for the dimethyl(dithio)carbene ligand as compared to CO .⁷

A comparison of the $\underline{k}(\text{CO})$ values of Ia (16.77 mdyn/Å) and $\{\text{Cp}(\text{CO})_2\text{Fe}(\text{PPh}_3)\}\text{PF}_6$ (16.74 mdyn/Å)²³ indicates that the dimethyl(dithio)carbene ligand has a π -acceptor/ σ -donor ratio which is very similar to that of the PPh_3 ligand.

It has been shown that the ^{13}C -NMR chemical shift of a CO ligand, $\delta(\text{CO})$, usually,^{12,27-30} but not always,^{31,32} moves to lower field as $\text{M}\rightarrow\text{CO}$ π -backbonding increases. For the $\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ complexes, the $\delta(\text{CO})$ values move to lower field as L is varied in the order: $\text{CO} > \text{CH}_3\text{NC} = \text{P}(\text{OPh})_3 > \text{P}(\text{OCH}_3)_3 > \text{CH}_3\text{CN} = \text{SbPh}_3 > \text{AsPh}_3 > \text{PPh}_3 > \text{C}_5\text{H}_5\text{N}$. The ^{13}C -NMR chemical shifts of the carbene carbons, $\delta(\text{carbene})$, move to lower field in the order: $\text{CO} > \text{P}(\text{OPh})_3 > \text{P}(\text{OCH}_3)_3 > \text{CH}_3\text{NC} \approx \text{SbPh}_3 > \text{AsPh}_3 \approx \text{PPh}_3 > \text{C}_5\text{H}_5\text{N} > \text{CH}_3\text{CN}$. With the exceptions of CH_3CN and the order of SbPh_3 , AsPh_3 , and PPh_3 , the $\delta(\text{CO})$ values follow the expected π -acceptor/ σ -donor trend.¹²⁻¹⁸ Except for the ordering of SbPh_3 , AsPh_3 , and PPh_3 , the $\delta(\text{carbene})$ values also follow this trend.

It has been shown that the barrier to rotation about the C(carbene)-O bond is lowered as the electron density on the carbene carbon is increased by varying the aryl carbene substituent in an extensive series of $(\text{CO})_5\text{Cr}-\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5\text{X}$ carbene complexes.³³ Temperature dependent

$^1\text{H-NMR}$ spectra of the $\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ carbene complexes indicate that the barrier to rotation about the C(carbene)-S bonds is sensitive to changes in electron density on the iron atom. At room temperature, Ia, IIa, and IIIa-g all have equivalent SCH_3 groups, but as the temperature is lowered, they become inequivalent because of syn-anti isomerization. These complexes are listed



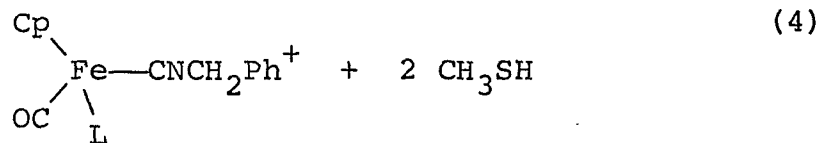
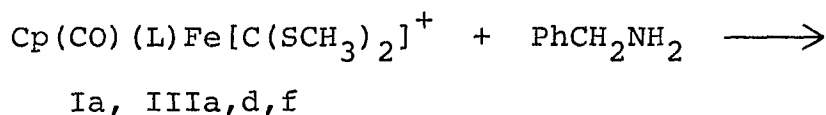
in Table IV in their order of decreasing free energies of activation, ΔG^\ddagger (calculated from the coalescence temperatures and peak widths at half height using the Eyring equation³⁴), for this isomerization. The greatest source of error³⁴ in the determination of these approximate values is the accuracy of the coalescence temperatures. These ΔG^\ddagger values generally follow the established trend¹²⁻¹⁸ for π -acceptor/ σ -donor ratios of the ligands. The higher barriers to rotation of the PPh_3 and AsPh_3 complexes as compared to those of $\text{P}(\text{OCH}_3)_3$ and $\text{P}(\text{OPh})_3$ is unexpected;

Table IV. Temperature dependent ^1H -NMR spectra of the carbene complexes arising from the syn-anti isomerization of the carbene ligand (in acetone- d_6)

Complex	L	T_c ($^\circ\text{C}$)	ΔG^\ddagger (kcal/mol)
Ia	CO	-2.5	13.6
IIa	CH_3CN	-28	12.2
III f	CH_3NC	-28	12.1
III c	PPh_3	-32	11.6
III d	AsPh_3	-48	11.1
III b	$\text{P}(\text{OCH}_3)_3$	-53	11.0
III a	$\text{P}(\text{OPh})_3$	-67	10.4
III e	SbPh_3	-60	10.3
III g	$\text{C}_5\text{H}_5\text{N}$	-71	10.1

the bulkiness³⁵ of the PPh₃ and AsPh₃ ligands may increase the barriers to rotation in these complexes. There is no obvious reason for the unusually high barrier to rotation in the CH₃CN complex.

Reactions of the Cp(CO)(L)Fe[C(SCH₃)₂]⁺ carbene complexes with amines Increased Fe→C(carbene) π-backbonding resulting from variations in the π-acceptor/σ-donor ratios of the ligands, L, is manifested in the reactivities of Ia and IIIa,d,f. Complexes Ia and IIIa,d,f all react at room temperature with benzylamine to give isocyanide derivatives (eq. 4), but only Ia and IIIa react with piperidine to form amino-thiocarbene complexes (eq. 5).



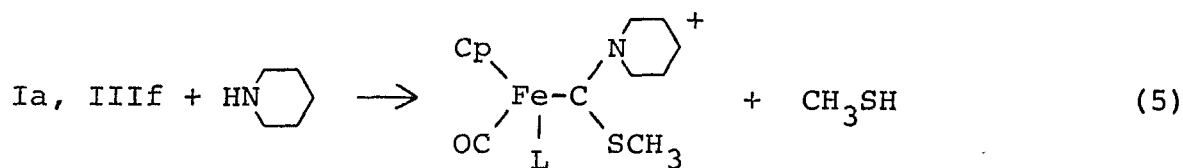
V, VIa,d,f

L = CO (Ia → V, 88%)

P(OPh)₃ (IIIa → VIa, 87%)

AsPh₃ (IIIId → VIId, 57%)

CH₃CN (IIIIf → VIIf, 58%)



VII, VIII

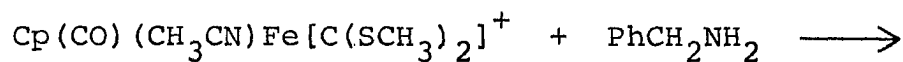
L = CO (VII, 69%)⁷CH₃NC (VIII, 73%)

The phosphine complex, IIIc, also reacts with benzylamine to yield the corresponding isocyanide complex, VIIC, but it has not been fully characterized. Stoichiometry is important in the reaction of IIIf with primary amines (eq. 4). If too large an excess of amine is used, the bis(isocyanide) complex, VIIf, which forms will react further to produce diaminocarbene complexes by addition of amine across a C≡N bond.^{24,36,37}

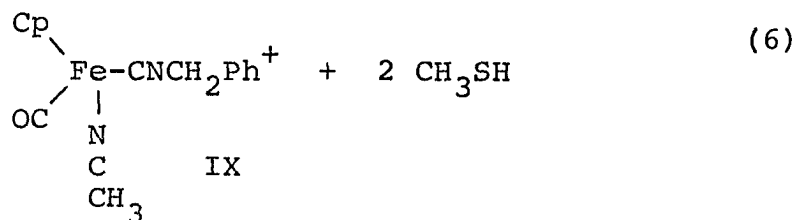
To determine the relative reactivities of these Cp(CO)(L)Fe[C(SCH₃)₂]⁺ complexes, equimolar amounts of two of the complexes were placed in CH₂Cl₂ or CH₃CN solutions, and the reactions with excess (2-5 fold) benzylamine were monitored by IR spectroscopy. Although overlap of the ν(CN) and ν(CO) bands between the complexes precluded the determination of accurate reaction rates, the observation of bands due to the slower reacting carbene

complex remaining after the faster reacting carbene complex had been consumed establishes the following order of decreasing rates of reaction with changes in L: $\text{CO} > \text{CH}_3\text{NC} > \text{P(OPh)}_3 > \text{AsPh}_3$. This is also the order of decreasing π -acceptor/ σ -donor ratios for these ligands,¹²⁻¹⁸ which suggests that electron-donor L groups increase electron density on the carbene carbon and reduce its rate of reaction with the nucleophilic amine. The lower electron donor properties of CO and CH_3NC account for the fact that Ia and IIIIf react with piperidine (eq. 5), while IIIa and IIIId do not. The reactivity of CO ligands towards nucleophiles has also been shown to decrease as $\text{M} \rightarrow \text{CO}$ π -backbonding increases.^{24,38,39}

The acetonitrile complex, IIa, which has unexpected IR, ^{13}C -NMR, and temperature dependent ^1H -NMR spectra, also displays rather unusual reactivity patterns. It reacts very slowly (24 h) with a ten-fold excess of benzylamine in CH_2Cl_2 to give a very low yield, by IR, of the corresponding isocyanide complex (eq. 6).



IIa



The only reaction observed between IIa and one equivalent of piperidine in CH_3CN is slow decomposition of IIa. These results are not unexpected, based on the assumed high electron donor ability of CH_3CN . This contrasts, however, with the rapid reaction of IIa with one equivalent of benzylamine in CH_3CN solution (eq. 6). Within two minutes of adding the amine, the IR spectrum of the reaction solution shows no bands for IIa, but rather absorption bands corresponding to IX and a band at $1985(\text{s})\text{ cm}^{-1}$ are observed. The band at 1985 cm^{-1} gradually disappears as the bands for IX grow in intensity. After approximately one hour, only IX is present. Complex IX is a yellow oil which is isolated in low (29%) yield and is characterized by its IR and $^1\text{H-NMR}$ spectra (Tables I and II). The band at 1985 cm^{-1} could correspond to $\text{Cp}(\text{CO})(\text{PhCH}_2\text{NH}_2)\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$. Reactions of other $\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ derivatives with amines do not show this solvent dependence, and the unique characteristics of $\text{Cp}(\text{CO})(\text{CH}_3\text{CN})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ are not presently understood.

EXPERIMENTAL SECTION

General information Reagent grade chemicals were used without further purification; $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{PF}_6$ (Ia),⁷ $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]\}\text{CF}_3\text{SO}_3$ (Ib),⁸ $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)\text{SCH}_3]\}\text{CF}_3\text{SO}_3$ (Ic),⁸ $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{OCH}_3)\text{NH}_2]\}\text{CF}_3\text{SO}_3$ (Id),⁹ $\{\text{Cp}(\text{CO})_2\text{Fe}(\text{CNCH}_2\text{Ph})\}\text{PF}_6$ (V),⁷ and $\{\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{N}(\text{CH}_2)_4\text{CH}_2]\}\text{PF}_6$ (VII)⁷ were prepared as reported previously. All irradiations were performed at 254 nm in borosilicate glassware equipped with a cooling probe using a reactor obtained from Bradford Scientific, Inc., Marblehead, Mass. The irradiations and subsequent CH_3CN displacement reactions were carried out under an N_2 atmosphere using solvents which were dried over CaSO_4 and purged with N_2 , although these precautions did not appear to be necessary. These precautions were not used for the reactions of $\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ with amines which were all run at room temperature. Infrared spectra were recorded on a Perkin-Elmer 281 spectrophotometer. All NMR studies were performed on a Jeol FX-90Q spectrometer; $\text{Cr}(\text{acac})_3$ (~ 0.1 M) was added to the ^{13}C samples to reduce data collection time.⁴⁰ Tetramethylsilane (TMS) was employed as the internal standard for all NMR spectra.

Preparation of the complexes. $\{\text{Cp}(\text{CO})(\text{CH}_3\text{CN})\text{Fe}[\text{C}(\text{SCH}_3)_2]\text{PF}_6$ (IIa) A 35 mL solution of CH_3CN containing Ia (0.10 g, 0.23 mmol) was irradiated at 254 nm until the $\nu(\text{CO})$ bands of Ia had disappeared (1-2 h). During this time, gas evolution was apparent, and the solution gradually changed color from bright yellow to red. The solution was then evaporated to a red oil which was washed with Et_2O . This oil was crystallized from CH_2Cl_2 with Et_2O at -20°C to give 0.091 g (88%) of IIa as dark red crystals. Mp $121\text{-}124^\circ\text{C}$ dec. Anal. calcd. for $\text{C}_{11}\text{H}_{14}\text{F}_6\text{FeNOPS}_2$: C, 29.95; H, 3.20; N, 3.17. Found: C, 30.06; H, 3.26; N, 3.10.

$\{\text{Cp}(\text{CO})(\text{CH}_3\text{CN})\text{Fe}[\text{C}(\text{OCH}_3)\text{SCH}_3]\text{CF}_3\text{SO}_3$ (IIc) This complex was prepared by the method used for IIa. Thus, the irradiation of Ic (0.060 g, 0.14 mmol) for 1 h afforded 0.021 g (34%) of IIc as red needles. Mp $81\text{-}83^\circ\text{C}$. Anal. calcd. for $\text{C}_{12}\text{H}_{14}\text{F}_3\text{FeNO}_5\text{S}_2$: C, 33.58; H, 3.29; N, 3.26. Found: C, 33.29; H, 3.25; N, 3.13.

$\{\text{Cp}(\text{CO})[\text{P}(\text{OPh})_3]\text{Fe}[\text{C}(\text{SCH}_3)_2]\text{PF}_6$ (IIIa) Crude IIa, generated from 0.500 g (1.13 mmol) of Ia, was dissolved in 20 mL of CH_2Cl_2 containing $\text{P}(\text{OPh})_3$ (350 μL , 1.34 mmol), and the solution was stirred for 6 h at room temperature.

The resulting yellow-brown solution was then evaporated to dryness, and the yellow residue was washed with Et₂O. Crystallization of this residue from acetone with Et₂O at -20° C yielded 0.63 g (78%) of IIIa as dark yellow crystals. Mp 133-135° C. Anal. calcd. for C₂₇H₂₆F₆FeO₄P₂S₂: C, 45.65; H, 3.69. Found: C, 45.25; H, 3.65.

{Cp(CO) [P(OCH₃)₃]Fe [C(SCH₃)₂] }PF₆ (IIIb) Trimethylphosphite (28 μL, 0.24 mmol) was stirred at room temperature with crude IIa, generated from Ia (0.10 g, 0.23 mmol), in 20 mL of CH₂Cl₂ for 5 h. The red solution was then evaporated to an oil which was washed with Et₂O and crystallized from CH₂Cl₂ with Et₂O at -20° C. The yield of IIIb, as orange crystals, was 0.060 g (49%). Mp 195° C dec. Anal. calcd. for C₁₂H₁₀F₆FeO₄P₂S₂: C, 27.50; H, 3.85. Found: C, 27.56; H, 3.80.

{Cp(CO) (PPh₃)Fe [C(SCH₃)₂] }PF₆ (IIIc) This complex was prepared by the same method as for IIIb. The reaction of PPh₃ (0.061 g, 0.23 mmol) and IIa, from 0.10 g (0.23 mmol) of Ia, afforded 0.089 g (58%) of IIIc as bright orange crystals after several recrystallizations from CH₂Cl₂ with Et₂O at -20° C to remove an unidentified black tar and a tan phosphorus-containing species. Mp 205° C dec. Anal. calcd. for C₂₇H₂₆F₆FeOP₂S₂: C, 48.96; H, 3.96. Found: C, 48.70; H, 3.99.

{Cp(CO)(AsPh₃)Fe[C(SCH₃)₂]}PF₆ (IIIId) The method used to prepare IIIb was also used for this complex. A 73% yield (0.12 g) of IIIId was obtained from the reaction of IIa, from 0.10 g (0.23 mmol) of Ia, and AsPh₃ (0.071 g, 0.23 mmol). Mp 180-184° C dec. Anal. calcd. for C₂₇H₂₆AsF₆FeOPS₂: C, 45.91; H, 3.71. Found: C, 45.98; H, 3.67.

{Cp(CO)(SbPh₃)Fe[C(SCH₃)₂]}PF₆ (IIIe) This derivative was prepared by the method used for IIIb. The reaction of IIa, generated from Ia (0.10 g, 0.23 mmol), and SbPh₃ (0.082 g, 0.23 mmol) afforded 0.13 g (74%) of IIIe as red needles. Mp 165° C dec. Anal. calcd. for C₂₇H₂₆F₆FeOPS₂Sb: C, 43.06; H, 3.48. Found: C, 43.19; H, 3.77.

{Cp(CO)(CH₃NC)Fe[C(SCH₃)₂]}PF₆ (IIIIf) The reaction of CH₃NC (13.5 μL, 0.230 mmol) and IIa, prepared from 0.10 g (0.23 mmol) of Ia, by the method used for IIIb afforded 0.065 g (65%) of IIIIf as orange-red crystals. Mp 128-130° C. Anal. calcd. for C₁₁H₁₄F₆FeNOPS₂: C, 29.95; H, 3.20; N, 3.17. Found: C, 29.89; H, 3.29; N, 3.53.

{Cp(CO)(C₅H₅N)Fe[C(SCH₃)₂]}PF₆ (IIIg) This complex was prepared by the route used for IIIb. Starting with

pyridine (19 μ L, 0.23 mmol) and IIa, from Ia (0.10 g, 0.23 mmol), 0.075 g (67%) of IIIg was isolated as dark red crystals. Mp 112-115° C dec. Anal. calcd. for $C_{14}H_{16}F_6FeNOS_2P$: C, 35.09; H, 3.37; N, 2.92. Found: C, 35.04; H, 3.37; N, 2.87.

$\{Cp(CO)[P(OPh)_3]Fe(CNCH_2Ph)\}PF_6$ (VIa) Complex IIIa
(0.10 g, 0.14 mmol) was stirred with $PhCH_2NH_2$ (30 μ L, 0.27 mmol) in 20 mL of CH_3CN for 9 h. The yellow solution was then evaporated to dryness, and the residue was washed with hexanes. Crystallization of the residue from CH_2Cl_2 with Et_2O at -20° C yielded 0.088 g (87%) of VIa as yellow crystals. Mp 126-128° C. Anal. calcd. for $C_{32}H_{27}F_6FeNO_4P_2$: C, 53.28; H, 3.77; N, 1.94. Found: C, 52.90; H, 3.79; N, 1.90.

$\{Cp(CO)(AsPh_3)Fe(CNCH_2Ph)\}PF_6$ (VIId) Benzylamine
(62 μ L, 0.57 mmol) and IIIId (0.040 g, 0.057 mmol) were stirred in 10 mL of CH_3CN for 18 h. The solution was then evaporated to a yellow oil which was washed with hexanes. The oil was crystallized from CH_2Cl_2 with Et_2O at -20° C to give 0.023 g (57%) of VIId as small yellow crystals. Mp 293-295° C. Anal. calcd. for $C_{32}H_{27}AsF_6FeNOP$: C, 53.58; H, 3.79; N, 1.95. Found: C, 53.39; H, 3.80; N, 1.88.

$\{\text{Cp}(\text{CO})(\text{CH}_3\text{NC})\text{Fe}(\text{CNCH}_2\text{Ph})\}\text{PF}_6$ (VIIf) A solution of 20 mL of CH_3CN containing IIIIf (0.10 g, 0.23 mmol) and PhCH_2NH_2 (27 μL , 0.25 mmol) was stirred for 4 h. The yellow solution was then evaporated to a yellow oil which could not be induced to crystallize. The yield of VIIf was approximately 0.060 g (58%). It was characterized by its infrared and ^1H -NMR spectra (Tables I and II).

$\{\text{Cp}(\text{CO})(\text{CH}_3\text{NC})\text{Fe}[\text{C}(\text{SCH}_3)\overline{\text{N}(\text{CH}_2)_4\text{CH}_2}]\}\text{PF}_6$ (VIII) Complex IIIIf (0.10 g, 0.23 mmol) was stirred with piperidine (225 μL , 2.27 mmol) in 20 mL of CH_3CN for 6 h. The resulting yellow solution was evaporated to an oil which was washed with hexanes. The oil was crystallized from CH_2Cl_2 with Et_2O at -20°C to afford 0.079 g (73%) of VIII as irregular, glass-like, yellow crystals. Mp $75-78^\circ\text{C}$. Anal. calcd. for $\text{C}_{15}\text{H}_{21}\text{F}_6\text{FeN}_2\text{OPS}$: C, 37.67; H, 4.43; N, 5.86. Found: C, 37.31; H, 4.45; N, 5.60.

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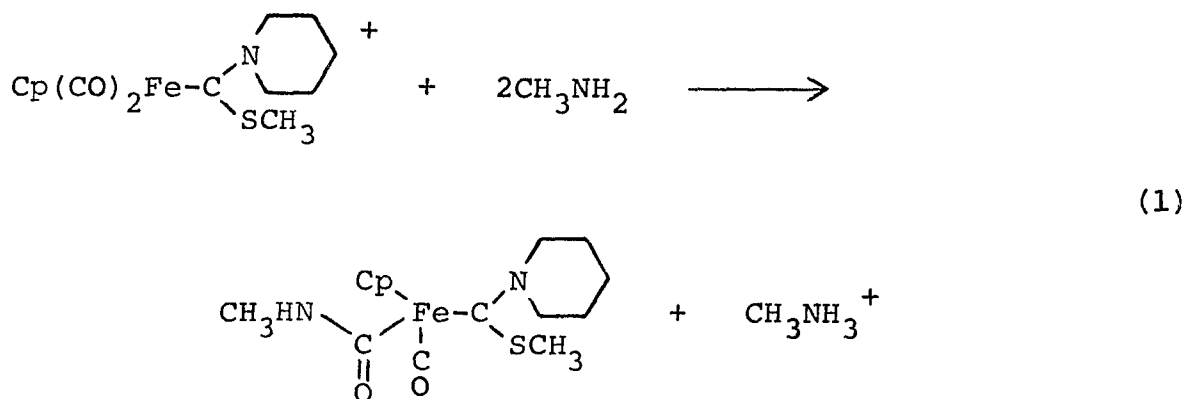
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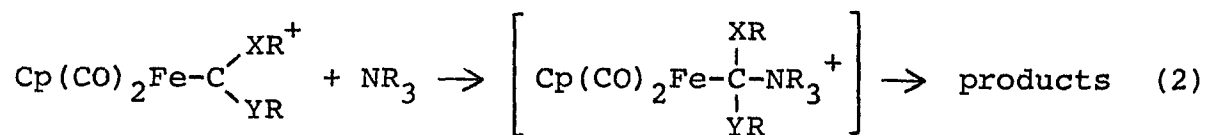
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SUMMARY

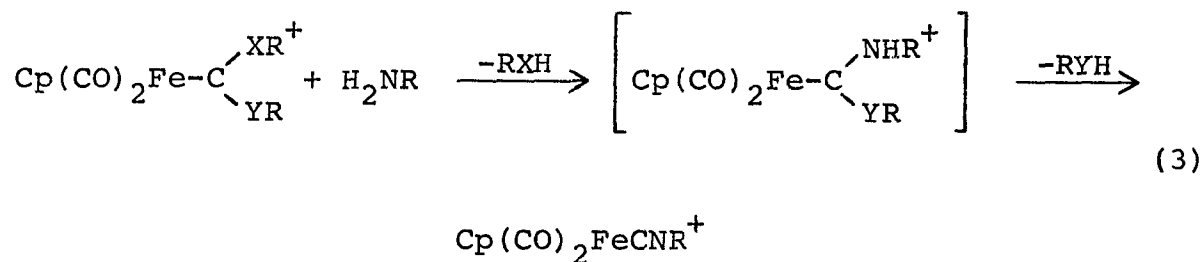
In an effort to more fully understand the chemistry of carbene complexes, two series of complexes, $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ and $\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ where X and Y are O, S, Se, and/or NR and L is CH_3NC , $\text{P}(\text{OPh})_3$, $\text{P}(\text{OCH}_3)_3$, PPh_3 , AsPh_3 , SbPh_3 , $\text{C}_5\text{H}_5\text{N}$, or CH_3CN , were prepared. Studies of their reactivity towards nucleophilic amines show that the electrophilicity of the carbene carbon decreases as π -donation from either the metal or the heteroatomic substituents increases. Sufficient π -donation, such as from amine groups, reduces the electrophilicity of the carbene carbon to the point that reactions with amines no longer occur at the carbene carbon (eq. 1).



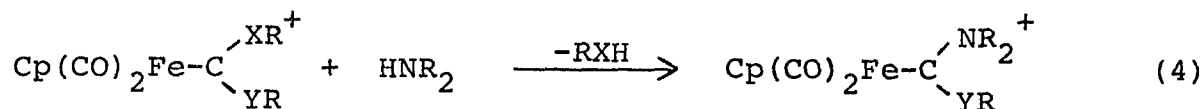
The reactions of the iron carbene complexes with amines appear to proceed by the formation of unstable ylide intermediates (eq. 2).



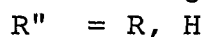
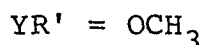
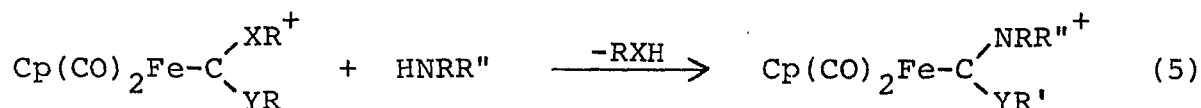
The collapse of these ylide intermediates to the observed products is controlled by the leaving group abilities of the heteroatomic carbene substituents, XR and YR. Carbene complexes with two good leaving groups, such as SePh, SPh, OPh, and SCH₃ groups, react with primary amines to give isocyanide complexes, probably in a step-wise manner (eq. 3).



These carbene complexes react with secondary amines to yield aminocarbene complexes by displacement of the better leaving group (eq. 4).

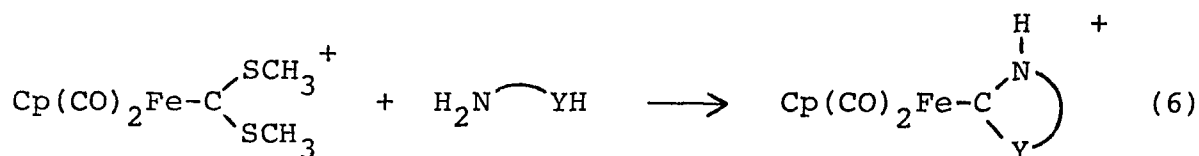


Carbene complexes with only one good leaving group react with primary and secondary amines to produce aminocarbene complexes by displacement of the good leaving group (eq. 5).



When both carbene substituents are poor leaving groups, uncharacterizable products generally result upon reaction of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ with amines. In the $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{XR})\text{YR}]^+$ carbene complexes, the methoxy group was the only carbene substituent which acted as a poor leaving group.

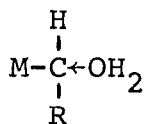
Heterocyclic carbene ligands are produced in the reactions of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ with appropriate diamines, amino alcohols, and amino thiols (eq. 6).



If the resulting carbene ligands can be effectively cleaved from the metal center, this could be a useful method for the

synthesis of five and six-membered organic heterocycles. The stability and reactivity of the $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ and $\text{Cp}(\text{CO})(\text{L})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ complexes suggest that these complexes could be useful reagents in organometallic synthesis.

The high sensitivity of the secondary carbene complex, $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{H}]^+$, towards H_2O may have relevance in the Fischer-Tropsch reaction. The reaction of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)\text{H}]^+$ and H_2O presumably involves nucleophilic attack by H_2O on the carbene carbon and the high reactivity of this complex may be due to the methylmercapto group, which has been shown to be a good leaving group in these iron carbene complexes. The metal-carbene species proposed as intermediates in the Fischer-Tropsch reaction, $\text{M}=\text{CHR}$ ($\text{R} = \text{H}$ or R), may not show this same reactivity towards H_2O , which is present in the process, but an ylide-type adduct



could form and, thus, affect the activity of the catalyst. The metathesis of olefins with polar functional groups may be difficult²² for similar reasons. The reactivity of Fischer-Tropsch and olefin metathesis catalysts towards nucleophilic reagents should be investigated further.

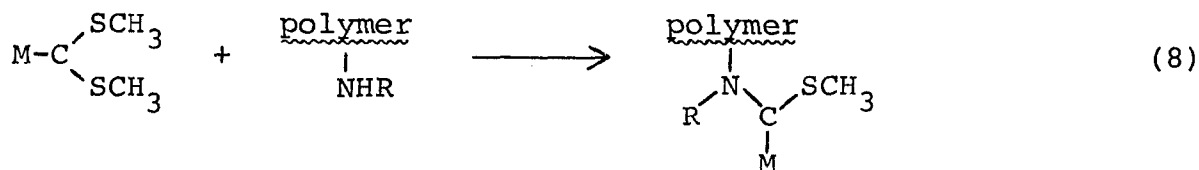
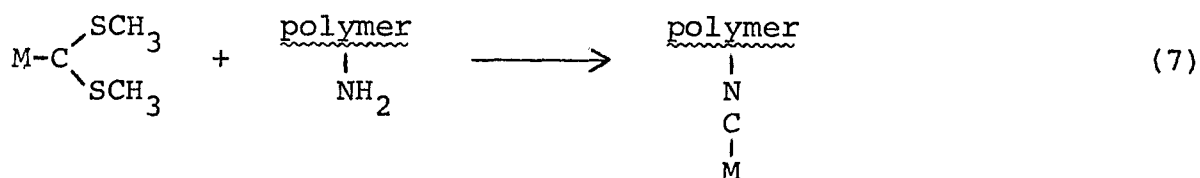
Spectroscopic studies indicate that the ability of the heteroatomic substituents in stabilizing the carbene carbon decreases in the order $N \gg \underline{Se} > S > O$ and that the $:C(SCH_3)_2$ ligand has a π -acceptor/ σ -donor ratio which is similar to that of PPh_3 . These studies also show that the degree of $Fe \rightarrow C(\text{carbene})$ π -backbonding may be controlled by varying the π -acceptor/ σ -donor ratio of the ligand, L, in the $Cp(CO)(L)Fe-[C(SCH_3)_2]^+$ complexes. This is important with respect to olefin metathesis and Fischer-Tropsch reactions as the amount of π -backbonding in the $M=CHR$ species should affect the activities of the catalysts.

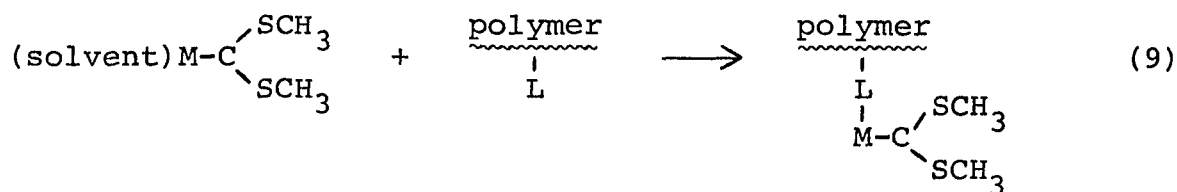
While the general trends found in the spectroscopic data for the $Cp(CO)_2Fe[C(XR)YR]^+$ and $Cp(CO)(L)Fe[C(SCH_3)_2]^+$ complexes are clear, certain discrepancies exist between the IR and ^{13}C -NMR data for these complexes. Mössbauer spectra and/or X-ray diffraction studies could be useful in understanding these discrepancies. As most of the carbene complexes crystallize readily, obtaining samples suitable for X-ray diffraction should not be a problem.

The present work has suggested several possibilities for future studies, some of which have already been mentioned. The secondary carbene complex is of interest as it may be a better model for Fischer-Tropsch catalysts. However, its high moisture sensitivity makes the study of this complex difficult. Ligand substituted derivatives, $Cp(CO)(L)Fe[C(SCH_3)H]^+$,

should be more stable⁴⁰ and more amenable to reactivity studies. The reactions of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ and $\text{Cp}(\text{CO})(\text{CH}_3\text{CN})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ with metal-carbonyl anions and other transition metal derivatives would be of interest as they could lead to di- and polynuclear metal carbene complexes.⁴¹⁻⁴³ Complexes of this type are thought to be important in the Fischer-Tropsch reaction.²⁴

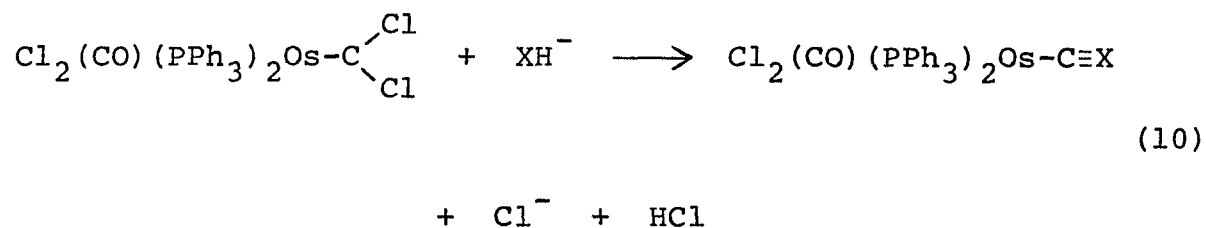
Owing to the stability and the synthetic steps required to prepare iron di(heteroatom)carbene complexes, it is doubtful that they could be active catalytic species. However, it is possible that they may be catalyst precursors. The behavior of these complexes under conditions normally found in olefin metathesis and Fischer-Tropsch systems could prove of interest. The reactions of $\text{Cp}(\text{CO})_2\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ with amines and the reactions of $\text{Cp}(\text{CO})(\text{CH}_3\text{CN})\text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ with π -acid ligands suggest possible methods of anchoring organometallic species to polymer supports (eq. 7-9).





These reactions would be of additional interest if the iron system showed any catalytic activity.

A dichloro carbene complex was recently reported for osmium, and the dichloro carbene ligand can be readily converted to CS, CSe, and CTe ligands (eq. 10).⁴⁴



X = S, Se, Te

As the dichloro carbene complex also reacts readily with primary amines to give isocyanide complexes,⁴⁴ $\text{Cp}(\text{CO})_2^- \text{Fe}[\text{C}(\text{SCH}_3)_2]^+$ may be a possible starting material for the synthesis of seleno- and tellurocarbonyl complexes.

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