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# The synthesis and reactivity of heterodinuclear iron, ruthenium, and cobalt compounds containing bridging dithiomethylene ligands. Attempted synthesis of the iron carbyne compound Cp(CO)Fe(triple bond)CSCH3

John R. Matachek

*Iowa State University*

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THE SYNTHESIS AND REACTIVITY OF HETERODINUCLEAR IRON, RUTHENIUM, AND COBALT COMPOUNDS CONTAINING BRIDGING DITHIOMETHYLENE LIGANDS.  ATTEMPTED SYNTHESIS OF THE IRON CARBYNE COMPOUND CP(CO)FE = CSCH(3)(1)

*Iowa State University*                                    PH.D.      1984

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The synthesis and reactivity of heterodinuclear

iron, ruthenium, and cobalt compounds containing

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synthesis of the iron carbyne compound $Cp(CO)Fe\equiv CSCH_3$


by


John R. Matachek


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## PREFACE

This dissertation is divided into two parts. Part I describes the synthesis and characterization of a series of dinuclear transition metal complexes containing bridging dithiomethylene ligands. The reaction of these compounds toward various nucleophiles and oxidizing agents is also presented. Conclusions are drawn about the structure and reactivity of these compounds based on the results of a molecular orbital calculation.

Part II of this dissertation describes the attempted synthesis of the iron carbyne (iron carbon triple bond)-containing compound $Cp(CO)Fe\equiv CSCH_3$. Although unsuccessful this study resulted in the synthesis of several new compounds containing iron carbon bonds and resulted in developing a new synthetic route to $Cp(CO)Fe[S_2CSCH_3]$.

Organizationally each of the two parts is independent of the other with the exception of the references which are numbered continuously throughout the entire dissertation.

PART I.  THE SYNTHESIS AND REACTIVITY OF

HETERODINUCLEAR IRON, RUTHENIUM,

AND COBALT COMPOUNDS CONTAINING BRIDGING

DITHIOMETHYLENE LIGANDS

# INTRODUCTION

The carbene group, :CRR', has been an object of study by the organic chemist for over half a century.[1] By themselves carbenes are very unstable and short lived. More recently, carbenes have been found to form stable complexes when bound to transition metals.[2] Several different modes of coordination between a carbene and a metal center can be envisioned (Fig. 1). Isolable examples of all four of these types are



| A | B | C | D |
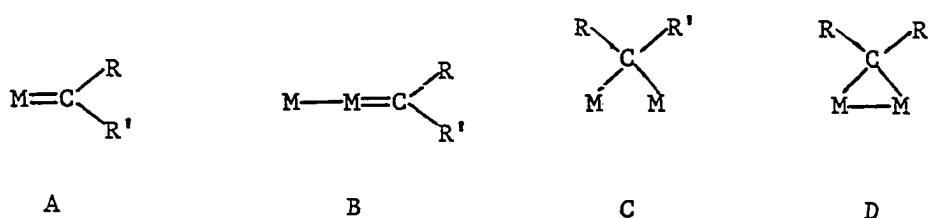
Figure 1. Possible coordination modes of carbene ligands to transition metals. For clarity all ancillary ligands have been omitted

known. To date, the most numerous of these are of the type represented by A (Fig. 1). Here the carbene carbon atom is $sp^2$ hybridized and acts as a two electron donor to the metal. Additional stabilization occurs as a result of d(pi)-p(pi) backbonding between the metal atom and the carbene carbon resulting in a multiple bond order (Fig. 2). Since the isolation



Figure 2. The sigma and pi bonding modes in terminal carbene-metal complexes

of the first such compound by Fischer and Massbol in 1964,[2] $(CO)_5W[C(OMe)Ph]$, literally hundreds of other examples have followed.

Several recent reviews have summarized this area of research.[3]

Although terminal carbene ligands in dinuclear metal compounds are known, as shown in B (Fig. 1), they are rare.[4] It appears that given the choice between bridging and terminal coordination modes the carbene favors the bridged position. The factors which govern this preference have yet to be delineated.

Carbene ligands have been found to bridge two metal atoms which are not joined by a metal-metal bond, as depicted in C (Fig. 1). In these cases, the presence of other bridging ligands is required. Examples of this include the Rh, Pd, Pt, and Au A-frame compounds synthesized by Balch, Puddephatt, and others which contain bridging phosphine ligands such as bisdiphenylphosphinomethane (dppm) in addition to the bridging carbene.[5] Compounds containing more than one bridging carbene and no direct metal-metal bond or other supporting ligands are also known.[6] There is a recent report of a diruthenium compound, $[CpRu(CO)_2]_2CH_2$, 1, which contains a single carbene bridge between two metals not joined by a metal-metal bond (d-Ru-Ru = 3.83 Å).[7] This represents the first isolated example of a bridging carbene complex in which the metals are not held together by a metal-metal bond or additional bridging ligands.

Compounds displaying the coordination mode depicted by D (Fig. 1) where the carbene bridges two metal atoms which are joined by a metal-metal bond have recently become of great interest. This is due to the proposed significance of the μ-carbene as an important intermediate (vide infra) in the metal surface-catalyzed reduction of carbon monoxide, or Fischer Tropsch reaction. The historical and continued importance of this

process require further discussion.

The Fischer Tropsch reaction in its simplest form is shown below (Eqn. 1). It represents a process whereby synthesis gas, a mixture of CO

$$nCO + 2nH_2 \xrightarrow{\text{catalyst}} -(CH_2)n- + nH_2O \quad (H = -39.4 \text{ Kcal/mole}) \tag{1}$$
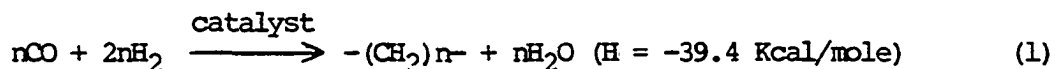
and $H_2$, is passed over a heterogeneous metal catalyst (typically Fe, Ru, Co, or Ni) at high temperature to give hydrocarbons and water. The primary products being straight chain alkanes and $\alpha$-olefins. Secondary products include branched hydrocarbons, alcohols, aldehydes, and carboxylic acids. The synthesis gas is derived from the combustion of coal in the presence of steam. Thus, this overall process represents a method in which coal, a relatively inexpensive and abundant material, can be converted into useful chemical feedstocks.

The discovery of this process and its first industrial scale application was pioneered by German scientists in the first quarter of this century. Prior to the mid-nineteen twenties several heterogeneous catalyst systems had been discovered which succeeded in converting synthesis gas into hydrocarbons. However the selectivity achieved was poor and the reactions required high temperatures and pressures to operate. At this point the industrialization of the process was not economically feasible. An important breakthrough was achieved in 1925 when Fischer and Tropsch reported an iron oxide/zinc oxide catalyst system capable of producing higher hydrocarbons from CO and $H_2$ at atmospheric pressure.[8] Although good selectivity was not achieved the Germans industrialized this process on a large scale to augment fuel supplies needed in time of war

and not available from other sources. During the peak production year of 1943, the German Fischer Tropsch plants were turning out 585,000 tons of products, the largest percentage of which was gasoline and diesel oil.[9]

The end of the war saw the end of this industry in Germany, and abundant supplies of cheap crude oil diminished interest in this process in general. Renewed interests in improving the selectivity and hence the economics of the Fischer Tropsch reaction have arisen since the oil embargoes of the early 1970s. The rising cost of crude oil brought about by the embargoes and the realization that supplies could become exhausted within a matter of decades have led to searches for alternate sources of energy. Coal, the source of the syngas which the Fischer Tropsch process utilizes, is available in vast quantities. The reserves in the United States are thought to be large enough to supply the energy needs of this country for two hundred years or more.

Current research efforts in Fischer-Tropsch chemistry are directed toward the development of more selective catlaysts. An immediate concern of this effort has been to elucidate the fundamental mechanistic steps involved in the catalytic cycle. Over the years several mechanisms have been proposed for this reaction.[10] Ironically, it appears that the primary steps involved in this reductive oligomerization of carbon monoxide are best described by the carbide/methylene mechanism as originally proposed by Fischer and Tropsch decades ago. The general scheme is outlined below (Figure 3).

It has been demonstrated that carbon monoxide and hydrogen adsorb dissociatively on the surfaces of metals commonly used as Fischer Tropsch

catalysts to give metal carbides, oxides, and hydrides.[10a] The carbides
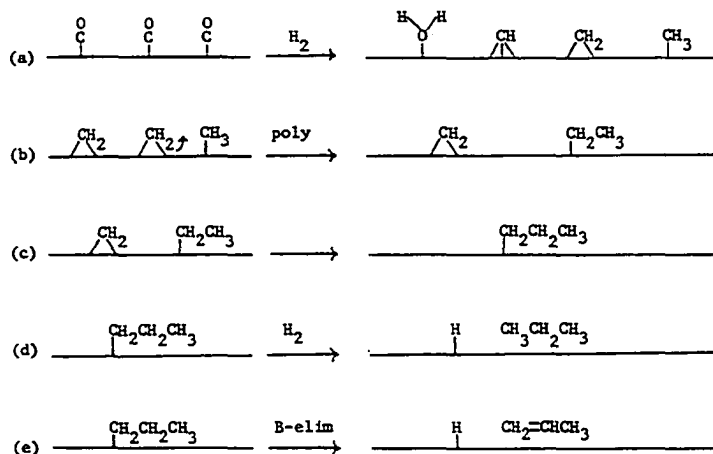


Figure 3. Basic Features of the Carbide/Methylene Mechanism

are then assumed to be successively hydrogenated by surface hydrides to give methylidyne, methylene, and methyl species. The surface oxygen atoms can be lost as water following hydrogenation. The exact mode of coordination of these species to the surface is still uncertain, although recent evidence suggests that each of these species interacts with more than a single metal center.[11] These $C(H)n$ (n = 0 to 3) fragments are also thought to have some mobility on the metal surface at the elevated reaction temperatures. As depicted in B (Fig. 3) surface methylene units undergo polymerization to form extended hydrocarbon chains. The presence of a methyl group has been shown to be necessary for polymerization to occur.[12]

The removal of the hydrocarbon chain from the metal surface can be envisioned as occurring in two ways. One involves further reaction with

an additional mole of $H_2$ dissociatively absorbed on the surface to give
the free hydrocarbon and a metal hydride as shown by D (Figure 3).
Alternatively the metal alkyl can undergo a β-hydride elimination reaction
to give the free α-olefin and a metal hydride. Both of these modes of
reactivity are well-established in homogeneous metal alkyl chemistry.[13]
The pathway through which oxygenated products are formed is not as clearly
understood. One can envision a mechanism in which a molecule of carbon
monoxide on the surface inserts into a metal alkyl bond prior to C-O bond
scission. This surface acyl species could then be reduced by metal
hydrides to form the corresponding alcohol. The insertion of CO into
metal alkyl bonds is also well documented in homogeneous solution
chemistry.[13] Surface formyls and hydroxy carbenes have also been proposed
as precursors to oxygenated products. The pathway through which the
oxygenated products are formed is still far from being understood.
Nevertheless the primary products of the Fischer-Tropsch reaction are
saturated and unsaturated hydrocarbons which are thought to evolve via
methylene polymerization.

The proposed intermediacy of the bridging carbene ligand in this
potentially important catalytic reaction has created a great deal of
interest in the synthesis of homogeneous transition metal compounds with
the metal-carbon coordination depicted in D (Fig. 1). The goal being to
develop an understanding of the reactivity and structural properties of
this ligand in order to help elucidate the types of reactions which one
might reasonably expect to observe on a heterogeneous surface. Although a
metal surface is different in many ways from a discrete homogeneous

complex certain patterns of chemical reactivity are expected to be common to both.[14]

With regard to nomenclature, IUPAC rules require that the term carbene refer to a divalent carbon atom (:CRR') which has $sp^2$ hybridization about carbon. If a carbene coordinates to just one metal center as depicted in A (Fig. 1) it has been shown by a large number of X-ray and neutron diffraction studies that the carbene carbon maintains $sp^2$ hybridization regardless of the nature of the substituents R and R'. Thus, the use of the term carbene in these cases is not contrary to established rules. This is not the case for compounds of type C and D (Fig. 1) where the carbene bridges two metal centers. These are best represented (vide-infra) as having distorted $sp^3$-hybridization at the bridgehead carbon. When a carbene is unsubstituted, as is true only in the case :$CH_2$, and bridging between metals, it is referred to as a μ-methylene ligand. When one hydrogen is substituted the ligand is then considered to be a μ-alkylidene derivative (e.g., "ethylidene for :$CH(CH_3)$). If both hydrogens are substituted the suffix "methylene" is used (e.g., :$C(SCH_3)_2$ is [bis(thiomethoxy)methylene]). This convention is followed here. Exception to this is made when generalizations are expressed referring to compounds containing bridging CRR' ligands in which R and R' may represent none, one, or two none hydrogen groups. In these cases, the general term carbene will be kept.

## Synthesis of bridging methylene compounds

The first methylene bridged transition metal complex to be isolated [CpMn(CO)$_2$]$_2$CH$_2$, 2, was prepared by Herrmann and coworkers in 1975 by

the reaction of CpMn(CO)$_2$THF with diazomethane at low temperature

(Eqn. 2).[15] Several years prior to this, the groups of Sternberg and

Wender in this country and Albanesi and Tovaglieri in Italy observed that

$$Cp\diagdown \underset{\underset{O^{C}\overset{|}{\underset{O}{C}}}{}{\overset{/}{Mn}}}(THF) \quad + \quad CH_2N_2 \quad \longrightarrow \quad Cp\diagdown \underset{O^{C}\overset{|}{\underset{O}{C}}}{Mn}\text{---}\underset{\diagdown Cp}{Mn}\text{---}CO \quad + \quad THF \qquad (2)$$

2
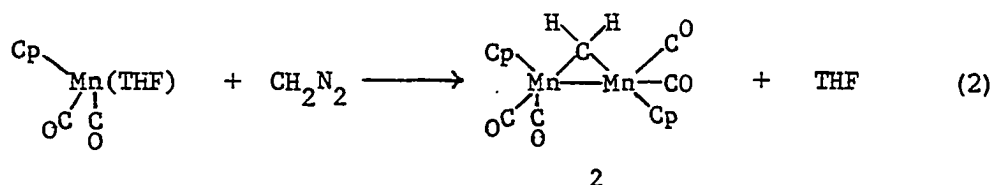
octacarbonyldicobalt reacted with CO and acetylene at elevated temperature

and pressure to yield a γ-lactone bridged compound (Eqn. 3).[16] Under more

$$Co_2(CO)_8 + C_2H_2 \xrightarrow{\ CO\ } (CO)_3Co\text{---}Co(CO)_3 \longrightarrow \qquad (3)$$
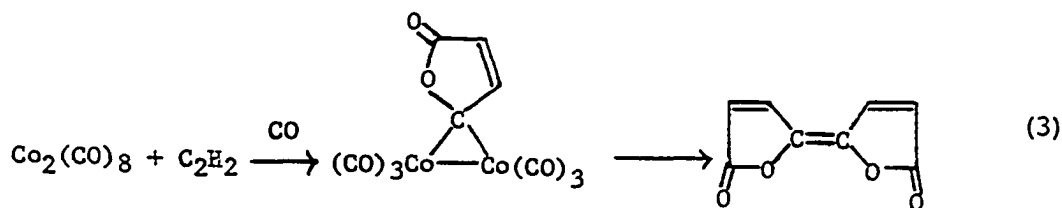
drastic conditions, further reaction occurred to yield bifurandione, a

product resulting from the coupling of two bridging γ-lactones. The

structure of the γ-lactone cobalt compound was later confirmed by an X-ray

diffraction study by Mills and Robinson.[17] This represented the first

synthesis of a bridging carbene compound, and also demonstrated the

ability of μ-carbene ligands to couple into larger hydrocarbon fragments.

At present, bridging carbene compounds have been characterized for

nearly all the transition metals. Several general synthetic routes to

compounds containing a carbene ligand bridging two metals connected

through a metal metal bond have been developed. The most widely used and

versatile of these involves the reaction of diazoalkanes with transition

metal compounds containing a labile two electron ligand or an unsaturated metal metal bond.[18] Both of these methods take advantage of the metal-induced elimination of nitrogen from the diazoalkane and concomitant carbene transfer to the metal substrate.

These reactions typically will occur under very mild conditions and produce high yields of μ-carbene products (Eqn. 4-8). The reaction between diazoalkane and the half-sandwich compounds of cobalt 3 and rhodium 4 are typical examples.[19] Activation of the saturated metal compound, presumably via CO loss in these cases is required prior to

$$\underset{3}{\overset{Cp}{\underset{\displaystyle}{}}}\text{Co(CO)}_2 \ + \ \text{NN=C}\underset{CO_2R}{\overset{R'}{}} \ \xrightarrow{\ C_6H_6 \ \text{reflux}\ } \ Cp \underset{O^C}{\overset{R' \ CO_2R}{\underset{Co-Co-CO}{}}} Cp \ + \ N_2 \ + \ 2CO \quad (4)$$

R= $CH_3$, $C_2H_5$, $t\text{-}C_4H_9$

R'= H, $CO_2CH_3$, $CO_2C_2H_5$, $CO_2(t\text{-}C_4H_9)$

$$\underset{4}{\overset{Cp}{\underset{\displaystyle}{}}}\text{Rh(CO)}_2 \ + \ \text{NN=C}\underset{CO_2C_2H_5}{\overset{CO_2C_2H_5}{}} \ \xrightarrow[\text{THF}]{\ hv\ } \ \underset{O^C}{\overset{H_5C_2O_2C \ CO_2C_2H_5}{\underset{Rh-Rh-CO}{}}} Cp \ + \ N_2 \ + \ 2CO \quad (5)$$

$$\text{Cp}-\underset{\underset{O}{N}}{\overset{\overset{O}{N}}{Fe=Fe}}-\text{Cp} \ + \ \text{NN=C}\underset{H}{\overset{H}{}} \ \xrightarrow{\ -80 \ \text{to} \ -25°\ } \ \underset{O^N}{\overset{H \ H}{\underset{Fe-Fe}{}}} Cp \ + \ N_2 \quad (6)$$

5           6

$$Cp'-Rh\overset{O}{\underset{C\atop O}{\overset{C}{=\!\!=}}}Rh-Cp' \;+\; NN{=}C\overset{Ph}{\underset{Ph}{<}} \longrightarrow Cp'\underset{OC}{\overset{Ph\diagdown C\diagup Ph}{\underset{}{Rh{-\!\!-}Rh}}}\overset{C}{\underset{Cp'}{\overset{O}{<}}} \xrightarrow[\text{THF}]{N_2CH_2} Cp'{-}Rh\overset{H\diagdown C\diagup H}{\underset{OC\diagdown C\diagup Ph\;Ph}{\underset{}{=\!\!=}}}Rh{-\!\!-}Cp' \quad (7)$$

| | | |
|---|---|---|
| 7 | 8 | 9 |

$$Cp' = C_5(CH_3)_5$$

$$(CO)_3Os\overset{(CO)_4}{\underset{H}{\overset{Os}{=\!\!=}}}Os(CO)_3 \;+\; NN{=}C\overset{H}{\underset{H}{<}} \longrightarrow (CO)_3Os\overset{(CO)_4}{\underset{\overset{H}{\underset{H\;H}{C}}}{\overset{Os}{Os{-\!\!-}Os}}}(CO)_3 \rightleftharpoons (CO)_3Os\overset{(CO)_4}{\underset{CH_3}{\overset{Os}{Os{-\!\!-}Os}}}(CO)_3 \quad (8)$$

| | | |
|---|---|---|
| 10 | 11a | 11b |

reaction with the diazo reagent. However, if a labile ligand is present such as THF (Eqn. 3) the reaction will proceed at or below room temperature. Subsequent metal-metal bond formation gives the final carbene bridged product. If the metal is in a coordinatively unsaturated environment as is the case for a pair of metals exhibiting a formal bond order greater than one, the reaction with the diazoalkane proceeds very readily. These reactions bear a resemblance to olefin cyclopropanation reactions where for example an olefin such as ethylene reacts with diazomethane to form cyclopropane. Theoretical calculations have in fact shown that the frontier orbitals involved in the reaction of a metal-metal double bond with a $CH_2$ fragment are very similar to what one finds for a simple olefin.[20] The nitrosyl bridged iron dimer 5 reacts under very mild conditions with diazomethane to give the black air stable methylene bridged compound 6 in yields of 90%.[21] The pentamethylcyclopentadienyl-

rhodium dimer **7** also reacts under very mild conditions with diphenyl-diazomethane to give an alkylidene-bridged rhodium dimer **8** with terminal carbonyl ligands.[22] This compound can be readily decarbonylated in refluxing THF to give the doubly bonded species [($C_5Me_5$)Rh(μ-CO)(μ-$CPh_2$)]$_2$ which when exposed to diazomethane gives the triply bridged structure **9**. Compound **9** was the first biscarbene-bridged species containing two different carbene ligands.

Unsaturated transition metal clusters are also reactive toward diazoalkanes. The dihydridoosmium cluster **10**, which exhibits a formal double bond between the two osmium atoms bridged by hydrogen, reacts with diazomethane to give a methylene-bridged hydrido osmium cluster **11**. This cluster exists in a tautomeric equilibrium in which the other tautomer contains bridging methyl and hydrido groups.[23]

The mechanism of the reaction between the unsaturated transition metal compounds and the diazoalkanes is thought to involve initial coordination of the terminal diazo nitrogen to the dimetal center. A cyclic five-membered transition state is thought to follow in which the diazoalkane carbon bends over to coordinate to one of the metals, rapid elimination of $N_2$ results in formation of the μ-alkylidene. Messerle and Curtis were able to isolate and crystallographically characterize the N-bound diazo intermediate in the reaction between $Cp_2Mo_2(CO)_4$ and $Ph_2CN_2$ in $CH_2Cl_2$ (Eqn. 9). This intermediate undergoes thermal decomposition in benzene at 60°C to form the alkylidene bridged species $Cp_2Mo_2(CO)_4$(μ-$CPh_2$).[24] A similar μ-diazoalkane intermediate has been observed by Shapley in the reaction of diazomethane with $Os_3(CO)_{10}(C_2Ph_2)$.[25]

$$\text{(9)}$$
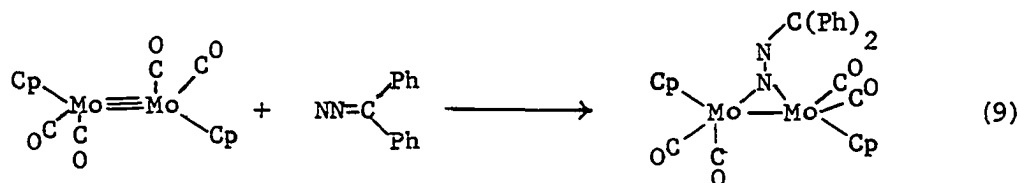
Another general synthetic route to bridging methylene compounds has been developed by Stone and coworkers. They found that Fischer-type mononuclear terminal carbene compounds (LxM=C(OR)R') will react with low valent electron rich metal complexes to form dinuclear bridging alkylidenes.[26] As shown below (Eqn. 10) the methoxyphenylcarbene of Cr,



$$\text{(10)}$$

M= Cr, Mo, W                    12
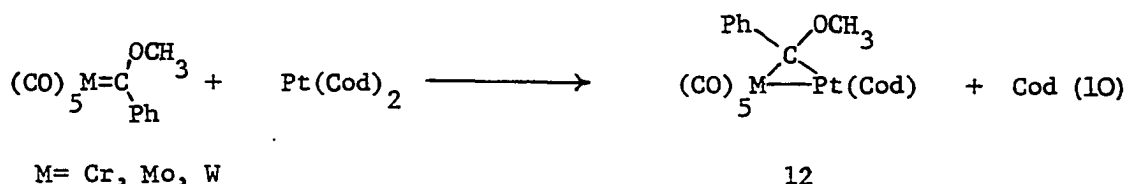
Mo. or W reacts with an ethylene-saturated light petroleum ether solution of Pt[Cod]$_2$ ant 0$^{\circ}$C to form the dark brown air-stable heterobimetallic methoxyphenylmethylene bridged product 12. The proposed mechanism of this reaction is indicated in Scheme I.
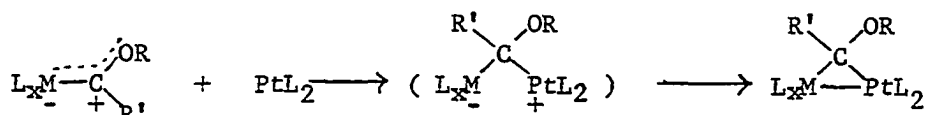


Scheme I

The dipolar nature of the Fischer-type carbene, which results from the presence of the heteroatoms on the carbene carbon atom provides an electrophilic site at which the electron rich Pt(0) compound can interact. The resulting dipolar intermediate can then collapse to form the metal-metal bonded product.

This synthetic route has also been extended to include di- and trinuclear metal systems from the reaction of Fischer-type carbene compounds with a variety of zero valent Ni, Pt, and Pd complexes. When $Cp(CO)_2Mn[C(OMe)Ph]$, **13**, is allowed to react with $Pt(Cod)_2$ (Eqn. 11) the manganese-platinum alkylidene bridged compound, **14**, is formed.[27]



$$13 \quad + \quad ML_2 \quad \longrightarrow \quad \text{(12)}$$



$$ML_2 = Ni(P(CH_3)_3)_2, \quad Pt(P(CH_3)_3)_2, \quad Pd(P(CH_3)_3)_2$$
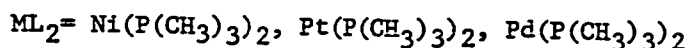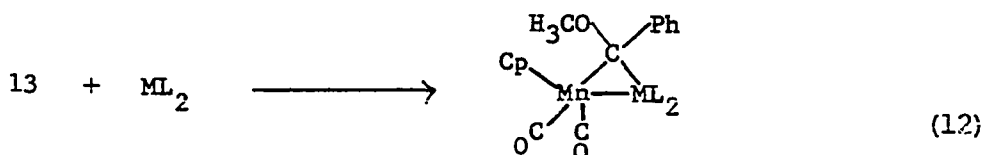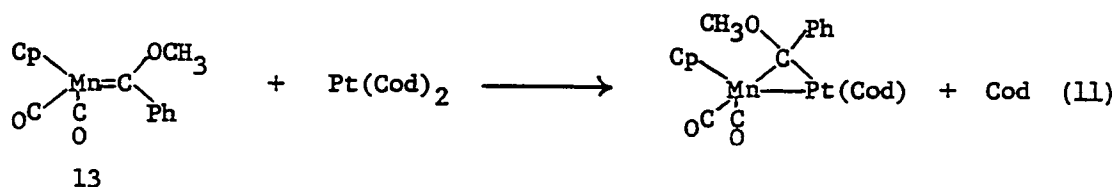
Reaction of $M(PMe_3)_2$ (M=Ni,Pt,Pd) with **13** also leads to the corresponding dinuclear μ-methoxyphenylmethylene compounds in good yield (Eqn. 12). If one starts with a bis olefin platinum complex a trinuclear Pt-M-Pt unit with the methoxyphenylmethylene ligand bridging between the two platinum atoms is obtained (Eqn. 13).[28] Interestingly, if a more bulky phosphine ligand such as $P(\underline{t}-Bu)_2Me$ is used, the reaction with **13** leads to the triplatinum compound, **14**, with two μ-methoxyphenylmethylene ligands.

$$(CO)_5 M=C \underset{Ph}{\overset{OCH_3}{\diagup}} \quad + \quad 2\ Pt(C_2H_4)_2PR_3 \quad \longrightarrow \quad \begin{array}{c} Ph \diagdown \quad \diagup OCH_3 \\ C \\ PR_3 \diagdown \quad \diagup PR_3 \\ Pt—Pt \\ \diagup \quad \diagdown \quad C_O \\ O C \diagdown M \diagup \\ (CO)_4 \end{array} \qquad (13)$$

M= Cr, W
PR$_3$= P(Bu$^t$)$_2$CH$_3$, P(C$_6$H$_{11}$)$_3$

$$\mathbf{13} \quad + \quad Pt(C_2H_4)P(Bu^t)_2CH_3 \quad \longrightarrow \quad \begin{array}{c} Ph \diagdown \quad \diagup OCH_3 \\ PR_3 \quad C \quad PR_3 \\ OC \diagdown Pt—Pt \diagup \quad OCH_3 \\ \diagdown \quad \diagup \quad C \diagdown \\ Pt \quad Ph \\ \diagup \\ PR_3 \end{array} \qquad (14)$$

**14**
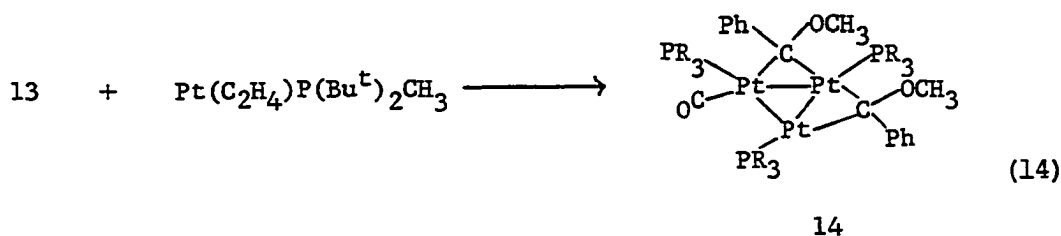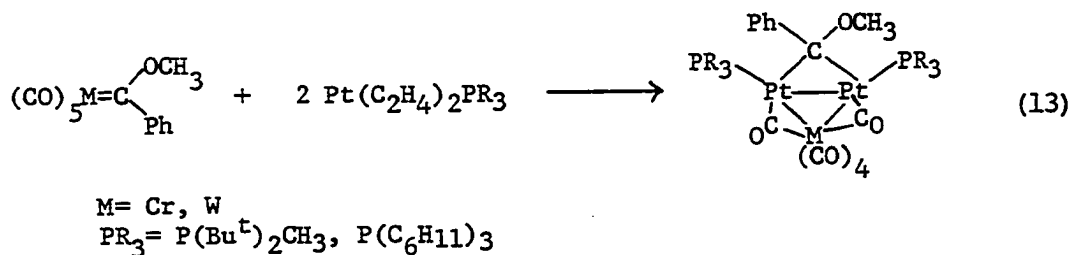
No stable Mn–Pt complex is observed. It was postulated that **14** arises via initial formation of an intermediate with a Mn[μ-C(OMe)Ph]Pt bridge which rearranges via carbene transfer to platinum. This carbene transfer reaction (Eqns. 13 and 14) was found to occur in a number of Mn–Pt systems and seems to be favored when bulky phosphine ligands are present. Consistent with this is the observation of Fischer and Beck who reported that the molybdenum complex [Mo{C(OMe)Ph}(CO)(NO)Cp] reacts with Ni(CO)$_4$ to give Ni$_3$(μ-C(OMe)Ph)$_3$(CO)$_3$.[29]

Another general method for preparing bridging carbene compounds involves the straight-forward reaction of a bridging carbyne ligand with a nucleophile. The variety of μ-carbenes that can be obtained from this route is illustrated below (Scheme II) by the research of Casey's group and also Pettit's.[30a,30b] The red cationic carbyne-bridged iron dimer

H  H
Cp\  C  /Cp
   Fe——Fe
O^C  C  C^O
      O

+  trans

16

H\  /PPh3
   C
O^C     C^O
   Fe——Fe
Cp^  C  ^Cp
      O

+

17

H\  /OC(CH3)3
   C
O^C     C^O
   Fe——Fe
Cp^  C  ^Cp
      O

20

|NaBH4

PPh3

K(OC(CH3)3)

H
C
Cp\  +  /Cp
   Fe——Fe
O^C  C  ^CO
      O

15

CO

N(CH3)3

H\  /C^O
   C
O^C     C^O
   Fe——Fe
Cp^  C  ^Cp
      O

+

18

Scheme II

H\  /N(CH3)3
   C
O^C     C^O
   Fe——Fe
Cp^  C  ^Cp
      O

+

19
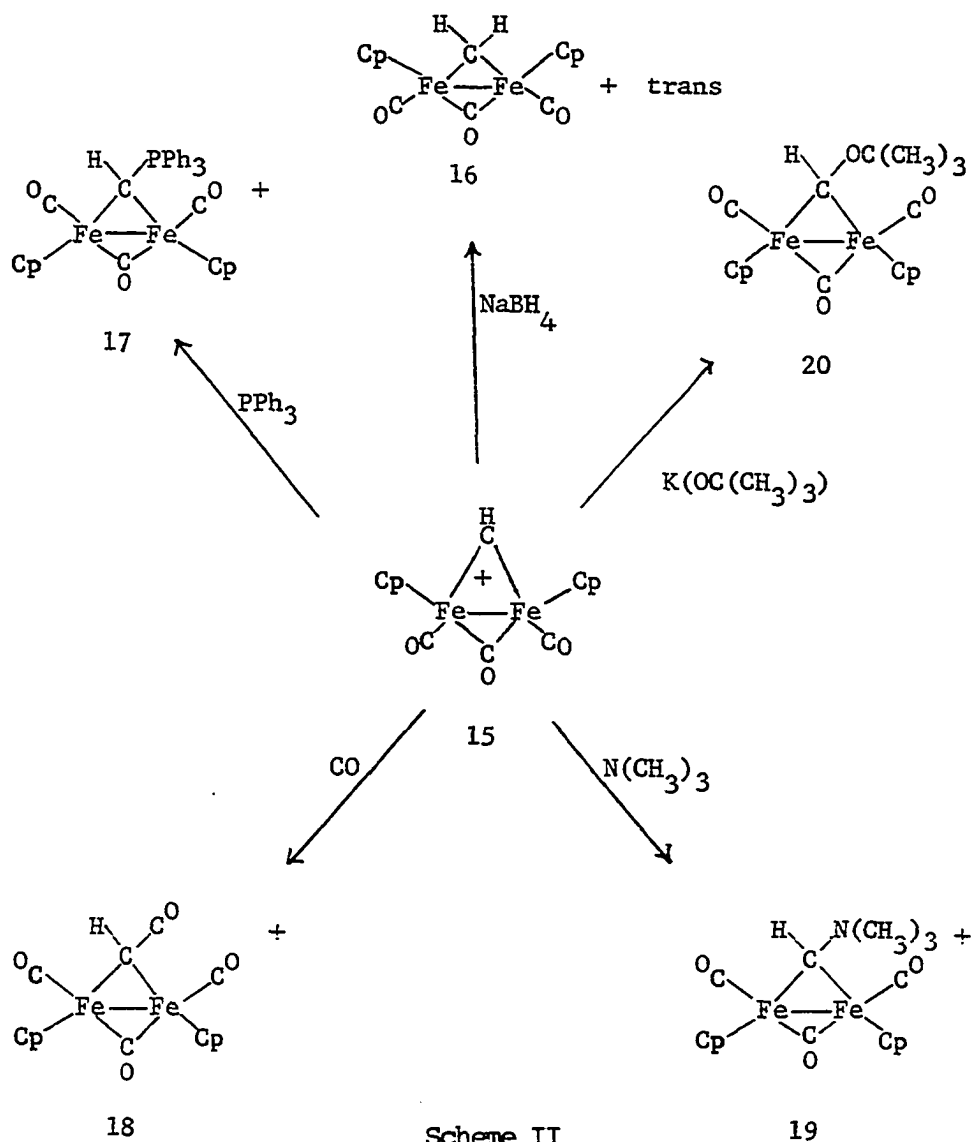
[cis-Cp$_2$Fe$_2$(CO)$_2$($\mu$-CH)]PF$_6$, 15, reacts with NaBH$_4$ in CH$_3$CN to yield an orange-red mixture of cis and trans isomers (3.2:1.0) of the methylene bridged compound, 16. Although separable by column chromatography the isomers interconvert in solution. Treatment of 15 with one equivalent of PPh$_3$ in CH$_2$Cl$_2$ gives the cationic red-brown phosphonium complex, 17, in

70% yield. The unusual acylium compound, **18**, is obtained when **15** is exposed to 500 torr of CO(g) at room temperature in $CH_2Cl_2$. The formulation of **18** as an acylium ion was confirmed by an X-ray structural analysis which showed the coordination of the CO group to the methylidyne carbon. In the presence of $NMe_3$ **15** reacts to form a 1:1 adduct with the structure proposed for **19**. Finally, when the potassium salt of t-butoxide is reacted with **15** the μ-carbene complex **20** is formed which contains an alkoxy group bound to the alkylidene carbon.

As noted, compound **16** exists as cis and trans isomers, the others mentioned above (**17-20**) exist solely as the cis isomer. Interconversion between cis and trans isomers also occurs for the μ-ethylidene compound **22** which is obtained by reacting the methyl analogue of **15** with tetra-carbonylhydridoferrate(-1) (Eqn. 15). The interconversion of cis and

$$Cp\underset{O^C}{\overset{CH_3}{\diagup\overset{C}{\underset{+}{\diagup}}\diagdown}}\underset{\overset{C}{O}}{\overset{Cp}{Fe\text{---}Fe}}\overset{Cp}{\diagdown^C_O} \quad + \quad HFe(CO)_4^- \quad \longrightarrow \quad Cp\underset{O^C}{\overset{H\diagdown\overset{CH_3}{\diagup}}{\diagdown}}\underset{\overset{C}{O}}{\overset{Cp}{Fe\text{---}Fe}}\overset{Cp}{\diagdown^C_O} \quad + \quad \text{trans} \quad (15)$$

**22**
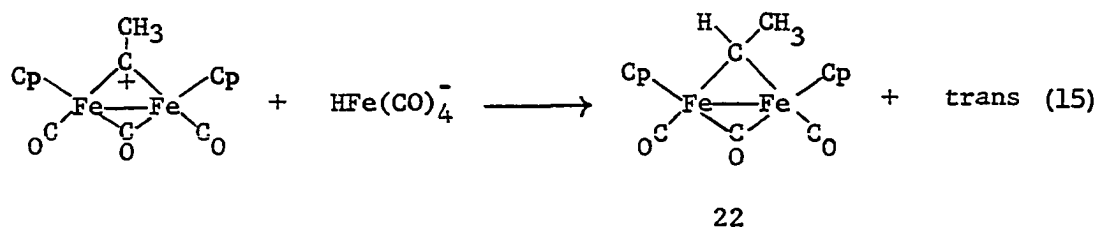
trans isomers of carbene bridged compounds is not uncommon and is believed to proceed through an intermediate in which the carbene ligand adopts a terminal coordination mode.[31]

When compound **22** is allowed to react with trityl cation $(Ph_3C^+BF_4^-)$ the purple solid μ-sigma,pi-vinyl complex **23** is obtained (Eqn. 16). Reaction of this compound with organolithium, RLi ($R=CH_3$, n-Bu), produces

$$22 \quad + \quad Ph_3C(BF_4) \longrightarrow \quad [\text{structure } 23] \quad \xrightarrow{RLi} \quad [\text{structure } 24] \qquad (16)$$

23                                    24
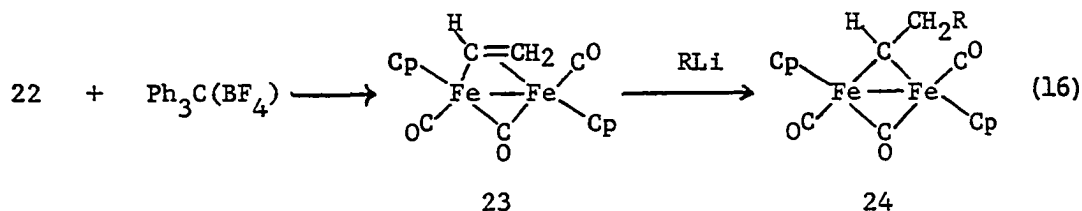
the corresponding μ-alkylidene compound, **24.**

Nucleophilic attack on a carbyne carbon in a ruthenium system has been shown by Knox and coworkers to generate a bridging alkylidene complex (Eqn. 17).[32]  In this case the cationic alkylidene-carbyne bridged

$$[\text{structure } 25] \quad + \quad NaBH_4 \longrightarrow \quad [\text{structure } 26]^- \qquad (17)$$

25                                    26
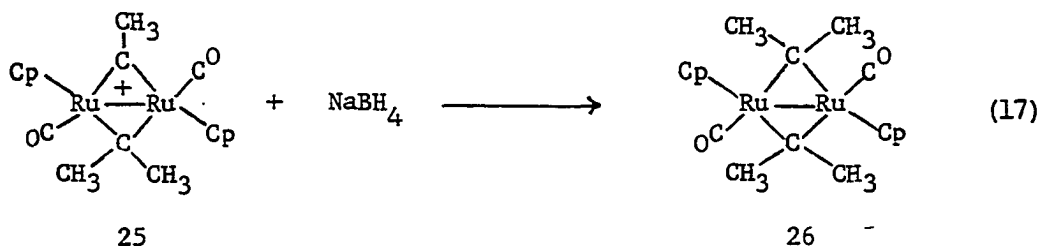
ruthenium dimer, **25,** when allowed to react with sodium borohydride yields a bis carbene bridged product, **26,** which is only observed as the trans isomer.  Stone and coworkers have also utilized the reaction of nucleophiles with bridging carbynes as a route to μ-carbene compounds the results of which have been summarized.[33]

Metal carbonyl anions have been found to react with haloalkanes in some instances to form bridging carbene compounds.  Pettit was the first to appreciate this in reaction of the tetraethylammonium salt of the metal

$$
Fe_2(CO)_8^{2-} \ + \ CH_2I_2 \ \longrightarrow \ \underset{\text{H}}{\overset{\text{H}}{\underset{}{}}}\text{C} \quad (CO)_4Fe\text{---}Fe(CO)_4 \ + \ 2I^- \quad (18)
$$

27                                    28
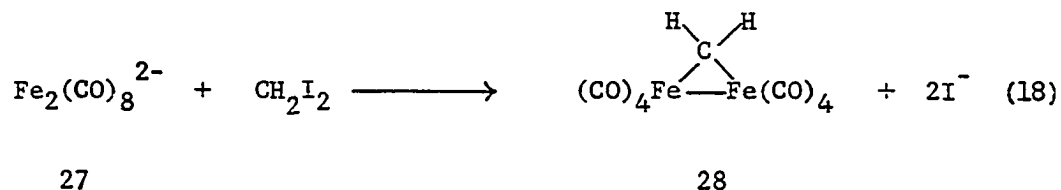
carbonyl dianion $[Fe_2(CO)_8]_2^-$, **27**, with geminal diiodoalkanes. When **27** and diiodomethane are mixed in acetone at $0^\circ C$ a reaction occurs resulting in a 60% yield of the methylene bridged dimer **28**.[34] A similar reaction occurs between **27** and 1,1-diiodoethane to give the corresponding bridging ethylidene compound. This reaction appears to be general for geminal diiodoalkanes. When dibromodimethylether and **27** are allowed to react under similar conditions a bridging methoxymethylene compound is formed (Eqn. 19). Reaction between two equivalents of acetyl bromide leads to a

$$
27 \ + \ Br_2CHOCH_3 \ \longrightarrow \ \underset{\text{H}}{\overset{\text{OCH}_3}{\underset{}{}}}\text{C} \quad (CO)_4Fe\text{---}Fe(CO)_4 \ + \ HBr \quad (19)
$$
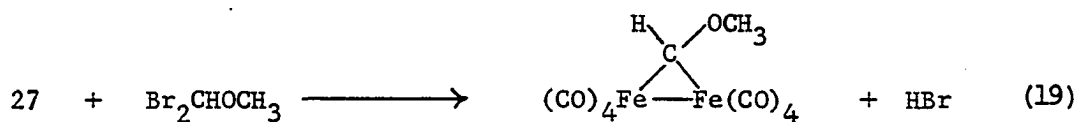
complex in which coupling has occurred between the acetyl units at the dimetal center. A bridging methoxymethylmethylene compound results in which one of the acetyl carbonyl groups binds to one of the iron atoms (Eqn. 20).

$$
27 \ + \ 2CH_3COBr \ \longrightarrow \ (CO)_4Fe\text{---}Fe(CO)_3 \ + \ CH_3CHO \quad (20)
$$
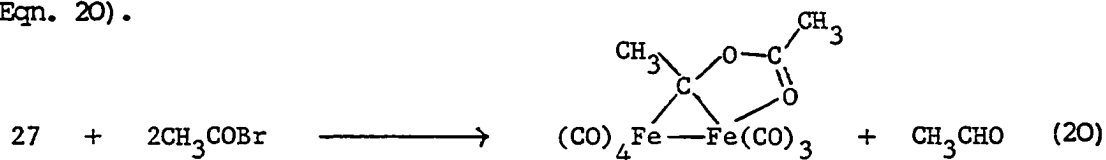
The radical anion, **29**, formed by the reduction of $Cp_2Co_2(CO)_2$ was found by Bergman to be reactive toward diiodomethane in THF to yield a methylene bridged cobalt dimer, **30** (Eqn. 21).[35] A mixture of cis and



$$Na(\ CpCo\!\!-\!\!CoCp\ )^{\underline{\cdot}}\ +\ CH_2I_2\ \longrightarrow\ \ \ \ \ \ +\ \ cis\ \ \ (21)$$

|  |  |
|---|---|
| **29** | **30** |
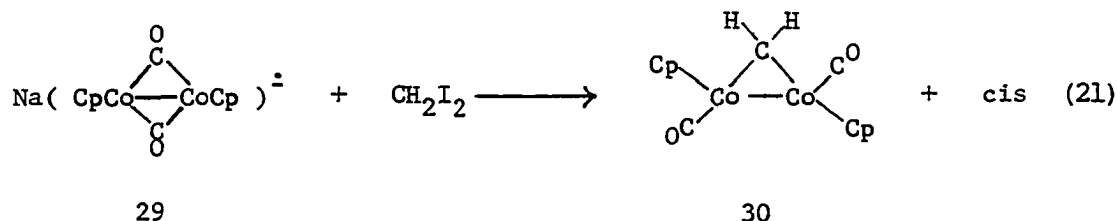
trans isomers of **30** are obtained in 48% yield. This reaction has also been found to be general for geminal diiodo alkanes.

One of the most interesting and perhaps pertinent synthetic routes to bridging carbene compounds involves the direct reduction of coordinated carbon monoxide. This involves nucleophilic attack of a carbanion at a carbonyl carbon followed either by acid induced loss of $H_2O$ to yield a cationic carbyne or direct reaction with a carbocation to yield an oxo containing carbene. The cationic carbyne can be further attacked with a nucleophile, as previously discussed, to give the carbene product. The intermediates in these reactions are usually not isolable. An example of each is given below. Knox has found that treatment of the pentamethyl-cyclopentadienylruthenium dimer, **31**, sequentially with methyl lithium, fluoroboric acid, and sodium borohydride leads to an ethylidene bridged compound, **32**.[32] Although not proven, it seems likely that initial attack of the carbanion occurs at a terminal carbonyl ligand giving an acyl anion which loses $H_2O$ upon reaction with two equivalents of fluoroboic acid leaving a bridging carbyne cation. This cation then yields the bridging

$$\text{(22)}$$

ethylidene following reaction with hydride. Alternatively the acyl anion can be methylated to give a methoxymethylene ligand as shown below (Eqn. 23).[36]



$$\text{(23)}$$

Geoffroy has shown that carbonyl ligands in metal carbonyl clusters can be reduced to $\mu$-carbenes in a similar stepwise fashion.[37] Treatment of $Os_3(CO)_{12}$ with $K[BH(O\text{-}i\text{-}Pr)_3]$ in THF at $0^\circ C$ leads to an unstable formyl complex $K[Os_3(CO)_{11}(CHO)]$, **33**, which upon acidification with aqueous $H_3PO_4$ leads to the cluster $Os_3(CO)_{11}(\mu\text{-}CH_2)$, **34**, (Eqn. 24). Attempted alkylation of **33** with $(CH_3)_3OBF_4$ also gave **34**. The mechanism through which **33** is transformed into **34** is still uncertain.

Finally, a general route to dirhenium compounds containing bridging carbene ligands has very recently been developed by Green using metal atom vapor techniques.[38] The co-condensation of rhenium atoms with benzene and

$$Os_3(CO)_{12} + K(BH(O\text{-}i\text{-}Pr)_3) \longrightarrow ((CO)_4Os\text{---}Os(CO)_4)^-$$

with $\overset{\displaystyle (CO)_4}{Os}$ bridging and a $\overset{|}{\underset{H}{C}}{=}O$ group

**33**

$\xrightarrow{H_3PO_4}$  (24)

cluster **34**: $\overset{(CO)_4}{Os}$ with $(CO)_3Os\text{---}Os(CO)_3$ bridged by $\overset{C}{\underset{H}{}}\overset{C}{\underset{H}{}}O$

**34**

saturated hydrocarbons, upon warming, leads to low yields (20%) of highly

air-sensitive, volatile, orange-yellow carbene bridged dimers

(μ-alkylidenes) (Scheme III). It is thought that initially the rhenium



Scheme III

atoms react with the arenes forming a highly reactive rhenium–arene species which then activates the methyl or methylene hydrogens of the saturated hydrocarbons. The detailed mechanism of this process is not understood.

Two other synthetic routes to bridging methylene compounds which have proven to be useful in a few isolated cases have been reported. The first involves reacting a transition metal alkyl complex, which contains a good leaving group on the α–carbon of the alkyl ligand, with a metal carbonyl anion. Nucleophilic displacement of the leaving group followed by metal–metal bond formation leads to the μ–methylene product (Eqn. 25).[39]



X= Cl, O(CO)CH$_3$

The second involves transforming dinuclear transition metal di–sigma or sigma–pi bound olefins into alkylidene bridged compounds by one of several routes.[5f,40]

Several carbene bridged species have been synthesized accidentally or by methods which have been proven to be unique to the particular system. These results have been summarized.[18]

## Reactions of bridging methylene compounds

Preliminary studies of the reactivity of bridging carbene ligands have dealt mainly with the bridging methylene ligand. Two types of reactivity are of principal importance in terms of the heterogeneous

catalytic reduction of carbon monoxide. The first involves the ability of the μ-methylene carbon-metal bond to undergo insertion reactions, which in effect results in an increase of the carbon chain length. This step is analogous to polymerization on the metal surface. The second important form of reactivity involves conversion of μ-methylene units into methyl species. As Pettit has shown, a methyl species needs to be present on the catalytic metal surface for polymerization to occur.[12] The conversion of a metal carbide to an alkylidyne (or CH) species is not well-studied; however, the conversion of alkylidynes into alkylidenes, which has been discussed, is well-known. The proposed role of the surface alkylidyne is currently limited to that of being an alkylidene precursor.

A large number of small organic molecules has been found to undergo the insertion reaction of the general type depicted in Scheme IV. In the



$$X = CO, \ SO_2, \ CS_2, \ C_2R_2, \ C_2R_4 \qquad\qquad 25$$
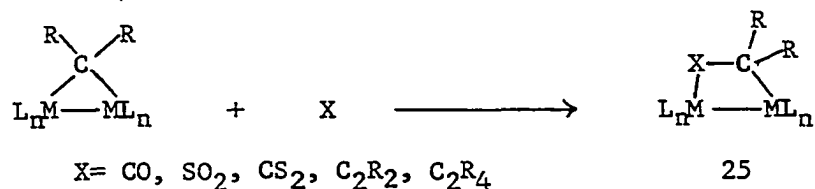
Scheme IV

cases where molcules of $SO_2$, $CS_2$, and $C_2H_4$ are able to insert into the μ-carbene metal bond, stable products of the type represented by 25 are often obtained. Carbon monoxide generally undergoes multiple insertions leading to an unstable organometallic product. Olefins generally insert and then rapidly eliminate a higher homologue organic species. For example, Herrmann has found that the μ-methylene dirhodium complex, 26,

reacts with $SO_2$ in THF at reduced temperature to give the sulfene bridged compound **27** in 93% yield (Eqn. 26).[41] Similarly it has been observed that

$$\text{26} \quad + \quad SO_2 \quad \xrightarrow{-80 \text{ to } -25^\circ} \quad \text{27} \quad (26)$$

$$Cp' = C_5(CH_3)_5$$

the unusual alkylidene bridged diiron complex **28** with the coordinated cyclopropylamine ligand readily reacts with $CS_2$ to give the insertion product **29** (Eqn. 27). The structure of this product was determined using X-ray diffraction techniques.[42]

$$\text{28} \quad + \quad CS_2 \quad \longrightarrow \quad \text{29} \quad (27)$$

Several examples of acetylene molecules inserting into carbene-metal bonds have been observed.[32,34,43] A typical example, taken from the research of Knox and coworkers illustrates this type of reaction (Eqn. 28).

$$\text{30} \quad + \quad HC\equiv CH \quad \xrightarrow{hv} \quad + \quad CO \quad (28)$$

$$M = Fe, Ru$$

Photolysis of **30** in an aromatic solvent in the presence of acetylene leads
to the formation of an alkylidene bridged product in which the original
alkylidene carbon is on the end of a metal coordinated olefin. The pro-
posed mechanism of this reaction is shown in Scheme V. Loss of CO is
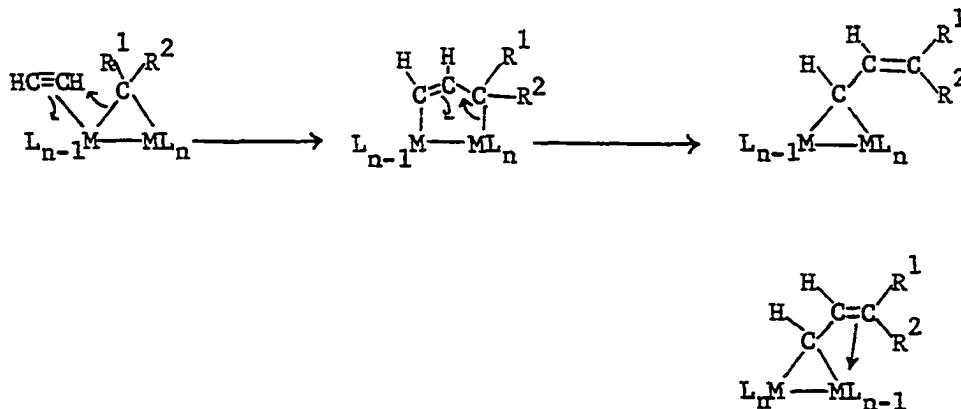


Scheme V

proposed as the primary result of photolysis. The vacant coordination
site allows entry of the acetylene molecule as a two electron donor.
Cyclization to form a five membered dimetallacyclopropene is thought to
occur followed by rearrangement to the final alkylidene product. The
olefin which is formed is able to coordinate to the metal center to fill
the site of unsaturation originally created by CO loss. When $R^2$ is a
group other than hydrogen dissociation of the coordinated olefin becomes
facile due to steric interaction with the metal. This allows a second
molecule of acetylene to enter the coordination sphere and undergo the
insertion process.

An exception to this type of acetylene insertion was observed in the

reaction of the cation $[Cp(CO)Co(\mu\text{-}CH(p\text{-}tolyl))W(CO)_2Cp]^+$ with 2-butyne.[43a]
As shown (Eqn. 29) alkylidene carbon attack has occurred rather than metal
carbon bond insertion. The reason for this unusual result has not been
clarified.



$$Cp(CO)_2W\text{---}Co(CO)Cp^+ \quad + \quad CH_3C\equiv CCH_3 \quad \longrightarrow \quad Cp(CO)W\text{---}Co(CO)Cp \quad (29)$$
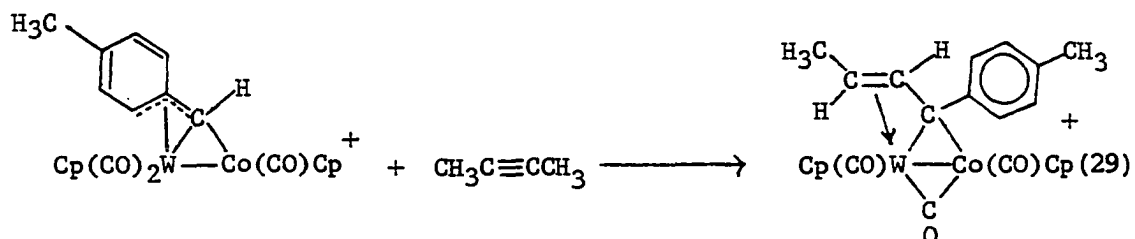
As mentioned, the insertion of olefins into metal-methylene bonds
results in unstable compounds which rapidly decompose.[34,35,43d,44] This
is in stark contrast to what was seen above in the case of acetylenes.
Pettit and coworkers observed the formation of propylene and tetracar-
bonyletheneiron when the alkylidene bridged diiron carbonyl compound 32
and ethylene were allowed to interact at elevated temperature (Eqn. 30).
The reaction is thought to occur via the formation of a coordinatively



$$(CO)_4Fe\text{---}Fe(CO)_4 \quad + \quad 3H_2C=CH_2 \quad \xrightarrow{55°} \quad CH_3CHCH_2 \quad + \quad 2\,\underset{CH_2}{\overset{CH_2}{||}}\text{---}Fe(CO)_4 \quad (30)$$
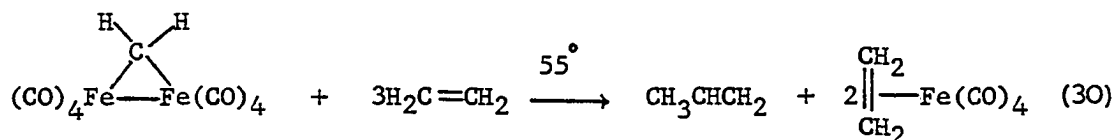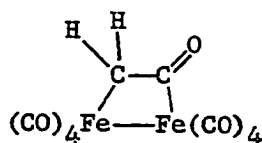
unsaturated dimetallacyclopentane intermediate similar to that in the case
of acetylene insertion. Once formed this intermediate is thought to
rapidly undergo a β-hydride elimination reaction forming a hydrido alkyl
intermediate. This pathway was blocked in the acetylene reaction because

of the unsaturation in the five-membered intermediate. The alkyl hydride formed here reductively eliminates from the metal center forming a free olefin and leaving an unsaturated metal complex. In this specific case, the iron is stabilized by further reaction with ethylene to give the indicated product. This pattern of reactivity is general in reactions of olefins with $\mu$-methylene compounds.

The direct coordination and insertion of a free carbon monoxide molecule into a $\mu$-methylene-metal bond has not been observed. No analogue to the ketene products seen in mononuclear carbyne chemistry has been detected.[45] Roper and coworkers have indirect evidence for such a species in reactions between alcohols and $CH_2(Fe(CO)_4)_2$. The product distribution resulting from deuteration studies suggest an intermediate such as 31 below.[46]

Shapley has isolated a ketenenylidene compound in the thermal decomposition reaction of $Os_3(CO)_{10}(\mu-CH_2)$ in the presence of methanol.[47] A reaction has been observed to occur between CO and $Cp_2(CO)_4Mo_2(\mu-CPh_2)$

$$\begin{array}{c} H \quad \overset{H}{\underset{|}{\phantom{.}}} \quad \overset{O}{\diagup} \\ \diagdown \underset{\diagup}{C}\!\!-\!\!\underset{\diagdown}{C} \\ (CO)_4Fe\!\!-\!\!Fe(CO)_4 \end{array}$$

31

to yield diphenylketene, although no stable organometallic product was isolated.[48] Several other authors have observed reactions to occur between $\mu$-methylene-containing compounds and CO which lead to the coupling products expected from CO insertion.[49] However, the actual ketene intermediates have eluded detection and isolation.

A reaction that is closely related to the insertion process described above involves the direct coupling of two μ-methylene ligands across a dimetal center. Clearly, the coupling of methylene ligands on a heterogeneous surface (providing they are indeed present) must be a facile process. Hence, one would hope to find a similar reactivity in homogeneous analogues. This type of reaction is observed to occur in homogeneous μ-methylene compounds. The di-μ-alkylideneruthenium complex **32** liberates 2-methyl-but-2-ene in 70% yield when heated to 200°C (Eqn. 31).[32] The nature of the metal containing products of this reaction



**32**
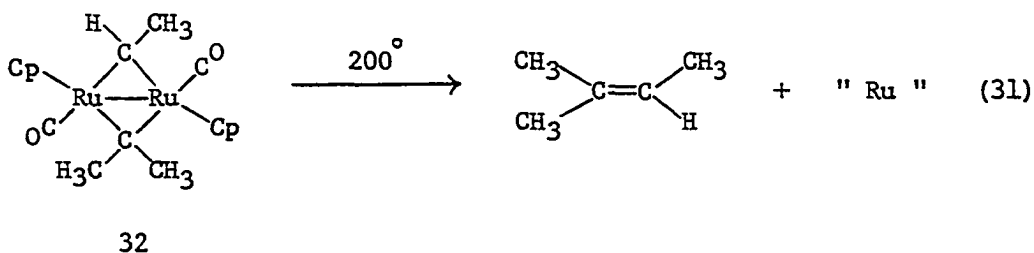
are unknown. A more dramatic example of this process has been observed by Maitlis in a dirhodium system.[50] In this case, a di-alkyl-bis-μ-methylene complex is observed to undergo thermolysis via carbene coupling and alkyl insertion (Eqn. 32). When heated to 350°C, the cis isomer of **33** yields



**33**     $Cp' = C_5(CH_3)_5$
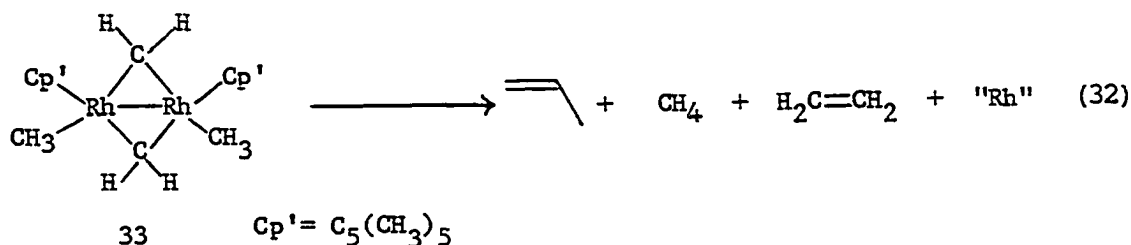
methane (48%), propene (30%), and ethylene (20%) as the major products.

The mechanism proposed for this reaction is presented in Scheme VI.
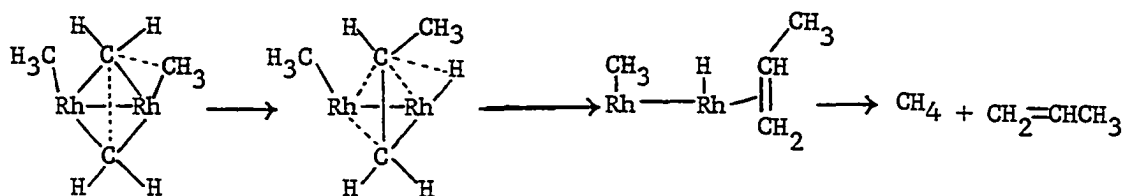


Scheme VI

Initially a double insertion occurs which couples the two methylene

ligands and a methyl group. If a β-hydride elimination then occurs an

intermediate alkyl hydride olefin complex results. This can then yield

the observed products via a reductive elimination of methane and dissocia-

tion of propene. No experiments have been done to confirm or deny the

validity of this mechanism. Further examples of carbene coupling

reactions are lacking due to the scarcity of multiple methylene bridged

compounds. The few other such compounds have not been explored for this

type of reactivity.[22a,6b]

Several well-documented examples of dinuclear μ-methylene compounds

being protonated to form methyl species have appeared.[5c,6a,35a,39b,51]

Protonation occurs in one of two ways. Generally if an electron rich

metal-metal bond is present protonation results there rather than at the

methylene bridge. However if an electron rich metal-metal bond is not

present, or is sterically unavailable protonation of the μ-methylene

carbon results.

When the methylene bridged rhodium compound, 34, is protonated at low

temperature, the cationic hydride bridged species **35** is isolated (Eqn. 33).[51d] Compound **35** has been characterized by IR, NMR, and



$$\text{(34)} \qquad \xrightarrow{\text{HX}} \text{(Cp(CO)Rh} \quad \text{Rh(CO)Cp)X} \xrightarrow{20°} (Cp_3Rh_3(CO)_2CH)X \qquad (33)$$

**34**            **35**

$$X = BF_4^-, \ CH_3CO_2^-, \ CF_3SO_3^-, \ FSO_3^-$$
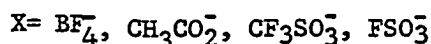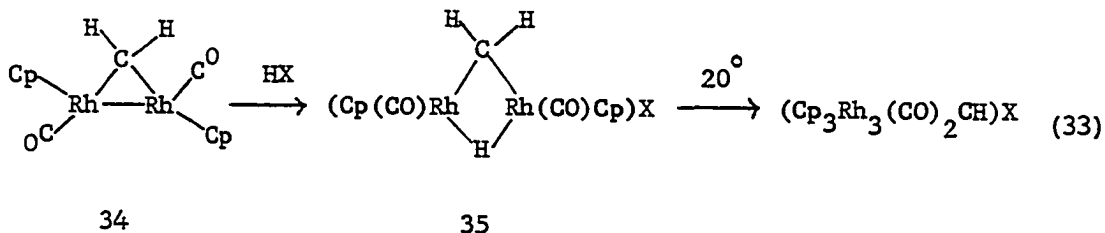
electrical conductivity measurements. The bridging hydride and methylene hydrogens were shown to exchange rapidly on the NMR time scale suggesting an intermediate methyl bridged structure. When **35** is allowed to warm to room temperature a trinuclear alkylidyne bridged structure, **36**, results. If a coordinating anion such as Cl⁻ or Br⁻ is used a different product results. Reaction of **34** with HCl or HBr at -80°C followed by slow warming results in the formation of Cp(CO)Rh(CH₃)Rh(X)(CO)Cp presumably via the same μ-methylene-μ-hydrido intermediate.

Reversible protonation at the methylene carbon was observed by Casey in the low temperature reaction between $HBF_4$ or $CF_3SO_3H$ and $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ in diethyl ether (Eqn. 34).[39b] Cationic **37** was isolated and



$$(34)$$

**37**
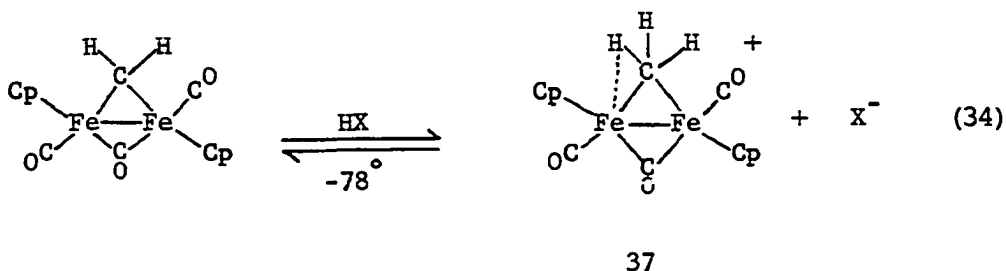
characterized by ¹H and ¹³C NMR. The large ¹³C–¹H coupling constant

($\delta$=23.4 ppm J=120 hz, X=SO$_3$CF$_3$) observed here corresponds to what is seen in other examples in which $\mu$-methylene-metal bonds have been proton-ated.[51c,52] Deuteration experiments on **37** have shown that the $\mu$-CH$_3$ is unsymmetrically bonded to the iron atoms and that there is a specific interaction of one iron atom with one CH bond of the $\mu$-CH$_3$ group. This type of interaction has also been seen in Os$_3$(CO)$_{10}$($\mu$-CH$_3$)H and {Cp$_2$Fe$_2$($\mu$-CO)[$\mu$-(C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$($\mu$-Ch$_3$)}$^+$, the latter case of which was confirmed using X-ray crystallography.[23,51c]

Wilkinson observed protonation of the triply methylene bridged ruthenium compound (Me$_3$P)$_3$Ru($\mu$-CH$_2$)$_2$($\mu$-CH$_3$)Ru(PMe$_3$)$_3$] {BF$_4$}.[6b] Upon further reaction of the cation with H$^+$ the dication [(PMe$_3$)$_3$Ru-($\mu$-CH$_2$)$_2$Ru(PMe$_3$)]{BF$_4$}$_2$ is formed along with methane. The presence of the three $\mu$-methylene ligands is thought to block initial protonation at the otherwise electron rich Ru-Ru bond.

Very recently, Stone has reported the first heterobimetallic assymmetrically bridged methyl complex {(CO)$_3$Re($\mu$-CH$_2$)($\mu$-CO)($\mu$-(C$_6$H$_5$)$_2$-PCH$_2$P(C$_6$H$_5$)$_2$W(CO)$_3$}$^+$, **38**, formed from the low temperature reaction between HBF$_4$, and (CO)$_3$Re($\mu$-CH$_2$)($\mu$-CO)($\mu$-(C$_6$H$_5$)$_2$PCH$_2$P(C$_6$H$_5$)$_2$)W(CO)$_3$ in CH$_2$Cl$_2$.[51c] One of the $\mu$-methyl CH bonds in **38** was found to interact with the tungsten atom. Further reaction of **38** with P(OMe)$_3$ causes the insertion of a CO ligand into the metal-methyl bond yielding a $\mu$-acyl ligand.

## Structure and bonding in bridging methylene compounds

Preliminary investigations into the structure and bonding of $\mu$-methylene containing compounds has led to some interesting results. Utilizing parameter-free Fenske-Hall molecular orbital calculations in

conjunction with He-I photoionization results Lichtenberger has developed
a fairly quantitative picture of the bonding, at the frontier orbital
level, in $[\mu\text{-}CH_2](CpMn(CO)_2)_2$.[53] The method used involves combining the
bonding and antibonding frontier orbitals for the fragment $CpMn(CO)_2$ into
the hypothetical dimer $[CpMn(CO)_2]_2$. This hybrid is then allowed to
interact with a similarly derived set of orbitals for $:CH_2$. A simplified
version of the resulting molecular orbital diagram is presented below.
(Fig. 4). The $\mu$-methylene ligand acts as a two electron donor to the
dinuclear metal fragment via overlap of the lone pair of electrons in an
orbital of sigma symmetry with an unoccupied (LUMO) metal orbital of the
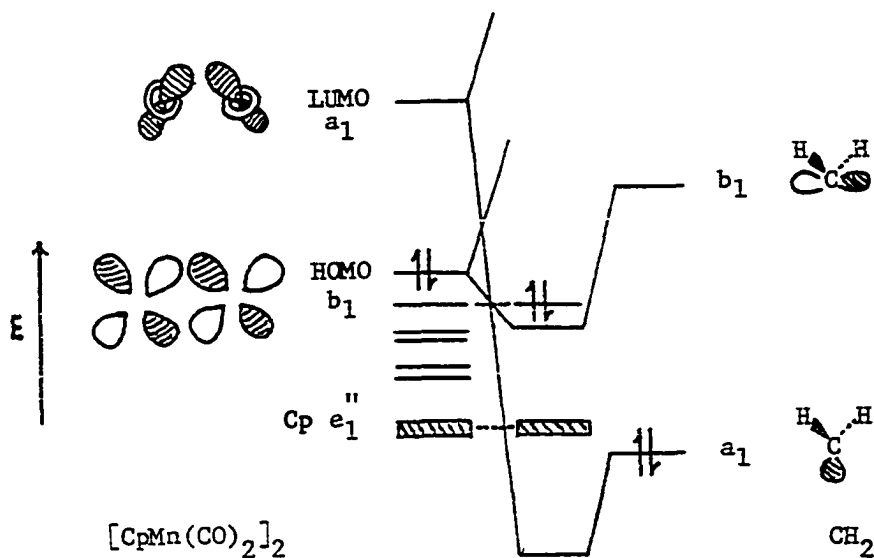


Figure 4. Molecular orbital diagram for $(CH_2)[CpMn(CO)_2]_2$.

same symmetry which is metal-metal bonding in character. This interaction strengthens the bonding between metal centers as well as to the methylene carbon. The $\mu$-methylene ligand also acts as a strong electron acceptor. The unoccupied p-pi orbital of $b_1$ symmetry is energetically positioned to interact with the HOMO of the dinuclear metal fragment, which is metal-metal antibonding in nature. With the $b_1$ methylene orbital being slightly below the HOMO of the metal fragment, this overlap effectively results in a charge transfer from metal to ligand. This interaction, by removing electron density from the antibonding HOMO of the dinuclear fragment strengthens the metal-metal bonding as well as contributing to the bonding of the methylene fragment. This metal to ligand charge transfer is such that a Mulliken orbital population analysis indicated a charge of -.529e on the methylene carbon atom. Similar conclusions have resulted from theoretical examinations of the molecules $(\mu\text{-}CH_2)Os_3(CO)_{10}$ and $(\mu\text{-}CH_2)[CpRh(CO)_2]_2$ by others.[54] It has been suggested that $\mu$-methylene is both a stronger sigma donor and pi acceptor than CO. Lichtenberger concluded that the pi acceptor ability of the $\mu$-methylene ligand was of more significance in the Mn system than was the sigma donation in terms of the contribution to the bonding.

The chemical and structural implications of these results are manifested in several ways. The high negative charge on the $\mu$-methylene carbon shown in calculations has been corroborated by an XPS study of the carbon 1s bonding energy in a series of $\mu$-methylene complexes[55] as well as by chemical shift data from $^{13}C$ NMR experiments.[56] In addition, the facile insertion of electrophilic molecules such as $CS_2$, $SO_2$, olefins, and

acetylenes into the μ-methylene metal bond as well as protonation of it are undoubtedly related to the high charge density at this center. This is in contrast to terminal Fischer-type carbene compounds (LxM=CROR') in which the carbene carbon is found to be very electrophilic.

It has also been observed that in comparison with the analogous μ-CO compounds, μ-methylene species tend to exhibit a shorter metal-metal bond distance by some 10 pm. This distance is still slightly longer (av. ca. 15 pm) than the values calculated from Pauling covalent radii for two "single bonded" metal atoms.[57] The structural features for all μ-methylene complexes reported up through early 1982 have been summarized.[18]

In homodinuclear compounds, the methylene ligand bridges symmetrically between the metal centers. This is not the case in heterodinuclear compounds or in complexes in which the metals exhibit vastly different electronic environments. This is undoubtedly the result of the strong influence of metal $d\pi$-$p\pi$ backbonding between the metal center and the μ-methylene ligand. The bridgehead carbon is observed to be drawn toward the metal center which is most electron rich and therefore best able to take part in backbonding. In the heterodinuclear methylene bridged compound $Cp(CO)Fe(\mu-CO)(\mu-CH_2)Mn(CO)_4$ the $\mu-CH_2$ is displaced toward the electron rich iron center [Fe–C(μ) av. 1.1927 (1)Å, Mn–C(μ) av. 2.087 (3)Å].[58] In a series of X-ray determinations involving heteroatom substituted μ-methylene ligands in Pt–Cr and Pt–W dinuclear systems Stone has observed the same effect.[26,59] In $(CO)_5W(\mu-CO)(\mu-C(OMe)Ph)Pt(PMe_3)_2$ the substituted μ-methylene ligand is greatly displaced toward the

electron rich Pt atom [W–C(μ) 2.48 (1)Å, Pt–C(μ) 2.04 (1)Å]. This can be regarded as a partial carbene transfer to platinum, and is consistent with the previous observation that reaction between electron deficient terminal Fischer-type carbenes and more electron rich platinum compounds can result in complete carbene transfer. In the nearly analogous compound $(PMe_3)(CO)_4W(\mu-C(tolyl)(OMe))Pt(PMe_3)_2$, in which a carbonyl on tungsten has now been replaced by $PMe_3$, the asymmetry of the bridge is lessened. [W–C(μ) 2.37 (1)Å, Pt–C(μ) 2.03 (1)Å]. This is expected in as much as the W center is made relatively less electron deficient by replacing the strong pi acceptor CO ligand by the excellent donor ligand $PMe_3$. The metal-metal separation is also found to decrease from 2.1861 (1) Å to 2.825 (1) Å respectively. Thus, the three center six electron bond which holds together these dimetallacyclopropane frames seems to be strengthened by increased electron density at the metal centers.

The research described in this dissertation explores further the chemistry of transition metal compounds containing μ–carbene ligands. More specifically a series of heterodinuclear metal complexes containing μ–dithioalkoxymethylene ligands is described. Compounds of this type are of special interest for several reasons. It has been shown that hetero-atom substituents on the carbene carbon such as N, O, S, and Se can greatly affect the reactivity of the carbene ligand.[60] This is thought to result from the ability of these atoms to donate sigma and pi electron density into the vacant p orbital of the carbene carbon. The donating ability was found to be N >> Se > S > O with the difference between S, Se, and O being small. The effect these substituents would have on the

bonding and hence the reactivity of μ-methylene ligands is largely unexplored. Inasmuch as oxygenated species are important products in heterogeneous CO oligomerization chemistry, knowledge of the reactivity of these types of ligands is of potential significance. Although dioxo and dithio carbenes are known in terminal carbene chemistry no examples of these ligands bridging metal centers has been reported.[61]

The development of a synthetic route to μ-bisdithioalkoxymethylene compounds evolved from the observation that certain cationic terminal dithiocarbene complexes of iron, such as $[Cp(CO)_2Fe[C(SMe)_2]\{PF_6\}$, **39,** were very readily attacked by nucleophiles such as phosphines and amines at the carbene carbon. It was thought that a metal anion, such as $Co(CO)_4^-$ might also react at the electrophilic carbene carbon and lead to the formation of a heterodinuclear thioalkoxymethylene derivative. The large number of metal carbonyl anions which can be readily synthesized make this an attractive route to heterodinuclear compounds, few first row transition metal examples of which are known. Cyclic five and six membered ring dithiocarbene analogues of **39** are also known and could lead to bridging cyclic carbene complexes. The chemistry of μ-cyclic carbenes is nearly unexplored. Finally, this research is part of a larger study of the organometallic chemistry of sulfur containing compounds.

## EXPERIMENTAL

General information:

The following solvents were distilled from the indicated desiccant and stored under an atmosphere of nitrogen in all glass apparatus: tetra-hydrofuran (sodium/benzophenone), dichloromethane ($P_4O_{10}$), diethylether ($NaK_{2.8}$). Reagent grade acetonitrile, acetone, pentane, and hexane were dried over molecular sieves (4Å) and purged with $N_2$ for 30 minutes prior to use. Piperidine was stirred over KOH, distilled, and stored over molecular sieves.

The metal carbonyl compounds $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ were obtained from Strem and sublimed prior to use. The following compounds were also obtained from Strem and used as received: $Fe(CO)_5$, $Cp_2Fe_2(CO)_4$, $Mo(CO)_6$, and $P(C_2H_5)_3$. The $Cp_2Ru_2(CO)_4$ was kindly provided by Dr. Alan Steinmetz. Triphenylphosphine was obtained from Aldrich Company and recrystallized from hot methanol before use.

All manipulations were carried out in Schlenkware or similar apparatus under $N_2$ using standard inert atmosphere techniques.[62] Infrared spectra were recorded on a Perkin-Elmer 681 spectrophotometer calibrated against CO and are thought to be accurate within $\pm 2$ cm$^{-1}$. Proton and carbon NMR spectra were obtained on a JEOL FX-90Q spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane. The shiftless relaxation agent Cr(acac)$_3$ (~0.1$\underline{M}$) was added to $^{13}$C samples to reduce data collection time. Electronic (UV-visible) spectra were recorded on a Beckman DU-8 instrument using quartz cells of 1 cm pathlength. Mass spectra were obtained on a Finnigan 400 GC-MS with an

INCOS 2300 data system, GC model 9610 at a source voltage of 20 eV.

Photochemical reactions were carred out at 254 nm in a quartz Schlenk tube

equipped with a cooling probe using a reactor obtained from Bradford

Scientific, Inc., Marblehead, MA. Melting points were determined with a

Thomas model 40 Micro Hot Stage and are not corrected.

The compounds: $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$, **39**[63],

$\{Cp(CO)(NCCH_3)Fe[C(SCH_3)_2]\}PF_6$, **40**[64], $\{Cp(CO)_2Fe[\overline{CSCH_2CH_2S}]\}PF_6$[41],

$\{Cp(CO)_2Fe[\overline{CSCH_2CH_2CH_2S}]\}PF_6$, **42**[60], $Cp_2FeFeCl_4$[65], $\{Fe(CO)_3NO\}PPN$, and

$\{Mn(CO)_2(NO)_2\}PPN$[66] were prepared by established routes.

Preparation of $\{Cp(CO)(NCCH_3)Fe[\overline{CSCH_2CH_2S}]\}PF_6$, **43**.  A 35 ml

acetonitrile solution of **41** (0.15 g, 0.35 mmole) was irradiated at 254 nm

for 2.5 hr. During this time, the bands due to **41** slowly diminished in the

IR spectra as a new band grew in at 2011 cm$^{-1}$. Gas evolution was apparent

and a gradual color change from bright yellow to red occurred. The

solvent was removed in vacuo (1 torr) leaving a red oil. The oil was

washed several times with Et$_2$O. Crystallization was induced by dissolving

the oil in a minimum amount of CH$_2$Cl$_2$, layering with Et$_2$O, and slowly

cooling to -20°C. Dark red air-stable crystals of **43** were obtained

(0.11 g, 64%). IR (CH$_2$Cl$_2$) ν(CO) 2016 cm$^{-1}$; $^1$H NMR (CD$_2$Cl$_2$) 4.83 (s,

5H, Cp), 3.14 (s, 4H, SCH$_2$), 2.32 (s, 3H, CH$_3$CN); $^{13}$C NMR (CD$_2$Cl$_2$,

Cr(acac)$_3$) 307.07 (s, carbene carbon), 214.49 (s, (CO)), 134.67 (s,

CH$_3$CN), 86.13 (s, Cp), 46.43 (s, SCH$_2$), 4.66 (s, $\underline{C}$H$_3$CN). Anal. calcd. for

C$_{11}$H$_{12}$ONF$_6$PS$_2$Fe: C, 30.08; H, 2.75. Found: C, 30.56; H, 2.99.

Preparation of $\{Cp(CO)(NCCH_3)Fe[\overline{CSCH_2CH_2CH_2S}]\}$ $PF_6$, **44.** This compound was prepared by the same method used for **43.** Thus, irradiation of **42** (0.12 g, 0.27 mmol). For 2.0 hr afforded 0.11 g (89%) of **43** as red air-stable crystals. Mp. 72-73°C. IR $(CH_2Cl_2)$ $\nu(CO)$ 1998 cm$^{-1}$; $^1H$ NMR $(CD_2CL_2)$ δ 4.78 (s, 5H, Cp), 3.20 (m, 4H, $SCH_2$), 2.50 (m, 2H, $CH_2$), 2.31 (s, 3H, $CH_3CN$); $^{13}C$ NMR $(CD_2Cl_2$, $Cr(acac)_3)$; 300.56 ppm (carbene carbon), 215.27 ppm (CO), 134.23 ppm (N$\underline{C}CH_3$), 84.66 ppm (Cp), 37.85 ppm ($SCH_2$), 19.22 ppm ($CH_2$), 4.66 ppm (NC$\underline{C}H_3$); Anal. calcd. for $C_{12}H_{14}ONF_6PS_2$: C, 31.80; H, 3.11. Found: C, 31.78; H, 3.00.

Preparation of $Cp(CO)_2RuC(S)SCH_3$ **45.**[67] The anion $Cp(CO)_2Ru^-$ was prepared as the sodium salt by stirring 0.80 g (1.8 mmol) of $Cp_2Ru_2(CO)_4$ in a 25 ml THF solution over a sodium amalgam (0.6 g Na, 15 ml Hg) for 2.5 hr. The amalgam was drained from the bottom of the flask and to the remaining muddy green solution was added 0.22 ml (0.28 g, 3.6 mmol) of $CS_2$. After two minutes of vigorous stirring the solution adopted a tan color. To this was immediately added 0.22 ml (0.52 g, 3.6 mmol) of $CH_3I$. The solution was then stirred an additional 30 min. during which time the color became dark brown. At this point it became possible to handle the solution in air, and the solvent was removed via rotoevaporation. The resulting residue was extracted with 3 x 30 ml portions of $Et_2O$. The combined extracts were filtered through Celite using a medium porosity glass frit. The yield of $Cp(CO)_2RuC(S)SCH_3$, **45**, after evaporation of the solvent was 83% (0.94 g, 3.0 mmol). IR $\nu(CO)$ (cyclohexane); 2040 cm$^{-1}$ (s), 1990 cm$^{-1}$ (s), $(CH_2Cl_2)$; 2041 cm$^{-1}$ (s), 1988 cm$^{-1}$ (s). $^1H$ NMR $(CD_2Cl_2/TMS)$ 5.31 (s, 5H, $C_5H_5$), 2.50 (s, 3H, $SCH_3$). $^{13}C$ NMR

(CD$_2$Cl$_2$/Cr(acac)$_3$); 268.8 ppm (thioester carbon), 198.8 ppm (CO), 90.6 ppm (C$_5$H$_5$), 25.0 ppm (CH$_3$).

Preparation of {Cp(CO)$_2$Ru[C(SCH$_3$)$_2$]} PF$_6$ **46** from **45**. In a 100 ml Schlenk flask was prepared a 50 ml CH$_2$Cl$_2$ solution containing 0.94 g (3.0 mmol) of **45**. With rapid stirring 0.24 ml (0.34 g, 3.0 mmol) of CH$_3$SO$_3$F was slowly dropped in via syringe. An IR spectrum of the reaction mixture after 1 hr. of stirring showed **45** to be completely gone and two new bands present at 2022(s) cm$^{-1}$ and 2060(s) cm$^{-1}$. No visible color change had occurred. The solvent was removed in vaccuo leaving a solid brown residue. This was extracted with 2 x 20 ml portions of Et$_2$O to remove traces of **45** or Cp$_2$Ru$_2$(CO)$_4$ leaving behind {Cp(CO)$_2$Ru[C(SCH$_3$)$_2$]}SO$_3$F. The SO$_3$F$^-$ anion was exchanged for PF$_6$$^-$ by stirring in acetone (30 ml) with 3 equivalents (1.7 g, 9.0 mmol) of K[PF$_6$] for 30 min. The solution was evacuated to dryness and the product {Cp(CO)$_2$Ru[C(SCH$_3$)$_2$]} PF$_6$, **46**, was extracted into 10 ml of CH$_2$Cl$_2$ and filtered through Celite. When the CH$_2$Cl$_2$ was removed in vaccuo 0.74 g (52%, 1.6 mmol) of **46** was obtained as a brown solid. Attempts to recrystallize **46** or the SO$_3$F$^-$ salt from CH$_2$Cl$_2$/Et$_2$O or acetone/Et$_2$O solutions yielded only brown air-stable oils. Spectroscopic data for **46**: IR $\nu$(CO) (CH$_2$Cl$_2$); 2066 (s) cm$^{-1}$, 2022 (s) cm$^{-1}$. $^1$H NMR (CDCl$_3$/TMS) $\delta$ 5.7 (s, 5H, C$_5$H$_5$), 3.1 (s, 6H, SCH$_3$). $^{13}$C NMR (CD$_2$Cl$_2$/Cr(acac)$_3$); 285.3 ppm (carbene carbon), 194.5 (Ru(CO)$_2$), 89.7 (C$_5$H$_5$), 30.5 (SCH$_3$).

Preparation of {Cp(CO)(NCCH$_3$)Ru[C(SCH$_3$)$_2$]} PF$_6$ **47** from **46**. The preparation of this compound was similar to that used for **40**. Irradiation of a 35 ml CH$_3$CN solution of **46** (0.10 g, 0.21 mmol), for 2 hours gave an

80% (0.080 g, 0.18 mmol) yield of **47** as a red air-stable oil. Spectroscopic data for **47**; IR $\nu(CO)$ (THF) 1981 (s) $cm^{-1}$, ($CH_3CN$) 1991 (s) $cm^{-1}$, $^1H$ NMR ($CDCl_3$/TMS) $\delta$ 5.2 (s, 5H, $C_5H_5$), 3.1 (s, 6H, $SCH_3$), 2.5 (s, 3H, $CH_3CN$). $^{13}C$ NMR ($CD_2Cl_2$/Cr(acac)$_3$); 297.9 ppm (carbene carbon), 199.4 ppm (Ru(CO)), 129.8 ($CH_3\underline{C}N$), 85.3 ppm ($C_5H_5$), 28.7 ppm ($SCH_3$), 4.22 ($\underline{C}H_3CN$).

Preparation of Cp(CO)Fe($\mu$-CO)[$\mu$-C(SCH$_3$)$_2$]Co(CO)$_2$ **48**. A solution of Na[Co(Co)$_4$] was prepared in situ by combining $Co_2(CO)_8$ (0.13 g, 0.38 mmol) with finely ground NaOH (1.30 g, 32.5 mmol) in THF (50 ml). After 30 min. with occasional shaking, the brown color of $Co_2(CO)_8$ disappeared. The resulting suspension was filtered through a medium glass frit into a Schlenk flask containing **40** (0.30 g, 0.68 mmol). Upon mixing, the color changed from red to dark brown. After 30 min., the solvent was removed under vacuum, and the residue was extracted with hot hexanes until the extracts were clear. The hexane extracts were combined, filtered through Celite, and evaporated under vacuum to dryness. The resulting purple residue was dissolved in a minimum volume of boiling hexanes; slow cooling to -20°C gave after 24 hr. 0.22 g (83%) of the air-stable, crystalline product: Mp 103-104°C; Anal. calcd. For $C_{12}H_{11}O_4S_2FeCo$: C, 36.20; H, 2.79. Found: C, 36.60; H, 2.93. MS (20 eV) m/e 398 ($m^+$). Spectroscopic data for the dinuclear $\mu$-methylene compounds are presented in Tables I, II, and III.

Preparation of Cp(CO)Fe($\mu$-CO)($\mu$-$\overline{CSCH_2CH_2S}$)Co(CO)$_2$ **52**. The procedure used here is similar to that used for **48**. A solution of Na[Co(CO)$_4$] was prepared by combining $Co_2(CO)_8$ (0.059 g, 0.17 mmol) with NaOH (0.60 g, 1.5 mmol) in THF. This was filtered into a flask containing 0.145 g (0.33

mmol) of **43** in 10 ml of THF. After 30 min., the reaction was complete and the solvent was removed at reduced pressure. The brown-black residue was extracted into 15 ml of $Et_2O$ and filtered through Celite. The filtrate was evaporated to dryness, redissolved in 1 ml of $CH_2Cl_2$ and chromatographed on silica-gel eluting with $CH_2Cl_2$/hexane 1:1. A single red band moved off the column (2 x 10 cm) this was collected and roto-evaporated to dryness yielding 0.055 g (61%) of **52** as a black solid. The solid was recrystallized from hot hexanes with minimal decomposition yielding violet needles. Mp. 72-74°C. Anal. calcd. for $C_{12}H_9O_4S_2FeCo$: C, 36.39; H, 2.29. Found: C, 36.63; H, 2.43. MS (20 eV), me/ 396 ($M^+$).

Preparation of $Cp(CO)Fe(\mu-CO)(\mu-\overline{CSCH_2CH_2CH_2S})Co(CO)_2$ **53**. This compound was prepared in the same manner as **52**. Thus, $Co_2(CO)_8$ (0.023 g, 0.067 mmol) and NaOH (0.050 g, 1.25 mmol) were combined to form $[Co(CO)_4]Na$ in 10 ml of THF. When this suspension was filtered into a 10 ml THF solution of **44** (0.060 g, 0.13 mmol) reaction occurred forming 0.039 g (72%) of **53**. After recrystallization from hot hexanes violet needles were obtained. Anal. calcd. for $C_{13}H_{11}O_4S_2FeCo$: C, 38.07; H, 2.70. Found: C, 37.72; H, 3.00. MS (20 eV) m/e 410 ($M^+$).

Preparation of $Cp(CO)Fe(\mu-CO)(\mu-C(SCH_3)_2)Fe(CO)(NO)$ **49**. To a 25 ml THF solution of **40** (0.206 g, 0.47 mmol) was added 0.33 g (0.47 mmol) of $PPN[(CO)_3Fe(NO)]$ against a countercurrent of $N_2$. The solution very slowly turned brown over the course of 12 hr. At this point, the solvent was removed in vacuo. The resulting brown residue was extracted into 20 ml of $Et_2O$ and filtered through Celite. After removing the solvent the black solid was chromatographed on silica-gel (2 x 8 cm) eluting with $CH_2Cl_2$/-

hexane 1:1. A single red band moved off the column. Upon rotoevaporation of the solvent 0.13 g (69%) of **49** resulted. Violet crystals could be obtained by dissolving the solid residue in a minimum of boiling pentane and slowly cooling to -20°C. Although stable in air for several hours, samples of **49** decomposed over the course of several weeks even under an atmosphere of $N_2$. This instability made elemental analysis impossible. Mp 89-91°C (decomp.).

Preparation of Cp(CO)Fe($\mu$-CO)($\mu$-$\overline{CSCH_2CH_2S}$)Fe(CO)CNO) **50**. Compound **49** was prepared and isolated in an analogous fashion to **49**. When 0.334 g (0.47 mmol) of [Fe(CO)$_3$NO]PPN was added to a 20 ml THF solution of **43** (0.206 g, 0.47 mmol), one obtained, after 12 hr. of stirring, 0.140 g (75%) of **50** as violet crystals. Like **49**, compound **50** was observed to decompose over a period of weeks. Ms (20 eV) m/e 395 (M$^+$).

Preparation of Cp(CO)Fe($\mu$-CO)($\mu$-$\overline{CSCH_2CH_2CH_2S}$)Fe(CO)(NO) **51**. This compound was prepared in the same manner as **49**. The addition of [Fe(CO)$_3$NO]PPN (0.21 g, 0.30 mmol) to 15 ml of THF containing 0.14 g (0.30 mmol) of **44** followed by 12 hr. of stirring led to the formation of 0.050 (g) (58%) of **51**. This compound slowly decomposed over a period of 2-3 weeks. Anal. calcd. for $C_{12}H_{11}O_4NS_2Fe_2$: C, 35.24; H, 2.71. Found: C, 35.43; H, 2.66.

Preparation of Cp(CO)Ru($\mu$-CO)($\mu$-C(SCH$_3$)$_2$)Co(CO)$_2$ **54**. A solution containing 0.150 g (0.31 mmol) of **47** in 20 ml of THF was prepared. Into this was filtered a solution of Na[Co(CO)$_4$] prepared by combining 0.048 g (0.14 mmol) of Co$_2$(CO)$_8$ and 0.12 g (1.4 mmol) of NaOH in 20 ml of THF as previously described. Upon mixing, the color slowly turned dark brown

over the course of 4 hr. The solvent was removed in vaccuo. The solid brown-black residue was extracted with 3 x 30 ml of hot hexane. The extracts were combined and reduced in volume to ~3 ml and then chromatographed on silica-gel eluting with $CH_2Cl_2$/hexane 2:3. A single reddish band moved off the column; this was collected and roto-evaporated to dryness. The residue was dissolved in a minimum volume of hot hexane and slowly cooled to -20°C. After 24 hr., a total of 0.14 g (62%) of small red crystals of **54** resulted. Mp. 110-112°C. Anal. calcd. for $C_{12}H_{11}O_4S_2RuCo$: C, 32.51; H, 2.50. Found: C, 32.19; H, 2.52. MS (20 eV), m/e 443.9 $M^+$).

Preparation of $Cp(CO)Fe(\mu-CO)(\mu-CSCH_2CH_2S)Co(CO)(PEt_3)$ **55**. When 52 $\mu l$ (0.35 mmol) of triethylphosphine was added to a $CH_2Cl_2$ (20 ml) solution of **52** (0.140 g, 0.35 mmol). A gradual color change from brown to amber occurred over a period of 2.5 hr. The solvent was removed at reduced pressure leaving a darkly-colored solid which was redissolved in ~1 ml of $CH_2Cl_2$ and eluted down silica-gel (2 x 15 cm) with $CH_2Cl_2$/hexane 2:1. A single amber colored band containing **55** moved off the column. This was collected and roto-evaporated to dryness. The resulting brown solid was dissolved in a minimum volume of hot heptane and slowly cooled to -20°C. After a period of two days 0.050 g (56%) of crystalline **55** was obtained. Some decomposition occurred during the recrystallization process; hence, the actual yield of the reaction was somewhat higher. Anal. calcd. for $C_{17}H_{24}O_3PS_2FeCo$: C, 41.99; H, 4.97. Found C, 41.86; H, 5.22. MS (20 eV) m/e 486 ($M^+$).

Preparation of $Cp(CO)Fe(\mu-CO)(\mu-C(SCH_3)_2)Co(CO)(PEt_3)$ **56**. This compound was prepared in the same fashion as **55**. Thus, the addition of

triethylphosphine (20 µl, 0.14 mmol) to a 30 ml $CH_2Cl_2$ solution of **48**

(0.052 g, 0.14 mmol) led, following recrystalllization from hexane, to a

79% yield (0.052 g) of **56**. Mp. 79-80°C. Anal. calcd. for

$C_{17}H_{26}O_3S_2PFeCo$: C, 41.82; H, 5.37. Found: C, 41.57; H, 5.33. MS (20 eV)

m/e 460 ($M^+$-CO).

Preparation of $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}C(SCH_3)_2)Fe(NO)(PEt_3)$ **57**. The prep-

aration of **57** was carried out in the same manner as **55**. When triethyl-

phosphine (39 µl; 0.26 mmol) was added to a 20 ml $CH_2Cl_2$ solution of **49**

(0.11 g, 0.26 mmol) and allowed to stir for 12 hr. The result was the

formation of 0.120 g (93%) of **57**. Recrystallization led to small, dark

brown-black cubic crystals. Mp 102-104°C. Anal. calcd. for $C_{16}H_{26}O_3$-

$NPS_2Fe_2$: C, 39.45; H, 5.38. Found: C, 39.34; H, 5.36. MS (20 eV) m/e

487 ($M^+$).

Reaction of **48** with $I_2$. When one equivalent of $I_2$ (0.038 g, 0.15

mmol) was added to a 20 ml $CH_2Cl_2$ solution of **48** (0.060 g, 0.15 mmol) a

rapid reaction occurred yielding a faint yellow-greenish solution. The IR

spectrum showed that within 10 min. the bands due to **48** had completely

diminished and new bands were present at 2058(s) $cm^{-1}$ and 2017 (s) $cm^{-1}$ in

the carbonyl region. These were identical to those reported for **39**. The

solution was filtered through Celite, reduced in volume to 3 ml, layered

with $Et_2O$, and slowly cooled to -20°C. Golden yellow crystals resulted

which had an $^1H$-NMR spectrum identical to that reported for **39**. The yield

of $Cp(CO)_2Fe[C(SCH_3)_2]^+$ was determined to be 75% by measuring the inten-

sity of the 2058 $cm^{-1}$ $\nu(CO)$ absorption of the reaction solution and

comparing it with intensities of standard solutions of **39**.

When the identical reaction was carried out in the presence of 2 equivalents of $PPh_3$ (0.079 g, 0.30 mmol) the IR showed two additional bands, at 1992 (s) $cm^{-1}$ and 1928 (vs) $cm^{-1}$. These bands were identified as belonging to $ICo(CO)_2(PPh_3)_2$. The yield of this cobalt(I) product, as determined by comparing the intensity of the 1928 $cm^{-1}$ band of the reaction solution to intensities of standard solutions of $ICo(CO)_2(PPh_3)_2$[68] was found to be 41%.

Reaction of **48** with $Br_2$. When one equivalent of $Br_{2(1)}$ (6.7 µl, 0.13 mmol) was added to a 20 ml $CH_2Cl_2$ solution of **48** (0.050 g, 0.13 mmol) an immediate reaction took place yielding a faint yellow-greenish solution. An IR spectrum showed the reaction to be complete in less than 2 min. Following the procedure used in the previous reaction involving $I_2$ the yield of $Cp(CO)_2Fe[C(SCH_3)_2]^+$ was found to be 90%.

Reaction of **48** with $[C_7H_7]BF_4$. The addition of 2 equivalents of $[C_7H_7]BF_4$ (0.053 g, 0.30 mmol) to a 20 ml $CH_2Cl_2$ solution of **48** (0.060 g, 0.15 mmol) initiated a slow reaction which after 24 hr. resulted in the production of $Cp(CO)_2Fe[C(SCH_3)_2]^+$. The yield, determined in the manner previously described, was 95%.

Reaction of **48** with $[Ph_3C]PF_6$. To a solution consisting of **48** (0.050 g, 0.13 mmol) dissolved in 20 ml of $CH_2Cl_2$ was added 2 equivalents of $[Ph_3C]PF_6$ (0.046 g, 0.26 mmol). Reaction occurred over the course of 20 min. yielding $Cp(CO)_2Fe[C(SCH_3)_2]^+$ (90%), based on IR measurements as previously described. When 1.5 (0.20 mmol) and 0.5 (0.07 mmol) equivalents of $[Ph_3C]PF_6$ were used in reaction with **48** under identical conditions the yield of $Cp(CO)_2Fe[C(SCH_3)_2]^+$ was found to be 77% and 23%

respectively.

Reaction of **48** with [Cp$_2$Fe]FeCl$_4$. An immediate color change to faint yellow-green occurred upon the addition of 2 equivalents of [Cp$_2$Fe]FeCl$_4$ (0.097 g, 0.26 mmol) to a 20 ml CH$_2$Cl$_2$ solution of **48** (0.021 g, 0.52 mmol). Following the procedure outlined above, the yield of Cp(CO)$_2$Fe[C(SCH$_3$)$_2$]$^+$ was found to be 75%. When the analogous reaction was carried out using 1 equivalent of [Cp$_2$Fe]FeCl$_4$ (0.13 mmol) the yield of Cp(CO)$_2$Fe[C(SCH$_3$)$_2$]$^+$ was observed to be 46%.

Reaction of **49** with [Cp$_2$Fe]FeCl$_4$. When a 15 ml CH$_2$Cl$_2$ solution of **49** (0.021 g, 0.053 mmol) was treated with 2 equivalents of [Cp$_2$Fe]FeCl$_4$ (0.040 g, 0.11 mmol) a rapid color change to a faint yellow-green occurred. After stirring for 15 min. the IR showed Cp(CO)$_2$Fe]C(SCH$_3$)$_2$]$^+$ to be the only CO-containing species present in solution. The solvent was removed at reduced pressure and replaced by 10.0 ml of CH$_2$Cl$_2$. The absorbance of the 2058 cm$^{-1}$ band was recorded, and the yield was determined to be 73% by comparison with the intensity of standard solutions of **39**. The product could be isolated in the crystalline state using the method given pre-viously for **48**. An $^1$H NMR spectrum of such crystals was in accord with published values for **39**. No attempt was made to trap the Fe(NO)(CO) fragment presumably also generated in this oxidation reaction.

Reaction of **50** with [Cp$_2$Fe]FeCl$_4$. The oxidation and characterization of the products of the reaction of **50** with [Cp$_2$Fe]FeCl$_4$ was performed in the same manner as for **49**. Thus, when **50** (0.030 g, 0.076 mmol) was allowed to interact with [Cp$_2$Fe]FeCl$_4$ (0.058 g, 0.15 mmol) in CH$_2$Cl$_2$, the IR (ν(CO)) showed a 75% yield of Cp(CO)$_2$Fe[$\overline{\text{CSCH}_2\text{CH}_2\text{S}}$]$^+$. The IR and $^1$H NMR

of this product are identical to published values for **41**.

Reaction of **51** with [Cp$_2$Fe]FeCl$_4$. The method used for this oxidation was the same as for compound **50**. If [Cp$_2$Fe]FeCl$_4$ (0.052 g, 0.13 mmol) was added to a CH$_2$Cl$_2$ (15 ml) solution of **51** (0.027 g, 0.067 mmol) one obtained Cp(CO)$_2$Fe[$\overline{\text{CSCH}_2\text{Ch}_2\text{CH}_2\text{S}}$]$^+$ in 99% yield.

Reaction of **52** with [Cp$_2$Fe]FeCl$_4$. The procedure used in this oxidation was the same as that used for **48**. When 2 equivalents of [Cp$_2$Fe]FeCl$_4$ (0.052 g, 0.14 mmol) were added to a 15 ml CH$_2$Cl$_2$ solution of **52** (0.027 g, 0.68 mmol), complete reaction occurred within 15 min. forming Cp(CO)$_2$Fe[$\overline{\text{CSCH}_2\text{CH}_2\text{S}}$]$^+$ (87%) as the only carbonyl containing species.

Reaction of **53** with [Cp$_2$Fe]FeCl$_4$. Using the procedure employed above for **52**, a solution of **53** (0.027 g, 0.068 mmol) was reacted with 2 equivalents of [Cp$_2$Fe]FeCl$_4$ yielding Cp(CO)$_2$Fe[$\overline{\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}}$]$^+$ (87%) as the only carbonyl-containing species.

Reaction of **54** with [Cp$_2$Fe]FeCl$_4$. The oxidation of **54** (0.028 g, 0.063 mmol) with 2 equivalents of [Cp$_2$Fe]FeCl$_4$ (0.048 g, 0.013 mmol) proceeded, under the same conditions used for **48**, in the same manner yielding a pale brown solution. An IR and $^1$H NMR analysis of the products of this reaction indicated the formation of Cp(CO)$_2$Ru[C(SCH$_3$)$_2$]$^+$ (80%, based on comparison of the IR spectrum to that of authentic samples) as the only soluble CO containing species.

Reaction of **56** with [Cp$_2$Fe]FeCl$_4$. The procedure followed here was the same as described for **48**. Reaction of **56** (0.067 g, 0.14 mmol) with 2 equivalents of [Cp$_2$Fe]FeCl$_4$ (0.105 g, 0.28 mmol) in 20 ml of CH$_2$Cl$_2$ resulted in the rapid formation of Cp(CO)$_2$Fe[C(SCH$_3$)$_2$]$^+$ (72%), as the only

soluble CO containing species.

Reaction of 55 with [Cp$_2$Fe]FeCl$_4$. Using the procedure outlined above led to the formation of Cp(CO)$_2$Fe($\overline{CSCH_2CH_2S}$)$^+$ in 53% yield from the reaction of 55 (0.040 g, 0.082 mmol) with 2 equivalents of [Cp$_2$Fe]FeCl$_4$ (0.63 g, 0.165 mmol) in CH$_2$Cl$_2$.

Reaction of 57 with [Cp$_2$Fe]FeCl$_4$. This reaction was carried out in the same manner as described for 48. The interaction of 57 (0.059 g, 0.12 mmol) with 2 equivalents of [Cp$_2$Fe]FeCl$_4$ led to the formation of Cp(CO)$_2$Fe[C(SCH$_3$)$_2$]$^+$ in 79% yield.

Reaction of 40 with Na[CpFe(CO)$_2$]. A 20 ml THF solution of Na[CpFe-(CO)$_2$] was generated by stirring 0.060 g (0.17 mmol) of Cp$_2$Fe$_2$(CO)$_4$ over a sodium amalgam (0.50 g, Na, 10 ml Hg) for 1.5 hr. This solution was transferred via cannula tube to a flask containing 0.10 g (0.23 mmol) of 40 dissolved in 10 ml of THF. The color of the solution rapidly became dark. After 2 hr. an IR spectrum of the reaction mixture showed only strong bands at 1966 cm$^{-1}$, 1958 cm$^-$, and 1788 cm$^{-1}$ which corresponded to Cp$_2$Fe$_2$(CO)$_4$. The bands for 40 were no longer present. The solution was evacuated to dryness and extracted with Et$_2$O. The red Et$_2$O extract was filtered through Celite and rotoevaporated to dryness. The red solid was dissolved in cyclohexane the IR spectrum of which only indicated the presence of Cp$_2$Fe$_2$(CO)$_4$.

Reaction of 40 with Na[CpRu(CO)$_2$]. A 20 ml THF solution of Na[CpRu-(CO)$_2$] was prepared by stirring 0.051 g (0.12 mmol) of Cp$_2$Ru$_2$(CO)$_4$ over a sodium amalgam (0.50 g Na, 10 ml Hg) for 2.5 hr. The THF solution of the anion was then transferred via cannula tube to a waiting solution of 40

(0.100 g, 0.23 mmol) in 15 ml of THF. The reaction was allowed to stir
for 2 hr. after which time the solvent was removed under reduced pressure.
The residue was extracted with 30 ml of $Et_2O$. The only carbonyl contain-
ing species present in the IR spectrum of this mixture was $Cp_2Fe_2(CO)_4$ and
$Cp_2Ru_2(CO)_4$.

Reaction of **40** with $Na[CpMo(CO)_3]$. The anion $CpMo(CO)_3^-$ was prepared
by adding 1.0 ml of a $NaK_{2.8}$ amalgam via syringe to $Cp_2Mo_2(CO)_6$ (0.200 g,
0.41 mmol) dissolved in 50 ml of THF. After 25 min., the IR spectrum
showed the presence of 3 bands, which corresponded to $CpMo(CO)_3^-$,[69] 1898
(s) $cm^{-1}$, 1790 (s) $cm^{-1}$, 1750 (s) $cm^{-1}$, while those of $Cp_2Mo_2(CO)_6$ had
diminished. This solution was filtered through a glass frit into a flask
containing **40** (0.21 g, 0.47 mmol) in 30 ml of THF. During 2 hr. of stir-
ring, the $\nu(CO)$ bands due to the anion disappeared while those due to **40**
persisted. After removing the solvent under reduced pressure the IR
(cyclohexane) $\nu(CO)$ of a $Et_2O$ extract showed $Cp_2Mo_2(CO)_6$ as the only
carbonyl containing species.

Reaction of **40** with $PPN[Mn(CO)_5]$. $Mn(CO)_5^-$ was prepared by the
reduction of $Mn_2(CO)_{10}$ in neat piperidine. To a flask containing 5 ml of
piperidine which had been purged with $N_2$ for 30 min. was added 0.080 g
(0.20 mmol) of $Mn_2(CO)_{10}$. Over a period of 15 min., the $Mn_2(CO)_{10}$ slowly
dissolved as reduction to $Mn(CO)_5^-$ occurred. To this was added a solution
of 0.132 g (0.23 mmol) of PPN[Cl] in 12 ml of $H_2O$/acetone 1:1. A yellow
precipitate formed immediately. The precipitate was collected on a glass
frit and dried under vacuum (1 torr) for 5 hr. yielding 0.199 g (0.27
mmol, 66%) of $PPN[Mn(CO)_5]$. An IR spectrum of this yellow precipitate in

THF showed bands at 1893 (m, br) $cm^{-1}$ and 1860 (s,br) $cm^{-1}$ which are in accord with published values for PPN[Mn(CO)$_5$].[70] This anion was then added to a 40 ml THF solution of **40** (0.12 g, 0.27 mmol). After 15 min. the IR bands due to Mn(CO)$_5^-$ had begun to diminish as those of Cp$_2$Fe$_2$(CO)$_4$ and Mn$_2$(CO)$_{10}$ appeared. The reaction was stirred for an additional 18 hr., by which time the prominent species in solution were Cp$_2$Fe$_2$(CO)$_4$ and Mn$_2$(CO)$_{10}$. The solvent was removed under reduced pressure. The IR spectrum $v$(CO) of a hexane extract of the residue confirmed Cp$_2$Fe$_2$(CO)$_4$ and Mn$_2$(CO)$_{10}$ as the only CO-containing products of this reaction.

Reaction of **40** with PPN[Mn(CO)$_2$(NO)$_2$]. A 30 ml THF solution of PPN[Mn(CO)$_2$(NO)$_2$] was prepared from 0.25 g (0.66 mmol) of [Mn(CO)$_5$-NCCH$_3$]PF$_6$ and 0.780 g (1.32 mmol) of PPN[NO$_2$] using the method of Glad-felter.[66] This solution was decanted via a cannula tube into a 40 ml THF solution containing 0.320 g (0.73 mmol) of **40**. The IR spectrum of the mixture changed slowly over the course of 20 hr. resulting in four bands: 1995 (s) $cm^{-1}$, 1775 (m) $cm^{-1}$, 1751 (m) $cm^{-1}$, and 1670 (m, br) $cm^{-1}$. The 1995 $cm^{-1}$ band was due to **40**. The solvent was removed at reduced pressure. The solid was extracted with 30 ml of Et$_2$O yielding a red solution. This red solution was filtered through Celite on a glass frit and evaporated to dryness. A small portion of the solid was dissolved in cyclo-hexane and displayed an IR spectrum $v$(CO) with bands at 1779 (s) $cm^{-1}$ and 1756 (s) $cm^{-1}$. This residue was sublimed at 40°C and 1 torr yielding a red crystalline material which showed a mass spectrum and $^1$H NMR identical to those reported for Roussin's red methyl ester (NO)$_2$Fe(u-SCH$_3$)$_2$Fe(NO)$_2$.[71]

The IR is in agreement as well. The source of the 1670 $cm^{-1}$ band in the IR of the reaction mixture is not known.

## RESULTS AND DISCUSSION

### Synthesis of u-dithiomethylene compounds

Cationic dithiocarbene complexes of iron such as

$\{Cp(CO)_2Fe[C(SCH_3)_2]\}$ $PF_6$, **39**, have been shown to be very reactive toward

nucleophilic attack at the carbene carbon by P, O, N, and S donors. In

some cases, the nucleophile simply remains attached to the carbon atom

without further reaction; in others, either a mercaptide group is cleaved

or rearrangement occurs (Scheme VII).[61a] The reactivity of compounds such
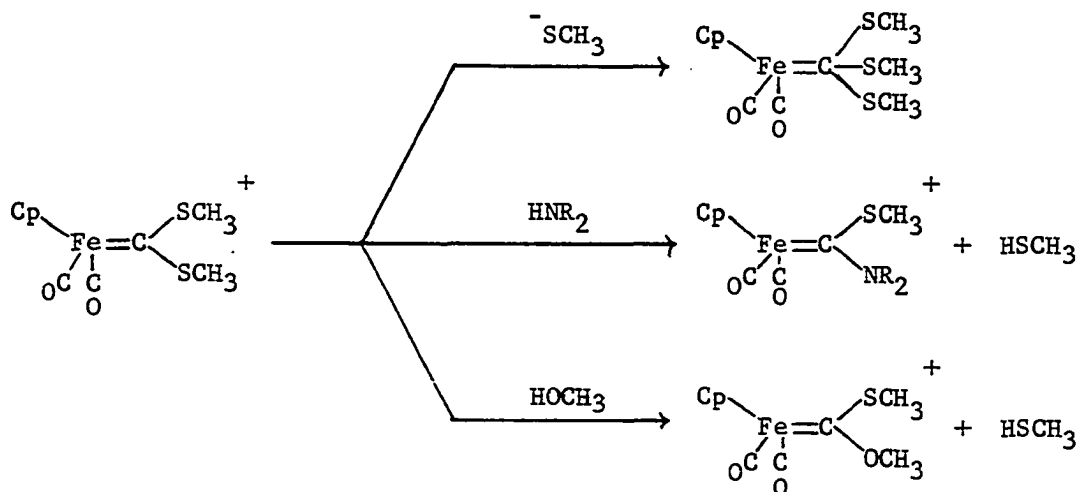


Scheme VII

as **39** or other Fischer-type carbene complexes toward nucleophilic transi-

tion metal carbonyl anions is virtually unexplored.[4a,30b]

The reaction of the terminal dithiocarbene complex $\{Cp(CO)(NCCH_3)$-

$Fe[C(SCH_3)_2]\}PF_6$, **40**, with $Na\{Co(CO)_4\}$ in THF at room temperature gives an

80% yield of the unusual bridging dithiomethoxymethylene complex, **48**, as

air-stable purple crystals according to equation 35. Compound **48** may also

be prepared from $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$, **39**, although in lower yield

(60%). No intermediates, such as $Cp(CO)Fe[\mu-(CO)][\mu-C(SCH_3)_2Co(CO)_3$, in

$$Cp\underset{O^C\underset{\underset{\dot{C}H_3}{C}}{\overset{\displaystyle +}{N}}}{\overset{}{Fe}}{=}C\overset{SCH_3}{\underset{SCH_3}{}} + Co(CO)_4^- \longrightarrow \quad H_3CS\underset{}{\overset{C}{}}SCH_3 \quad Cp\underset{O^C}{\overset{}{Fe}}{-}\underset{\underset{O}{C}}{Co}(CO)_2 + CO + NCCH_3 \tag{35}$$

40                                          48
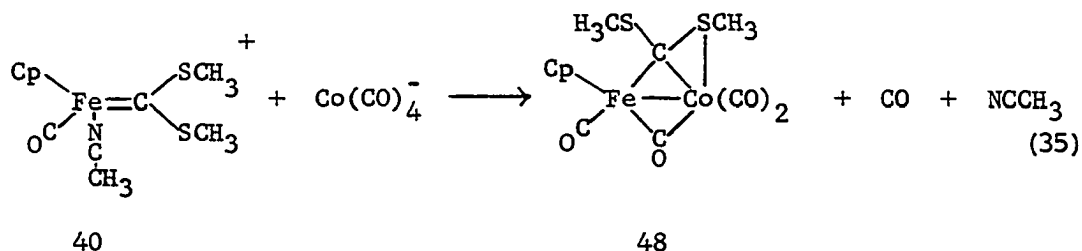
which the sulfur atom is not coordinated to cobalt are observed in the IR

during the formation of **48**. The $^{13}C$ NMR spectrum of **48** (Table 1) shows a

resonance at 176.4 ppm which is in the region normally assigned to $\mu$-

methylene carbon atoms.[18] A single resonance corresponding to a bridging

carbonyl is observed at 249.6 ppm. The carbonyl region also shows a

resonance at 212.5 ppm, diagnostic of a CpFe(CO) moiety and two broadened

resonances at 208.8 ppm and 201.1 ppm which can be assigned as carbonyls

bound to the quadrupolar cobalt nucleus (59-Co I=7/2 100%). Two singlets

are observed for the methyl groups in the $^1H$ NMR spectrum of **48** (Table 2)

one at 2.70 ppm and the other at slightly higher field, 2.23 ppm. The

shift of one of the methyl resonances to higher field is consistent with

the coordination of one of the sulfur atoms to one of the metal centers

forming a three-membered metallothiocyclopropane ring. King and Bisnette

observed a similar shift to higher field of the mercaptide methyl protons

upon coordination of the sulfur atom in the sigma to pi conversion of a

series $(Ln)M-CH_2SCH_3$ compounds, an example of which is shown below

Table 1.  $^{13}C$ NMR Spectra of the μ-dithiomethylene Complexes in $CD_2Cl_2$ (ppm).[a]

| Complex | μ-CC | Fe(CO)[b] | μ-methylene carbon | Cp | Other Resonances |
|---|---|---|---|---|---|
| **48** | 249.59 | 212.50 | 176.44 | 83.27 | 208.77, 201.06 $(Co(CO)_2)$, 30.01, 24.85 $(SCH_3)_2$ |
| **49** | 260.34 | 212.31 | 188.77 | 84.52 | 222.31 (Fe(CO)), 29.71, 27.54 $(SCH_3)_2$ |
| **50** | 260.08 | 213.02 | 197.33 | 85.00 | 222.46 (Fe(CO)), 43.57 $(SCH_2)$, 38.99 $(SCH_2)$ |
| **51** | 260.08 | 212.84 | 181.90 | 84.66 | 222.20 (Fe(CO)), 40.71 33.78 $(SCH_2)_2$, 19.22 $(CH_2)$ |
| **52** | 249.85 | 213.80 | 185.90 | 84.14 | 208.64, 201.75 $(Co(CO)_2)$, 42.45, 39.50 $(SCH_2)_2$ |
| **53** | 249.85 | 213.54 | 168.38 | 84.05 | 209.22, 201.50 $(Co(CO)_2)$, 43.23, 33.95 $(SCH_2)_2$, 19.39 $(CH_2)$ |

[a]All resonances are singlets unless otherwise noted.  Spectra were recorded at -78°C in the presence of 0.1 M Cr(acac)₃.

[b]Refers to the carbonyl bound to the Fe coordinated to Cp.

Table 1. (Continued)

| Complex | μ-CO | Fe(CO)[b] | μ-methylene carbon | Cp | Other Resonances |
|---------|------|-----------|--------------------|----|------------------|
| **54** | 236.23 | — | 161.71 | 86.18 | 208.36, 201.64 (Co(CO)$_2$), 199.70 (Ru(CO)), 30.65, 24.24 (SCH$_3$)$_2$ |
| **55** | 253.41(d)[c] | 214.67 | 169.73(d)[d] | 82.23 | 206.22 (d, Co(CO)[e], 30.49, 24.42 (SCH$_3$)$_2$, 17.53 (d, PCH$_2$CH$_3$),[f] 6.91 (S, PCH$_2$CH$_3$) |
| **56** | 251.67(br) | 215.53 | 180.09(d)[g] | 82.84 | 206.60 (br, Co(CO)), 41.49, 39.24 (SCH$_2$)$_2$, 17.70 (d, PCH$_2$CH$_3$)[h], 7.08 (S, PCH$_2$) |
| **57** | 263.12(br) | 213.45 | 179.22(br) | 83.01 | 29.10, 26,41 (SCH$_3$)$_2$, 17.23 (d, PCH$_2$)[i], 6.82 (PCH$_2$CH$_3$) |

[c]$^2J_{PC}$ = 5.86 hz.

[d]$^2J_{PC}$ = 17.58 hz.

[e]$^2J_{PC}$ = 7.81 hz.

[f]$^1J_{PC}$ = 21.53 hz.

[g]$^2J_{PC}$ = 19.48 hz.

[h]$^1J_{PC}$ = 21.5 hz.

[i]$^1J_{PH}$ = 23.48 hz

(Eqn. 36).[72] In all cases the methyl group bound to the sulfur shifted to

$$Cp-Mo(CO)_3-CH_2SCH_3 \xrightarrow{-CO} \quad + \quad CO \quad (36)$$

higher field in the $^1$H NMR spectrum upon formation of the metallothio-cyclopropane product $(Ln-1)M-CH_2SCH_3$ in which the sulfur became coordinated to the metal following the loss of CO. The IR (Table 3) spectrum of **48** is very similar in the number and shape of the bands to what is observed for $CpFeCo(CO)_6$[73], both terminal ($2037cm^{-1}$ (m), 1988 (br,s) and bridging (1836 $cm^{-1}$ (m)) carbonyl groups are present. The broadness of the 1988 $cm^{-1}$ band suggests the overlapping of two carbonyl bands. The mass spectrum of **48** shows the parent ion plus fragments corresponding to the loss of one to four carbonyl ligands.

Although the coordination of one of the sulfur atoms to cobalt was suggested by these data a single-crystal X-ray diffraction study was undertaken by Fenske and coworkers to confirm the structure of **48** and provide the accurate bond distances and angles necessary to carry out a molecular orbital calculation (vide infra). Prior to this study no di-heteroatom substituted μ-methylene compounds had been isolated and characterized.[74]

The results of the crystal structure determination of **48** have been published in full and will only be summarized here.[74] The atom labeling scheme and molecular geometry of the bridged dithiomethylene complex are

Table 2. $^1$H NMR Spectra of the Complexes in $CD_2Cl_2$ $(\delta)^a$

| Complex | $C_5H_5$ | Other Resonances |
|---------|----------|------------------|
| **48** | 4.70 | 2.70 (3H, $SCH_3$), 2.23 (3H, $SCH_3$) |
| **49** | 4.57 | 2.79 (3H, $SCH_3$), 2.55 (3H, $SCH_3$) |
| **50**$^b$ | 4.55 | 3.40 (m, 3H, $(SCH_2)_2$) |
| **51** | 4.55 | 3.17 – 2.92 (br (m), $(SCH_2)_2$), 2.41 (m, $CH_2$)$^c$ |
| **52**$^b$ | 4.69 | 3.59–2.89 (br(m), 4H, $(SCH_2)_2$) |
| **53** | 4.69 | 2.96 (m, 4H, $(SCH_2)_2$), 2.31 (m, 2H, $CH_2$) |
| **54** | 5.16 | 2.57 (3H, $SCH_3$), 2.19 (3H, $SCH_3$) |
| **55** | 4.58 | 2.76 (3H, $SCH_3$), 2.12 (3H, $SCH_3$), 1.7 (m, 6H, $PCH_2$), 1.1 (m, 9H, $CH_3$)$^d$ |
| **56** | 4.66 | 3.67 – 2.78 (m, 4H, $SCH_2$), 1.80 (q, 6H, $PCH_2$), 1.09 (p, 9H) ($CH_3$) |
| **57** | 4.53 | 2.92 (3H, $SCH_3$), 2.46 (3H, $SCH_3$), 1.90 (br(m), 6H, $PCH_2$), 1.14 (m, 9H, $CH_3$) |

$^a$All resonances are singlets unless otherwise indicated.

$^b$Recorded in $CDCl_3$.

$^c$Poor separation of peaks makes meaningful integration impossible.

$^d3J_{PH} = 13.7$ Hz, $^2J_{PH} = 0.5$ Hz.

Table 3. IR Spectra of the Complexes in Cyclohexane $(cm^{-1})$[a]

| Complex | $\nu(CO)^T$ | $\nu(CO)^B$ | $\nu(NO)$ |
|---|---|---|---|
| Cp(CO)Fe($\mu$-CO)($\mu$-C(SMe)$_2$)Co(CO)$_2$ **48** | 2036 (m), 1989 (s, br) | 1836 (m) | |
| Cp(CO)Fe($\mu$-CO)($\mu$-C(SCH$_3$)$_2$)Fe(CO)(NO) **49** | 2003 (m), 1983 (s) | 1830 (m) | 1752 (s) |
| Cp(CO)Fe($\mu$-CO)($\mu$-CSCH$_2$CH$_2$S)Fe(CO)(NO) **50** | 2002 (m), 1985 (s) | 1832 (m) | 1739 (s) |
| Cp(CO)Fe($\mu$-CO)($\mu$-CSCH$_2$CH$_2$CH$_2$S)Fe(CO)(NO) **51** | 2005 (m), 1981 (s) | 1827 (m) | 1739 (s) |
| Cp(CO)Fe($\mu$-CO)($\mu$-CSCH$_2$CH$_2$S)Co(CO)$_2$ **52**) | 2032 (m), 1985 (s), 1973 (sh) | 1831 (m) | |
| Cp(CO)Fe($\mu$-CO)($\mu$-CSCH$_2$CH$_2$CH$_2$S)Co(CO)$_2$ **53** | 2032 (m), 1982 (s), 1971 (m) | 1830 (m) | |
| Cp(CO)Ru($\mu$-CO)($\mu$-C(SMe$_2$)Co(CO)$_2$ **54** | 2040 (m), 1987 (s), 1983 (sh) | 1841 (m) | |
| Cp(CO)Fe($\mu$-CO)($\mu$-C(SCH$_3$)$_2$)Co(CO)PEt$_3$ **55** | 1978 (s), 1953 (m) | 1794 (m) | |
| Cp(CO)Fe($\mu$-CO)($\mu$-CSCH$_2$CH$_2$S)Co(CO)PEt$_3$ **56** | 1976 (s), 1934 (m) | 1791 (m) | |
| Cp(CO)Fe($\mu$-CO)($\mu$-C(SCH$_3$)$_2$)Fe(NO)PEt$_3$ **57** | 1970 (s) | 1779 (s) | 1706 (s) |

[a]The superscripts T and B refer to terminal and bridging carbony ligands respectively.

shown in Figure 5. Selected bond distances and angles are given in
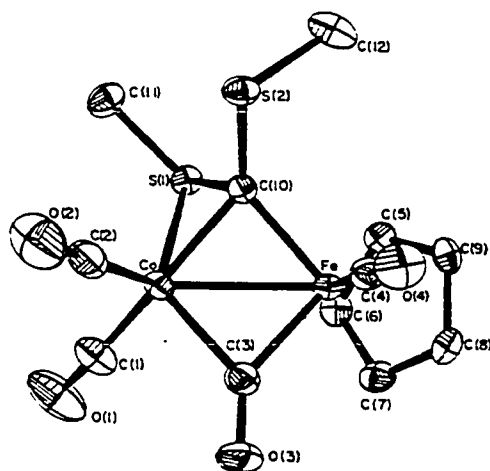


Figure 5. ORTEP drawing of compound **48**.

Table 4. The Fe—Co distance of 2.502 (1) $\overset{\circ}{A}$ in **48** is somewhat shorter than

the corresponding distances in $(CO)_3Co[\mu-CO]_2Fe(CO)Cp$, 2.545 (1) $\overset{\circ}{A}$ [75], and

the indenyl analogue $(CO)_3Co[\mu-CO]_2Fe(\eta-C_9H_7)(CO)$, 2.552 (2) $\overset{\circ}{A}$ [76]. The

bridging system is non-planar with the angle between the Co—C(10)—Fe and

Co—C(3)—Fe planes being 154.4°, which compares with 143.5° and 148.0° in

the carbonyl derivatives.

The geometry around the bridging carbene carbon C(10) is unusual in

the sense that C(10), S(1), S(2), and Fe are nearly co-planar; the sum of

the angles around C(10) to S(1), S(2), and Fe are 356.8°. The Fe—C(10)

bond distance of 1.996 (2) $\overset{\circ}{A}$ is very similar to those observed in other

Fe(CO)Cp methylene bridged compounds: $(\mu-CO)(\mu-CHCH_3)[Fe(Cp)(CO)]_2$, 1.987

(1) $\overset{\circ}{A}$ [77]; $(\mu-CO)(\mu-CHCO_2-t-bu)[Fe(Cp)(CO)]_2$, 1.97 (3) $\overset{\circ}{A}$, 2.00 (2) $\overset{\circ}{A}$.[78] It

is, however, longer than the average distance of 1.921 $\overset{\circ}{A}$ observed in the

disordered structure $(CO)_4Mn(\mu-CO)(\mu-CH_2)Fe(Cp)(CO)$.[48] The Co—C(10) bond

Table 4. Selected Bond Lengths (Å) and Angles (deg)

## Bond Lengths

| | | | | | |
|---|---|---|---|---|---|
| Fe-Co | 2.502(1) | Co-C(1) | 1.800(2) | C(3)-O(3) | 1.176(3) |
| Fe-C(3) | 1.952(2) | Co-C(2) | 1.761(3) | C(4)-O(4) | 1.143(3) |
| Fe-C(6) | 1.769(2) | Co-C(3) | 1.899(2) | C(5)-C(6) | 1.420(3) |
| Fe-C(5) | 2.117(2) | Co-C(10) | 1.916(2) | C(6)-C(7) | 1.424(3) |
| Fe-C(6) | 2.118(2) | S(1)-C(10) | 1.789(2) | C(7)-C(8) | 1.402(4) |
| Fe-C(7) | 2.122(2) | S(1)-C(11) | 1.810(3) | C(8)-C(9) | 1.427(4) |
| Fe-C(8) | 2.110(2) | S(2)-C(10) | 1.770(2) | C(5)-C(9) | 1.406(3) |
| Fe-C(9) | 2.087(2) | S(2)-C(12) | 1.810(3) | | |
| Fe-C(10) | 1.966(2) | C(1)-O(1) | 1.139(3) | | |
| Co-S(1) | 2.275(1) | C(2)-O(2) | 1.149(3) | | |

## Bond Angles

| | | | | | |
|---|---|---|---|---|---|
| C(1)-Co-C(3) | 97.74(10) | Co-Fe-C(3) | 48.56(7) | S(2)-C(10)-Fe | 127.41(12) |
| C(1)-Co-Fe | 50.75(6) | Co-C(3)-Fe | 81.04(9) | Co-S(1)-C(10) | 54.70(7) |
| Fe-Co-C(3) | 50.40(7) | Co-C(10)-Fe | 80.25(8) | Co-S(1)-C(11) | 108.30(10) |
| C(10)-Co-S(1) | 49.64(6) | Co-C(10)-S(1) | 75.66(8) | C(10)-S(2)-C(11) | 100.1(1) |
| C(10)-Fe-Co | 49.00(6) | S(1)-C(10)-S(2) | 117.69(12) | C(10)-S(2)-C(12) | 107.0(1) |
| C(10)-Fe-C(3) | 94.36(9) | | | | |

length of 1.916 (2) Å compares with the following values in other cobalt

bridging methylene complexes: $(\mu\text{-}CO)[M\text{-}\overline{CCH\text{=}CHC(\text{=}O)O}][Co(CO)_3]_2$, 1.93 Å

(av);[17] $(\mu\text{-}CHCO_2Et)[Co(Cp)(CO)]_2$, 1.95 Å (av);[19] $[\mu\text{-}\overline{CC(\text{=}O)C_6H_4C(\text{=}O)}]$-

$[Co(Cp)(CO)]_2$, 1.916 (4) Å, 1.973 (4) Å;[79] $(\mu\text{-}CO)(\mu\text{-}CH_2)[Co(C_5(CH_3)_5]_2$,

1.909 (9) Å;[80] and $(\mu\text{-}CH_2)[Fe(C_5(CH_3)_5)(CO)]_2$, 1.907 (10) Å, 1.943 (8)Å.[81]

The Co-C(10)-Fe angle of 80.25°(8) is in the range (76-81°) which is

typical of $\mu$-methylene compounds.[18]

The plane described by the Co, C(10), and S(1) triangle makes an

angle of 115.5° with the plane defined by Co, C(10), and Fe. The Co,

C(10), S(1) triangle is reminiscent of mononuclear $M\text{-}\overline{CH_2SCH_3}$ complexes

in which the following CS bond distances in the three-membered ring are

known: $(Ph_3P)_2Pd(\eta^2\text{-}CH_2SCH_3)^+$, 1.77 (4) Å, 1.678 (14) Å;[82]

$(Ph_3P)(Cl)Pd(\eta^2\text{-}CH_2SCH_3)$, 1.756 (6) Å;[83] $Cp(CO)_2Mo(\eta^2\text{-}CH_2SCH_3)$, 1.78

(1)Å;[84] $[(CH_3)_2Ga(N_2C_3H_3)(OCH_2CH_2N(CH_3)_2)]Mo(CO)_2(\eta^2\text{-}CH_2SCH_3)$, 1.744

(3)Å.[85] While the C(10)-S(1) distance, 1.789 (2) Å in **48** is comparable to

these values, it is shorter than C-S single bonds in ethylene sulfide

(1.819 (1) Å)[86] and tetrahydrothiophene (1.839 (1) Å).[86] It is, however,

similar to $C(sp^2)$-S distances in the following molecules:
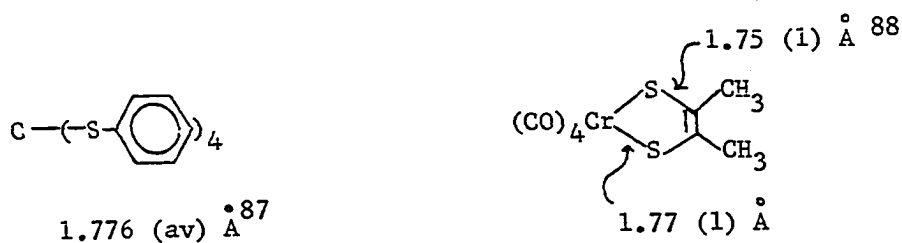


It is evident even from this limited comparison, that C-S bond distances

in triangular M-C-S units result in a somewhat ambiguous interpretation of

the bonding between the C and S atoms and the C and S bonding interactions

with the metal. For this reason molecular orbital calculations were of particular interest (vide infra).

The facility with which $Co(CO)_4^-$ reacted with **40** suggested that the isoelectronic anion $Fe(CO)_3NO^-$ might show similar reactivity. When **40** is allowed to react with one equivalent of $PPN\{Fe(CO)_3NO\}$ in THF at room temperature the dinuclear dithiomethyoxymethylene compound, **49**, is obtained in 69% yield (Eqn. 37). The spectrum of **49** shows a single strong band in the $\nu(CO)$ region at 1830 cm$^{-1}$ as well as bands at 2003 cm$^{-1}$ and 1983 cm$^{-1}$ which correspond to the two terminal carbonyl ligands. The terminal nitrosyl group gives rise to a strong band at 1752 cm$^{-1}$. The $\mu$-dithiomethylene carbon atom appears as a sharp singlet at 188.7 ppm in



$$\mathbf{40} \qquad\qquad \mathbf{49}$$
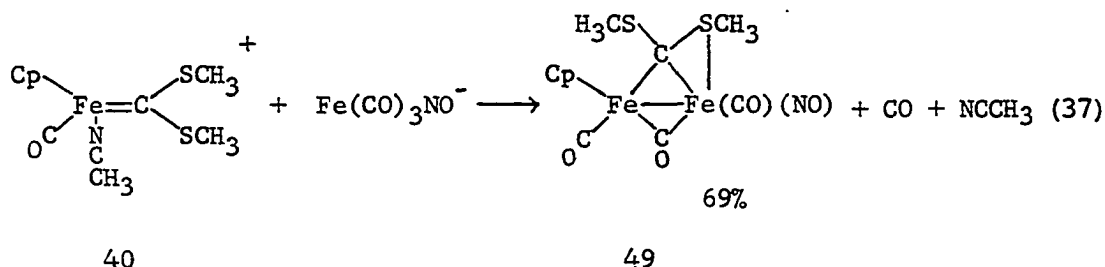
the $^{13}$C NMR spectrum of **49**. The low field region also shows a resonance at 212.3 ppm, which is in the region normally assigned to $CpFe(CO)$ carbonyl carbons, in addition to a resonance at 222.3 ppm which is assigned to the CO ligand on the nitrosyl containing Fe atom. The methyl region of the proton NMR spectrum of **49** shows two peaks, as was the case for **48**, one shifted to slightly higher field (2.79 ppm and 2.55 ppm). These are consistent with the presence of the two $SCH_3$ groups, in one of which the sulfur is bound to the Fe. The highest peak in a low energy mass spectrum of **48** occurs at m/e 397 which corresponds to the parent ion. In addition,

peaks appear with masses which correspond to fragments in which 1-3

carbonyl groups and a nitrosyl group have been lost by the parent. These

data are in accord with the formulation of 49 as having one sulfur atom of

the μ-dithiomethoxymethylene ligand coordinated to the nitrosyl containing

iron atom, similar to what was observed for 48.

Similar results are obtained upon reacting the five- and six-membered

cationic dithiocarbene complexes of iron {Cp(CO)(NCCH$_3$)Fe[$\overline{\text{CSCH}_2\text{CH}_2\text{S}}$]}PF$_6$,

43, and {Cp(CO)(NCCH$_3$)Fe[$\overline{\text{CSCH}_2\text{CH}_2\text{CH}_2\text{S}}$]}PF$_6$, 44, with PPN{Fe(CO)$_3$NO} as

shown in Equation 38. It was thought that perhaps the constraint of the

cyclic carbene would make sulfur coordination to the iron atom less

favorable. However, the spectral data presented in Tables 1, 2, and 3



$$\text{Cp}\diagdown\text{Fe}=\text{C}\diagup\text{S} (\text{CH}_2)_n \text{ + Fe(CO)}_3\text{NO}^- \longrightarrow \text{Cp}\diagdown\text{Fe}\text{—Fe(CO)(NO) + CO + NCCH}_3 \quad (38)$$

| 43, n= 2 | 50, n=2  75% |
|---|---|
| 44, n= 3 | 51, n=3  58% |
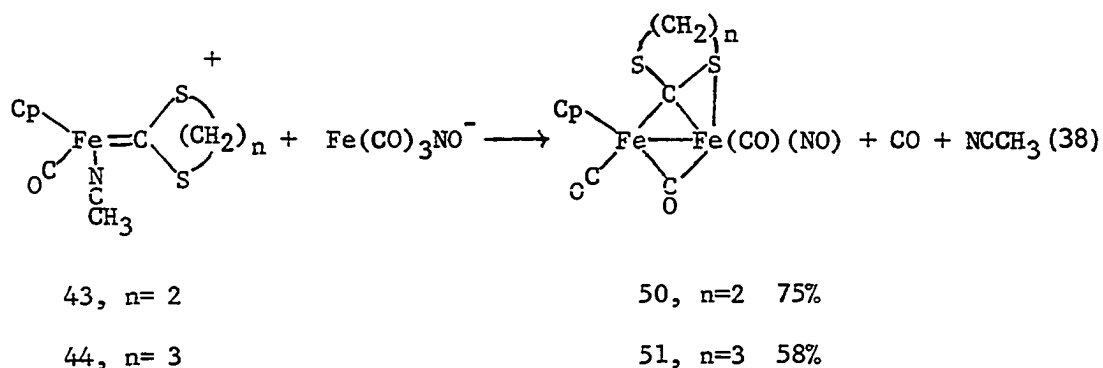
show compounds 50 and 51 to be similar in structure to 49. The μ-carbon

atom of the dithiomethylene ligands appear at 197.3 ppm and 181.9 ppm,

respectively. In the mass spectrum of 50 and 51 the highest peak (m/e)

corresponds to the parent ion for the sulfur coordinated structure. Peaks

corresponding to the fragments formed from the loss of 1-3 carbonyls and

the nitrosyl ligand are also apparent. The coordination of the sulfur to

the iron atom bearing the nitrosyl ligand is again based on the observation of only a single CO carbon resonance in the $FeNO(CO)_x$ region of the $^{13}C$ NMR (222.5 ppm and 222.2 ppm for **50** and **51** respectively), and the observation of a CO resonance in the CpFe(CO) region (**50**, 213.0 ppm; **51**, 212.8 ppm). If the sulfur were not coordinated to the iron bearing the nitrosyl ligand an additional CO carbon resonance would be expected in the region of 222 ppm. The protons in the μ-cyclicdithiomethylene ligands appear as unresolved multiplets in the $^1H$ NMR spectra of **50** and **51**. This results because of the strong coupling between these protons complicated by the fact that they are all magnetically nonequivalent. However, the methylene carbons in the cyclic ring all appear as well-resolved singlets in the $^{13}C$ NMR (Table 1).

As was the case for **40**, both **43** and **44** react with $Na\{Co(CO)_4\}$ in THF at room temperature to form the corresponding dithiomethylene-bridged compounds (Eqn. 39). Again, the spectroscopic data indicate the

$$43 \text{ or } 44 + Co(CO)_4^- \longrightarrow \quad + CO + NCCH_3 \quad (39)$$
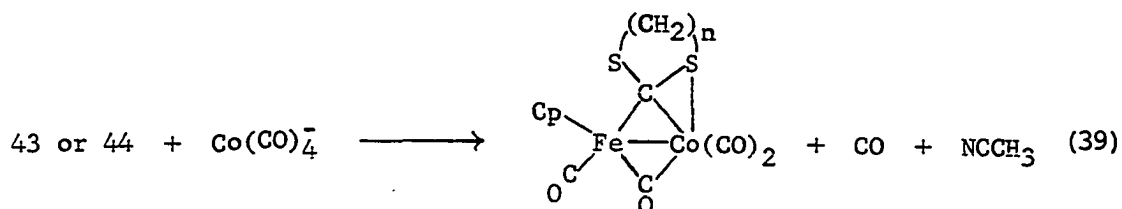
52, n= 2    61%

52, n= 3    72%

coordination of one of the sulfur atoms of the μ-cyclicdithiomethylene ligand to the cobalt. Both **52** and **53** have IR spectra nearly identical to **48**. The ν(CO) region of **52** contains four bands, 2032 cm$^{-1}$ (s), 1985 (s),
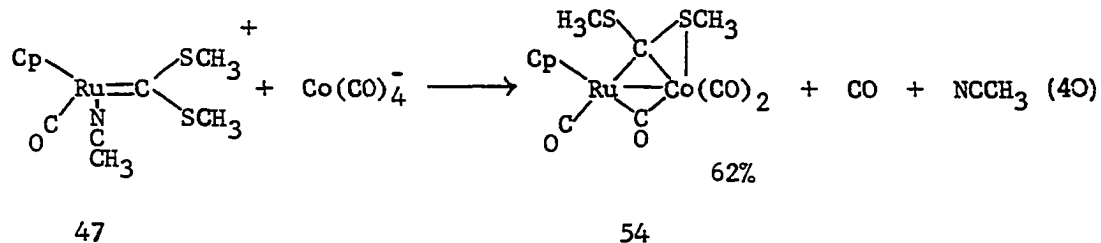
methylene carbon atoms appear at 13.4 ppm and 14.3 ppm higher field (236.2 ppm, 161.7 ppm, respectively) than those in the analogous Fe compound, **48**. This shift to higher field is expected when the first row iron atom is replaced by its heavier congener ruthenium. This has been observed in other μ-methylene compounds as well.[26] The $^1$H NMR spectrum of **54** exhibits a resonance at 5.16 ppm corresponding to the protons of the Cp ligand, whereas in the iron analogues **48–53**, the Cp resonances fall in the range 4.55–4.70 ppm. The thiomethoxy methyls in **54** appear at 2.57 ppm and 2.19 ppm which is at slightly higher field than in **48**. Again the methyl resonance at higher field (2.19 ppm) is believed to be the one coordinated to cobalt. The IR spectrum of **54** shows four bands in the carbonyl region, three terminal (2040 cm$^{-1}$ (m), 1987 (s), 1983 (sh)) and one in the bridging region (1841 cm$^{-1}$ (m)). The highest peak (m/e) observed in the mass spectrum of **54** corresponds to the parent ion; in addition peaks correponding to fragments formed from the loss of 1–4 carbonyl ligands are also apparent.

Compound **47** proved to be unreactive toward PPN{Fe(CO)$_3$NO} in THF at room temperature. Presumably the carbene carbon in **47** is less electro-

philic than that of the iron analogue, **40**, due to the more basic (better pi donor) second row ruthenium atom.

Attempts were made to prepare $\mu$-dithioalkoxymethylene compounds from the reaction of **40** with the anions $CpFe(CO)_2^-$, $CpRu(CO)_2^-$, $CpMo(CO)_3^-$, $Mn(CO)_5^-$, and $Mn(CO)_2(NO_2)^-$. None of these reactions gave the desired product. Reaction between **40** and $Na\{CpFe(CO)_2\}$ in THF rapidly leads to the reduction of **40** ultimately forming $Cp_2Fe_2(CO)_4$ as the only carbonyl containing species in solution. A similar reaction occurs between **40** and $Na\{CpRu(CO)_2\}$ or $Na\{Mn(CO)_4\}$. In the former, a rapid reaction occurs yielding $Cp_2Ru_2(CO)_4$ and $Cp_2Fe_2(CO)_4$ while in the latter a slow reaction occurs (18 hr.) resulting in the formation of small amounts of $Cp_2Fe_2(CO)_4$ and $Mn_2(CO)_{10}$. The anion $Na\{CpMo(CO)_3\}$ seems unreactive toward **40**. After 24 hr. of stirring in THF the only new bands present in the IR correspond to $Cp_2Mo_2(CO)_6$ while those of **40** have diminished. Finally, reaction between **40** and $PPN\{Mn(CO)_2(NO)_2\}$ leads to the slow formation (12 hr.) of Roussin's red methyl ester, $(NO)_2Fe(\mu\text{-}SCH_3)_2Fe(NO)_2$ as the only carbonyl containing species in solution.[71]

## Reaction with PEt$_3$

Although not common, the displacement of a sulfur intramolecularly coordinated in a metallothiocyclopropane ring has been observed. Okawara found that in the presence of excess triphenylphosphine the sulfur atom bound to Pd in $(\eta^2\text{-}CH_2SCH_3)Pd(PPh_3)Cl$ was displaced, in an equilibrium fashion, to give the $(\eta^1\text{-}CH_2SCH_3)(PPh_3)_2Pd(Co)$ complex (Eqn. 41).[82,89] When one equivalent of triethylphosphine is added to a dark brown dichloromethane solution of **48**, a slow color change to amber occurs over the

$$\underset{\substack{\text{H}_2\text{C} \\ | \\ \text{S} \\ | \\ \text{CH}_3}}{\overset{\displaystyle \text{PPh}_3}{\text{Pd}}}\text{Cl} \quad + \quad \text{PPh}_3 \quad \rightleftharpoons \quad (\text{PPh}_3)_2\text{ClPd}(\eta^1\text{-CH}_2\text{SCH}_3) \qquad (41)$$
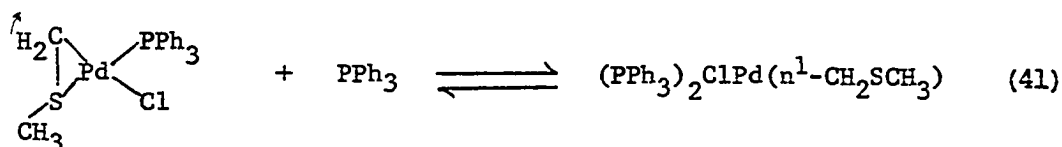
course of 30 min. Analysis of the product indicates that the $\text{PEt}_3$ has

displaced a CO ligand from the cobalt, leaving the sulfur coordination

intact (Eqn. 42). The IR spectrum of the carbonyl region of **56** consists

$$\underset{\textbf{48}}{\overset{\displaystyle \text{H}_3\text{CS}\diagdown\quad\diagup\text{SCH}_3}{\text{Cp}\diagdown\overset{\text{C}}{\underset{\text{Fe}\overline{\quad\quad}\text{Co(CO)}_2}{\diagup\diagdown}}}} \quad + \quad \text{PEt}_3 \quad \longrightarrow \quad \underset{\textbf{56}}{\overset{\displaystyle \text{H}_3\text{CS}\diagdown\quad\diagup\text{SCH}_3}{\underset{79\%}{\text{Cp}\diagdown\overset{\text{C}}{\underset{\text{Fe}\overline{\quad\quad}\text{Co(CO)(PEt}_3)}{\diagup\diagdown}}}}} \quad + \quad \text{CO} \quad (42)$$
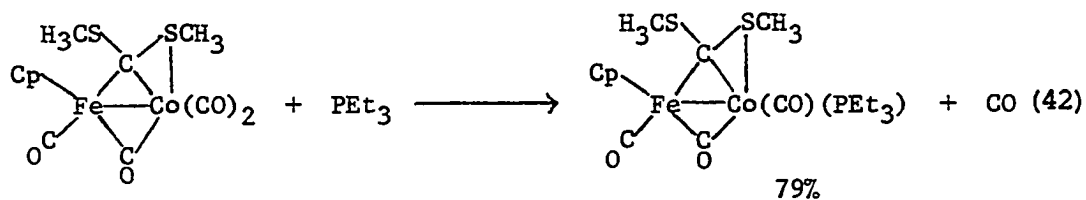
of two terminal bands (1978 $\text{cm}^{-1}$ (s), 1953 (m)) and one bridging (1794

$\text{cm}^{-1}$ (m)), all shifted to lower energy from what was observed in **48**. This

is consistent with the replacement of the good pi acceptor CO ligand with

the poor pi acceptor/strong sigma donor $\text{PEt}_3$. Integration of the $^1\text{H}$ NMR

spectrum of **56** indicates the presence of only one $\text{PEt}_3$ ligand. No split-

ting of the Cp ring is observed in either the $^1\text{H}$ or $^{13}\text{C}$ NMR spectra. Only

one resonance is present in the cobalt carbonyl region of the $^{13}\text{C}$ NMR

spectrum, a doublet centered at 206.20 ppm ($J_{PC}$=7.81 hz). The CpFe(CO)

region of the 13-C NMR displays a single resonance at 214.67 ppm. The

$\mu$-dithiomethylene carbon and $\mu$-CO resonances are split into doublets by

coupling to phosphorus: 169.73 ppm ($J_{CP}$=17.58 hz) and 253.13 ppm ($J_{CP}$=5.86

hz) respectively. The highest mass observed in a low energy (20 eV) mass

spectrum of **56** occurs at m/e 487 which corresponds to the molecular ion

for Cp(CO)Fe(μ-CO)(μ-C[SCH$_3$]$_2$)Co(CO)PEt$_3$, **56.** All these data are consistent with the replacement of a single carbonyl ligand on cobalt by PEt$_3$. Reaction of **48** with more than one equivalent of PEt$_3$ does not lead to further substitution. The weaker nucleophile PPh$_3$ is unreactive toward **48** under similar conditions.

The five-membered ring μ-dithiomethylene compound **52** also reacts with PEt$_3$ via simple CO substitution to give Cp(CO)Fe(μ-CO)(μ-CSCH$_2$CH$_2$S)Co(CO)-PEt$_3$ **55.** Quite surprisingly **49** reacts with PEt$_3$ with loss of the only terminal CO ligand on the iron bearing the coordinated sulfur atom to give Cp(CO)Fe(μ-CO)(μ-C(SCH$_3$)$_2$)Fe(NO)PEt$_3$, **57.** Thus the metallothiocyclopropane ring in these compounds appears quite robust with loss of CO favored over displacement of the intramolecular sulfur coordination in reactions with PEt$_3$ even when only one terminal CO ligand is present on the metal atom.

Upon substitution of a CO ligand by PEt$_3$ in compounds **48, 49,** and **52** one observes a shift of the carbonyl resonance in the $^{13}$C NMR spectra to lower field for the remaining terminal and bridging CO ligands. For example, the terminal CO on iron in **48** appears in the $^{13}$C NMR spectra at 212.50 ppm. When one of the carbonyl ligands on cobalt is replaced with PEt$_3$ giving **56** the terminal CO on iron is shifted to 214.67 ppm. This type of shift has been observed before, and, in general, for carbonyl ligands the $^{13}$C CO resonance shifts to lower field as the pi backbonding increases. This chemical shift trend has also been reported for the $^{13}$C resonances of terminal carbene carbon atoms.[64] In contrast, the μ-dithiomethylene carbon resonances in **55, 56,** and **57** all come at higher

field than in the non-phosphine substituted analogues. The shift to higher field is 5-10 ppm. This is opposite in direction to what is observed for carbonyls and terminal carbene ligands which are strong pi acceptors ligands. Knox has reported that on substitution of a carbonyl ligand in $Cp(CO)Ru(\mu\text{-}CO)(\mu\text{-}C(CH_3)_2)Ru(CO)Cp$ by $PMe_2Ph$ to form $Cp(CO)Ru(\mu\text{-}CO)(\mu\text{-}C(CH_3))RuCp(PMe_2Ph)$ the position of the $\mu$-propylidene carbon shifts from 175.8 ppm to 167.5 ppm respectively.[40b] This is in accord with our observations. The reason for this change in the direction of the chemical shift in $\mu$-methylene compounds is not currently understood.

## Reactions with oxidizing agents

In a reaction not previously reported for bridging methylene compounds, **48** is readily oxidized to yield a mononuclear dithiocarbene complex of iron, **39'** (**39'** refers to $Cp(CO)_2Fe[C(SCH_3)_2]^+$ which equals **39** when the counter ion is $PF_6^-$ (Eqn. 43). Reactions with two equivalents of

$$H_3CS, C, SCH_3 \quad Cp, Fe—Co(CO)_2 + (OX) \xrightarrow{-2e} Cp, Fe=C, SCH_3 + \text{ " }Co^I(CO)_2\text{ " } (43)$$

48                                 39'

the oxidizing agents $I_2$, $Br_2$, $Ph_3C\{PF_6\}$, $Cp_2Fe\{FeCl_4\}$, and $C_7H_7\{BF_4\}$ in $CH_2Cl_2$ under $N_2$ gives $\{Cp(CO)_2Fe[C(SCH_3)_2]\}^+$, **39'**, as the only carbonyl-containing product. In the reaction with $I_2$ in the presence of two equivalents of $PPh_3$ the cobalt fragment is isolated (41%) as $ICo(CO)_2(PPh_3)_2$, which is identified by comparing its IR spectrum with that of an authentic sample.[90,91] In the absence of $PPh_3$, no identifiable Co(I) complex is

isolated. The yield of the iron product **39'** in the reaction of **48** with two equivalents of I$_2$ without added PPh$_3$ is 91% after 10 min, as determined by measuring the intensity of the 2058 cm$^{-1}$ CO absorption and comparing it with intensities of standard solutions of **39**. The analogous reaction with Br$_2$ gives a 90% yield of **39'** after 5 min. Two equivalents of C$_7$H$_7${BF$_4$} give a 95% yield of **39'** after 24 hr. After only 1 min, two equivalents of Cp$_2$Fe{FeCl$_4$} give a 75% yield of **39'**, whereas one equivalent gives a 46% yield. Reactions of Ph$_3$C{PF$_6$} after 20 min give the following yields with different numbers of equivalents of the oxidizing agent: 23% (0.5 equiv), 77% (1.5 equiv), 90% (2.0 equiv). These reactions establish that two equivalents of oxidant are required. No intermediates are observed even in reactions involving fewer than 2 equivalents.

In order to explore further the generality of this process, reactions were carried out between μ-dithiomethylene compounds **49-57** and the oxidant Cp$_2$Fe{FeCl$_4$}. These results are summarized in Table 5. In all cases the terminal dithiocarbene cation is formed in high yield. The highest yields (greater than 90%) are obtained from the compounds with the bridging six-membered cyclic dithiomethylele ligand, **51** and **53**. The bridging dithiomethoxymethylene and five-membered cyclic dithiomethylene complexes generally gave yields of 70-80%. Substitution of a CO ligand by PEt$_3$ does not influence the outcome of the oxidation process in a general way. For example, the yield of **39'** obtained in the oxidation of **48** is essentially the same as **56**. A comparison of the yields of the oxidation reactions of the iron-cobalt versus iron-iron compounds show there to be little variation. It appears that in the reactions of these μ-dithiomethylene

Table 5.   Results of the Oxidation of μ-dithioalkoxymethylene complexes with two equivalents of $Cp_2FeFeCl_4$

| Compound | Product | % Yield[a] |
|---|---|---|
| **48** | $Cp(CO)_2Fe[C(SMe)_2]^+$ | 75 |
| **40** | $Cp(CO)_2Fe[C(SMe)_2]^+$ | 73 |
| **50** | $Cp(CO)_2Fe[CSCH_2CH_2S]^+$ | 75 |
| **51** | $Cp(CO)_2Fe[CSCH_2CH_2CH_2S]^+$ | 99 |
| **52** | $Cp(CO)_2Fe[CSCH_2CH_2S]^+$ | 87 |
| **53** | $Cp(CO)_2Fe[CSCH_2CH_2CH_2S]^+$ | 93 |
| **54** | $Cp(CO)_2Ru[C(SMe)_2]^+$ | 80 |
| **55** | $Cp(CO)_2Fe[C(SMe)_2]^+$ | 72 |
| **56** | $Cp(CO)_2Fe[CSCH_2CH_2S]^+$ | 53[b] |
| **57** | $Cp(CO)_2Fe[C(SCH_3)_2]^+$ | 79 |

[a]The yield of $Cp(CO)_2Fe[C(SMe)_2]^+$ was determined by measuring the intensity of the 2058 $cm^{-1}$ $\nu(CO)$ absorption and comparing it with intensities of standard solutions of $Cp(CO)_2Fe[C(SMe)_2]^+PF_6^-$ **39**. The yields of $Cp(CO)_2Fe[CSCH_2CH_2S]^+$, $Cp(CO)_2Fe[CSCH_2CH_2CH_2S]^+$ and $Cp(CO)_2Ru[C(SCH_3)_2]^+$ were determined in an analogous fashion using the 2065 $cm^{-1}$, 2057 $cm^{-1}$ and 2066 $cm^{-1}$ bands in **41**, **42**, and **46**, respectively.

[b]The low yield in this case may be due in part to a side reaction between liberated $PEt_3$ and $Cp(CO)_2Fe[CSCH_2CH_2S]^+$.

containing compounds with $Cp_2Fe\{FeCl_4\}$ that the variations in the yields

of the terminal carbene cations are more dependent upon the nature of the

dithiomethylene ligand than in changes in the electronic nature of the

dimetal center. Since the two electrons removed from the HOMO are metal-

metal bonding in nature (vide infra), one might expect changes in the

electronic environment of the metal center to be a larger factor.

The mechanism through which the oxidation process leads to the

formation of the terminal carbene cations is not clear. The general lack

of bridging methylene compounds in systems unsupported by metal-metal

bonds or other bridging ligands suggests that the removal of two electrons

involved in metal-metal bonding may render the complex unstable toward

heteronuclear cleavage. However, Geiger has recently reported that a one

electron electrochemical oxidation of the dimanganese $\mu$-methylene complex,

$[CpMn(CO)_2]_2CH_2$ is reversible and forms a radical cation in which the

Mn-Mn bond is not retained.[57] A preliminary study of the cyclic-

voltammetry of **48** in $CH_2Cl_2$ (0.2 M $(t-bu)_4N\{BF_4\}$) using platinum wire

electrodes shows only irreversible oxidation and reduction waves.

## Molecular orbital calculation on $Cp(CO)Fe(\mu-CO)(\mu-C(SCH_3)_2)_2Co(CO)_2$

A molecular orbital calculation was carried out by Fenske and

coworkers on compound **48** using the Fenske-Hall method.[74a] This method is

devoid of empirical parameters with eigenvalues and eigenvectors

determined completely by the geometry of the molecule as well as by the

size and nature of the atomic basis set. Separate calculations were first

carried out on the ligands CO, $\mu$-CO, Cp, and $\mu$-C(SCH_3)_2$. The resulting

molecular orbitals of the free ligands were combined with Fe and Co

functions (from the tables of Richardson) to generate the molecular orbital diagram.[74b]

The molecular orbital diagram of the frontier orbitals of the dithiomethylene ligand is shown in Figure 6, and the arrangement of atomic orbitals in each of the energy levels is shown in Figure 7. From the molecular orbital diagram and orbital sketches of Figures 6 and 7, it is apparent that the p orbitals are responsible for interactions between the ligand atoms at the level of the frontier orbitals. Level 13 consists of p orbitals on all three atoms but is located primarily on sulfur 1, the sulfur atom that is part of the three-membered ring. Level 14 is a non-bonding level that consists only of two sulfur atoms that interact minimally due to the distance that separates them. This level is located
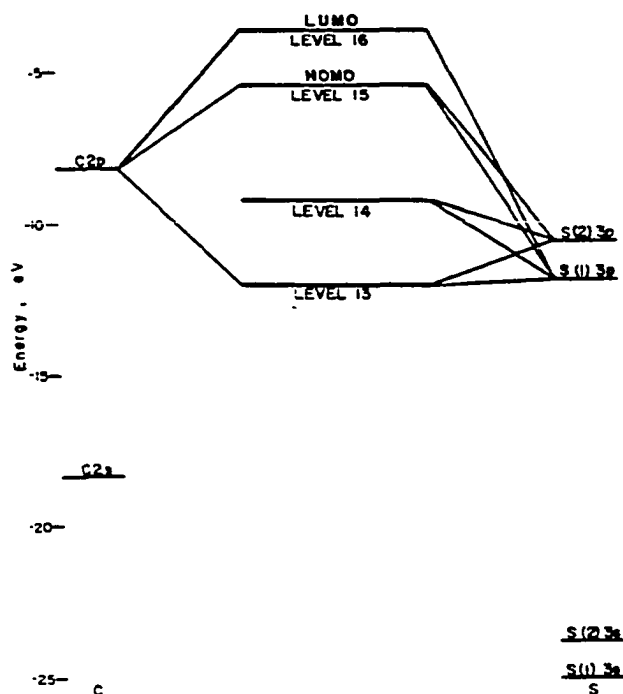


Figure 6. Molecular orbital diagram depicting the frontier orbitals of the dithiomethylene ligand in compound **48**.
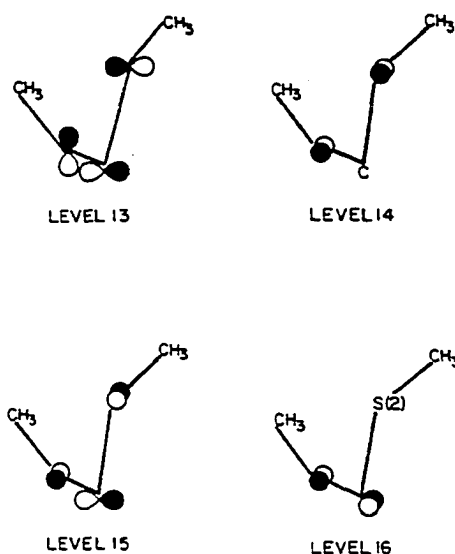
Figure 7.  Arrangement of the atomic orbitals of the dithiomethylene
ligand

primarily on sulfur 2, the sulfur atom that does not participate in the

ring formation. Level 15 is the HOMO of the dithiomethylene ligand and

consists of the orbitals located on all three atoms. This level is

located primarily on the methylene carbon atom, and the p orbitals of the

sulfur atoms contribute equal amounts of character but much less character

than the carbon. Level 16, the LUMO, is an antibonding orbital and is the

most significant ligand orbital. This level consists essentially of the

methylene carbon atom and the sulfur atom that participates in the ring

structure.

A molecular orbital diagram depicting metal-dithiomethylene

interactions is shown in Figure 8. The lowest level of energy at which

the metal center interacts with the frontier orbitals of the

dithiomethylene ligand (designated level (a) in Figure 8) is at -15.62 eV.

Dithiomethylene ligand level 13 interacts in a stabilizing manner with a
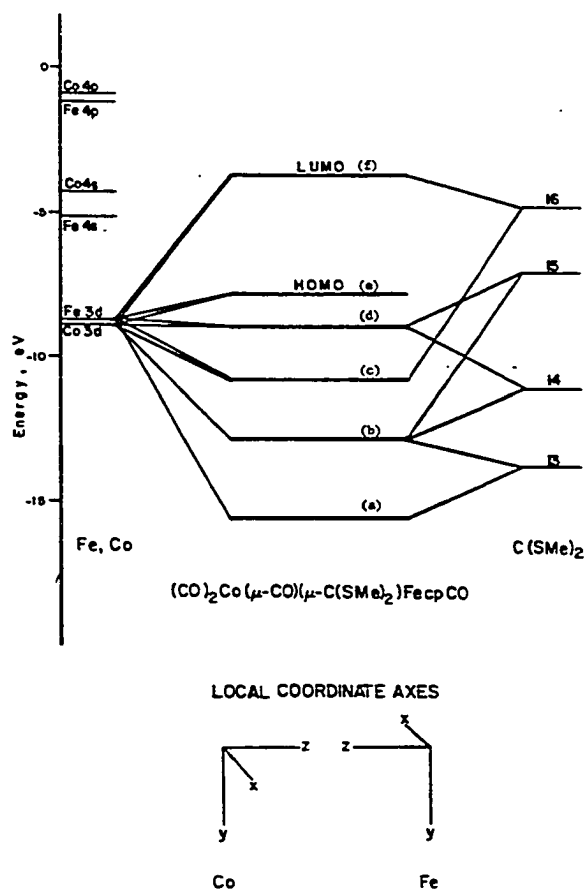
Figure 8. Molecular orbital diagram of compound **48** showing only
dithiomethylene interactions with Fe and Co

linear combination of d orbitals on the iron atom that hybridize to

accommodate the ligand orbital. The primary interaction in this orbital

is the formation of a sigma bond between the iron and methylene carbon

atom. Although orbitals on both sulfur atoms are available for bonding

they are too distant to interact with the iron. The level above this

one, orbital (b) at -12.92 eV is more complicated in composition and

interaction. Here dithiomethylene ligand levels 13, 14, and 15 linearly

combine to produce a rehybridized ligand orbital that interacts with an

appropriately hybridized linear combination of cobalt d functions. This interaction composes the basic triangular framework among the cobalt, sulfur, and methylene carbon atoms. Dithiomethylene ligand level 16, the LUMO of the dithiomethylene fragment, interacts with the metal centers in a slightly different manner than levels 13, 14, and 15. In level (c), iron and cobalt character are present in almost equal amounts. Their interaction with dithiomethylene ligand level 16 can be described as follows. The iron d functions overlap with the carbon p orbital alone since the sulfur orbital is too distant. The cobalt, however, can overlap with both the methylene carbon and the sulfur atom that compose the triangular ring, forming a pi bond between the metal and the ligand. The interaction of both metal atoms with the dithiomethylene ligand in this molecular orbital results in a net flow of electrons from filled metal orbitals into an empty ligand orbital. The extent of this interaction is quite large; Mulliken population analysis shows 0.809 electrons reside in a formerly empty ligand LUMO.

Orbital (d) at -8.97 eV is composed of iron and cobalt d orbitals and dithiomethylene ligand levels 14 and 15. Ligand levels 14 and 15 have rehybridized forming a symmetry equivalent complement to the available combination of metal d orbitals. The result of this last metal-ligand interaction is a sigma bond between the methylene carbon and each metal atom.

The HOMO for compound 48 occurs at -7.85 eV and is nonbonding to the dithiomethylene ligand and consists exclusively of iron and cobalt d orbital interactions. The LUMO, level (f), at -3.54 eV results from the

interaction of iron and cobalt d orbitals with level 16, the LUMO of the dithiomethylene ligand.

To a first approximation, these results agree with those obtained by Hoffmann in his calculation on the μ-methylene compound CpRh(CO)$_2$(μ-CH$_2$)RhCp,[20] and Licthenberger in his on μ-CH$_2$[CpMn(CO)$_2$]$_2$.[53] The general conclusion these authors drew is that while the μ-methylene ligand is a strong sigma donor its real strength is that of being an exceptionally good pi acceptor. The ability of the formally empty pz orbital on the μ-methylene fragment to accept pi electron density from filled metal Pi$^*$ orbitals greatly enhances the bonding in the dimetallocyclopropane ring. Most notably by accepting electron density from orbitals which are largely metal-metal antibonding. As was noted, this interaction is significant for compound **48** as well. The presence of the coordinated sulfur atom of the dithiomethylene ligand complicates the M.O. picture such that other direct comparisons with the previous theoretical results are difficult.

The driving force for the coordination of the sulfur atom to cobalt in compound **48** can be clearly understood in terms of the results of the molecular orbital calculation. The ability of a lone pair of electrons on an uncoordinated S atom to participate in pi bonding with the formerly unoccupied methylene pz orbital diminishes the ability of the μ-methylene ligand to function as a pi acceptor with the metals. As stated previously, the ability of the μ-methylene ligand to accept metal pi$^*$ electron density is important in stabilizing the dimetallocyclopropane ring. The displacement of a CO ligand by a sulfur atom of the μ-dithiomethylene ligand has two consequences. Firstly, it diminishes the

competition between the sulfur lone pair electrons and the metal pi[*]
system for the formerly unoccupied μ-methylene pz orbital thus
strengthening the bonding in the dimetallocyclopropane ring (particularly
the metal-metal bonding). Secondly, as was noted, electron-releasing
ligands enhance the bonding in dimetallocyclopropane rings by increasing
the electron density available for pi backbonding. By replacement of the
strong pi acceptor CO ligand with the electron donating S atom, the complex
gains additional electron density in the pi system and hence enhanced
bonding in the dimetallocyclopropane ring. Thus, the coordination of the
sulfur atom to cobalt by displacement of a CO ligand would be expected to
lead to a more stable complex in terms of the bonding between the
μ-methylene ligand and the dimetal center.

These results suggest that μ-dioxomethylene-containing compounds may
be less stable than the corresponding μ-dithiomethylene analogues. It has
been demonstrated in terminal carbene compounds that S and O atoms, when
bound to the carbene carbon, are capable of interacting to a considerable
extent with the vacant pz orbital of the carbene carbon.[60] The difference
between O and S was found to be small. How this translates when the
'carbene' ligand bridges two metals is not obvious. However, the coor-
dination of the sulfur ligand to cobalt in compound **48** and others like it
suggest that energetically the more stable compound is one in which the
lone pair electrons on heteroatoms do not interact with the methylene pz
orbital in a way which interferes with the pi backbonding to the dimetal
center. The poorer nucleophile oxygen would not be expected to displace a
ligand such as CO from a neighboring metal center to form a metallocyclo-

propane ring. The diminished pi bonding between the dimetal center and the μ-methylene carbon atom due to competition from oxygen lone pair interactions may lead to weak dimetallocyclopropane ring bonding. This may render the terminal coordination mode to be preferred for dioxocarbene containing compounds. No examples of μ-dioxocarbenes have been reported; however a terminal dioxo carbene has been observed in a dinuclear system.[4a] The same generalization can be made for diaminocarbenes. No μ-diaminocarbenes have been reported although terminal diaminocarbene containing compounds tend to be very stable. Lappert has prepared dinuclear compounds containing terminal diaminocarbenes.[4d] This is in contrast to methylene ligands in general where the bridging mode is nearly always preferred.

The oxidative cleavage of the μ-dithiomethylene compounds to terminal carbene products can be partially understood in terms of the molecular orbital results. Oxidation of compound 48 involves removal of electrons from the HOMO which is metal-metal bonding in nature. It is not surprising that this leads to fragmentation of the dimetal center. The question of the cleavage of the sulfur-cobalt bond is not as clear cut. Inspection of orbital (c) in Figure 8 shows that pi bonding is in part responsible for the sulfur-cobalt interaction. In general, oxidation would result in a decrease in the available pi electron density in the complex and would be expected to diminish the extent of this pi interaction. Thus oxidation would be expected to weaken the sulfur-cobalt bond. The fact that it is actually cleaved is probably the result of several factors which are not as simply understood.

## CONCLUSION

The reaction of cationic terminal dithiocarbene complexes of Fe and Ru with transition metal carbonyl anions serves as a useful route to homo and heterodinuclear complexes containing μ-dithiomethylene ligands. The coordination of one of the sulfur heteroatoms in the μ-methylene ligand to one of the metal centers leads to a very stable metallothiocyclopropane ring. While rings of this type are common in mononuclear compounds this is the first example of a dinuclear complex of this type. The inability of nucleophilic phosphine ligands to disrupt this ring structure by displacement of the sulfur is also in accord with the general trends observed in mononuclear analogues. In view of the enhanced bonding in the dimetallocyclopropane ring in these complexes gained through the displacement of a CO by the sulfur heteroatom, as determined in the molecular orbital calcuation on **48**, other compounds which contain a μ-methylene ligand with one or two S heteroatoms would be expected to exhibit this same structural feature.

The metal carbonyl anions which fail to give dinuclear μ-methylene compounds tend instead to reduce **40** to $Cp_2Fe_2(CO)_4$. Other cationic terminal dithiocarbenes which are not so easily reduced may readily react with metal anions to give μ-dithiomethylene compounds. A knowledge of the electrochemistry of terminal dithiocarbenes would facilitate the choice of likely candidates. Inasmuch as neutral dithiocarbene containing complexes are known their reactivity toward metal carbonyl anions would be worth exploring as well.

The oxidation reaction which was found to occur for the μ-dithio-

methylene compounds may be a general reaction for μ-methylene compounds. This has yet to be determined. The dithiomethylene ligand is uniquely suited for the study of this reaction because of the very stable terminal carbene complex which it forms. In most of the μ-methylene compounds known, the terminal carbene product which would be expected to result from the oxidation would be very reactive and not isolable as such. In those cases (μ-CH$_2$ or μ-CRR where R = alkyl or aryl) a carbene coupling product such as a olefin might be expected with the fate of the organometallic product being unpredictable.

This oxidative reactivity may have implications in metal surface chemistry. The conversion between bridging and terminal coordination modes for the carbene ligand on the metal surface may present a mechanism for the mobility of these ligands. On an active catalytic surface metal oxides are constantly forming and being removed as water. If an oxide forms near to or adjacent to a μ-methylene ligand it may 'oxidize' the local metal environment enough to cause the μ-methylene to become terminal. The terminal carbene would then be expected to become bridging again in the direction of a more electron rich environment, such as metal hydride or alkyl. As mentioned, μ-methylene ligands always 'lean' toward the more electron rich metal center. This sort of mobility would then promote chain growth as the carbene would be migrating toward surface species capable of reacting with it.

PART II. ATTEMPTED SYNTHESIS OF THE

IRON CARBYNE COMPOUND

$Cp(CO)Fe \equiv CSCH_3$

# INTRODUCTION

As free organic species carbynes, CR, are radicals containing
monovalent carbon atoms with five valence electrons. They are transient
species which are unstable because of an incomplete valence shell. The
simplest of these, CH, is fairly well characterized spectroscopically and
found to be extremely reactive.[92,93] Like so many other valence electron-
poor organic species, carbynes have been found to form stable complexes
when coordinated to transition metals.

In a molecular orbital sense this stabilization results from the
donation of the electron pair in the HOMO of the carbyne ligand (C-R[+])
into the LUMO of the metal fragment creating a sigma bond, and by back-
donation from the two highest occupied orbitals of the metal fragment into
the lowest empty orbitals of the carbyne, forming a pi bond (Figure 1).

$$\underset{\sigma\text{-HOMO}}{\bigodot\!\!:\!C\!\!-\!\!R^{+}} \qquad\qquad \underset{\pi\text{-LUMO}}{C\!\!-\!\!R^{+}}$$
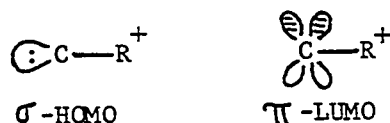
Figure 1. Frontier bonding orbitals of a carbyne ligand

The sigma and two pi bonds form a formal metal-carbon triple bond.[94] For
purposes of electron counting carbynes are considered as 3 e$^-$ donors.

Since E.O. Fischer reported the first mononuclear carbyne containing
compound in 1973, trans-X(CO)$_4$M≡CR, (M=Cr, Mo, W, R=CH$_3$, C$_6$H$_5$, X=Cl, Br,
I) from the reaction of (CO)$_5$M=C(R)(OR) with BX$_3$ numerous other such
compounds have followed.[95] Carbyne compounds are now known for groups
5[96,97], 6[95,98], 7[99,100], and 8 metals.[101]

The group R (CR) has been varied to include alkyl[102,103], alkynyl[104],

amino [99,105], chloro[106], hydrido[107], silyl[108], and thio[109,110] moieties.
In addition carbynes have been found to occupy double and triply bridged
positions in di and polynuclear transition metal complexes.[111]

General interest in the chemistry of the carbyne ligand has arisen
for several reasons. The chemistry of metal carbon double bonds
(carbenes) has been found to be quite varied and to reflect in may ways
that of the carbon-carbon double bond in olefins.[18] The question of to
what extent a metal-carbon triple bond will resemble that of the carbon-
carbon triple bond in acetylenes is eagerly being explored. In a more
practical sense carbyne containing compounds have come under scrutiny
because of their potential use as catalysts. Recently, Schrock
demonstrated that the tungsten (VI) carbyne compound, $[(CH_3)_3CO)_3W\equiv CCH_3]$,
catalyzes the homogeneous metathesis of acetylenes (Eqn. 1).[112] The

$$M\equiv CR \xrightarrow{+ RC\equiv CR'} \begin{array}{c} R \\ M= \\ R' \quad R \end{array} \longrightarrow \begin{array}{c} R \\ M \\ R' \quad R \end{array} \xrightarrow{-RC\equiv CR} M\equiv CR' \qquad (1)$$
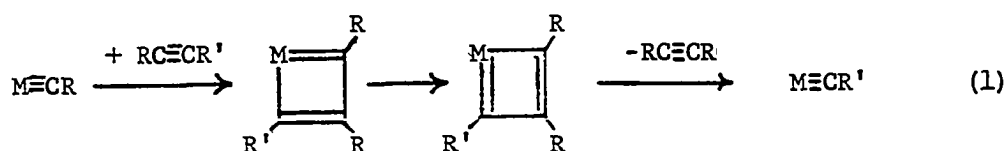
activity of the carbyne compounds toward acetylene metathesis were found
to exceed those reported for heterogeneous catalysts.

In addition, hydroxycarbyne complexes (R = OH) have recently been sug-
gested as possible intermediates in the homogeneous transition-metal-
catalyzed reduction of carbon monoxide.[113] Theoretical and experimental
data indicate that hydroxycarbynes may be more favorable than the pre-
viously supposed formyl (-C(O)H) species as the primary product resulting
from the interaction of a metal hydride with coordinated CO (Eqn. 2).

$$(CO)_nM\underset{\underset{O}{C}}{\overset{H}{<}} \rightleftharpoons \begin{array}{l} (CO)_nM-C\overset{\displaystyle O}{\underset{\displaystyle H}{<}} \\ \\ (CO)_nM\equiv C-OH \end{array} \tag{2}$$
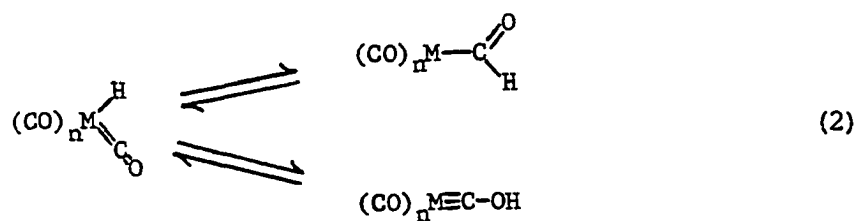
For these reasons interest in developing effective synthetic routes to carbyne-containing compounds and exploring their reactivity has grown rapidly.

Synthetic methods for the preparation of carbyne complexes can be classified into four major categories: lewis acid assisted abstraction of an alkoxy group from a terminal carbene,[95,100c,102,105,108,114-118] intra or intermolecular-hydrogen abstraction also from a terminal carbene,[96-98,119] transformation of a vinyl or vinylidene ligand,[103,120] or via the addition of an electrophilic reagent to a thiocarbonyl or isonitrile ligand.[99,109,110,121,122,123] A few carbyne compounds have been prepared which do not fall into one of these categories.[101,124-128]

To date, alkoxy and hydroxycarbyne complexes have eluded isolation or detection.[113] This has precluded studying directly the types of intermediates proposed in homogeneous CO reduction chemistry. However, it has proven to be possible to isolate and characterize the analagous thioalkoxycarbyne compounds. Angelici and coworkers have shown that the thiocarbonyl ligand in certain electron rich tungsten thiocarbonyl complexes ($\nu(CS) < 1200$ cm$^{-1}$) can be alkylated at the thiocarbonyl sulfur atom with $CH_3OSO_2F$, $CH_3I$, or $R_3O^+$ to give the corresponding thiocarbyne compounds (Eqn. 3).[109,122] The most significant result of this reaction

is the reduction in the C–S bond order from 3 to 1. The reduction of the

$$\text{Cp}\diagdown\underset{\underset{O}{\overset{|}{C}}}{\overset{OC}{W}}\text{--CS}^{-} \qquad \qquad \text{Cp}\diagdown\underset{\underset{O}{\overset{|}{C}}}{\overset{OC}{W}}\text{≡C--S}\diagdown\text{R} \qquad (3)$$

or        + RX  ⟶  or

$$\text{HB(pz)}_3\text{W(CO)}_2\text{CS}^{-} \qquad\qquad \text{HB(pz)}_3\text{(CO)}_2\text{W≡C--S}\diagdown\text{R}$$
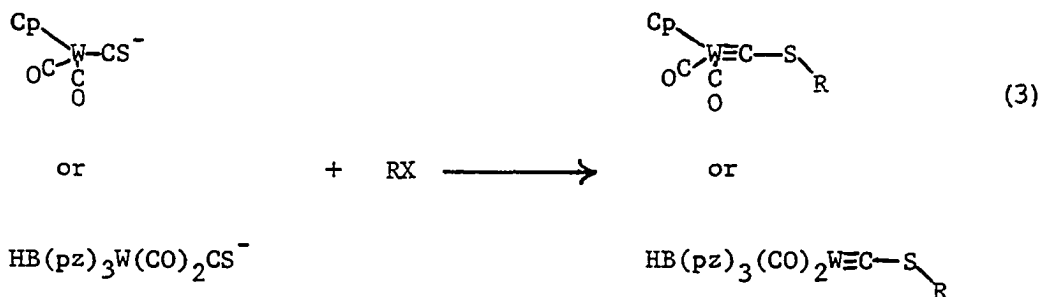
R = 2,4-dinitrophenyl, methyl, orthyl and X = Cl or I

C–O bond order from 3 to 1 is an important step in the catalytic reduction

of carbon monoxide to form hydrocarbons. In a more unusual reaction it

was found that the thiocarbyne compound, Cp(PPh$_3$)(CO)W≡CSPh, could be

produced from the reaction of Cp(PPh$_3$)(CO)W(CS)I with Li{Ph} (Eqn. 4).[110]

$$\text{Cp}\diagdown\underset{\underset{PPh_3}{}}{\overset{OC}{W}}\diagup^{I}\text{--CS} + \text{Ph}^{-} \longrightarrow \text{Cp}\diagdown\underset{\underset{PPh_3}{}}{\overset{OC}{W}}\text{≡C--S}\diagdown_{\text{Ph}} + \text{I}^{-} \qquad (4)$$
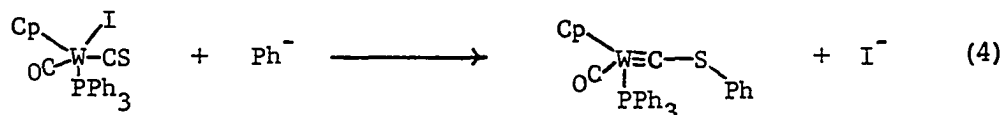
The identification of the product of reaction 4 as a thiocarbyne was

confirmed by an X-ray diffraction study. It was postulated that the

reaction occurred through a charge-transfer-radical mechanism rather than

direct nucleophilic attack of Ph- on the CS sulfur. Very recently it was

discovered that the thiocarbyne carbon in the hydrotris(pyrazoly-

borate)mercaptocarbyne complex [HB(pz)$_3$](CO)$_2$W(≡CSCH$_3$) could be protonated

to give the C- and S- coordinated mercaptocarbene complex

[HB(pz)$_3$](CO)$_2$W[$\eta^2$-CH(SCH$_3$)]$^{+}$ (Eqn. 5).[129] An X-ray structural

determination confirmed the $\eta^2$-CH(SCH$_3$) coordination. This represented

the first observation of such a ligand and only the second report of the

$$HB(pz)_3(CO)_2W\equiv C-S_{CH_3} \quad \underset{:B}{\overset{H^+}{\rightleftharpoons}} \quad HB(pz)_3(CO)_2W-C\overset{H}{\underset{S_{CH_3}}{\diagup}}{}^+ \qquad (5)$$
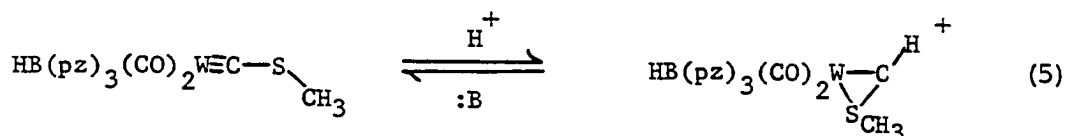
addition of $H^+$ to a carbyne carbon.[101,130] This result led to the

proposition that the protonation of a hydroxycarbyne $M\equiv COH$ to give $M[\eta^2-$

$CH(OH)]$ is a possible step in the catalytic hydrogenation of $CO$, Scheme I.

$$M\equiv C-O\overset{H}{\diagup} \quad \overset{H^+}{\longrightarrow} \quad M\overset{O-H}{\underset{C}{\diagdown}}\overset{}{\underset{H}{}} \quad \longrightarrow \quad M\overset{O-H}{\underset{C}{\diagdown}}\overset{}{\underset{H}{}} \quad \longrightarrow \quad H_2O + \text{hydrocarbons}$$
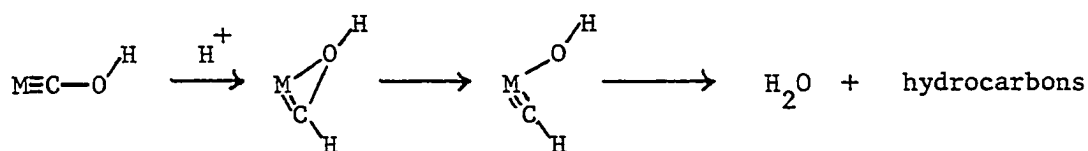
Scheme I

The reverse of reaction 5 was found to occur in low yield in the presence

of a base. The deprotonation of the $\eta^2$-carbene represents a new and

potentially important synthetic route to thiocarbyne-containing compounds.

Metallothiocyclopropane rings ($\overline{M-CHR-SR'}$) are quite common in organo-

metallic chemistry.[89] If one has a situation where R is some

group such as an alkoxide or mercaptide which can readily be cleaved to

yield the $\eta^2-CH(SR')$ carbene, deprotonation to the carbyne may be possible

(Eqn. 6). Thus an investigation was begun exploring the possibility of

$$L_nM-\overset{H}{\underset{S}{\overset{|}{C}}}-R \quad \overset{-R}{\longrightarrow} \quad L_nM-C\overset{H}{\underset{S}{\diagup}}{}^+ \quad \overset{Base}{\longrightarrow} \quad L_nM\equiv C-S_{R'} \qquad (6)$$
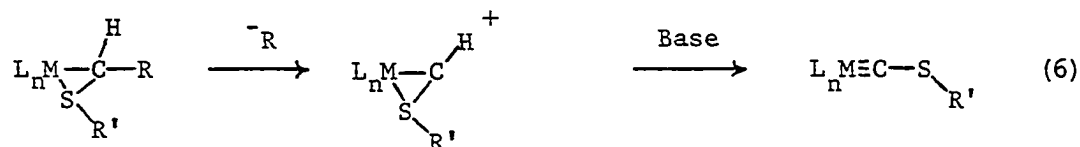
using $\eta^2$-carbene ligands as precursors to carbyne containing compounds.

As a starting point it was decided to pursue the synthesis of the $\eta^2-$

thiocarbene complex $Cp(CO)\overline{FeCHSCH_3}^+$ for use as a precursor to the iron

thiocarbyne compound $Cp(CO)Fe\equiv CSCH_3$. The iron carbyne compound $Cp(CO)Fe\equiv$

$CSCH_3$ was speculated by Quick and Angelici to result in low yield from the

interaction of methyliodide with a THF solution containing $CpFe(CO)^{2-}$ and

$CpFe(CO)(CS)^-$ generated in-situ from the reduction of the thiocarbonyl

compound $Cp_2Fe_2(CO)_3CS$ with Na(Hg) (Eqn. 7).[131] Alkylation of the

$$\begin{array}{c} Cp \\ \diagdown \\ \underset{\underset{O}{C}}{Fe}-CS^- \end{array} + CH_3I \longrightarrow \begin{array}{c} Cp \\ \diagdown \\ \underset{\underset{O}{C}}{Fe}\equiv C-SCH_3 \end{array} + I^- \qquad (7)$$
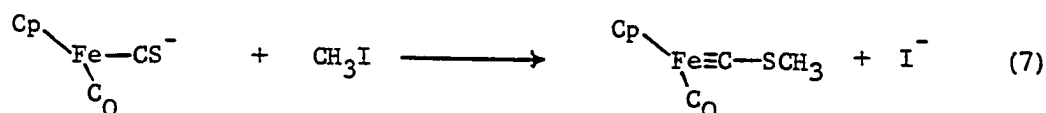
thiocarbonyl sulfur to yield the iron thiocarbyne is analogous to what had

been observed in the similar tungsten thiocarbonyl compounds discussed

above. The product of Equation 7 was chromatographed giving an orange

colored compound which was tentatively characterized by its IR and ^{1}H NMR

spectra as the thiocarbyne. The IR ($\nu(CO)$, $CS_2$) showed a single strong

band at 1960 cm$^{-1}$ while the NMR showed two resonances ($\delta$, $CS_2$), one at

4.57 ppm (s, 5H) corresponding to the Cp ligand and another at 2.53 ppm

(s, 3H) corresponding to the $SCH_3$ group. No band was seen in the $\nu(CS)$

region of the IR which was taken as evidence for the alkylation at sulfur

as opposed to iron. The position of the $SCH_3$ in the NMR was also consis-

tent with what had been observed in other thiomethoxycarbyne compounds.

However the low yield obtained in this case and the difficulty in obtain-

ing $CpFe(CO)(CS)^-$ made this synthetic route to $Cp(CO)Fe\equiv CSCH_3)$ undesir-

able. The complete characterization of $Cp(CO)Fe\equiv CSCH_3$ was never com-

pleted. The availability of the iron dithioketal complex

$Cp(CO)_2Fe[CH(SCH_3)_2]$ in good yield suggested that it would be worthwhile

to attempt to obtain the iron thiocarbyne from this compound via the $\eta^2$-carbene route discussed above.[132] The necessary series of transformations are shown below in Scheme II.



$$\text{Cp}\diagdown\underset{\underset{0}{\overset{|}{\underset{\text{C}}{\text{Fe}}}}}{}\text{—C}\overset{\text{H}}{\underset{\text{SCH}_3}{\diagdown}}\text{—SCH}_3 \quad \xrightarrow{\text{-CO}} \quad \text{Cp}\diagdown\underset{\underset{\text{S}}{\overset{C'}{\text{Fe}}}}{}\text{—C}\overset{\text{H}}{\underset{\text{SCH}_3}{\diagdown}}\text{—SCH}_3 \quad \xrightarrow{\text{-SCH}_3} \quad \text{Cp}\diagdown\underset{\underset{\text{S}}{\overset{C'}{\text{Fe}}}}{}\text{—C}\overset{\text{H}}{\underset{\text{CH}_3}{\diagdown}} \quad +$$

Base

$$\text{Cp}\diagdown\underset{\underset{\text{O}}{\overset{|}{\text{C}}}}{\text{Fe}}\equiv\text{C—SCH}_3$$
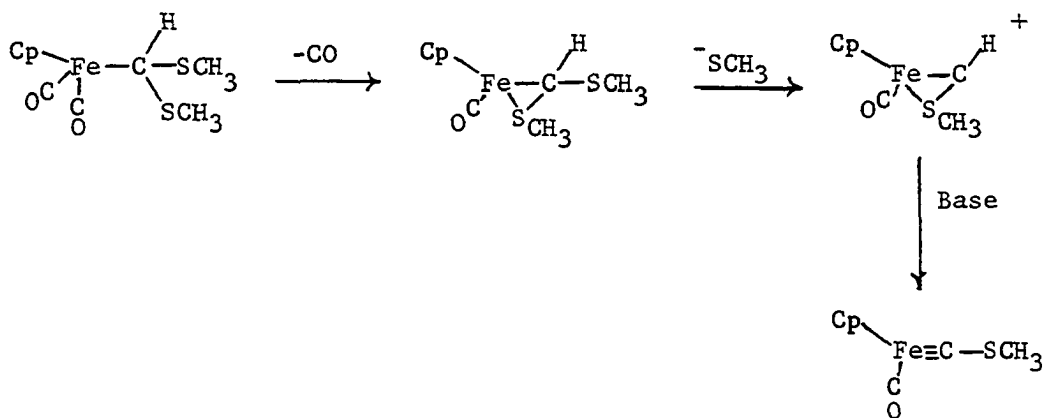
Scheme II

The first step, which involves formation of the metallothiocyclopropane ring, occurs as a result of CO loss from the dithioketal. Loss of CO from organometallic sulfur containing compounds such as $Cp(CO)_3$-$MoCH_2SCH_3$ and $(CO)_5MnCH_2SCH_3$ to give the corresponding cyclized products $Cp(CO)_2\overline{MoCH_2SCH_3}$ and $(CO)_4\overline{MnCH_2SCH_3}$ has been shown to occur thermally or under photochemical conditions.[133] This reactivity is well documented for thiomethoxymethyl transition metal complexes but completely unexplored for the dithioketals. The next step in Scheme III involves removal of the free mercaptide from the cyclic dithioketal forming the sulfur-coordinated carbene cation. A similar reaction has been observed in the removal of $SCH_3^-$ from the dithioketal $Cp(CO)_2FeCH(SCH_3)_2$ using $H^+$ or trityl cation to yield the cationic hydridothiocarbene $Cp(CO)_2Fe[CHSCH_3]^+$.[134] Similarly, the trithioketal $Cp(CO)_2FeC(SCH_3)_3$ has been found to react with $H^+$ to

yield the cationic dithiocarbene $Cp(CO)_2Fe]C(SCH_3)_2]^{+}$.[135] Whether the coordination of one of the mercaptide groups to the iron center would affect the lability of the other mercaptide in reactions with $H^+$ or trityl is not known. Removal of the proton from the coordinated carbene would then occur as a result of treatment with the appropriate base as discussed above yielding the thiocarbyne.

The outcome of the experiments just discussed suggested (see Results and Discussion) that an alternative structure needs to be considered for the product of Equation 7, which was tentatively assigned as the thio-carbyne, $Cp(CO)Fe\equiv CSCH_3$. Knox has reported that the reaction of $CpFe(CO)_2^-$ with excess $CS_2$ in THF for 1 hr. followed by methylation with methyliodide leads to the production (5-10% yield) of the trithiocarbonate complex $Cp(CO)Fe(S_2CSCH_3)$ (Eqn. 8).[136] No other organometallic products

$$Cp\diagdown Fe(CO)_2^- \xrightarrow[\text{2. } CH_3I]{\text{1. } CS_2 \text{ 1 hr.}} Cp\diagdown Fe\diagdown^{S}_{C\diagdown O}\diagdown^{S}_{S}\diagdown C-SCH_3 \quad (8)$$
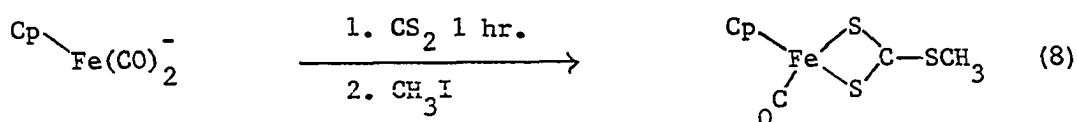
of this reaction are reported. This trithiocarbonate has physical and spectroscopic properties similar to those reported for $Cp(CO)Fe\equiv CSCH_3$. The IR of the trithiocarbonate complex shows a single $\nu(CO)$ absorption ($CH_2Cl_2$) at 1956 $cm^{-1}$ and exhibits two resonances in the $^1H$ NMR spectrum ($CS_2$) at 4.60 ppm and 2.55 ppm. The trithiocarbonate product of Equation 8 may be the actual product of Equation 7. Recall that in the preparation of the iron thiocarbyne that $CpFe(CO)_2^-$ is present as well as $CpFe(CO)(CS)^-$. And, most importantly, the product is extracted with $CS_2$

following the methylation step. This result by Knox is somewhat in conflict with the report of Dombek and Angelici who reported that the reaction of $CpFe(CO)_2^-$ with a stoichiometric amount of $CS_2$ followed by immediate methylation with $CH_3I$ leads to good yields of the dithioester complex $Cp(CO)_2FeC(S)SCH_3$ (Eqn. 9).[132] The important difference between

$$Cp\diagdown \underset{\underset{O}{C}}{\overset{}{Fe}}-CO^- \qquad \xrightarrow[\text{2. } CH_3I]{\text{1. } CS_2} \qquad Cp\diagdown \underset{\underset{O}{C}}{\overset{\overset{S}{\parallel}}{Fe}}-C-SCH_3 \qquad (9)$$
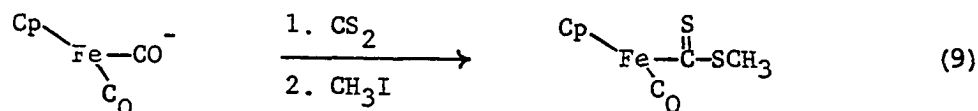
reactions (8) and (9) seems to be the difference in reaction times. It was speculated by Knox that the trithiocarbonate results from either the decomposition of the thioester during the longer reaction time, or, more likely by prior formation of the iron trithiocarbonate anion $Cp(CO)_2FeS_2C(S)^-$ which then reacts with $CH_3I$ to give the observed methylated product. There is precedence in the literature for the formation of the trithiocarbonate anion. The reaction of $PPN\{Mn(CO)_5\}$ with $CS_2$ in THF was found to result in the slow formation of $PPN\{(CO)_4MnS_2C(S)\}$ in high yield (Eqn. 10).[137] No evidence for

$$Mn(CO)_5^- \quad + \quad CS_2 \quad \xrightarrow{\text{4 days}} \quad (CO)_4Mn\diagdown\diagdown\diagdown_{S}^{S}\diagdown C\text{-}S^- \qquad (10)$$
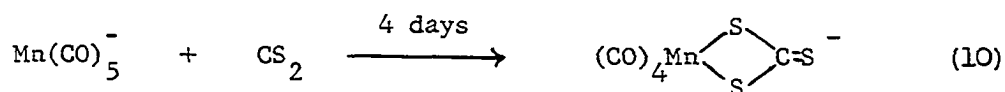
$Cp(CO)_2FeS_2C(S)^-$ was reported during the course of reaction (8). Methylation of the anionic product of equation (10) with $CH_3I$ or $SFO_2(OCH_3)$ generates the neutral complex $(CO)_4MnS_2CSCH_3$ in 40% yield.

The original preparation of $Cp(CO)FeS_2CSCH_3$ was carried out some time

ago.[138] The reaction of CpFe(CO)$_2$X (X = Cl, Br, I) with methyltrithio-
carbonate anion was found to occur via nucleophilic displacement of halide
to give dicarbonylcyclopentadienyl(methyltrithiocarbonate)iron. When
allowed to stand in solution for long periods or photolyzed this compound
loses CO to form carbonylcyclopentadienyl(methyltrithiocarbonate)iron in
78% yield, Scheme III. Alkyl trithiocarbonate metal carbonyl complexes



Scheme III
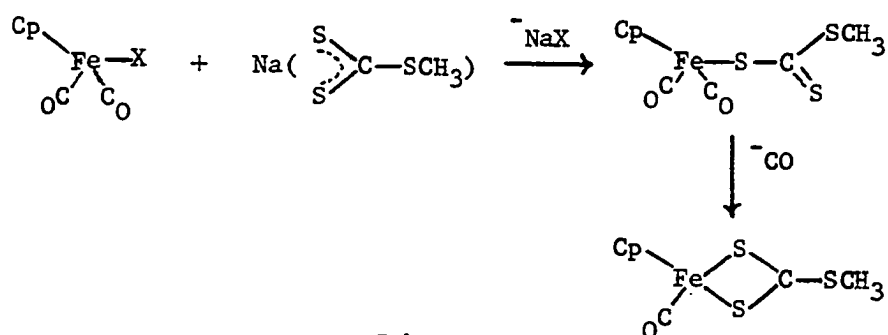
have also been prepared through the insertion of a molecule of CS$_2$ into a
metal alkylsulfide bond (Eqn. 11).[139] Transition metal complexes



$$\text{(11)}$$
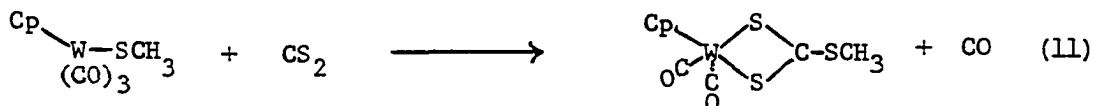
containing only trithiocarbonate ligands or other noncarbon ligated
groups such as Cl or OR etc. are well known. In these cases, the trithio-
carbonate ligand is referred to as a thioxanthate. The first metal
thioxanthate complex was prepared by Hofmann in 1897.[140] The chemistry of
these compounds, including the results of several crystal structures has
been reviewed.[141]

## EXPERIMENTAL

### General procedures

All manipulations were carried out under an atmosphere of dry $N_2$ in 24/40 Standard-type Schlenk-type glassware. Reduced pressures and $N_2$ were provided by a dual manifold vacuum/$N_2$ line using 3-way evacuated stopcocks. Solutions were transferred via stainless steel double ended needles (cannula tubes) or Leuer-lock syringes. Filtrations were done using Celite (diatamaceous earth) filter aid and medium porosity sintered glass frits.

Inert atmosphere chromatography was carried out in a specially designed column depicted below. Typically, 400-mesh silica gel (30 ml) was
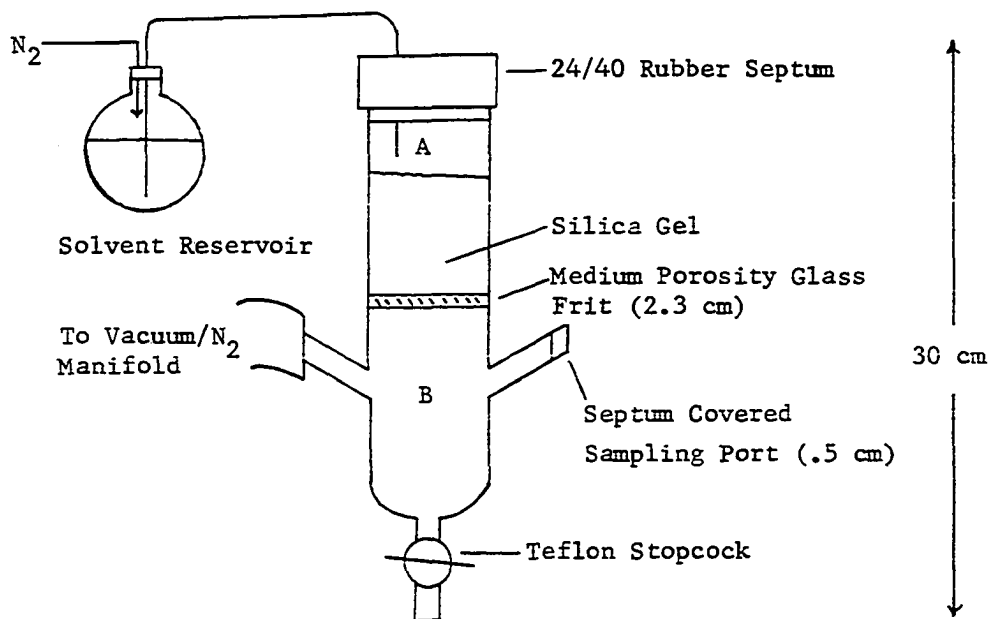


introduced in the column, and the system was degassed by 5 cycles of vacuum ($10^{-3}$ torr) and $N_2$ purging. The eluent was then siphoned into

chamber A through a cannual tube from the solvent reservoir by inserting a needle through the 24/40 septum, allowing $N_2$ to escape. When all the silica gel was wet, gentle shaking resulted in a homogenous suspension. Reduction of the pressure in chamber B caused eluent to draw through the frit and allowed the silica gel to pack. Once the column was packed, sample was introduced on top of the column via syringe or cannula tube. Chromatography was carried out by slightly reducing the pressure of chamber B. Unwanted portions are simply flushed out through the bottom stopcock, while desirable portions were removed through the sampling port.

## Solvents

Most solvents were of reagent grade or better and purified prior to use. All distillations were carried out under an atmosphere of dry $N_2$ and distillates were stored over 4 Å molecular sieves. The sieves were activated prior to use by heating to 300°C at $10^{-3}$ torr for 6 hours followed by cooling under $N_2$. The solvents $CH_2Cl_2$, $CH_3CN$, and $CH_3OH$ were distilled from $CaH_2$. Tetrahydrofuran (THF) and diethylether were distilled from sodium/benzophenone. The solvents $CS_2$, acetone, pentane, and hexanes were simply stored over sieves for a period of days and purged with $N_2$ for a minimum of 30 min. prior to use.

## Reagents

The reagents $CF_3SO_3H$, $Ph_3C\{PF_6\}$, $HBF_4 \cdot Et_2O$, and $Li\{OC(CH_3)_3\}$ were obtained from Aldrich and used without further purification. Proton sponge ([1,8-bis-[dimethylamino]-napthalene]) was obtained from Aldrich and recrystallized from pentane prior to use. Methanethiol ($HSCH_3$) was

also obtained from Aldrich and distilled prior to use. Trimethylamine-N-oxide dihydrate was obtained from Aldrich and was sublimed before use to remove the water of hydration. The hydride donating reagents $Li\{AlH_4\}$, $Li\{((CH_3)_3CO)_3AlH\}$, and NaH (as a 50% mineral oil dispersion) were obtained from Alpha as was n-butyllithium (2.5 $\underline{M}$ in hexane).

The compounds $[Cp(CO)(NCCH_3)Fe\{C(SMe)_2\}]PF_6$,[64] $Cp(CO)_2Fe\{C(H)(SMe)_2\}$[134], $[Cp(CO)_2Fe\{C(SMe)_2\}]PF_6$[63], and $Li\{SCH_3\}$[142] were prepared by literature methods.

## Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 681 grating infrared spectrophotometer. The spectrometer calibration was routinely checked by using a sample of CO gas (300 torr, pathlength = 4 cm). Frequencies reported are accurate to $\pm 2$ cm$^{-1}$. All spectra were recorded in solution; the cells employed NaCl plates separated by a 1 mm teflon spacer. In the short time necessary to obtain spectra in the $\nu(CO)$ region anaerobic conditions and degassed solvents were not required.

Nuclear magnetic resonance spectra were recorded on either a JEOL FX90Q (90 MHz $^1H$, 22.5 MHz $^{13}C$) or Nicolet NT300 (300 MHz $^1H$, 75 MHz $^{13}C$) Fourier transform spectrometer. For $^1H$ spectra chemical shifts are reported in ppm downfield ($\delta$) from tetramethylsilane (TMS). For $^{13}C$ spectra all samples were proton-decoupled, and chemical shifts were referenced indirectly to the chemical shift of the solvent signal: $CDCl_3$, 77.06 ppm; $CD_2Cl_2$, 53.80 ppm. In order to reduce data collection time, 0.1 $\underline{M}$ $Cr(acac)_3$ was added to all $^{13}C$ samples. To prevent decomposition

during data collection all samples were freeze-thaw degassed. All signals
are singlets unless noted otherwise.

Photochemical experiments were carried out using a water-jacketed
quartz immersion type reactor with a solution volume of 125 mL. A 100
watt medium pressure mercury arc lamp was used as a photon source. Nitro-
gen gas was vigorously purged through the solutions during photolysis.

Mass spectra were obtained on a Finnigan 4000 mass spectrometer at an
ionization potential of 20 eV. Melting points were determined using a
Thomas model 40 Miro Hot Stage and are not corrected. Elemental analyses
were performed by the Ames Laboratory.

Preparation of $Cp(CO)Fe[CH(SCH_3)(SCH_3)]$, **2**, from the photolysis of
$Cp(CO)_2Fe[CH(SCH_3)_2]$, **1.** Compound **1** was prepared by reaction of either
$LiAlH_4$ or $Li[(CH_3)_3CO]_3AlH$ with $Cp(CO)_2Fe[C(SCH_3)_2]\{Pf_6\}$ in THF. Due to
the difficulty in obtaining solid samples of **1** it was used in-situ and not
isolated. Yields of 80-85% were typical.[134] In a typical preparation,
0.40 g (0.94 mmol) of $Cp(CO)_2Fe[C(SCH_3)_2]\{Pf_6\}$ was combined with 0.26 g
(1.02 mmol) of $Li[(CH_3)_3CO]_3AlH$ in 40 ml of THF. After stirring for 60
min., the solvent was removed under reduced pressure leaving a brown oily
residue. The residue was extracted with 40 ml of hexane and filtered
through Celite on a glass frit. At this point, the solution was
transferred into a photolysis vessel and additional hexane was added to
give a total volume of 125 mL. Photolysis was carried out with a vigorous
$N_2$ purge; gas evolution was apparent. The reaction required 7.5 min. to go
to completion, at which time the color had become black and the IR $v(CO)$
showed a single strong absorption band at 1933 $cm^{-1}$. Prolonged photolysis

led to decomposition. The solution was filtered through Celite over a glass frit into a 250 ml roundbottom flask with sidearm. The hexane was removed under reduced pressure. The black residue was chromatographed under $N_2$ using the column and supporting material described above. Elution with a mixture of hexane/$CH_2Cl_2$ (1:1) caused a single dark band to move down the column. Some tailing occurred. Evaporation of the solvent left a black oily residue of 0.19 g (80%) of 2. This compound decomposed immediately upon exposure to the atmosphere and was only stable for short periods of time under $N_2$. Compound 2 is very soluble in nonpolar solvents. Attempted crystallization by slow cooling of pentane heptane, diethylether, or hexane solutions led to unstable oils. This procedure was found to be the best method for the preparation of 2. IR ($CH_2Cl_2$) $\nu$(CO): 1925 (s) $cm^{-1}$; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 4.50 (s, 5H, Cp), 2.26 (s, 1H, CH), 2.19 (s, 3H, $SCH_3$), 1.60 (s, 3H, $SCH_3$); $^{13}C$ NMR ($CD_2Cl_2$) 217.18 ppm (CO), 79.54 ppm (Cp), 68.10 ppm (CH), 27.19 ppm ($SCH_3$), 24.07 ppm ($SCH_3$); Mass Spec. m/e 256 ($M^+$), see Results and Discussion.

Preparation of Cp(CO)Fe[CH(SCH₃)SCH₃], 2, from the reaction of 1 with (CH₃)₃NO. As described previously 1 was prepared by combining 0.21 g (0.48 mmol) of $Cp(CO)_2Fe[C(SCH_3)_2]\{Pf_6\}$ and 0.14 g (0.55 mmol) of $Li[(CH_3)_3CO]_3AlH$ in 30 ml of THF. The isolated oil was redissolved in 20 ml of THF and excess $(CH_3)_3NO$ (0.060 g, 0.79 mmol) was added. Over the course of 4 hr. a band gradually grew in at 1923 $cm^{-1}$ as the bands due to 1 diminished. Based on the relative intensity of the IR $\nu$(CO) bands the reaction only proceeded to approx. 60% completion. The solvent was removed at reduced pressure, extracted with $CH_2Cl_2$, and filtered through

Celite over a glass frit. A brown oily residue resulted after removal of the $CH_2Cl_2$. The IR of this residue ($\nu(CO)$, 1933 (s) $cm^{-1}$, hexane) was consistent with the formation of **2**. Longer reaction times or refluxing did not increase the amount of **2** formed. When $CH_3CN$ was used as the reaction solvent **1** was only formed to the extent of approx. 20%.

Preparation of $Cp(CO)Fe[CH(SCH_3)(SCH_3)]$, **2**, from the reaction of $Cp(CO)(NCCH_3)Fe[C(SCH_3)_2]\{PF_6\}$, **3**, with NaH. To a 30 ml THF solution of **3** (0.20 g, 0.45 mmol) was added 0.022 g (0.46 mmol) of NaH (as a 50% mineral oil dispersion). The reaction was stirred for 4 hr. during which time the solution became dark brown. The IR $\nu(CO)$ showed the starting material to be gone, and the band due to **2** to be present as well as some $Cp_2Fe_2(CO)_4$. Some precipitate had also formed. The solution was filtered through Celite over a glass frit and the resulting residue was chromatographed as described above. The single band which eluted, upon removal of the solvent, yielded 0.070 g (60%) of **2**. The $^1H$ NMR and IR were the same as the results obtained above.

Attempted reaction of $Cp(CO)Fe[CH(SCH_3)(SCH_3)]$, **2**, with $PEt_3$. A sample of **2** was generated as described above by allowing 0.40 g (0.94 mmol) of $Cp(CO)_2Fe[C(SCH_3)_2]\{PF_6\}$ and 0.26 g (1.02 mmol) of $Li[(CH_3)_3CO]_3AlH$ to react in THF, followed by the indicated workup and photolysis for 7.5 min. in hexane. The resulting hexane solution of **2** was filtered through Celite over a glass frit and reduced in volume to 30 ml. To this solution was added 0.30 ml (2.0 mmol) of $PEt_3$. After stirring for 24 hr. no change in the position or intensity of the 1933 $cm^{-1}$ IR absorption band of **2** had occurred. Refluxing for 4 hr had no effect.

Reaction of Cp(CO)Fe[CH(SCH₃)(SCH₃)], **2**, with H{BF₄}. To a 0°C 125

ml hexane solution of **2**, generated as described above by photolysis of a

solution of **2** (prepared from 0.40 g (0.94 mmol) of

Cp(CO)₂Fe[C(SCH₃)₂]{PF₆} and 0.26 g (1.02 mmol) of Li{[(CH₃)CO]₃AlH} was

added 130 ul (0.94 mmol) of H{BF₄} · Et₂O. Over the course of 1 hr the

solution became clear as a voluminous darkly colored precipitate formed.

The IR ν(CO) showed **2** to be gone. The hexane was decanted away and the

precipitate washed with 20 ml of Et₂O. When pumped to dryness the preci-

pitate Cp(CO)Fe[CHSCH₃]{BF₄}, **4**, (0.14 g 0.48 mmol, 80% based on **2**)

appeared pale green in color and was sparingly soluble in CH₂Cl₂ giving a

red-green solution which exhibited a single strong band in the IR ν(CO) at

1993 cm⁻¹. Compound **4** was found to be very soluble in CH₃CN (IR: 2000 (s)

cm⁻¹) and acetone (IR: 1985 (s) cm⁻¹). All attempts to crystallize or

chromatograph **4** failed. Although somewhat broadened by paramagnetic iron

impurities, a ¹H NMR spectrum of **4** was obtained. This spectrum, taken of

the crude reaction product (CD₃CN NMR solvent) showed peaks at 4.92 ppm

(s), 2.24 ppm (s), and 2.14 ppm (s) of approximate integrated intensity

ratios of 5:3:1 in addition to a quartet (3.88 ppm) and triplet (1.26 ppm)

of much larger intensity caused by the diethyl ether present in the fluor-

oboric acid. Compound **4** was found to decompose to a totally insoluble

residue upon exposure to the atmosphere.

Reaction of Cp(CO)Fe[CH(SCH₃)(SCH₃)], **2**, with Ph₃C{PF₆}. An oily

black sample of **2** was prepared in the same manner as described in the

preceding experiment starting from 0.40 g (0.94 mmol) of

Cp(CO)₂Fe[C(SCH₃)₂]{PF₆} and 0.26 g (1.02 mmol) of Li{[(CH₃)₃CO]₃AlH}.

This was dissolved in 30 ml of $CH_2Cl_2$, and 0.36 g (0.94 mmol) of $Ph_3C\{PF_6\}$ was added. Over the course of 30 min. the IR $\nu(CO)$ band of **2** diminished as the solution developed a red-green color and two new bands appeared at 2020 $cm^{-1}$ (sh) and 1993 $cm^{-1}$ (s). The 1993 $cm^{-1}$ band corresponded to what had been observed for the formation of the carbene cation, **4**, above, while the identity of the shoulder at 2020 $cm^{-1}$ is unknown. Using excess $Ph_3C-\{PF_6\}$ did not alter the results of the reaction.

General Procedure for the Preparation of **4**. In all subsequent reactions involving **4** the following procedure was used for its preparation inasmuch as it was found to give the cleanest product and highest yields. In all cases $Cp(CO)_2Fe[C(SCH_3)_2]\{PF_6\}$ and a slight molar excess (~10-20%) of $Li\{[(CH_3)_3CO]_3AlH\}$ were allowed to stir for 1 hr in THF. The solution was evaporated to dryness under reduced pressure. The residue was extracted into 40 ml of hexane, filtered through Celite over a glass frit, and immediately transferred into a photolysis vessel. The solution volume was increased to 125 ml by the addition of hexane. Photolysis was carried out with a rapid $N_2$ purge until an IR of the reaction mixture showed **1** to be completely gone. At this point the solution was filtered again through Celite over a glass frit (a small amount of a black insoluble precipitate was always present) and cooled to $0^{o}C$ in an ice-water bath. To this black solution was added 1 equivalent of $H\{BF_4\}$ (based on an 80% yield of **2**). The solution was stirred for 1 hour during which time it became clear as the voluminous red-green precipitate was formed. The hexane was decanted away and the residue was washed with 2 x 20 ml portions of $Et_2O$. This

residue was then used immediately in subsequent reactions. The yield of **4** obtained was approximately 51% based on $Cp(CO)_2Fe[C(SCH_3)_2]\{PF_6\}$.

Attempted preparation of $Cp(CO)Fe{\equiv}CSCH_3$, **5**, from $Cp(CO)Fe[CH(SCH_3)]\{BF_4\}$, **4**.

A. Using $K_2CO_3$:

A sample of **4** was prepared using the general procedure outlined above starting with 0.40 g (0.94 mmol) of $Cp(CO)_2Fe[C(SCH_3)]\{PF_6\}$. This was partially dissolved in 20 ml $CH_2Cl_2$ and 0.19 g (1.4 mmol) of $K_2CO_3$ was added. After 12 hr. of stirring, a small band appeared at 1955 $cm^{-1}$ in the IR $\nu(CO)$. The amount of **4** present was greatly diminished due to decomposition. The solution was evacuated to dryness and a $CS_2$ extract was taken. An IR $\nu(CO)$ of this red-orange extract showed a single strong band at 1960 $cm^{-1}$ plus a trace of $Cp_2Fe_2(CO)_4$. Evaporation of the $CS_2$ extract at reduced pressure left only a few mg of orange material which although presumed to be **5** was not further characterized. Employing longer reaction times or carrying out the reaction in acetone solvent failed to increase the yield of **5**. When the reaction was carried out in $CH_3CN$ under the same conditions a green solution exhibiting a single strong IR band at 2020 $cm^{-1}$ resulted. The nature of this reaction was not pursued.

B. Using Proton Sponge:

Addition of proton sponge [1,8-bis-(dimethylamino)napthalene] (0.20 g, 0.93 mmol) to a solution of **4** (formed from 0.40 g (0.94 mmol)) of $Cp(CO)_2Fe[C(SCH_3)_2]\{PF_6\}$ using the general procedure outlined above) in 25 ml of $CH_2Cl_2$, acetone, $CH_3CN$, or THF gave yields of

less than 1% of the orange compound presumed to be **5**, which exhibited

the single IR band at 1960 cm$^{-1}$ in $CS_2$. The reaction occurred imme-

diately but did not proceed to completion. Addition of a large excess

of proton sponge did not alter the outcome of the reaction. A slight

increase in the yield of the 1960 cm$^{-1}$ ($CS_2$) product was observed.

When the $BPh_4^-$ salt of **4**, prepared via metathesis of **4** with $Na\{BPh_4\}$

in $CH_3OH$, was allowed to react with $K_2CO_3$ in $CH_2Cl_2$. However, the

increase in yield was very slight (3%) and significant decomposition

of **4** occurred during the metathesis process. Chromatography (silica-

gel, 2 x 6 cm, $CH_2Cl_2$/hexane 1:1) of the product of this latter

reaction, performed with no special precautions to exclude the atmos-

phere resulted in the isolation of a single orange band. A $CS_2$ ex-

tract of the residue left after evaporation of the solvent from this

band was red-orange in color and exhibited a single strong IR band

$\nu(CO)$ at 1960 cm$^{-1}$. A $^1H$ NMR spectrum, taken in $CDCl_3$ solvent, was

obtained on this sample (~2 mg). The spectrum showed a resonance at

4.65 (s) ppm and another at 2.55 (s) ppm in relative integrated inten-

sity 5:3. These data were consistent with the formation of **5** or **7**

(see Results and Discussion).

C. Using NaH:

When 1 equivalent of NaH (50% mineral oil dispersion) was added

to a $CH_2Cl_2$ solution of **4**, prepared following the general procedure,

the only reaction found to occur was the slow solution decomposition

of **4**. After stirring for 6 hr. the solvent was removed at reduced

pressure. A $CS_2$ extract of this residue was colorless and silent in the $\nu(CO)$ region of the IR.

D. **Using NaBH$_4$:**

When 1 equivalent of NaBH$_4$ was added to a $-78°C$ acetone solution of **4**, prepared following the general procedure, a rapid reaction occurred. A hexane extract of the residue left after evaporation of the solvent at reduced pressure showed the formation of $Cp_2Fe_2(CO)_4$ plus a small amount of a compound which exhibited an IR $\nu(CO)$ band at 1932 cm$^{-1}$ (vide infra).

E. **Using Li$\{[(CH_3)_3CO]_3AlH\}$:**

When 1 equivalent of Li$\{[(CH_3)_3CO]_3AlH\}$ was stirred in THF for 3 hr. with **4**, prepared following the general procedure, no reaction occurred. When the reaction was run in THF a reaction slowly occurred over the course of 10 hr. Evaporation of the solvent and extraction with $CS_2$ gave a solution which exhibited two bands in the IR $\nu(CO)$; 1960 (s) cm$^{-1}$, 1920 (m) cm$^{-1}$. Chromatography on silica-gel (using the inert atmosphere apparatus described previously, $CH_2Cl_2$/hexane, 1:1) resulted in the separation of two bands. The first to elute was orange in color and corresponded to **5**. The second was amber in color. Evaporation of the solvent from this second band gave a darkly colored oily-solid which was very soluble in hexane exhibiting a single band in the IR $\nu(CO)$ at 1932 cm$^{-1}$. A $^1$H NMR spectrum of this material taken in CDCl$_3$ exhibited resonances at 4.34 (s) ppm, 1.84 (s, ppm, 1.66 (s) ppm, and 1.39 (s) ppm in relative integrated intensity ratios of 5:1:3:1, respectively, and was tentatively assigned the structure

Cp(CO)Fe[CH$_2$SCH$_3$], **6**. Compound **6** was found to readily decompose in solution upon exposure to the atmosphere.

F.  Using Li{OC(CH$_3$)$_3$}:

To a 20 ml CH$_3$CN solution of **4**, generated using the general procedure starting from 0.13 g (0.31 mmol) of Cp(CO)$_2$Fe[C(SCH$_3$)$_2$]{PF$_6$}, was added 0.036 g (0.32 mmol) of Li{OC-(CH$_3$)$_3$}. Within 10 min. the solution developed a brown coloration. The IR ν(CO) indicated that in addition to a large amount of **4** new peaks had appeared at 1950 cm$^{-1}$ and 1921 cm$^{-1}$. Over the course of 30 min. the 1921 cm$^{-1}$ band became dominant. No further change in the IR resulted over the next several hours. The solvent was removed under reduced pressure and a CS$_2$ extract was taken. This extract showed traces of Cp$_2$Fe$_2$(CO)$_4$ and a product containing a single strong IR ν(CO) band at 1927 cm$^{-1}$ presumed to be the oxothioketal Cp(CO)Fe[CH(SCH$_3$)(OC(CH$_3$)$_3$].

When **4** was dissolved in CH$_3$OH and 2 equivalents of K$_2$CO$_3$ were added, a slow reaction occurred generating a small amount of a product which when extracted into CS$_2$ gave an IR ν(CO) band at 1928 cm$^{-1}$. Based on the above result this was thought also to be an oxothioketal, Cp(CO)Fe[CH(SCH$_3$)(OCH$_3$)] generated from the reaction of **4** with ⁻OCH$_3$.

Preparation of Cp(CO)Fe[S$_2$C(SCH$_3$)], **7**, from the reaction of Cp(CO)Fe[CH(SCH$_3$)] with ⁻SCH$_3$ in presence of CS$_2$. Although not proven in every case it is believed that reactions between **4** and ⁻SCH$_3$ in the presence of CS$_2$ proceeded via prior formation of ⁻S$_2$C(SCH$_3$) to yield **7**.

A. Using Li{SCH$_3$} generated in situ, in THF:

To a sample of **4**, prepared in the general manner from 0.40 g

(0.94 mmol) of Cp(CO)$_2$Fe[C(SCH$_3$)$_2$]{PF$_6$}, was added a 15 ml THF solu-

tion prepared from 2.0 ml of HSCH$_3$ and 0.30 g (1.18 mmol) of

Li{[(CH$_3$)$_3$CO]$_3$AlH} which had stirred for 12 hr. This was followed by

25 ml of CS$_2$. The solution was then cooled to 0°C and allowed to stir

for 3 hr. during which time the solution developed a blood red colora-

tion. In the absence of CS$_2$ no color change occurred. The solvent

was removed at reduced pressure. Maintenance of an inert atmosphere

was no longer required. The red solid which resulted was extracted

with 2 x 10 ml of CS$_2$, the extracts were combined and filtered through

Celite. The CS$_2$ solution was rotoevaporated to dryness and the

residue chromatographed on 400-mesh silica-gel (2 x 6 cm) eluting with

hexane/CH$_2$Cl$_2$ 10:1. A single red band moved down the column. This

was collected and rotoevaporated to dryness, then dried under vacuum

(10$^{-3}$ torr) for 30 min. A yield of 37% (0.94 g. 0.35 mmol). based on

Cp(CO)$_2$Fe[C(SCH$_3$)$_2$]{PF$_6$}, of Cp(CO)Fe[S$_2$C(SCH$_3$)], **7**, was obtained.

Crystals of **7** resulted upon slow cooling of a saturated petane solu-

tion to -20°C (see Results and Discussion for X-ray diffraction data).

At 0°C or below, solutions or crystals of **7** are stable for indefinite

periods; however, at room temperature decomposition begins in a matter

of hours. Compound **7** is very soluble in organic solvents. Data for

**7**: Anal. Calcd.: C$_8$H$_8$OS$_3$Fe; C: 35.30, H: 2.96. Found: C: 35.56, H:

3.04. Melting Point: 40-41°C; IR (CS$_2$): 1960 cm$^{-1}$; $^1$H NMR (CD$_2$Cl$_2$):

4.60 (s, 5H, Cp), 2.48 (s, 3H, SCH$_3$); (CS$_2$): 4.47 (s, 5H, Cp), 2.53

(s, 3H, SCH$_3$); $^{13}$C NMR: 238.55 ppm (s, S$_2$$\underline{C}$(SCH$_3$)), 216.29 (s, CO), 79.50 (s, Cp), 16.54 (s, SCH$_3$).

B. Using Li{SCH$_3$} generated in situ, in CH$_2$Cl$_2$:

A solution containing 1.0 ml of HSCH$_3$ and 0.24 g (0.94 mmol) of Li{[(CH$_3$)$_3$CO]$_3$AlH} in 20 ml of THF was stirred for 12 hr. The solvent and excess HSCH$_3$ were removed at reduced pressure and 20 ml of CH$_2$Cl$_2$ was added to the white oily Li{SCH$_3$} residue partially dissolving it. This suspension was added to a sample of **4**, prepared using the general procedure from 0.40 g (0.94 mmol) of Cp(CO)$_2$Fe[C(SCH$_3$)$_2$]{PF$_6$}. The solution immediately developed a slight red coloration. After stirring for 10 min. the solvent was removed at reduced pressure. The CS$_2$ extract was blood red in color. Following the workup described in the preceding experiment (A) 0.086 g (0.32 mmol, 34%) of **7** was obtained. When LiAlH$_4$ (0.040 g, 1.1 mmol) was used in place of Li{[(CH$_3$)$_3$CO]$_3$AlH} to generate Li{SCH$_3$} the yield of **7** was 20%.

C. Using solid Li{SCH$_3$} in THF:

A sample of **4**, prepared using the general procedure from 0.25 g (0.58 mmol) of Cp(CO)$_2$Fe[C(SCH$_3$)$_2$]{PF$_6$}, was dissolved in 10 ml of THF. To this was added 10 ml of CS$_2$ followed by 0.040 g (0.74 mmol) of Li{SCH$_3$}. Over the course of 3 hr., the solution became blood red in color. The solvent was removed at reduced pressure. Following the workup described above in (A) resulted in the isolation of 0.037 g (0.14 mmol, 23%) of **7**.

D. Using Na{SCH$_3$} in THF:

A 20 ml THF solution of Na{SCH$_3$} was generated by allowing 0.050 g

(1.0 mmol) of NaH (as a 50% mineral oil dispersion) and 2 ml of HSCH$_3$ to

stir for 3 hr. This was added directly to a sample of **4**, prepared using

the general procedure from 0.40 g (0.94 mmol) of Cp(CO)$_2$Fe[C(SCH$_3$)$_2$]{PF$_6$}.

After a period of 3 hr. the solution had become chocolate brown in color.

The solvent was removed at reduced pressure. A CS$_2$ extract gave a blood

red solution, the IR of which showed only the presence of **7**. The CS$_2$ was

evaporated leaving 0.020 g (0.96 mmol, 10%) of **7** as a red oil.

Reaction of Cp(CO)Fe[S$_2$C(SCH$_3$)], **7**, with PEt$_3$. To a cherry red solu-

tion of **7** (0.20 g, 0.074 mmol) in 20 ml of CH$_2$Cl$_2$ was added 0.050 ml

(0.059 g, 0.51 mmol) of PEt$_3$. Over the course of 2 hr. the solution

developed a deep burgundy color as the IR band of **7** slowly diminished, no

precipitation occurred. The solution was evaporated to dryness at reduced

pressure. The residue was dissolved in hexane giving a purple solution.

The IR of the hexane extract showed no bands in the region 2100–1500 cm$^{-1}$.

The formation of the CO substitute product Cp(PEt$_3$)Fe[S$_2$C(SCH$_3$)] seemed

likely.

## RESULTS AND DISCUSSION

The photolysis of a yellow hexane solution of $Cp(CO)_2FeC(SCH_3)_2H$, 1, results in the formation of a black, homogenous, extremely air-sensitive solution which exhibits a single strong band in the IR $v(CO)$ at 1933 $cm^{-1}$ (Eqn. 12). Gas evolution is apparent during this process. Exposure

$$
\begin{array}{ccc}
\underset{1}{Cp\diagdown\!Fe\!-\!\overset{H}{\underset{|}{C}}\!-\!SCH_3} & \xrightarrow[-CO]{h\nu} & \underset{2\quad 80\ \%}{Cp\diagdown\!Fe\!-\!\overset{H}{\underset{|}{C}}\!-\!SCH_3} + CO \qquad (12)
\end{array}
$$

of this solution to oxygen results in the immediate formation of a black insoluble precipitate which is silent in the $v(CO)$ region of the IR. The black oily residue left after photolysis and evaporation of the solvent could be quickly chromatographed under anaroebic conditions on silica-gel by eluting with dichloromethane/hexane 1:1. The single black band which eluted down the column was collected and found to be sufficiently free of paramagnetic iron impurities for NMR spectroscopy. Other attempts to purify the product of equation 12 such as recrystallization or sublimation failed to yield a solid material; only oily residues were obtained. The $^1H$ NMR spectrum of 2 in $CDCl_3$ (Table 1) is consistent with structure 2 in which loss of CO is accompanied by coordination of one of the mercaptide sulfur atoms to iron. In addition to the resonance for the Cp ligand are peaks at 2.26 ppm (s, 3H), 2.19 ppm (s, 1H), and 1.60 ppm (s, 3H). These three resonances are assigned to the dangling mercaptide, the hydrogen on the ketal carbon, and the mercaptide bound to both the iron and ketal

Table 1. Infrared and $^1$H NMR ($\delta$) of the Complexes

| Complex | IR, $\nu$(CO), cm$^{-1}$ | Cp | CH | CH$_2$ | SCH$_3$ | Ref |
|---|---|---|---|---|---|---|
| Cp(CO)$_2$Fe[CH$_2$SCH$_3$] | 2029 (s), 1981 (s)[a] | 4.79[b] | --- | 2.32 | 2.09 | 133 |
| Cp(CO)$_3$Mo[CH$_2$SCH$_3$] | 2029 (s), 1952–1943 (vs)[c] | 5.38[b] | --- | 2.38 | 2.18 | 133 |
| Cp(CO)$_2$Mo[CH$_2$SCH$_3$] | 1922 (s), 1838 (s)[c] | 5.15[b] | --- | 2.67 ave. 1.89 2.28 | 1.88 | --- |
| Cp(CO)$_2$Fe[CH(SCH$_3$)$_2$], 1 | 2018 (s), 1968 (s)[d] | 4.93[e] | 3.97 | --- | 2.22 | 60 |
| Cp(CO)Fe[CH(SCH$_3$)(SCH$_3$)], 2 | 1933 (s)[f] | 4.50[e] | 2.26 | --- | 2.19 1.60 | --- |
| Cp(CO)Fe[CH(SCH$_3$)]$^+$, 4 | 1993 (s)[d] | 4.92[g] | 2.14 | --- | 2.24 | --- |
| Cp(CO)Fe[C(SCH$_3$)], 5 | 1960 (s)[b] | 4.57[b] | --- | --- | 2.53 | 131 |
| Cp(CO)Fe[CH$_2$SCH$_3$], 6 | 1932 (s)[f] | 4.34[e] | --- | 1.84 1.39 | 1.66 | --- |
| Cp(CO)Fe[S$_2$C(SCH$_3$)], 7 | 1956 (s)[d] | 4.60[b] | --- | --- | 2.55 | --- |

[a]CCl$_4$ solvent.
[b]CS$_2$ solvent.
[c]Halocarbon mull.
[d]CH$_2$Cl$_2$ solvent.
[e]CDCl$_3$.
[f]Hexane solvent.
[g]CD$_3$CN solvent.

carbon atom, respectively. The shift to higher field of the ketal proton

and the protons in the iron bound mercaptide are consistent with the

observations of King who reported similar $^1$H chemical shift differences

in the sigma to pi conversion of $Cp(CO)_3MoCH_2SCH_3$ to $Cp(CO)_2MoCH_2SCH_3$

(Table 1) (Eqn. 13).[133] The unbound $SCH_3$ group in the sigma complex

$$Cp\diagdown Mo{-}CH_2SCH_3 \xrightarrow[-CO]{} Cp\diagdown Mo{-}\overset{H}{\underset{\underset{O}{C}\ \underset{O}{C}\ S_{CH_3}}{C}}{-}H \quad + \quad CO \quad (13)$$
$$(CO)_3$$

resonates at 2.18 ppm while in the pi complex the metal bound $SCH_3$ group

appears at 1.88 ppm. The $^{13}$C NMR spectrum of 2 is also consistent with

the indicated structure. In addition to resonances for the CO and Cp

ligands (Table 2) are two others, one at 27.19 ppm and the other at 24.07

ppm corresponding to the methyl carbon of the dangling and iron bound

mercaptide protons. The resonance observed at 68.10 ppm is assigned to

the ketal carbon atom. It is not evidence which of the methyl carbon

resonances corresponds to the iron bound versus dangling mercaptide

groups; no mononuclear analogues to 2 have had their $^{13}$CNMR spectra

recorded. The similar dinuclear metallothiocyclopropane ring containing

compound $Cp(CO)Fe(\mu{-}CO)(\mu{-}C(SCH_3)_2)Fe(NO)(CO)$ (see Results and Discussion

Part I) which also has one dangling and one free mercaptide group shows

resonances for the mercaptide carbon atoms at 29.71 ppm and 27.54 ppm.

These are similar in chemical shift and separation to what is observed

above for 2. The chemical shift of the ketal carbon atom in 2 is

approximately 30.1 ppm to lower field than what is found for 1. The

reasons for this decrease in the magnetic shelding of the ketal carbon

Table 2. $^{13}C$ NMR spectra of compounds discussed in Part II. All spectra were recorded in $CD_2Cl_2$ solvent and are reported in ppm relative to TMS = 0 ppm

| Compound | (CO) | C$_5$H$_5$ | CR$_3$ | SCH$_3$ |
|---|---|---|---|---|
| Cp(CO)$_2$Fe[C(SCH$_3$)$_3$] | 217.0 | 90.9 | 60.7 | 19.6 |
| Cp(CO)$_2$Fe[(CH)(SCH$_3$)$_2$], 1 | 215.9 | 87.5 | 37.5 | 20.4 |
| Cp(CO)Fe[(CH)(SCH$_3$)(SCH$_3$), 2 | 217.2 | 79.5 | 68.1 | 27.2 24.1 |
| Cp(CO)Fe[S$_2$C(SCH$_3$)], 7 | 216.3 | 79.5 | 238.6 | 16.5 |

upon going from **1** to **2** are not clear. It is interesting that coordination of the sulfur atom to iron on going from **1** to **2** shifts the ketal carbon to much lower field in the $^{13}$CNMR spectrum while in the $^{1}$HNMR spectrum the ketal proton resonance is shifted to higher field.

A low energy mass spectrum of **2** shows a parent ion at m/e 256 plus peaks corresponding to the fragments shown below. As can be seen, all the



major fragments are observed beginning with the loss of CO. Two additional peaks of low intensity at m/e 356 and 279 were observed and are of unknown origin. They may represent products resulting from the decomposition of **2** during the loading of the sample into the mass spectrometer, a process which requires short exposure to the atmosphere. Due to its oily nature and rapid decomposition in the presence of dioxygen further characterization of **2** by means such as elemental analysis or vapor pressure osmometry was not possible.

It was discovered that compound **2** could also be synthesized in two other ways. When the cationic carbene compound Cp(CO)(NCCH$_3$)Fe-

$[C(SCH_3)_2]\{PF_6\}$, **3**, is allowed to react with NaH in THF at room temperature a rapid reaction occurs leading to a darkly colored extremely air-sensitive solution (Eqn. 14). The IR, proton, and carbon NMR spectra

$$Cp\diagdown \underset{\underset{O}{\overset{|}{C}}\,\underset{\overset{|}{C}}{N}}{Fe}=C\overset{\displaystyle +}{\diagup\diagdown}\underset{SCH_3}{\overset{SCH_3}{}} \quad + \quad H^- \quad \longrightarrow \quad 2 \quad + \quad NCCH_3 \qquad (14)$$

of the product of this reaction are identical to those of **2** as obtained above by the photochemical route. The yield obtained from this route is 60%. Similar yields result when $LiAlH_4$ or $Li\{[(CH_3)_3CO]_3Al\}$ are used as the hydride donors. It seems likely that **2** results from attack of the hydride at the carbene carbon followed by displacement of the labile acetonitrile ligand by sulfur. For either electronic reasons or problems of constraint the sulfur atom in **3** cannot displace the weakly bound acetonitrile ligand. The nucleophilicity of the sulfur in **3** is expected to be less than in an intermediate such as $Cp(CO)(NCCH_3)Fe[C(SCH_3)_2H]$ because of the interaction of the sulfur lone pair with the carbene carbon in **3**. In addition, once hydride attacked occurs forming the $sp^3$ ketal carbon from the $sp^2$ carbene the constraint on the rotation of the sulfurs is relieved making interaction with the iron atom easier. Alternatively, a mechanism can be envisioned in which the hydride initially displaces the acetonitrile ligand and migrates to the carbene carbon as the sulfur fills the open coordination site. Migration of a metal hydride to a carbene ligand has been proposed to occur as a reversible process in low temperature matrix isolation experiments.[143] However, attack of hydride ligands on other cationic iron carbene compounds have been found generally to occur at the

carbene carbon atom as is most likely occurring here.[144]

Compound 2 can also be obtained from the interaction of $(CH_3)_3NO$ and 1 in refluxing THF (Eqn. 15). The conversion to 2 does not go to

$$\underset{\underset{\displaystyle O}{C}}{\overset{\displaystyle Cp}{\underset{\displaystyle \overset{|}{C}}{\overset{|}{Fe}}}} - C \overset{\displaystyle H}{\underset{\displaystyle SCH_3}{\overset{\displaystyle SCH_3}{\diagup}}} + (CH_3)_3NO \longrightarrow 2 + CO_2 + (CH_3)_3N \qquad (15)$$

completion even when large excesses of $(CH_3)_3NO$ and long reaction times are used. A significant quantity of unreacted 3 always remains. Presumably this reaction occurs as a result of the oxidation of coordinated CO to $CO_2$ by $(CH_3)_3NO$ followed by the formation of an intermediate amine complex which rapidly rearranges to 2 by sulfur displacement of $(CH_3)_3N$. No such intermediates are detected in this case. The ability of $(CH_3)_3NO$ to react with metal carbonyl compounds via attack at coordinated CO forming $CO_2$ is well documented.[145]

These chemical results along with the spectroscopic data strongly suggest that the formulation of 2 as a simple dithioketal in which one of the mercaptide sulfur atoms is bound to the iron atom forming a metallothiocyclopropane ring is correct. King and coworkers tried to obtain the cyclic thioketal $Cp(CO)\overline{FeCH_2SCH_3}$ by the photolysis of $Cp(CO)_2$-$FeCH_2SCH_3$ without success.[133] They reported that chromatography of the products of the photolysis resulted only in the recovery of unchanged starting material and trace amounts of an unknown intensely green colored substance. No mention was made of performing the chromatography under an atmosphere of dinitrogen, which was found to be necessary for the isolation of 2.
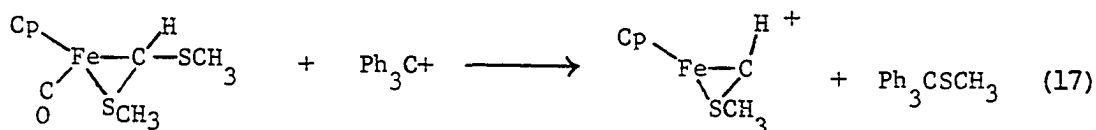
Attempts to either displace the iron coordinated mercaptide group or the carbonyl ligand in 2 with the strong nucleophile $PEt_3$ failed. When stirred with a two-fold excess of $PEt_3$ for 24 hr. in hexane no change in the position or intensity of the 1933 $cm^{-1}$ IR band of 2 was detected.

The acid induced loss of a $-SCH_3$ from 1 or $Cp(CO)_2Fe[C(SCH_3)_3]$ leading to the formation of the corresponding cationic carbene complexes $Cp(CO)_2Fe[C(SCH_3)H]^+$ and $Cp(CO)_2Fe[C(SCH_3)_2]^+$ has been found to be a facile process.[134,135] The reaction between 2 and one equivalent of $H\{BF_4\}$ in hexane at $0°C$ leads to the immediate formation of an insoluble red-green precipitate (Eqn. 16). When dry the precipitate appears pale



$$
\underset{O}{\overset{Cp}{\underset{C}{\diagdown}}} Fe\!-\!\overset{H}{\underset{S}{\overset{|}{C}}}\!-\!SCH_3 \quad + \quad H^+ \quad \longrightarrow \quad \underset{O}{\overset{Cp}{\underset{C}{\diagdown}}} Fe\!-\!\overset{H}{\underset{S}{C}}\!\overset{+}{\phantom{C}} \quad + \quad HSCH_3 \quad (16)
$$

green and is stable for a period of a few hours under an atmosphere of dinitrogen. The product of reaction (16), 4, is sparingly soluble in $CH_2Cl_2$ giving a red green solution exhibiting a single strong IR $\nu(CO)$ band at 1933 $cm^{-1}$. In the more polar solvents $CH_3CN$ and $(CH_3)_2CO$ compound, 4 is very soluble exhibiting carbonyl bands at 2000 $cm^{-1}$ and 1985 $cm^{-1}$ respectively. Decomposition of 4 in the solid state occurs over the course of a few hours leading to an increasingly insoluble green material of unknown composition. When the preparation of 4 is carried out in $CS_2$ or diethyl ether at $0°C$, 5 is obtained as a red-green oil. Attempts to recrystallize or chromatograph 4 failed yielding only oily

residues (recrystallization) or totally insoluble precipitates. Due to impurities and paramagnetic broadening NMR characterization of **4** was not conclusive. An $^1$H NMR spectrum of the crude reaction product ($CD_3CN$) contained peaks at 4.92 ppm (s), 2.24 ppm (s), and 2.14 ppm (s) but was dominated by a quartet at 3.88 ppm and a triplet at 1.26 ppm due to the diethyl ether present in the fluoroboric acid. The position and relative intensity of the nonether resonances are consistent with the structure of **4** as being a product simply resulting from the loss of $SCH_3^-$ from **2**. The resonance at 4.92 is readily assigned to the Cp ligand and is downfield shifted .42 ppm from its position in the netraul **2**. When **1** is converted to the cationic carbene compound $Cp(CO)_2Fe[C(SCH_3)_2]^+$ the Cp is similarly downfield shifted from 4.93 ppm to 5.57. The bound mercaptide methyl is assigned as the resonance at 2.24 ppm based on relative intensities; this is shifted downfield .64 ppm from its position in **2**. The ketal proton in **4** is assigned the resonance at 2.14 ppm and is upfield shifted slightly from its position in **2** by .12 ppm. With the exception of this slight upfield shift of the ketal proton on going from **2** to **4** the $^1$H-NMR data are consistent with the formulation of this product as being a cationic carbene-like compound in which the one mercaptide ligands is bound to the iron. Although not conclusive in itself the shift to higher energy of the CO band in the IR is also consistent with the conversion of **2** to **4**.



$$Cp-Fe(CO)-C(H)(SCH_3)(SCH_3) \ + \ Ph_3C^+ \ \longrightarrow \ [Cp-Fe-C(H)(SCH_3)]^+ \ + \ Ph_3CSCH_3 \quad (17)$$

The trityl cation has also recently been found to remove mercaptide groups from thioketals to yield cationic thiocarbene compounds.[134] Reaction of 2 with one equivalent of $Ph_3C\{PF_6\}$ in $CH_2Cl_2$ leads to the production of 4 over the course of .5 hr. (Eqn. 17). An additional IR band appears at 2020 $cm^{-1}$ in this preparation as a shoulder on the 1985 $cm^{-1}$ absorption $(CH_2Cl_2)$ of 4. The appearance and IR spectral proper-ties of 4 obtained by this route are identical to those of the $H^+$ reaction (Eqn. 16). The source of the 2020 $cm^{-1}$ band in this case is not known.

Attempts to prepare the iron carbyne $Cp(CO)Fe\equiv CSCH_3$, 5, by deprotonation of 4 met with limited success (Eqn. 18).[131] The



$$\text{4} \qquad\qquad\qquad\qquad\qquad \text{5}$$

deprotonation of $[HB(pz)_3](CO)_2W[\eta^2-CH(SCH_3)]^+$, giving the neutral tungsten carbyne complex $[HB(pz)_3](CO)_2W\equiv CSCH_3$ was found to proceed with NaH, $K_2CO_3$, and $NEt_3$ in about 10% yield.[129] Similar reactions carried out on 4 led to the production of very small quantities of an orange compound with IR and $^1H$ NMR spectra consistent with the formation of 5 (vida infra).
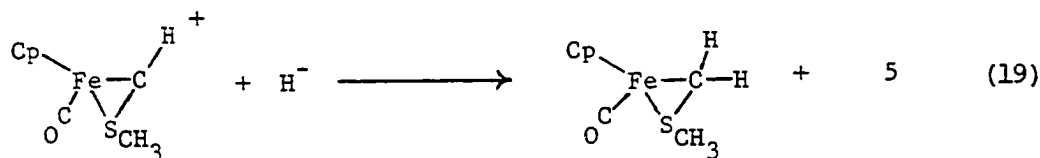
When an excess of $K_2CO_3$ is added to a $CH_2Cl_2$ solution of 4 at room temperature a very slow reaction occurs resulting in the growth of a small band at 1955 $cm^{-1}$ in the IR $\nu(CO)$ over the course of 12 hr. The major reaction occurring over this time is the decomposition of 4. A $CS_2$

extract of the solid left after removal of the solvent appears orange in color and exhibits IR $\nu(CO)$ bands corresponding to a very small quantity of $Cp_2Fe_2(CO)_4$ in addition to a single band at 1960 $cm^{-1}$ ($CS_2$) presumed to be **5**. The yield of what is presumed to be **5** obtained by this route is less than 1%. The same result is obtained when the reaction is carried out in acetone solvent. Surprisingly, the reaction between **4** and $K_2CO_3$ in acetonitrile leads exclusively to the production of a soluble green compound exhibiting a single strong band at 2020 $cm^{-1}$ in the IR. This compound resembles the by-product obtained in the reaction between **2** and trityl. Reaction of **4** with $NEt_3$ in $CH_2Cl_2$ gives trace amounts of $Cp_2Fe_2(CO)_4$ as the only $CS_2$ soluble product.

Slightly greater yields of the compound presumed to be **5** were obtained in the reaction of the more soluble tetraphenylborate salt of **4** with proton sponge ([1,8-bis-(dimethylamino)naphthalene]) in $CH_2Cl_2$. During the metathesis of **4** with $Na\{BPh_4\}$ in methanol a significant amount of decomposition occurs, in addition to the formation of a shoulder in the IR $\nu(CO)$ at 2020 $cm^{-1}$ similar to what was observed in reactions of **4** with $K_2CO_3$ in $CH_3CN$. When the $BPh_4$ salt of **4** is allowed to react with one equivalent of proton sponge a small band rapidly appears in the IR spectrum of the crude reaction mixture at 1960 $cm^{-1}$. Chromatography of a $CS_2$ extract of the solid residue left after evaporation of the solvent yields a small quantity of what is believed to be **5** as a bright orange slightly air sensitive oil. A $^1H$ NMR spectrum of this oil in $CDCl_3$ shows a single sharp resonance at 4.65 ppm consistent with the presence of the Cp ligand as well as a smaller peak (area 5:3) at 2.55 ppm corresponding
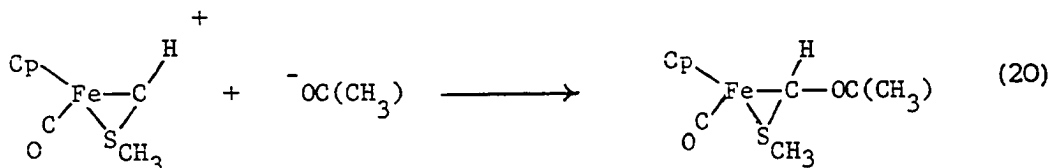
to the mercaptide methyl protons. In the similar mercapto-carbyne

compounds trans-$IW(CO)_4CSCH_3$ and $[HB(pz)_3](CO)_2W$ $CSCH_3$ the mercaptide

resonances appeared at 2.60 and 2.59 ppm respectively in the ^{1}H NMR

spectra.[123] The yield from this preparation is approximately 1%.

Several hydride donors were tried as bases in reactions aimed at

deprotonating **4** to form **5**. Sodium hydride was found to be unreactive

toward **4** in $CH_2Cl_2$ or THF. Reaction of **4** with $NaBH_4$ in acetone was found

to lead to the formation of a significant amount of $Cp_2Fe_2(CO)_4$ as the

only soluble carbonyl containing species. When $Li\{[(CH_3)_3CO]_3AlH\}$ is

allowed to stir for 10 hr. in the presence of **4** in THF a small amount of **5**

appears to form, similar to what was observed for proton sponge in $CH_2Cl_2$.

In addition, a previously unobserved weak band appears at 1930 $cm^{-1}$. When

chromatographed on silica-gel under $N_2$ ($CH_2Cl_2$/Hexane 1:1) two bands are

observed to elute down the column. The first is orange in color, and

corresponds to the compound presumed to be **5**. The second is darkly-

colored giving rise to an amber colored solution. The solid which results

upon removal of the solvent from this band readily dissolves in hexane

giving a single sharp peak in the IR $\nu(CO)$ at 1932 $cm^{-1}$. This product is

likely to result from the direct attack of $H^-$ on the carbene carbon on **4**

(Eqn. 19). Compound **6** is the cyclic thiomethoxymethyl derivative which



$$(19)$$

**6**

King tried but failed to isolated in the photolysis of

$Cp(CO)_2Fe(CH_2SCH_3)$.[133] A $^1H$ NMR spectrum $(CDCl_3)$ of **6** shows a resonance

at 4.34 ppm which is in the Cp region as well as one at 1.66 ppm which is

slightly broadened and of 3:5 integrated intensity with the one at 4.34.

The region around 1.6 ppm is noisy but singlets appear above the noise at

1.84 ppm and 1.39 ppm in integrated intensity of approximately 1 each.

These correspond with what would be expected for the methylene protons in

a compound such as **6**. In the similar compound $Cp(CO)_2Mo(\eta^2-CH_2SCH_3)$ the

two methylene protons are found to be nonequivalent and resonate at 2.67

and 1.89 ppm in the $^1H$ NMR. The methyl group of the mercaptide resonates

at 1.86 ppm.[133] Compound **6** was not characterized further.

Reaction of **4** with oxo-anions appears to lead to attack at the

carbene carbon as was partially the case for $H^-$. When potassium

t-butoxide is added to a $CH_3CN$ solution of **4** a small band develops in the

IR at 1921 $cm^{-1}$ within 10 min (Eqn. 20). No formation of **5** is evident.

$$
\begin{array}{c}
\overset{+}{\underset{\displaystyle \underset{O}{\overset{\displaystyle Cp}{\diagdown}}}{\underset{\displaystyle C}{\overset{\displaystyle \diagup}{\phantom{.}}}}Fe{-}C\overset{\displaystyle H}{\underset{\displaystyle \underset{CH_3}{\overset{\displaystyle S}{\diagup}}}{\diagup}}
\end{array}
\;+\; {}^-OC(CH_3)_3 \;\longrightarrow\;
\begin{array}{c}
\underset{\displaystyle \underset{O}{\overset{\displaystyle Cp}{\diagdown}}}{\underset{\displaystyle C}{\overset{\displaystyle \diagup}{\phantom{.}}}}Fe{-}C\overset{\displaystyle H}{\underset{\displaystyle \underset{CH_3}{\overset{\displaystyle S}{\diagup}}}{\diagup}}{-}OC(CH_3)_3
\end{array}
\qquad (20)
$$

After 20 hr. of stirring the IR shows no further change except for the

formation of a small quantity of $Cp_2Fe_2(CO)_4$. A $CS_2$ extract showed only

$Cp_2Fe_2(CO)_4$ and the presumed oxothioketal at 1927 $cm^{-1}$ in the IR. When

**4** was dissolved in methanol and one equivalent of $K_2CO_3$ was added, a

similar reaction occurred. A $CS_2$ extract of this reaction mixture

following removal of the solvent showed the presence of $Cp_2Fe_2(CO)_4$ and

another product which had a single strong band at 1928 cm$^{-1}$ which is presumed to be the methoxy analogue $Cp(CO)Fe(\eta^2\text{-}CH(SCH_3)OCH_3$. The low yields obtained in these reactions (less that 5%) precluded their further study.

In reaction with **4** -SCH$_3$ seemed likely, in view of the results with oxo-anions, to either reform **2** or to act as a base and deprotonate **4** to give **5**. Neither of these results occur to any extent. When a solution of Na$\{SCH_3\}$, gene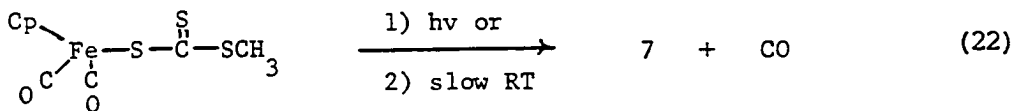rated from NaH and HSCH$_3$ in THF, is added to **4** the color gradually becomes dark over the course of 18 hr. During this period the IR shows the gradual disappearance of **4**, no new bands appear. An Et$_2$O extract of the solid residue left after removal of the solvent is silent in the 2100-1800 cm$^{-1}$ region of the IR. However, when CS$_2$ is used to extract the crude reaction product the extract appears orange and has a single band in the IR $\nu(CO)$ at 1955 cm$^{-1}$ indicating the likely formation of **5**. Since **5** is expected to be soluble in Et$_2$O this result suggests that the presence of the thiocarboxylate anion, $^-SC(S)SCH_3$, formed by the reaction of unreacted -SCH$_3$ with CS$_2$, was either acting as a base to deprotonate **4** presumably forming **5** or reacting in some previously unsupposed fashion with **4**. Experiments in which CS$_2$ was added directly to solutions containing **4** and -SCH$_3$ in THF were found to drastically increase the yield of the 1955 cm$^{-1}$ band in the IR giving a blood red color to the solution over the course of 20 min. Removal of the solvent gave a deeply-colored red residue which was very soluble in CS$_2$, exhibiting a single sharp band at 1960 cm$^{-1}$ in the $\nu(CO)$ region of the IR. Chromatography on silica-gel with CH$_2$Cl$_2$/hexane 1:1 lead to the elution of a

single orange-red colored band. A $^1$H NMR of this product showed

resonances (CS$_2$) at 4.47 ppm (s, 5H) and 2.53 ppm (s, 3H) which were in

good accord with those observed for the product of the reaction of **4** with

proton sponge. However, further characterization of the product of this

reaction indicated that a thiocarboxylate iron compound, **7**, had been

formed in 49% yield rather than the thiocarbyne (Eqn. 21). Crystals were



(21)

obtained by slow cooling of a saturated pentane solution of **7**. The mass

spectrum (m/e 272, M+) and elemental analysis are consistent with the

formulation of **7** as a methyl(trithiocarbonato)cyclopentadienyl iron

carbonyl. A $^{13}$C NMR spectrum is also consistent (Table 3) with this

formulation. The thiocarboxylate carbon resonates at 238.55 ppm in the

$^{13}$C NMR which is at higher field than would be expected for a thiocarbyne

carbon.[123] The methyl resonance appears at 16.54 ppm which is close to

the value obtained in the thiocarbyne [HB(pz)$_3$](CO)$_2$W CSCH$_3$ of 17.4 ppm.

No similar thiocarboxylate compounds have had their $^{13}$C NMR spectra

recorded for comparison to the values obtained here. Compound **7** was

originally prepared by Knox and coworkers via the photolysis or slow



(22)

solution decomposition of $Cp(CO)_2FeSC(S)SCH_3$ in 78% yield (Eqn. 22). They

reported **7** as a deep-red air-stable crystalline material with a single

band in the IR $v(CO)$ at 1956 cm$^{-1}$ ($CH_2Cl_2$) and two singlets in the $^1H$ NMR

at 4.60 ppm and 2.55 ppm ($CS_2$). These values are in accord with the

values obtained above for **5**.

The formation of **7** from the reaction of **4** with methyltrithiocarbonate

can be envisioned as occurring as shown below (Scheme IV). Initially the



Scheme IV

sulfur anion must displace the mercaptide sulfur bound to the iron leading

to the intermediate carbene. This can then rearrange via displacement of

the carbene ligand by the thione sulfur to give **7**. The fate of the

liberated carbene ligand is not known. Although much less common than

nucleophilic displacement of CO, the displacement of carbene ligands from

transition metals by things such as phosphines has been observed

before.[133,146] This mechanism is in accord with the observations of Knox

who found that the sulfur coordinated trithiocarbonate complex

$Cp(CO)_2FeSC(S)SCH_3$ can slowly rearrange in solution with loss of CO to

form **7** (Eqn. 22).[138]

The crystal structure of **7** was determined.[147] An ORTEP drawing is shown in Figure 1 indicating the geometry of the molecule and the atom labeling scheme. A few selected bond distances and angles are presented in Table 3. The molecule adopts a three-legged piano stool configuration. The four membered chelate ring (Fe, S1, C3, S3) is symmetrical about a plane drawn through C3 and Fe. The S3 and S1 to Fe bond distances of 2.287 (3) $\overset{o}{A}$ and 2.279 (3) $\overset{o}{A}$ are approximately 0.6 longer than the C3-S1 (1.691 (9)$\overset{o}{A}$) and C3-S3 (1.684 (8) $\overset{o}{A}$) bond



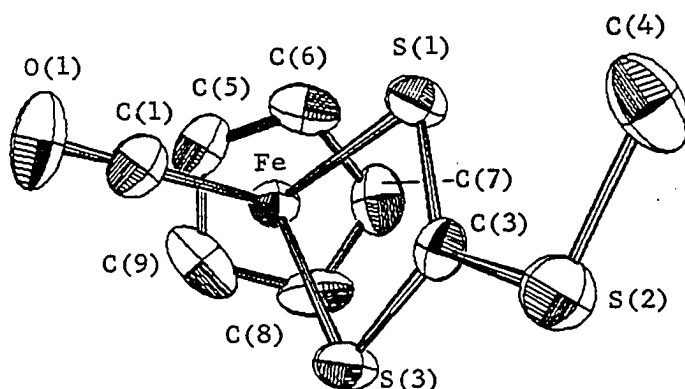Figure 1. ORTEP drawing of **7** showing the atomic labeling scheme.

Table 3. Selected bond distances and angles in **7**

| Distances | | Angles (degrees) | |
|---|---|---|---|
| Fe S1 | 2.287 (3) | S3 Fe S1 | 75.14 (9) |
| Fe S2 | 2.279 (3) | S3 C3 S1 | 111.1 (5) |
| C3 S3 | 1.684 (8) | Fe S3 C3 | 86.7 (3) |
| C3 S1 | 1.691 (9) | Fe S1 C3 | 86.8 (3) |
| C3 S2 | 1.717 (8) | C3 S2 C4 | 102.5 (4) |

distances. The geometry around C3 is planar; the sum of the angles around C3 to S1, S2, S3 are 359.99° (5). These values are in accord with those typically observed in transition metal thiocarboxylate complexes (or thioxanthate complexes as they are commonly referred to).[141] The C3-S2 distance of 1.717 (8) Å is slightly shorter than the $C(sp^2)$-S distance in $C(SPh)_4$ (1.776 Å average).[87] The S2-C4 distance of 1.816 (9) Å is typical for a carbon-sulfur single bond (ethylene sulfide C-S single bond distance is 1.819 (1) Å).[86]

Although unclear it is possible that the compound obtained by Quick and Angelici which was thought to be the thiocarbyne complex Cp(CO)Fe $CSCH_3$, 5, may simply be the thiocarboxylate 7. There are two reasons for considering this possibility. Firstly, the IR (in the CO region), $^1H$ NMR, and physical characteristics are (Table 4) very nearly identical. Both compounds are similar in color, very soluble in organic solvents, and chromatograph on silica-gel. Unfortunately, the yield of 5 obtained by

Table 4. A comparison of the spectroscopic and physical properties of 7 with those proposed by Quick and Angelici for Cp(CO)Fe $CSCH_3$), 5

| | IR ($CS_2$, cm$^{-1}$) | $^1H$-NMR ($CS_2$, δ) | | Color | Stability |
|---|---|---|---|---|---|
| | | $C_5H_5$ | $SCH_3$ | | |
| Cp(CO)FeS$_2$CSCH$_3$, 7 | 1960 | 4.47 | 2.53 | orange | slow dec. in solution |
| Cp(CO)Fe≡CSCH$_3$, 5 | 1960 | 4.55 | 2.53 | orange | "rather unstable" as an oil |

Quick was so poor that further characterization was not completed.

Secondly, Knox has reported that when CpFe(CO)$_2^-$ is reacted with excess

$CS_2$ followed by alkylation with $CH_3I$ that **7** is obtained in 5-10% yield (Eqn. 23).[136] No mechanism was put forth to explain this transformation.

$$\underset{O}{\overset{Cp}{\underset{C}{\phantom{.}}}}\overset{-}{Fe}\overset{C}{\underset{O}{\phantom{.}}} \qquad \xrightarrow[\text{2) } CH_3I]{\text{1) } CS_2} \qquad 7 \qquad\qquad (23)$$

This represents a plausible route to **7** from the reaction conditions employed by Quick. In Quick's case $CpFe(CO)_2^-$ was present in the reaction mixture as well as $CpFe(CO)(CS)^-$. After the addition of $CH_3I$ the product, thought to be **5**, was extracted into $CS_2$. If unreacted $CpFe(CO)_2^-$ had remained in the flask at the time of the $CS_2$ extraction the reaction described in Eqn. 23 could have occurred resulting in the production of **7**, which in view of the circumstance, i.e., the known reactivity of thiocarbonyl anions toward $CH_3I$, was mistaken for **5**. Whether or not this was the case cannot be decided without further experiments along the lines of Quick's original work.

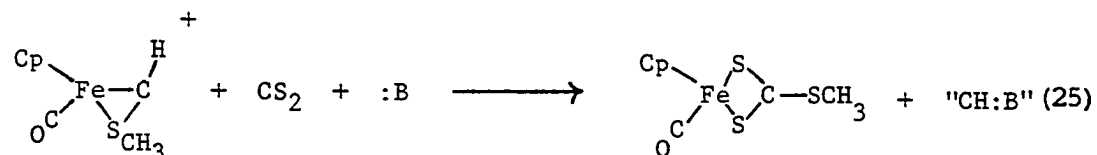One also has to reconcile the fact that small amounts of a compound thought to be **5** were obtained in the reaction of **4** with bases as described above. In all cases where the product **5** was thought to be forming, the product had been extracted into $CS_2$. This suggests two possibilities. Either compound **5** was actually formed in small amounts from the deprotonation of **4** or $CS_2$ was somehow interacting with **4** and the base present to form **7**. There is some precedence for this last proposition. Carbon disulfide has been found to insert in metal-sulfide bonds to form

thiocarboxylate ligands (Eqn. 24).[148] It is conceivable that the

$$Cp\text{—}W(CO)_3\text{—}SCH_3 \quad + \quad CS_2 \quad \longrightarrow \quad Cp\text{—}W(\text{CO})(C)(S)_2C\text{—}SCH_3 \quad + \quad CO \qquad (24)$$

presence of a base such as $K_2CO_3$ or proton sponge could promote the

insertion of $CS_2$ into the metal-sulfide bond of **4** (Eqn. 25). Partial or

full deprotonation of **4** may create an intermediate which more readily

$$Cp\text{—}Fe\text{—}C(H)(SCH_3) \quad + \quad CS_2 \quad + \quad :B \quad \longrightarrow \quad Cp\text{—}Fe(S)_2C\text{—}SCH_3 \quad + \quad "CH:B" \quad (25)$$
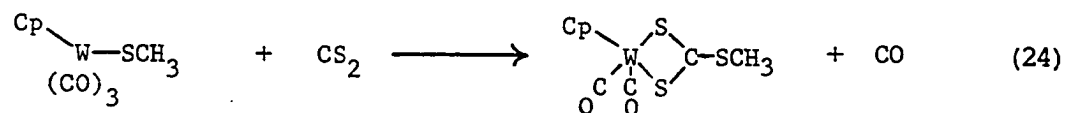
interacts with $CS_2$ than **4** itself, which is totally unreactive in the

presence of $CS_2$ alone. The experiments described herein do not allow this

question to be answered. At this point it is not possible to say for

certain whether compound **5**, the iron thiocarbyne, really has existed. If

it has not, then a transformation such as the one described in Equation 25

must be responsible for the conversion of **4** to **7**.

## CONCLUSION

The work described in this section is obviously not a complete story. It would be worthwhile to try making enough of **5** from Quick's route to find out for certain if it is the thiocarbyne or simply the thiocarboxylate compound, **7**.[131] If it is the former as originally proposed then further investigations involving the deprotonation of **4** seem worthwhile. If it is the latter further experimentation on the iron system seems less appropriate in view of the extremely low yields of organometallic products obtained. Certainly the preparation of **7** developed here in the search for **5** is not a particularly good one.

As a synthetic route to transition metal-thiocarbyne compounds the deprotonation of coordinated $\eta^2$-CHSCH$_3$ ligands seems promising. While the difficulties encountered in the iron system described above were severe, the large number of possible compounds which have yet to be tried suggest hope. In principle one need only be able to make a dithiomethoxymethyl transition metal carbonyl compound as a starting point in preparing $\eta^2$-CHSCH$_3$ containing compounds. As it seems clear from the work described here and the work of others cited, the coordination of one of the sulfurs of the dithiomethoxymethyl ligand to the metal center by displacemet of a CO ligand is a facile process. One need only be able to cleave off a mercaptide group from the $\eta^2$-CH(SCH$_3$)$_2$ ligand to have the desired $\eta^2$-CHSCH$_3$ configuration. As described, this is readily achieved with acid or trityl cation.

Inasmuch as carbynes are a very interesting and important class of ligands in organometallic chemistry the pursuit of synthetic routes to

thiocarbyne containing compounds will continue in earnest. The synthetic route briefly explored here seems likely to be of continued value in this regard.

## GENERAL SUMMARY

The research presented in Part I of this dissertation demonstrates that mononuclear terminal dithiocarbene ligands can be converted into bridging dithiomethylene ligands through reaction with suitable metal carbonyl anions. The resulting bridging dithiomethylene ligands are unusual in the sense that one of the sulfur atoms becomes coordinated to a metal center forming a three-membered metallothiocyclopropane ring. The results of a molecular orbital calculation on this ligand arrangement indicates that the formation of the metal-sulfur bond through displacement of a CO ligand significantly enhances the bonding in the dimetallocyclopropane ring. In a unique reaction these bridging dithiomethylene containing compounds were found to react with oxidizing agents resulting in the formation of terminal dithiocarbene ligands.

The work described in Part II of this dissertation deals with attempts to prepare the thiocarbyne compound $Cp(CO)Fe\equiv CSCH_3$. It was thought that deprotonation of the $\eta^2$-thiocarbene complex $\{Cp(CO)Fe(CHSCH_3)\}BF_4$ would lead to formation of the thiocarbyne. This was not successful to any extent. Reactions employing numerous types of bases under a diverse set of conditions failed to yield the iron thiocarbyne compound.

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