"The Synthesis and Reactivity of Thiolate Bridged Diiron Hexacarbonyl Complexes"

by

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B.S., The Pennsylvania State University
(1983)

SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE

DEGREE OF

DOCTOR OF PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 1987

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This Thesis is Dedicated with love
to my wife, Elaine,
and to my parents

"The Synthesis and Reactivity of Thiolate Bridged Diiron Hexacarbonyl Complexes"

by

Jeffrey Barmont Hoke

Submitted to the Department of Chemistry
on May 22, 1987 in partial fulfillment of the
requirements for the Degree of Doctor of Philosophy

ABSTRACT

Chapter 1: "Synthesis of $(\mu\text{-R}^1\text{C=NR}^2)(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$"

New μ-iminoacyl complexes of the type $(\mu\text{-R}^1\text{C=NPh})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ were prepared from the reactions of triiron dodecacarbonyl with thioimidates $(\text{R}^1\text{C(SR)=NR}^2)$. The geometry of the bridging iminoacyl and thiolate ligands was determined primarily from IR and ^{13}C NMR spectral correlations to related acyl and thioacyl systems. In related work, reaction of $[\text{Et}_3\text{NH}][(\mu\text{-CO})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]$ with N-phenyl benzimidoyl chloride was found to be an alternate and superior route to complexes of this class.

Chapter 2: "Synthesis and Reactivity of $(\mu\text{-}\sigma,\pi\text{-C}\equiv\text{CR}^1)(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$"

New μ-acetylide complexes of the type $(\mu\text{-}\sigma,\pi\text{-C}\equiv\text{CR}^1)(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ were prepared from the reactions of $[\text{Et}_3\text{NH}][(\mu\text{-CO})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]$ with 1-bromoalkynes. Fluxionality of the alkyne derived, bridging acetylide ligands was illustrated in the variable temperature ^{13}C NMR study of $(\mu\text{-}\sigma,\pi\text{-C}\equiv\text{CSiMe}_3)(\mu\text{-}^t\text{BuS})\text{Fe}_2(\text{CO})_6$. Subsequent reaction of these acetylide products with diethylamine, aniline, t-butylamine, and triphenylphosphine generated products derived from nucleophilic attack of the base at the β-carbon atom of the bridging acetylide ligand. In addition, reaction of $(\mu\text{-}\sigma,\pi\text{-C}\equiv\text{CR}^1)(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ with dicobalt octacarbonyl and diiron nonacarbonyl yielded unusual homo- and heterometallic acetylide clusters, four of which have been characterized by X-ray crystallography. Surprisingly, the specific cluster isolated depended not only on the added metal carbonyl $(\text{Co}_2(\text{CO})_8$ vs. $\text{Fe}_2(\text{CO})_9)$, but also on the particular substituent (R^1) in $(\mu\text{-}\sigma,\pi\text{-C}\equiv\text{CR}^1)(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$.

Chapter 3: "Reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with Acetylenes and α,β-Unsaturated Acid Chlorides"

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with alkyl and aryl acetylenes ($R^1C{\equiv}CR^2$) produced neutral μ-vinyl complexes of the type $(\mu\text{-}\sigma,\pi\text{-}R^1C{=}CHR^2)(\mu\text{-}RS)Fe_2(CO)_6$. Presumably, formation of these products resulted from the in-situ protonation of an intermediate vinylic anion by the triethylammonium cation. ^1H NMR correlations have shown that overall addition of the diiron and proton units has occurred in a cis fashion. In some cases, reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with acetylenes generated the α,β-unsaturated acyl complexes $(\mu\text{-}R^1C({=}CHR^2)C{=}O)(\mu\text{-}RS)Fe_2(CO)_6$ as well. Formation of these acyl products resulted not only from protonation by the triethylammonium cation, but also from insertion of carbon monoxide into an iron-vinyl σ-bond. Bridging acyl complexes of this general class were prepared directly from the reactions of α,β-unsaturated acid chlorides ($R^1(R^2)C{=}CHC(O)Cl$) with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$. In refluxing THF, these vinylacyl complexes were decarbonylated to the respective μ-vinyl derivatives.

Chapter 4: "Reactions of $[Li][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with Acetylenes"

Unexpectedly, reaction of acetylenes ($R^1C{\equiv}CR^2$) with $[Li][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ followed by reaction of the anionic intermediate with an electrophile generated products derived from complex intramolecular rearrangement chemistry involving vinyl, carbonyl, and thiolate ligands. In the abscence of the in-situ triethylammonium proton source, unusual vinyl complexes which have incorporated a carbonyl ligand into the organic framework (and in some cases, with concurrent involvement by the thiolate ligand) were prepared and characterized by X-ray crystallography. Unexpectedly, the specific type of product obtained depended on the organic group of the RS ligand, the substituents on the acetylene, the reaction temperature, and the added electrophile. Of particular interest was the crystal structure of a novel, delocalized vinylcarbene complex.

Chapter 5: "Synthesis of $(\mu_3,\eta^2\text{-}C{=}CHR)(\mu\text{-}CO)Fe_3(CO)_9$"

Trinuclear vinylidene complexes of the type $(\mu_3,\eta^2\text{-}C{=}CHR)(\mu\text{-}CO)Fe_3(CO)_9$ were prepared from the reactions of 1-bromoalkynes ($R^1C{\equiv}CBr$) with $[Et_3NH][HFe_3(CO)_{11}]$. Structure assignment by the standard analytical and spectroscopic techniques was confirmed by X-ray crystallography. Presumably, formation of these products resulted from an intramolecular hydride migration to an initially formed acetylide intermediate.

Thesis Supervisor: Dr. Dietmar Seyferth (Prof. of Chemistry)

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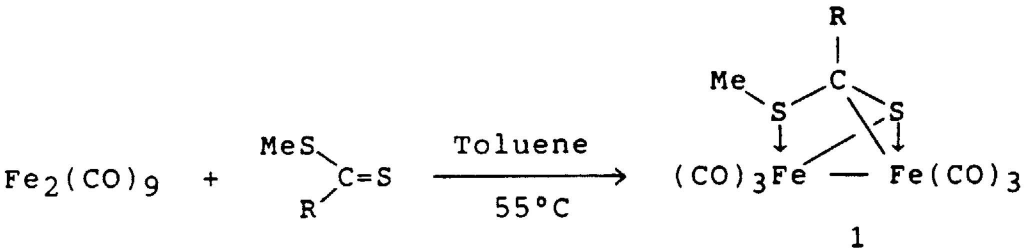
EXPERIMENTAL

Chapter 1

"Synthesis of $(\mu\text{-}R^1C{=}NR^2)(\mu\text{-}RS)Fe_2(CO)_6$"

INTRODUCTION

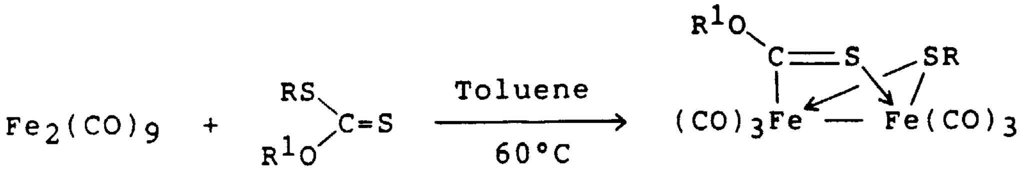
The reactions of iron carbonyls with organic thiocarbonyl compounds have received considerable attention in the literature. These include the reactions of O-alkyl thioesters,[1,2] dithioesters,[3] O-alkyl, S-alkyl dithiocarbonates,[4] trithiocarbonates,[5] O-alkyl thioformates,[2,4b] dithioformates,[2] thioketones,[6] thioureas,[7] and thioamides.[7] Diiron hexacarbonyl complexes are typically isolated in these instances with the organic thiocarbonyl substrate retaining its structural integrity and bonding to the diiron centers as a formal six electron donor (e.g. Eq. 1).[3] In some cases, however, diiron hexacarbonyl complexes are isolated where cleavage of an additional C-S bond has occurred with subsequent formation of bridging, three electron thiolate and thioacyl ligands (e.g. Eq. 2).[4a] This type of cleavage reaction also has



(1)

1

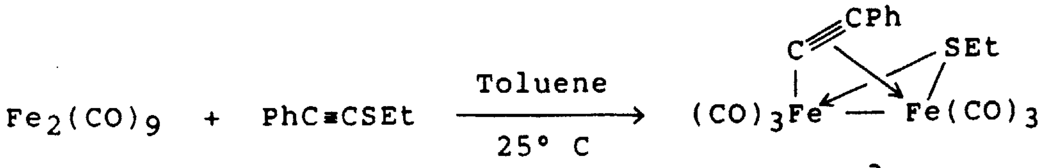
R = alkyl, aryl



(2)

2

$R = R^1$ = alkyl, aryl



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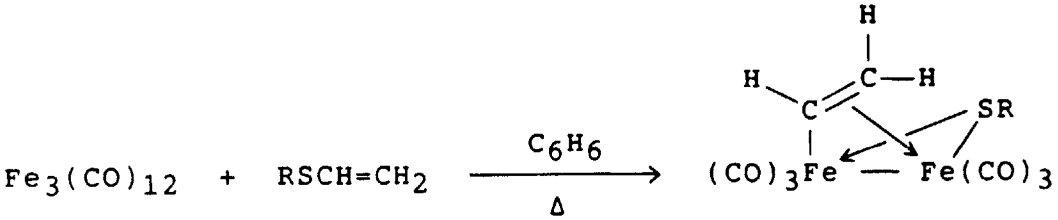
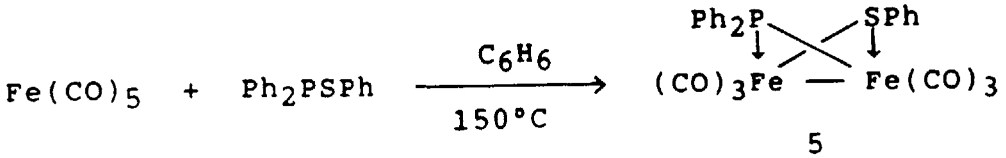


4

(4)

R = Me, Et, Vi, ^{i}Pr

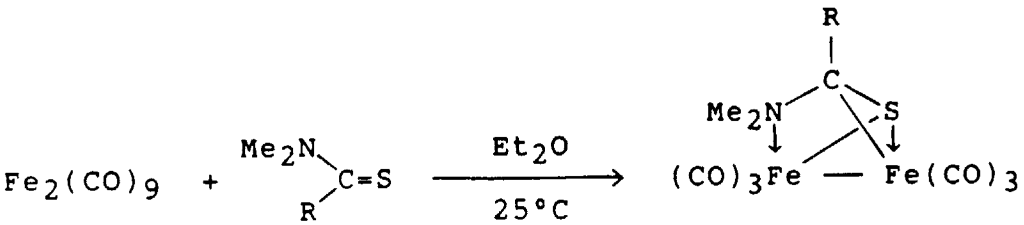


5

(5)

been observed in the synthesis of other thiolate bridged diiron hexacarbonyl complexes as well (Eqs. 3, 4, and 5).[8]

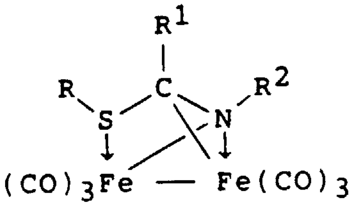
Alper has shown that reaction of diiron nonacarbonyl with N,N-dimethyl thioamides generates, in very low yield, diiron hexacarbonyl species, 6, in which the organic ligand has remained intact (Eq. 6).[7] In light of this result and our continuing interest in the synthesis of thiolate bridged diiron hexacarbonyl complexes, we wondered if reaction of the isomeric thioimidates ($R^1C(SR)=NR^2$) with diiron nonacarbonyl would produce related complexes of type 7 or



6

(6)

R = NMe_2, Me, Ph



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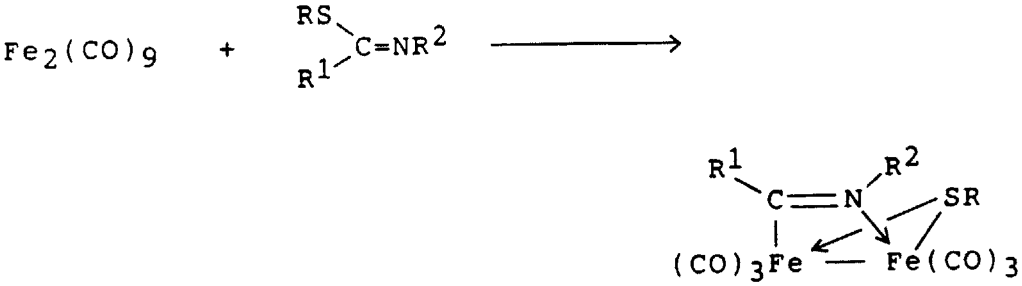


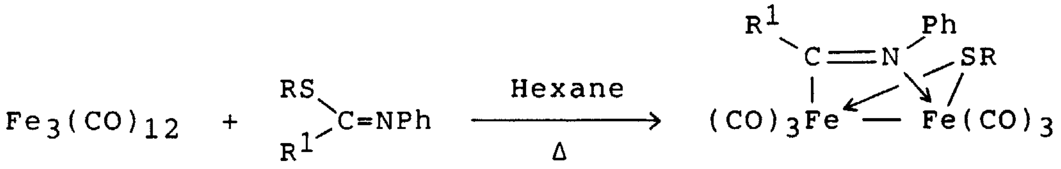
(7)

8

ones of type 8 derived from cleavage of the C-S bond (Eq. 7). While mononuclear η^1- and η^2-iminoacyls[9-15] and trinuclear μ_2- and μ_3,η^2-iminoacyls[16-18] are well known for the transition metals, binuclear μ_2-iminoacyl complexes of type 8 are not common in the literature. Mays has reported the synthesis of a μ-formimidoyl dirhenium complex, although supporting structural information was not given.[19] Evans has also reported the synthesis of a bis(formimidoyl) bridged diyttrium complex although an X-ray crystal structure indicated that the bridge bonding was formally more σ,π in nature.[20] Isoelectronic μ-acyl complexes are well known for the transition metals,[21] and in fact, a wide variety of thiolate and acyl bridged diiron hexacarbonyl complexes have been prepared.[22] Clearly, however, the analogous, dinuclear μ-iminoacyl complexes have little precedent.

RESULTS AND DISCUSSION

Reaction of $Fe_3(CO)_{12}$ with thioimidates, $R^1C(SR)=NPh$ ($R = R^1$ = alkyl, aryl), in refluxing hexane produced diiron hexacarbonyl complexes in moderate yields which have been characterized as bridging iminoacyl derivatives of type 8 (Eq. 8). (Although reaction with $Fe_2(CO)_9$ proceeded



(8)

8

a	R = Me	R^1 = Ph	43%
b	R = Me	R^1 = Me	49%
c	R = Me	R^1 = Et	52%
d	R = Et	R^1 = Me	34%

analogously, superior yields were obtained with $Fe_3(CO)_{12}$.) While products of type 8 all gave consistent carbon/hydrogen combustion analyses, EI mass spectra, and ^1H NMR spectra, the coordination of the bridging ligands was determined primarily from the infrared and ^{13}C NMR spectra. The IR spectra of 8a-d all displayed a strong absorption in the range of 1555 - 1570 cm^{-1} assigned to $\nu_{C=N}$ of the μ-iminoacyl ligands. As expected for bridging ligands of this type (e.g. μ-acyl), this band is shifted somewhat to lower frequency (~ 60 cm^{-1}) when compared to the parent thioimidates ($\nu_{C=N}$ 1610 - 1632 cm^{-1}). In contrast, $\nu_{C=N}$ of isomers of type 7 (Eq. 7) should be shifted to much lower wavenumbers typical for a C-N single bond (ca. 1030 - 1230 cm^{-1}).[23] Similarly, if the bonding of the μ-iminoacyl ligands was σ,π in nature (Fig. 1), then $\nu_{C=N}$ should be shifted considerably to lower frequency. Although one would expect an absorption indicative of a bond order between one or two for (μ-σ,π-$R^1C=NR^2$)(μ-RS)$Fe_2(CO)_6$, 9, Evans surprisingly has reported $\nu_{C=N}$ to be around 1530 cm^{-1} for the related σ,π-bis(formimidoyl) bridged yttrium complexes, [$(CpR)_2Y(\mu-\sigma,\pi-HC=N^tBu)]_2$, 10, (Fig. 2).[20] In general, since the isomers 8 and 9 are structurally very similar, differentiation between the two based on spectroscopic data alone is very difficult without appropriate comparisons in the literature. The structure of (μ-$R^1C=NR^2$)(μ-RS)$Fe_2(CO)_6$, 8, however, seems more consistent with the observed infrared data.

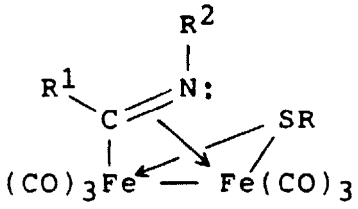


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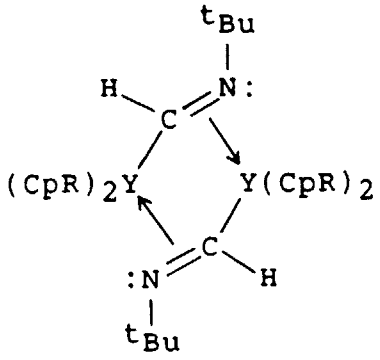
Figure 1

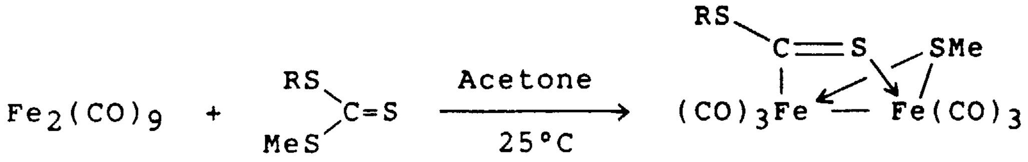
In the ^{13}C NMR spectra of 8a-d, the "carbene-like" iminoacyl carbons are observed at low field, δ_C ~ 233. These values are shifted approximately 65 ppm downfield from



10

Figure 2

the corresponding signals of the parent thioimidates. Patin has observed similar trends in the reactions of $Fe_2(CO)_9$ with S-alkyl xanthates (Eq. 2)[4] and ferrocenyl trithiocarbonates (Eq. 9)[5] where products derived from



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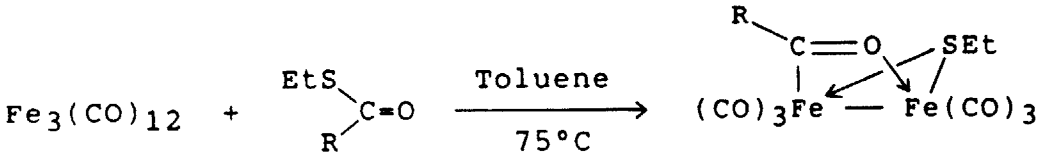
(9)

R = $(Cp_2Fe)CH_2$

cleavage of a C-S bond (with subsequent formation of bridging thiolate and thioacyl ligands) were isolated. In these two cases, the thioacyl carbon resonances of the reaction products (δ_C ~ 293 and 304) were shifted approximately 65 and 80 ppm downfield from the respective di- and trithiocarbonates. Similarly, Womack has obtained



12

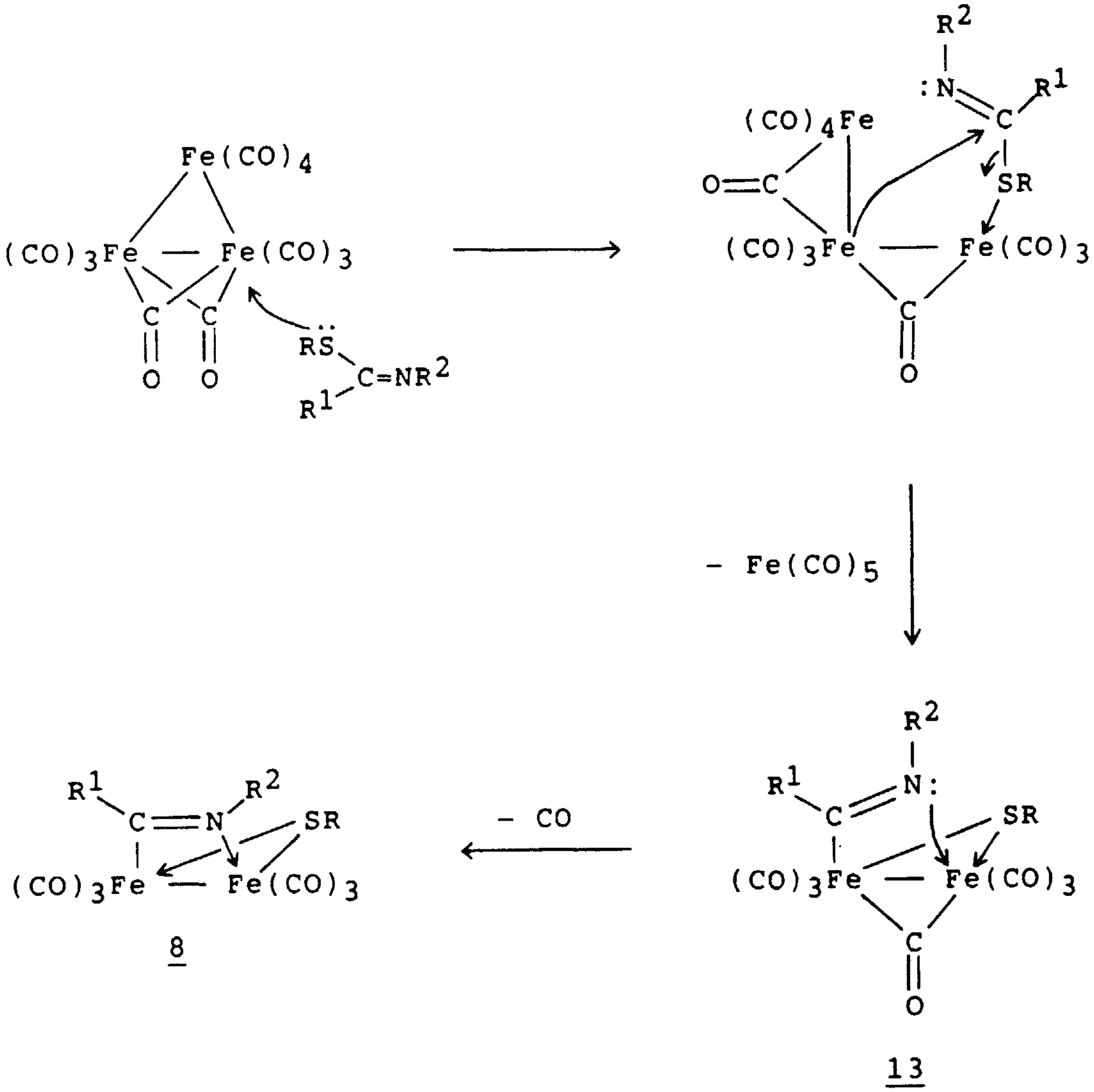
(10)

R = Me, ^{t}Bu, Ph

analogous results from the reaction of S-alkyl thioesters with triiron dodecacarbonyl (Eq. 10); the resulting μ-acyl products showed a downfield shift of approximately 105 ppm (δ_C ~ 295) for the respective acyl carbon atoms as compared to the parent thioesters (δ_C ~ 190).[2]

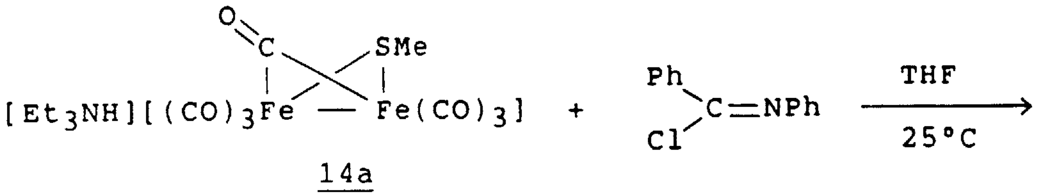
In contrast to these results, Patin has observed an opposite trend in the reactions of dithioesters with diiron nonacarbonyl. Diiron hexacarbonyl complexes were isolated where the original organic thiocarbonyl substrate had not been cleaved (Eq. 1).[3] In this instance, however, the thiocarbonyl resonances in the ^{13}C NMR spectra (δ_C ~ 75) were shifted approximately 150 ppm upfield as compared to the free dithioesters. Womack has likewise noted this trend in the related reactions of dithioformates and O-alkyl thioesters with diiron nonacarbonyl.[2]

A possible mechanistic scheme accounting for the formation of the μ-iminoacyl products, 8, is proposed in Scheme 1 (see ref. 5). The first step likely involves nucleophilic attack by sulfur at iron with concomitant cleavage of an Fe-Fe bond and migration of carbon monoxide to a new bridging position. Attack by the neighboring iron atom at the electrophilic thioimidate carbon then can lead to cleavage of the C-S bond, and, with loss of $Fe(CO)_5$, the terminal iminoacyl intermediate 13. Subsequent bridging by the nitrogen lone pair with loss of carbon monoxide then gives 8.



Scheme 1

To provide further structural proof for the generation of μ-iminoacyl complexes of this type, we have synthesized 8a alternately by the reaction of $[Et_3NH][(\mu$-$CO)(\mu$-$MeS)Fe_2(CO)_6]$, 14a, with N-phenyl benzimidoyl chloride (Eq. 11). Reaction of anionic transition metal reagents with imidoyl chlorides has previously been shown to be a viable route to the synthesis of mononuclear iminoacyl complexes.[9b,15] Furthermore, anions of the general type



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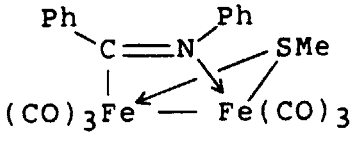
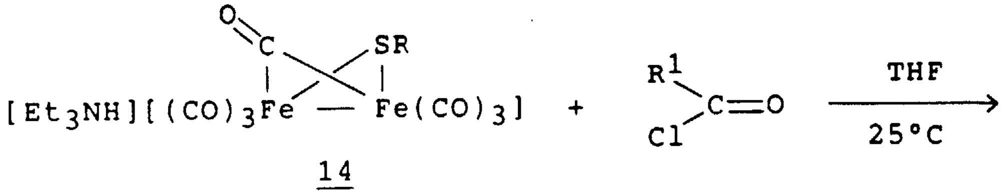


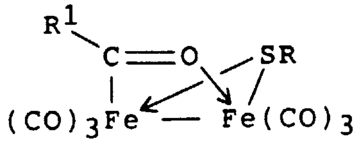
8a, 61%

$[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$, 14, have been shown to be versatile reagents for the synthesis of a wide variety of thiolate bridged diiron complexes. Typically, reaction with an electrophile leads to net substitution of the bridging carbonyl ligand with a new bridging group.[22c,24] For example, reaction of $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$, 14, with acid chlorides ($R^1C(O)Cl$, R^1 = alkyl, aryl) yields neutral bridging acyl complexes of type 12, $(\mu\text{-}R^1C{=}O)(\mu\text{-RS})Fe_2(CO)_6$, in variable yields (Eq. 12).[22a-c] Subsequently, reaction of



(12)

$R = R^1$ = alkyl, aryl



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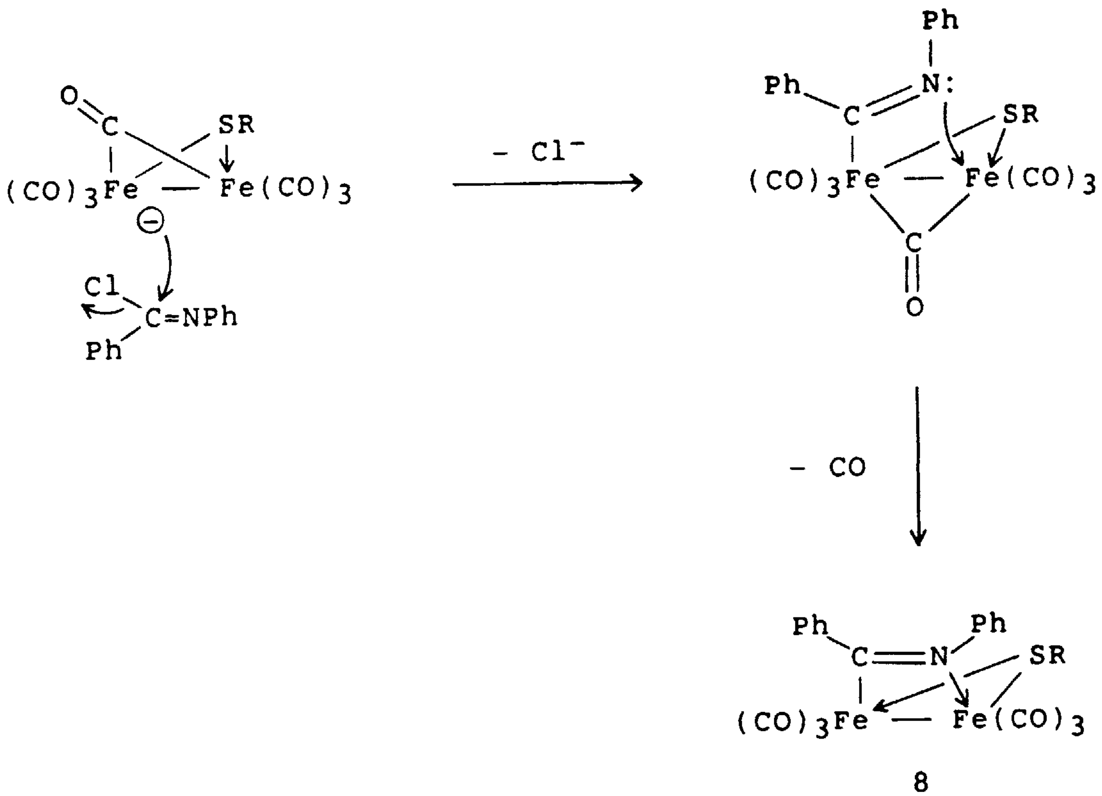
14a with benzimidoyl chloride yielded the expected product, 8a, in good yield. Analogously, (μ-PhC=NPh)(μ-^{t}BuS)$Fe_2(CO)_6$, 8e, was prepared in 85% yield by the reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}^tBuS)Fe_2(CO)_6]$, 14b, with benzimidoyl chloride. Not surprisingly, in the ^{13}C NMR spectrum of 8e the methyl resonance of the t-butyl group (δ_C 34.18) is observed in the region typically found for thiolate bridged diiron hexacarbonyl complexes (see Chapter 4).

Mechanistically, formation of the iminoacyl derivatives by this route can be envisioned as a simple S_N2 process with attack of an iron centered anion at the imino carbon and concomitant elimination of chloride ion (Scheme 2). Subsequent bridging of the dangling iminoacyl ligand by the nitrogen lone electron pair with loss of carbon monoxide then produces 8.



8

Scheme 2

EXPERIMENTAL

General Comments

All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl. Hexane was distilled under nitrogen from lithium aluminum hydride. Triethylamine was distilled under nitrogen from calcium hydride. Tert-butyl mercaptan and methyl mercaptan (Matheson) were used without further purification. Triiron dodecacarbonyl ($Fe_3(CO)_{12}$)[25] and N-phenyl benzimidoyl chloride (PhC(Cl)=NPh)[26] were prepared by literature methods. N-phenyl,S-methyl methylthioimidate (MeC(SMe)=NPh), N-phenyl,S-methyl ethylthioimidate (EtC(SMe)=NPh), N-phenyl,S-methyl phenylthioimidate (PhC(SMe)=NPh), and N-phenyl,S-ethyl methylthioimidate (MeC(SEt)=NPh) were all prepared by literature methods[27] and characterized fully by the standard analytical and spectroscopic techniques. Characterizing data are included below. All solvents and liquid reagents were purged with nitrogen prior to use. Solid thioimidates were recrystallized. Butyllithium (2.4 M in hexane) was purchased from Alfa and used as received.

The progress of all reactions was monitored by thin layer chromatography (Baker Flex - Silica Gel 1B-F). Purification by filtration chromatography in which the reaction products were dissolved in a suitable solvent and chromatographed on a bed of Mallinckrodt 100 mesh silicic acid (ca. 200 ml) in a 350 ml glass fritted filter funnel was used in most cases. Further purification by column chromatography was accomplished with a 350x25 mm column using Mallinckrodt 100 mesh silicic acid. All chromatography was completed without exclusion of atmospheric moisture or oxygen. Solid products were recrystallized from deoxygenated solvents at -20°C.

Solution or neat infrared spectra (NaCl optics) were obtained using a Perkin-Elmer Model 1430 double beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a JEOL FX-90Q or a Bruker WM-250 NMR spectrometer operating at 90 or 250 MHz respectively. Carbon-13 NMR spectra were obtained using a Bruker WH-270 spectrometer operating at 67.9 MHz. Electron impact mass spectra were obtained using a Finnigan-3200 mass spectrometer operating at 70 eV. Masses were correlated using the following isotopes: ^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{32}S, and ^{56}Fe. Melting points were determined in air on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were perfomed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Characterizing Data for EtC(SMe)=NPh **JBH-37-II**

bp: 92.0 -94.0°C @ 4 torr

Anal. Calcd. for $C_{10}H_{13}NS$: C, 66.99; H, 7.31 %. Found: C, 66.98; H, 7.29 %.

IR(neat): 3090w, 3077w, 3041w, 3030w, 2985m, 2938m, 2887w, 2430vw, 1630vs-br(C=N), 1600vs, 1485s, 1465s, 1452m, 1445m, 1380w, 1315w, 1265vw, 1218vs, 1172m, 1150vs, 1100w, 1075m, 1069m, 1042s, 970m, 940s, 902w, 890w, 792m, 769s, 730vw, 700vs, 613m, 585w, 508m cm^{-1}.

^{1}H NMR(CD_2Cl_2; 90 MHz): δ 1.12 (t, J = 7.57 Hz, 3H, $CH_2C\underline{H}_3$), 2.41 (m, 5H, SCH_3 and $C\underline{H}_2CH_3$), 7.59 (m, 5H, C_6H_5).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 12.55 (q, J = 128.5 Hz, $CH_2\underline{C}H_3$), 12.64 (q, J = 141.1 Hz, SCH_3), 28.33 (t, J = 128.4 Hz, $\underline{C}H_2CH_3$), 119.72 (d, J = 160.0 Hz, C_6H_5), 122.80 (d, J = 164.0 Hz, C_6H_5), 128.84 (d, J = 160.0 Hz, C_6H_5), 150.68 (s, ipso C_6H_5), 171.81 (s, C=N).

Mass Spectrum (EI); m/z (relative intensity): 179 (M^+, 10), 150 (MeSC=NPh, 1), 135 (SC=NPh, 3), 132 (EtC=NPh, 100), 117 (CH_2C=NPh, 4), 104 (C=NHPh, 13), 103 (C=NPh, 3), 77 (Ph, 68).

Characterizing Data for MeC(SMe)=NPh JBH-10-II

bp: 89.0 - 91.0°C @ 6 torr

Anal. Calcd. for $C_9H_{11}NS$: C, 65.41; H, 6.72 %. Found: C, 65.57; H, 6.68 %.

IR(neat): 3080w, 3075w, 3041w, 3010vw, 2940w, 1632vs-br(C=N), 1600s, 1582m, 1490s, 1452w, 1431m, 1368m, 1318w, 1222m, 1165m, 1145vs, 1072m, 1030m, 1002w, 990w, 905w, 805w, 882s, 737w, 703s, 690m, 640vw, 590w, 505w cm^{-1}.

^1H NMR(CD_2Cl_2; 90 MHz): δ 2.02 (s, 3H, CCH_3), 2.43 (s, 3H, SCH_3), 6.59 - 7.63 (m, 5H, C_6H_5).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 12.63 (q, J = 141.0 Hz, SCH_3), 20.94 (q, J = 129.7 Hz, CCH_3), 119.65 (d, J = 158.6 Hz, C_6H_5), 122.75 (d, J = 162.2 Hz, C_6H_5), 128.59 (d, J = 159.5 Hz, C_6H_5), 150.47 (s, ipso C_6H_5), 165.71 (s, C=N).

Mass Spectrum (EI); m/z (relative intensity): 165 (M^+, 12), 135 (SC=NPh, 2), 118 (MeC=NPh, 100), 103 (C=NPh, 1), 91 (NPh, 1), 77 (Ph, 86).

Characterizing Data for PhC(SMe)=NPh JBH-71-I

mp: 62.5 - 63.5°C

Anal. Calcd. for $C_{14}H_{13}NS$: C, 73.97; H, 5.76 %. Found: C, 73.86; H, 5.80 %.

IR($CHCl_3$): 3090vw, 3070vw, 3015w, 2935vw, 1610s-br(C=N), 1594vs, 1585sh, 1485m, 1445m, 1311w, 1190vw, 1168w, 1000w, 970m, 955m, 700m, 695m, 670m cm^{-1}.

^{1}**H NMR**($CDCl_3$; 90 MHz): δ 2.37 (s, 3H, CH_3), 6.48 - 7.72 (m, 10H, C_6H_5).

Mass Spectrum (EI); m/z (relative intensity): 227 (M^+, 10), 180 (PhC=NPh, 100), 135 (SC=NPh, 1), 121 (SCPh, 3), 103 (C=NPh, 1), 77 (Ph, 68).

Characterizing Data for MeC(SEt)=NPh JBH-14-II

bp: 85.0 - 110.0°C @ 4 torr

Anal. Calcd. for $C_{10}H_{13}NS$: C, 66.99; H, 7.31 %. Found: C, 66.91; H, 7.29 %.

IR(neat): 3360vw-br, 3240vw-br, 3090w, 3072w, 3042w, 3035w, 2980m, 2938m, 2880w, 2105vw, 1940vw-br, 1865vw-br, 1800vw-br, 1630vs-br(C=N), 1599vs, 1490s, 1450m, 1369s, 1267m, 1241s, 1171m, 1141vs, 1071m, 1059m, 1028m, 1000m, 982m, 965m, 905m, 807m, 781s, 762m, 710s, 696s, 669w, 640w, 586w, 529w, 502m cm^{-1}.

^{1}**H NMR**(CD_2Cl_2; 90MHz): δ 1.33 (t, J = 7.32 Hz, 3H, $SCH_2C\underline{H}_3$), 1.98 (s, 3H, $N{=}CCH_3$), 3.03 (q, J = 7.32 Hz, 2H, $SC\underline{H}_2CH_3$), 6.69 - 7.41 (m, 5H, C_6H_5).

^{13}**C NMR**($CDCl_3$; 67.9 MHz): δ 13.92 (q, J = 128.0 Hz, CH_3), 21.44 (q, J = 129.7 Hz, CH_3), 24.00 (t, J = 140.4 Hz, $S\underline{C}H_2CH_3$), 119.89 (d, J = 158.7 Hz, C_6H_5), 122.63 (d, J = 162.3 Hz, C_6H_5), 128.89 (d, J = 159.6 Hz, C_6H_5), 150.78 (s, ipso C_6H_5), 165.56 (s, C=N).

Mass Spectrum (EI); m/z (relative intensity): 179 (M^+, 11), 151 (MeC(SH)=NPh, 10), 150 (MeC(S)=NPh, 2), 136 (HSC=NPh, 1), 135 (SC=NPh, 1), 118 (MeC=NPh, 100), 77 (Ph, 70).

Synthesis of (μ-PhC=NPh)(μ-MeS)$Fe_2(CO)_6$ JBH-8-II

A 300 ml three necked, round bottomed flask equipped with a reflux condenser, glass stopper, stir-bar, and rubber septum was charged with 1.12 g (2.22 mmol) of $Fe_3(CO)_{12}$ and 0.50 g (2.21 mmol) of N-phenyl,S-methyl phenylthioimidate and subsequently degassed by three evacuation/nitrogen-backfill cycles. The flask was then charged with 50 ml of hexane by syringe and the resulting dark green solution was heated at reflux for 28 h. The solvent from the now red reaction mixture was removed in vacuo and the red, oily residue which remained was purified by filtration chromatography. Pentane eluted a yellow band which gave 0.09 g (0.24 mmol, 22% based on S) of (μ-MeS)$_2$$Fe_2(CO)_6$, identified by its ^{1}H NMR spectrum.[28] Further elution with pentane yielded an orange band which gave 0.48 g (0.95 mmol, 43%) of (μ-PhC=NPh)(μ-MeS)$Fe_2(CO)_6$, 8a, as an air-stable, red solid, mp 162.0-165.0°C after recrystallization from pentane.

Anal. Calcd. for $C_{20}H_{13}Fe_2NO_6S$: C, 47.37; H, 2.58 %. Found: C, 47.57; H, 2.75 %.

IR($CHCl_3$): 3105vw, 3092vw, 3072vw, 3000vw, 2965w, 2937w, 2840w, 1595m(Ph), 1588m(Ph), 1577m(Ph), 1555vs-br(C=N), 1488s, 1451m, 1441m, 1430w, 1318m, 1262w, 1072m, 1025m, 1000w, 947s, 897m, 708s, 698s, 670m, 665m, 630s, 618vs, 610vs, 580vs, 567s cm^{-1}.
Terminal carbonyl region (pentane): 2075s, 2038vs, 1998vs, 1981m, 1971w cm^{-1}.

^{1}H NMR(CD_2Cl_2; 90 MHz): δ 2.39 (s, 3H, SCH_3), 6.52-7.53 (m, 10H, C_6H_5).

^{13}C NMR(CD_2Cl_2; 67.9 MHz): δ 23.07 (q, J = 139.7 Hz, SCH_3), 121.51 - 130.46 (m, C_6H_5), 147.44 (s, ipso C_6H_5), 153.75 (s, ipso C_6H_5), 209.71, 210.56, and 214.09 (all s, Fe-CO), 233.02 (s, C=N).

Mass Spectrum (EI); m/z (relative intensity): 507 (M^+, 7), 479 (M^+ - CO, 8), 451 (M^+ - 2CO, 32), 423 (M^+ - 3CO, 18), 395 (M^+ - 4CO, 14), 367 (M^+ - 5CO, 26), 339 (M^+ - 6CO, 100), 324 ($SFe_2PhC{=}NPh$, 3), 298 (SFe_2Ph_2, 8), 247 ($SFe_2C{=}NPh$, 11), 221 (SFe_2Ph, 41), 180 (PhC=NPh, 57), 170 ($SFe_2C{=}N$, 4), 144 (SFe_2, 48), 77 (Ph, 40).

Synthesis of (μ-MeC=NPh)(μ-MeS)$Fe_2(CO)_6$ JBH-12-II

In an experiment similar to the synthesis of 8a, a hexane solution containing 4.03 g (8.01 mmol) of $Fe_3(CO)_{12}$ and 1.23 ml (8.00 mmol) of N-phenyl,S-methyl methylthioimidate was heated at reflux for 50 h, during this time a gradual color change from dark green to red was observed. The solvent from the reaction mixture was then removed in vacuo and the resulting brown-red tar was purified by filtration chromatography. Pentane eluted an orange band which gave 0.21 g (0.56 mmol, 14% based on S) of (μ-MeS)$_2Fe_2(CO)_6$, identified by its ^{1}H NMR spectrum.[28] Further elution with pentane yielded a second orange band which gave 1.73 g (3.89 mmol, 49%) of (μ-MeC=NPh)(μ-MeS)$Fe_2(CO)_6$, 8b, as an air-stable, red solid, mp 98.0-100.0°C after recrystallization from pentane.

Anal. Calcd. for $C_{15}H_{11}Fe_2NO_6S$: C, 40.49; H, 2.49 %. Found: C, 40.64; H, 2.59 %.

IR($CHCl_3$): 3100vw, 3000vw, 2960vw, 2933w, 2840vw, 1595m(Ph), 1570vs(C=N), 1490s, 1451m, 1430m, 1357m, 1317m,

1169vw, 1112s, 1071w, 1025w, 1000vw, 965w, 955w, 947w, 912vw, 700s, 612s, 575s cm^{-1}.
Terminal carbonyl region (pentane): 2069s, 2027s, 1995vs, 1977m, 1969s, 1942vw cm^{-1}.

^1H NMR(CD_2Cl_2; 90 MHz): δ 2.03 (s, 3H, $C\underline{H}_3C{=}NPh$), 2.40 (s, 3H, SCH_3), 6.42-7.52 (m, 5H, C_6H_5).

^{13}C NMR(CD_2Cl_2; 67.9 MHz): δ 22.98 (q, J = 139.3 Hz, SCH_3), 34.83 (q, J = 128.5 Hz, $\underline{C}H_3C{=}NPh$), 121.97 (d, J = 161.1 Hz, C_6H_5), 126.87 (d, J = 161.6 Hz, C_6H_5), 129.79 (d, J = 160.8 Hz, C_6H_5), 152.78 (s, ipso C_6H_5), 210.60 and 213.84 (both s, Fe-CO), 230.87 (s, C=N).

Mass Spectrum (EI); m/z (relative intensity): 445 (M^+, 11), 417 (M^+ - CO, 16), 389 (M^+ - 2CO, 23), 361 (M^+ - 3CO, 24), 333 (M^+ - 4CO, 13), 305 (M^+ - 5CO, 27), 277 (M^+ - 6CO, 100), 262 ($SFe_2MeC{=}NPh$, 18), 247 ($SFe_2C{=}NPh$, 6), 236 (SFe_2MePh, 19), 221 (SFe_2Ph, 39), 185 ($SFe_2MeC{=}N$, 11), 170 ($SFe_2C{=}N$, 5), 165 (MeS(Me)C=NPh, 6), 159 ($MeSFe_2$, 10), 144 (Fe_2S, 53), 138 ($Fe_2C{=}N$, 1), 118 (MeC=NPh, 27), 77 (Ph, 20).

Synthesis of (μ-EtC=NPh)(μ-MeS)$Fe_2(CO)_6$ JBH-39-II

In an experiment similar to the synthesis of 8a, a hexane solution containing 2.01 g (3.99 mmol) of $Fe_3(CO)_{12}$ and 0.70 ml (4.00 mmol) of N-phenyl,S-methyl ethylthioimidate was heated to reflux for 20 h during which time a gradual color change from dark green to brown-red was observed. The solvent from the reaction mixture then was removed in vacuo and the resulting dark red oil was purified by filtration chromatography. Pentane eluted an orange band which gave 0.14 g (0.36 mmol, 18% based on S) of (μ-MeS)$_2Fe_2(CO)_6$ identified by its ^1H NMR spectrum.[28] Further elution with pentane yielded a second orange band which gave 0.95 g (2.06 mmol, 52%) of (μ-EtC=NPh)(μ-MeS)$Fe_2(CO)_6$, 8c, as an air-stable, red solid, mp 92.5-97.0°C after recrystallization from pentane.

Anal. Calcd. for $C_{16}H_{13}Fe_2NO_6S$: C, 41.86; H, 2.85 %. Found: C, 41.76; H, 2.86 %.

IR($CHCl_3$): 3100vw, 3080vw, 2992m, 2952m, 2940m, 2890w, 2845w, 1599m(Ph), 1590m(Ph), 1565vs(C=N), 1560vs(Ph), 1491s, 1463m, 1452s, 1432m, 1380m, 1319m, 1199m, 1171w, 1132m, 1075m, 1030m, 1015w, 960m, 950m, 937s, 911vw, 702vs, 610vs, 580vs cm^{-1}.
Terminal carbonyl region (pentane): 2070s, 2032vs, 1995vs, 1978m, 1970m cm^{-1}.

^{1}H NMR($CDCl_3$; 250 MHz): δ 0.88 (t, J = 7.63 Hz, 3H, $C\underline{H}_3CH_2C{=}NPh$), 1.96 (m, 1H, $CH_3C\underline{H}_2C{=}NPh$ diastereotopic CH_2), 2.14 (m, 1H, $CH_3C\underline{H}_2C{=}NPh$ diastereotopic CH_2), 2.32 (s, 3H, SCH_3), 6.60-7.30 (m, 5H, C_6H_5).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 10.96 (q, J = 128.3 Hz, $\underline{C}H_3CH_2C{=}NPh$), 22.71 (q, J = 139.2 Hz, SCH_3), 39.51 (t, J = 129.3 Hz, $CH_3\underline{C}H_2C{=}NPh$), 121.24 (d, J = 161.0 Hz, C_6H_5), 126.42 (d, 161.7 Hz, C_6H_5), 129.44 (d, J = 161.0 Hz, C_6H_5), 152.83 (s, ipso C_6H_5), 210.04, 210.34, and 213.46 (all s, Fe-CO), 236.06 (s, C=N).

Mass Spectrum (EI); m/z (relative intensity): 459 (M^+, 10), 431 (M^+ - CO, 12), 403 (M^+ - 2CO, 33), 375 (M^+ - 3CO, 29), 347 (M^+ - 4CO, 16), 319 (M^+ - 5CO, 37), 291 (M^+ - 6CO, 100), 276 ($SFe_2EtC{=}NPh$, 4), 262 ($MeSFe_2C{=}NPh$, 13), 248 ($HSFe_2C{=}NPh$, 9), 247 ($SFe_2C{=}NPh$, 8), 221 (SFe_2Ph, 30), 170 ($SFe_2C{=}N$, 5), 159 ($MeSFe_2$, 8), 145 (Fe_2SH, 6), 144 (Fe_2S, 40), 132 (EtC=NPh, 30), 118 ($CH_2C{=}NHPh$, 8), 77 (Ph, 22), 56 (Fe, 6).

Synthesis of (μ-MeC=NPh)(μ-EtS)$Fe_2(CO)_6$ JBH-19-II

In an experiment similar to the synthesis of 8a, a hexane solution containing 4.04 g (8.01 mmol) of $Fe_3(CO)_{12}$ and 1.30 ml (7.33 mmol) of N-phenyl,S-ethyl methylthioimidate was heated to reflux for 16 h during which time a gradual color change from dark green to red was observed. The solvent from the reaction mixture then was removed in vacuo and the resulting brown-red tar was purified by filtration chromatography. Pentane eluted an orange band which gave 0.22 g (0.56 mmol, 15% based on S) of (μ-EtS)$_2Fe_2(CO)_6$ identified by its mass and ^{1}H NMR spectra.[28c,29] Further elution with pentane yielded a second orange band which gave 1.14 g (2.48 mmol, 34%) of (μ-MeC=NPh)(μ-EtS)$Fe_2(CO)_6$, 8d, as an air-stable, red solid, mp 81.0-82.5°C after recrystallization from pentane.

Anal. Calcd. for $C_{16}H_{13}Fe_2NO_6S$: C, 41.86; H, 2.85 %. Found: C, 41.83; H, 2.87 %.

IR($CHCl_3$): 3090vw, 3077vw, 2990m, 2973m, 2935m, 2917w, 2873w, 2852vw, 1594s(Ph), 1570vs-br(C=N), 1488s, 1450s, 1432m, 1378m, 1356s, 1259s, 1200m, 1170w, 1112vs, 1070m, 1045w, 1025m, 1000w, 917m, 912vw, 849vw, 700vs, 615vs, 580vs cm^{-1}.
Terminal carbonyl region (pentane): 2062s, 2045vw, 2020vs, 1990vs, 1972m, 1965m, 1940vw cm^{-1}.

^{1}**H NMR**(CD_2Cl_2; 90 MHz): δ 1.50 (t, J = 7.32 Hz, 3H, $SCH_2C\underline{H}_3$), 1.96 (s, 3H, $C\underline{H}_3C$=NPh), 2.61 (q, J = 7.32 Hz, 2H, $SC\underline{H}_2CH_3$), 6.51-7.65 (m, 5H, C_6H_5).

^{13}**C NMR**($CDCl_3$; 67.9 MHz): δ 18.37 (q, J = 128.1 Hz, $SCH_2\underline{C}H_3$), 33.88 (t, J = 140.0 Hz, $S\underline{C}H_2CH_3$), 34.55 (q, J = 127.8 Hz, $\underline{C}H_3C$=NPh), 121.52 (d, J = 160.4 Hz, C_6H_5), 126.43 (d, J = 162.0 Hz, C_6H_5), 129.25 (d, J = 161.8 Hz, C_6H_5), 152.29 (s, ipso C_6H_5), 209.94, 210.07, and 213.91 (all s, Fe-CO), 230.83 (s, C=N).

Mass Spectrum (EI); m/z (relative intensity): 459 (M^+, 14), 431 (M^+ - CO, 15), 403 (M^+ - 2CO, 36), 375 (M^+ - 3CO, 38), 347 (M^+ - 4CO, 16), 319 (M^+ - 5CO, 48), 291 (M^+ - 6CO, 100), 263 ($HSFe_2MeC{=}NPh$, 49), 221 (SFe_2Ph, 29), 185 ($SFe_2MeC{=}N$, 30), 170 ($SFe_2C{=}N$, 6), 145 ($HSFe_2$, 18), 144 (Fe_2S, 63), 118 (MeC=NPh, 31), 104 (HC=NPh, 6), 77 (Ph, 32), 56 (Fe, 8).

Preparation of $[Li][(\mu\text{-}CO)(\mu\text{-}MeS)Fe_2(CO)_6]$ JBH-55-III

A 200 ml Schlenk flask equipped with a stir-bar and rubber septum was charged with 1.51 g (3.00 mmol) of $Fe_3(CO)_{12}$, degassed by three evacuation/nitrogen-backfill cycles, and then charged with 20 ml of THF by syringe. A cloudy solution of 3.00 mmol of lithium methanethiolate in 20 ml of THF (prepared in a separate flask at 0°C by the reaction of an excess of methyl mercaptan with 3.00 mmol of n-butyllithium) was subsequently added by cannula. An immediate reaction ensued (with brisk gas evolution) and a gradual color change from dark green to brown-red was observed. The resulting $[Li][(\mu\text{-}CO)(\mu\text{-}MeS)Fe_2(CO)_6]$ reagent solution was stirred for 20 min at room temperature and subsequently used in-situ without further purification.

Reaction of $[Li][(\mu\text{-}CO)(\mu\text{-}MeS)Fe_2(CO)_6]$ with Ph(Cl)C=NPh JBH-55-III

To the previously prepared $[Li][(\mu\text{-}CO)(\mu\text{-}MeS)Fe_2(CO)_6]$ reagent solution (3.00 mmol) was added by cannula 0.65 g (3.01 mmol) of N-phenyl benzimidoyl chloride dissolved in a separate flask in 20 ml of THF. After the resulting reaction mixture had been stirred for 60 h at room temperature, the solvent was removed in vacuo to yield a brown-red tar which was purified by filtration chromatography. Pentane eluted an orange band which gave 0.21 g (0.56 mmol, 37% based on S) of $(\mu\text{-}MeS)_2Fe_2(CO)_6$ identified by its ^1H NMR spectrum.[28] Pentane eluted a second orange band which gave 0.94 g (1.84 mmol, 61%) of (μ-PhC=NPh)(μ-MeS)$Fe_2(CO)_6$, 8a, identified by comparison of its ^1H NMR spectrum to that of an authentic sample (JBH-8-II).

Preparation of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ JBH-56-III

A 250 ml Schlenk flask equipped with a spin bar and rubber septum was charged with 1.51 g (3.00 mmol) of $Fe_3(CO)_{12}$ and degassed by three evacuation/nitrogen-backfill cycles. The flask was then charged with 50 ml of THF, 0.42 ml (3.00 mmol) of triethylamine, and 0.34 ml (3.00 mmol) of t-butyl mercaptan by syringe. The reaction mixture was stirred for 20 min at room temperature during which time slow gas evolution as well as a color change from dark green to brown-red were observed. The resulting $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ reagent solution subsequently was used in-situ without further purification.

Synthesis of $(\mu\text{-}PhC{=}NPh)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ JBH-56-III

To the previously prepared $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ reagent solution (3.00 mmol) cooled to -78°C was added by cannula 0.65 g (3.01 mmol) of N-phenyl benzimidoyl chloride dissolved in a separate flask in 20 ml of THF (also cooled to -78°C). The reaction mixture was stirred for 15 min at -78°C, warmed to room temperature, and then stirred for 40 h at room temperature. Subsequently, the solvent was removed in vacuo to yield a red, oily solid which was purified by filtration chromatography. Pentane eluted an orange band which was not collected. Pentane eluted a second orange band which gave 1.40 g (2.54 mmol, 85%) of $(\mu\text{-}PhC{=}NPh)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$, 8e, as a red, air-stable solid, mp 124.0-126.0°C after recrystallization from pentane.

Anal. Calcd for $C_{23}H_{19}Fe_2NO_6S$: C, 50.30; H, 3.49 %. Found: C, 50.46; H, 3.61 %.

IR($CHCl_3$): 3099vw, 3085vw, 2987w, 2952w, 2933w, 2909w, 2873vw, 1599w(Ph), 1589w(Ph), 1579w(Ph), 1555m(C=N), 1490m, 1475w, 1470w, 1455w, 1441w, 1395vw, 1365m, 1329vw, 1155m, 1072w, 1025vw, 1000vw, 945m, 898w, 790vs, 740vs, 710vs, 670vs, 625s, 615s, 610s, 599vs, 590vs cm^{-1}.
Terminal carbonyl region (pentane): 2068m, 2025vs, 1998vs, 1990vw, 1980vw cm^{-1}.

^1H NMR(CD_2Cl_2; 90 MHz): δ 1.55 (s, 9H, $SC(CH_3)_3$), 6.55-7.22 (m, 10H, C_6H_5).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 34.18 (q, J = 126.2 Hz, $SC(\underline{C}H_3)_3$), 49.22 (s, $S\underline{C}(CH_3)_3$), 120.84-129.92 (m, C_6H_5), 146.75 (s, ipso C_6H_5), 153.18 (s, ipso C_6H_5), 209.23, 210.96, and 213.74 (all s, Fe-CO), 232.88 (s, C=N).

Mass Spectrum (EI); m/z (relative intensity): 549 (M^+, 4), 521 (M^+ - CO, 2), 493 (M^+ - 2CO, 15), 465 (M^+ - 3CO, 16), 437 (M^+ - 4CO, 7), 409 (M^+ - 5CO, 15), 381 (M^+ - 6CO, 58), 325 ($HSFe_2PhC{=}NPh$, 67), 247 ($SFe_2PhC{=}N$, 19), 221 (SFe_2Ph, 35), 213 (HSPhC=NPh, 15), 180 (PhC=NPh, 100), 145 (Fe_2SH, 5), 144 (Fe_2S, 43), 77 (Ph, 54), 57 (^tBu, 11), 56 (Fe, 7).

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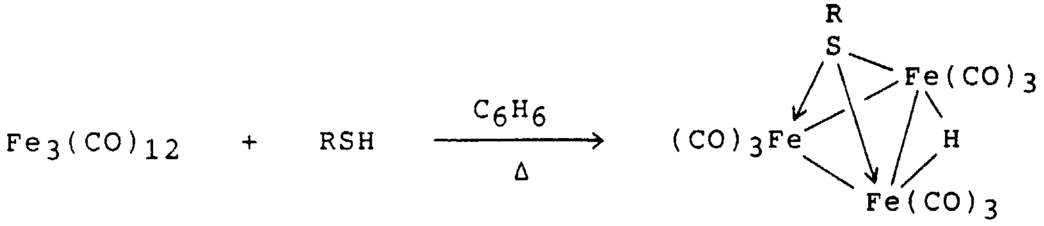
Chapter 2

"Synthesis and Reactivity of $(\mu-\sigma,\pi-C{\equiv}CR^1)(\mu-RS)Fe_2(CO)_6$"

INTRODUCTION

In 1970, Haines reported the synthesis of new trinuclear iron clusters, $(\mu_3\text{-RS})(\mu\text{-H})Fe_3(CO)_9$, 1, from the reactions of secondary and tertiary alkyl thiols with triiron dodecacarbonyl (Eq. 1).[1] Huttner and coworkers

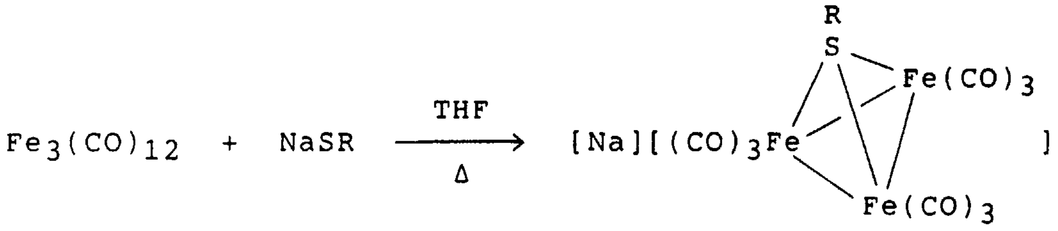


1

(1)

R = ^{i}Pr, ^{s}Bu, ^{t}Bu

subsequently discovered that these iron hydrides (R = ^{t}Bu, c-C_6H_{11}) could be deprotonated by amines and that the resulting anionic intermediate 2, reacted with potentially bridging electrophiles such as R_2PCl, R_2AsCl, RSCl, $RPCl_2$ (all R = alkyl, aryl), $POCl_3$, and Cl_2 to yield new $Fe_3(CO)_9$ complexes.[2] In related work, Markó reported that primary, secondary, and tertiary sodium thiolates react with $Fe_3(CO)_{12}$ in refluxing THF to yield the same reactive anion, $[(\mu_3\text{-RS})(\mu\text{-H})Fe_3(CO)_9]^-$, 2 (Eq. 2).[3] Surprisingly, Womack

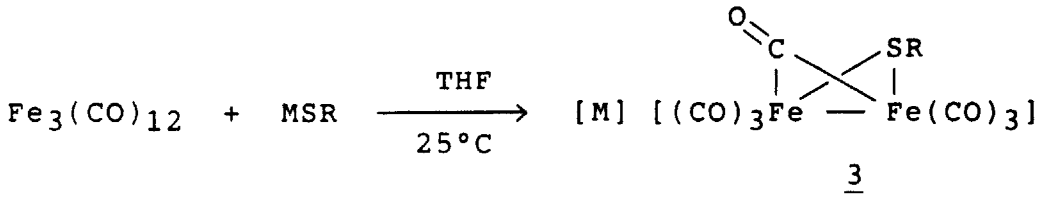


2

(2)

R = Et, ^{n}Bu, ^{s}Bu, ^{t}Bu

discovered that reaction of alkyl and aryl thiolates with $Fe_3(CO)_{12}$ in THF at room temperature generates reactive <u>dinuclear</u> anions of the form $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$, 3 (Eq. 3).[4a] These dinuclear anions have proven to be very

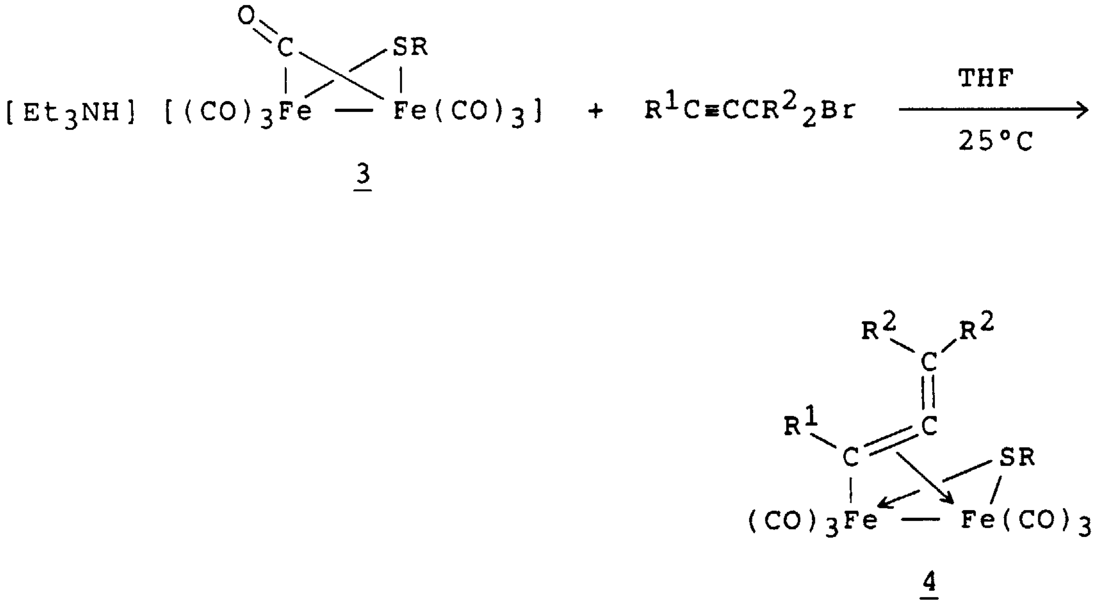


(3)

M = Li^+, Na^+, Et_3NH^+

R = Et, ^{t}Bu, Ph

reactive starting materials which yield a wide variety of thiolate-bridged diiron hexacarbonyl complexes upon reaction with organic or heteroatom-containing electrophiles.[4] Since Womack has shown that reaction of $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ with propargyl halides, $R^1C{\equiv}CR^2{}_2X$, yielded unusual allenyl complexes of the type $(\mu\text{-}\sigma,\pi\text{-}R^1C{=}C{=}CR^2{}_2)(\mu\text{-RS})Fe_2(CO)_6$, 4 (Eq. 4),[4a] it was of particular interest to extend the

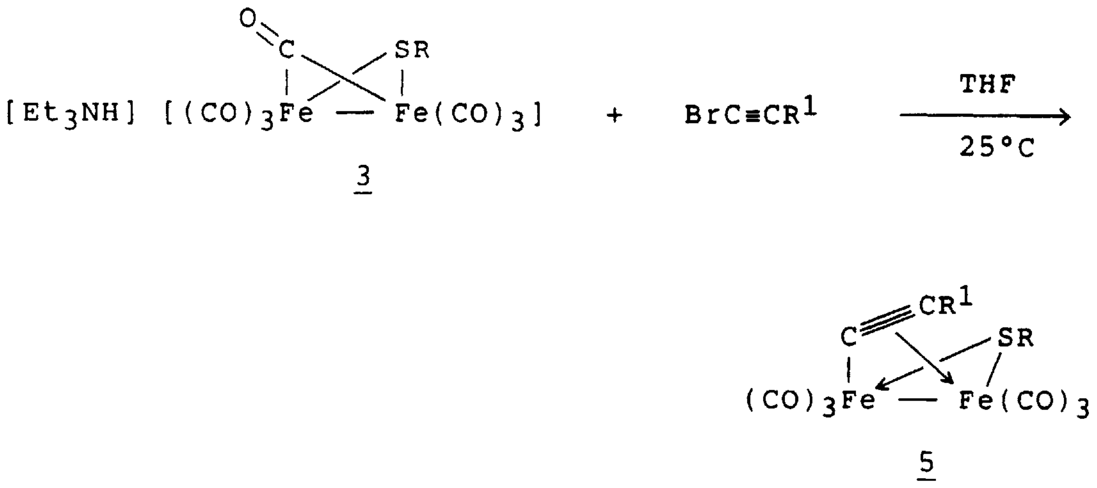


(4)

chemistry of 3 to include the related α-bromoacetylenes as well.

RESULTS and DISCUSSION

Reaction of 1-bromoalkynes, $R^1C{\equiv}CBr$ (R^1 = Ph, ^{t}Bu, $SiMe_3$), with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$, 3 (R = ^{t}Bu, Et, Ph), generated the expected acetylide-bridged diiron complexes, $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR^1)(\mu\text{-}RS)Fe_2(CO)_6$, 5, in high yield (Eq. 5). Addition of the acetylene to a brown-red THF solution of the thiolate anion typically resulted in rapid reaction with brisk gas evolution (CO), dramatic color change (cherry red), and formation of a white precipitate ($[Et_3NH][Br]$). After chromatographic workup, the acetylide products were isolated as a mixture of two inseparable isomers (identified in the respective ^1H and ^{13}C NMR



(5)

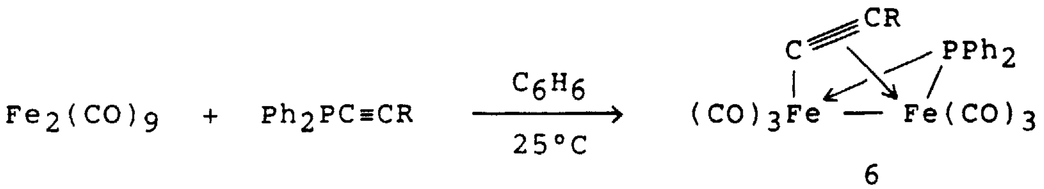
a	R = ^{t}Bu	R^1 = Ph	88%
b	R = ^{t}Bu	R^1 = ^{t}Bu	88%
c	R = ^{t}Bu	R^1 = $SiMe_3$	93%
d	R = Et	R^1 = Ph	84%
e	R = Et	R^1 = ^{t}Bu	71%
f	R = Ph	R^1 = ^{t}Bu	66%

a e

Figure 1

spectra). Presumably, these isomers arise from either an axial (a) or equatorial (e) orientation of the organic substituent and the lone electron pair on the bridging sulfur atom with respect to the Fe_2S plane (Fig. 1). In general, the ^1H NMR spectra of these complexes show thiolate resonances of the major isomer shifted slightly downfield from those of the minor isomer. For instance, the major t-butyl resonance in complex 5a appears at δ_H 1.38 while the minor resonance appears at δ_H 1.21. Prior correlations have shown that protons on axial thiolate ligands resonate at higher field than the corresponding equatorial protons.[5] Consequently, the high-field signals in our system can be attributed to the axial (minor) isomer and the low-field signals to the equatorial (major) isomer. The fact that the major isomer formed is that with the equatorial orientation seems reasonable based on steric arguments. In related work, Carty has reported the synthesis of analogous phosphido-bridged μ-σ,π-acetylide complexes by the reaction of diiron nonacarbonyl with phosphinoacetylenes (Eq. 6).[6] Other mono- and polynuclear acetylide species also are known.[6d,e,7-14]

In comparison to proposed mechanisms for nucleophilic substitution of α-bromoacetylenes,[27] the initial step in our system likely results from attack of an iron-centered anion on the bromine atom of the acetylene with subsequent elimination of bromide ion (Scheme 1). Bridging of the

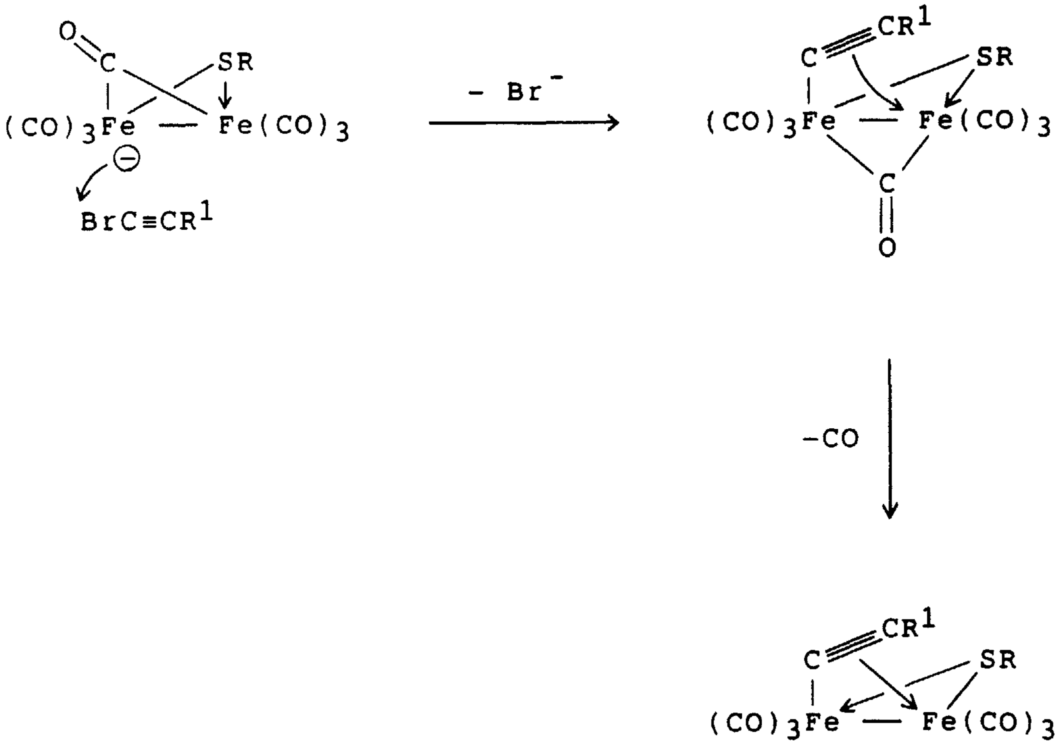


(6)

6

~25%

R = Ph, ^tBu, ^iPr, c-C_6H_{11},
p-C_6H_4OMe, p-C_6H_4Br



5

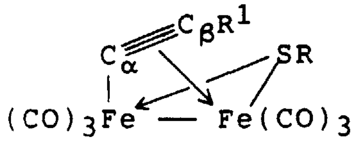
Scheme 1

terminal alkynyl moiety of the resulting heptacarbonyl intermediate with elimination of CO then produces 5.

In the infrared spectra, only 5c shows a band assignable to the carbon-carbon stretch of the triple bond ($\nu_{C\equiv C}$ 1910 cm^{-1}). The appearance of this band is consistent with coordination of the alkynyl fragment resulting in a decrease of the stretching frequency from that of a free carbon-carbon triple bond (ca. 2100 - 2250 cm^{-1}).[15] Similarly, Carty has observed this effect in the related phosphido-bridged complexes, $(\mu-\sigma,\pi-C\equiv CPh)(\mu-Ph_2P)Fe_2(CO)_6$, 6a, and $(\mu-\sigma,\pi-C\equiv CPh)(\mu-Ph_2P)Fe_2(CO)_5PPh_3$, 7, where $\nu_{C\equiv C}$ was observed at 1930 and 1900 cm^{-1}, respectively.[6b] The corresponding absorption in the other thiolate-bridged, μ-σ,π-acetylide complexes which we have prepared (5a,b,d-f) were not located due to overlap with the terminal carbonyl bands. Only the strongly electron-withdrawing trimethylsilyl group[16] in 5c shifted $\nu_{C\equiv C}$ far enough to lower frequency to be observed distinctly.

Although the alkynyl bond typically is not observable in 5 via IR spectroscopy, the acetylenic carbon atoms themselves are easily assigned in the corresponding ^{13}C NMR spectra (Table 1). In all cases except 5c (where R^1 = Me_3Si), the acetylide carbon atoms (C_α and C_β) resonate in the range δ_C 95 - 120. As expected, Carty has noted similar behavior in the series of related acetylides $(\mu-\sigma,\pi-C\equiv CR)(\mu-Ph_2P)Fe_2(CO)_6$, 6. However, whereas we cannot assign C_α and C_β unambiguously, Carty could differentiate between C_α and C_β based on differences in coupling constants to the bridged phosphorus atom. In addition, he noted that the relative position of C_α and C_β, and hence the charge distribution of the triple bond, depended on the group bonded to C_β. When R was t-butyl (charge donating), C_α was observed at higher field (δ_C 98.4) than C_β (δ_C 107.0). However, when R was phenyl (charge withdrawing), C_α was observed at lower field (δ_C 110.4) than C_β (δ_C 92.1). Whether this substituent derived reversal in polarization occurs in our acetylide system cannot be determined with certainty, although direct

Table 1: ^{13}C NMR Data for 5



	R	R^1	$\delta C\alpha/\beta$
a	^tBu	Ph	92.39, 95.43, 114.46, 114.95
b	^tBu	^tBu	102.34, 109.60
c	^tBu	$SiMe_3$	90.95, 95.27, 141.32, 143.24
d	Et	Ph	93.09, 93.87, 113.21, 119.00
e	Et	^tBu	101.50, 105.48, 107.72
f	Ph	^tBu	100.85, 104.75, 108.26, 111.01

comparison to Carty's correlations seems reasonable. It is interesting to note that for 5c (R = Me_3Si), C_α and C_β are separated by approximately 50 ppm, indicating a much larger degree of polarization than for the other acetylide complexes. This likely results from the stongly electron withdrawing nature of the trimethylsilyl group.[16]

Structurally, complexes 5 are interesting in that the bridging acetylide ligand is fluxional. This is illustrated in the variable temperature ^{13}C NMR study of $(\mu-\sigma,\pi-C{\equiv}CSiMe_3)(\mu-{}^tBuS)Fe_2(CO)_6$, 5c (Fig. 2). At room temperature, the ^{13}C NMR spectrum shows two signals in the terminal carbonyl region (δ_C 208.12 - minor isomer; δ_C 209.48 - major isomer) each of which can be assigned to all the carbonyl ligands of each isomer. However, 5c is a statically unsymmetrical molecule. The two tricarbonyliron fragments in each isomer are chemically inequivalent, and,

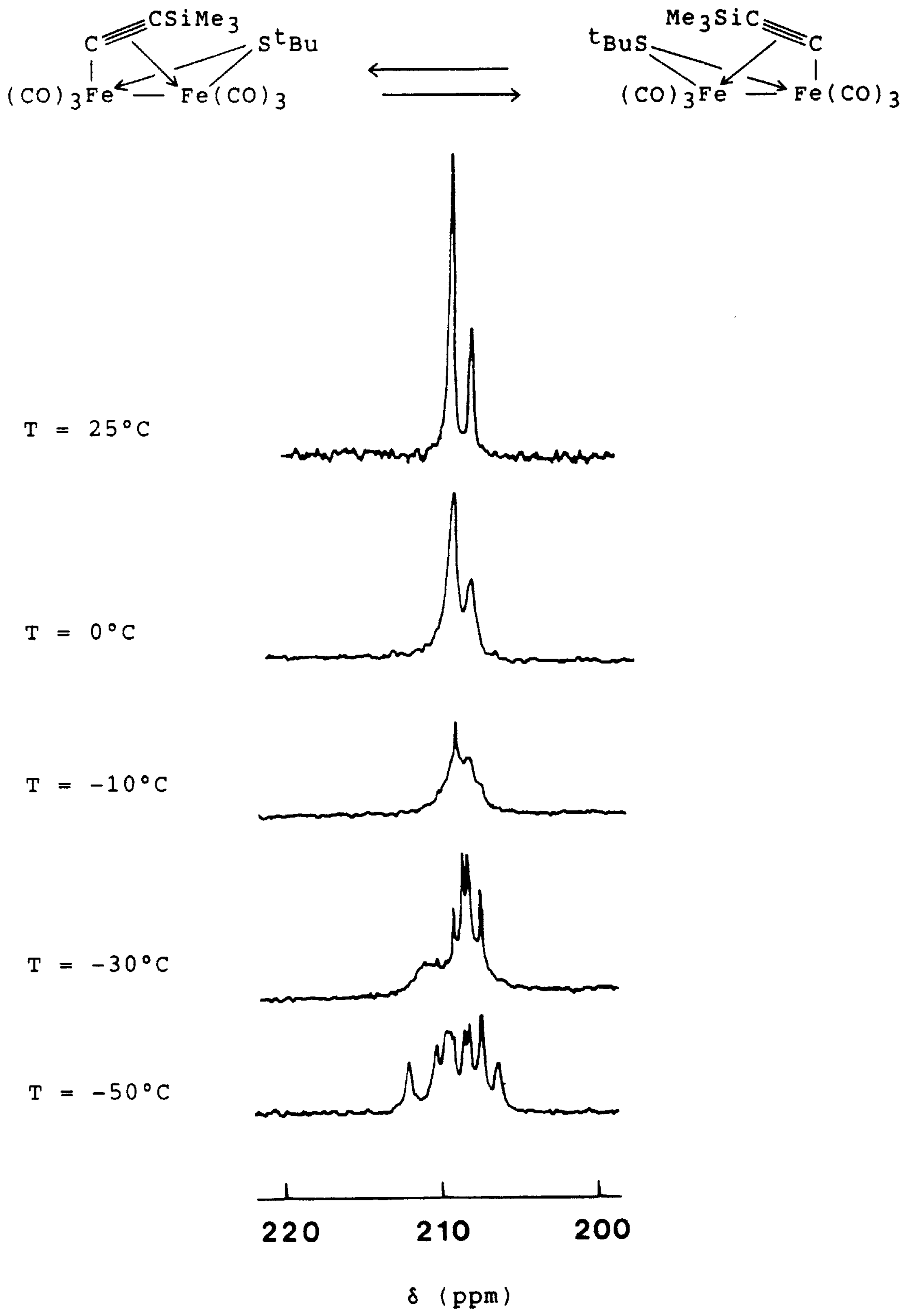
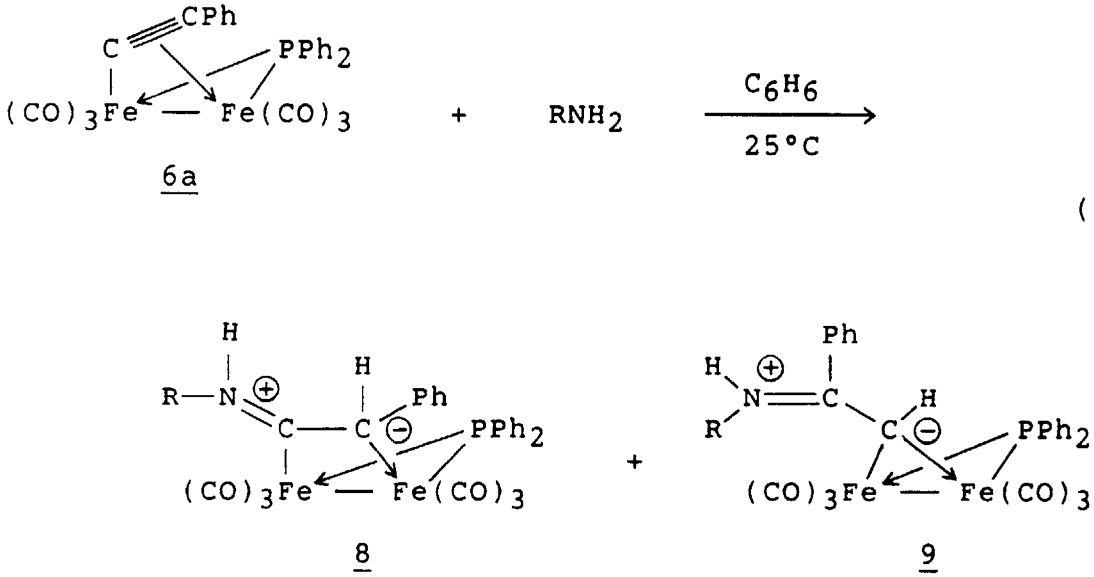


Figure 2: Variable Temperature ^{13}C NMR Study for 5c

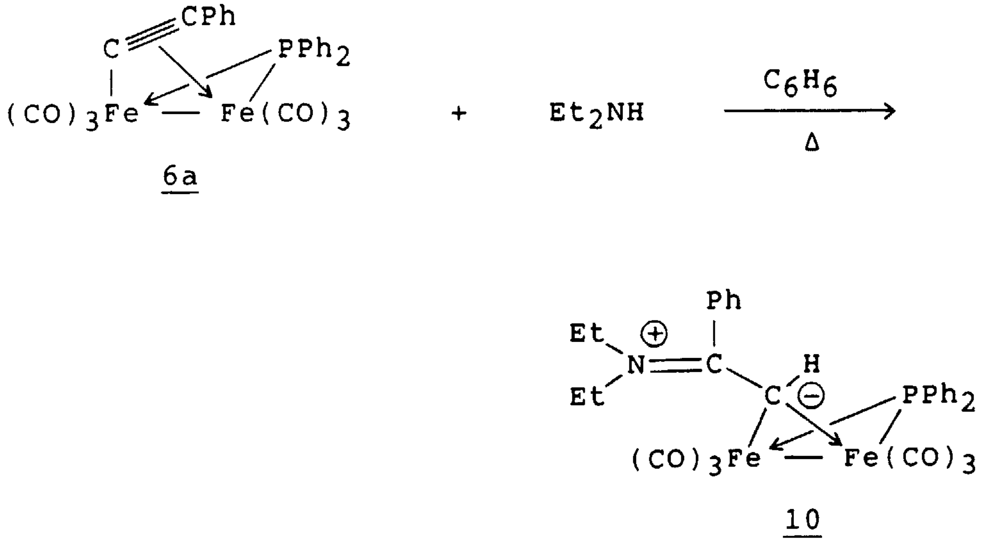
therefore, should give rise to two carbonyl resonances (a total of four including both isomers) assuming that the three carbonyl ligands on each metal center are locally equilibrated between themselves by rapid rotation. Consequently, some type of fluxional motion involving the bridging acetylide ligand must occur at room temperature which equilibrates the two tricarbonyliron fragments, and hence, all carbonyl ligands in each isomer on the NMR time scale. As illustrated in Figure 2, the two inequivalent tricarbonyliron fragments of each isomer can be equilibrated by a flipping motion of the acetylide ligand over the face of the Fe_2S core. Not surprisingly, this motion can be frozen out at low temperature. As the temperature is lowered, the two singlets broaden, and then, at -30°C, each is split into two distinct resonances (δ_C 207.47 and 209.23 - minor isomer; δ_C 208.23 and 208.60 - major isomer) corresponding to the now inequivalent $Fe(CO)_3$ fragments of each isomer. A broad hump has also begun to form to the left of these four peaks indicative of the slowing down of the localized carbonyl rotations on each iron center. Further cooling causes further slowing until at -50°C, nine distinct CO peaks are visible in the range δ_C 207.42 - 210.29. As expected, this fluxionality is reversible. Subsequent warming of the sample to room temperature results in the appearance of the original two carbonyl signals. This type of fluxional process has been proposed for other bridged vinyl and acetylide complexes as well.[17]

Because of the polarizable and relatively unhindered nature of their bridging acetylide ligands, complexes 5 appeared to be likely candidates for further reactivity studies. Carty has extensively explored the chemistry of the corresponding phosphido-bridged acetylide derivatives $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)(\mu\text{-}Ph_2P)Fe_2(CO)_6$, 6. Included in these studies were the reactions of 6 with amines, phosphines, and phosphites. Depending on the particular amine or phosphine/phosphite utilized, new phosphido-bridged iron complexes were isolated resulting from nucleophilic attack on the triple bond with subsequent incorporation of the base into a new bridging ligand (Eqs. 7 - 11).[6b,18] Based on

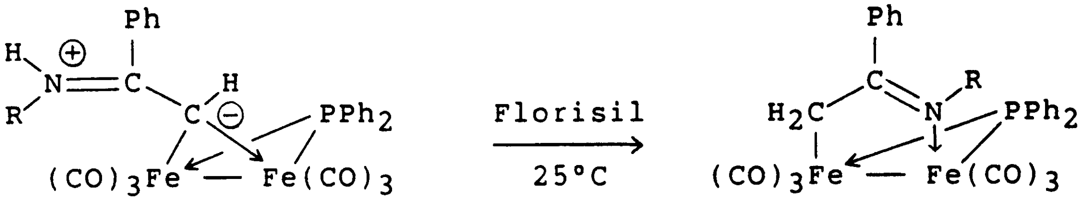


(7)

R = Me, Et

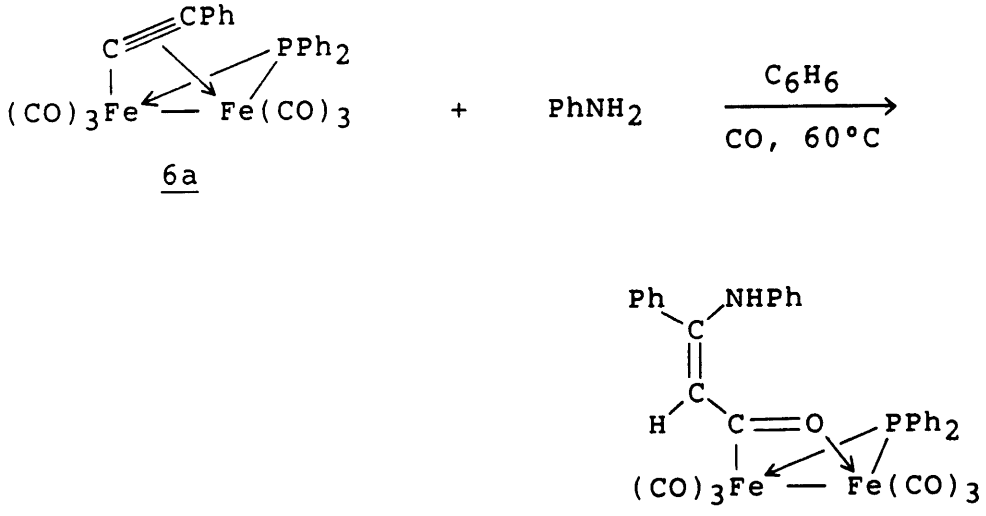


(8)



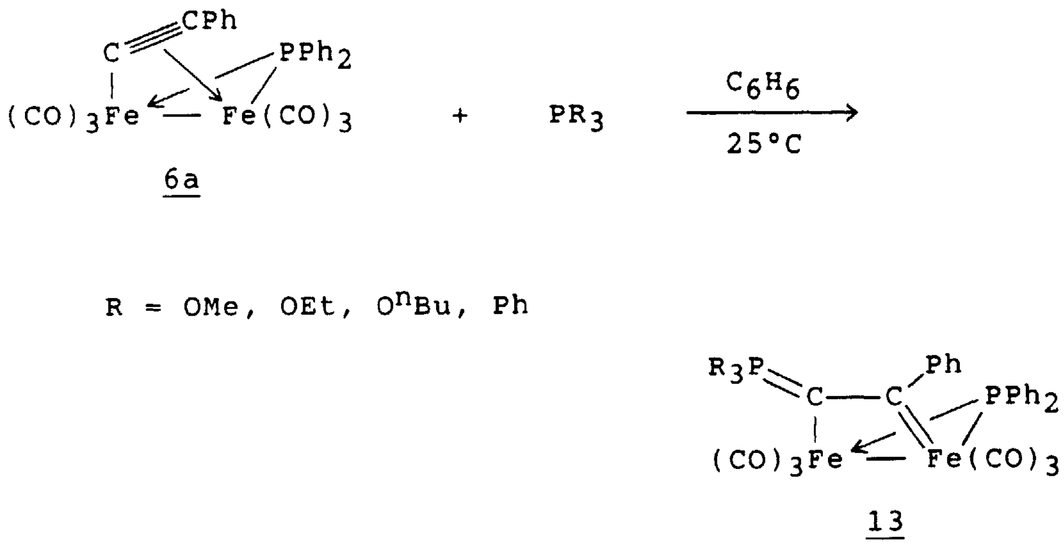
9 11 (9)

R = Me, Et



6a (10)

12

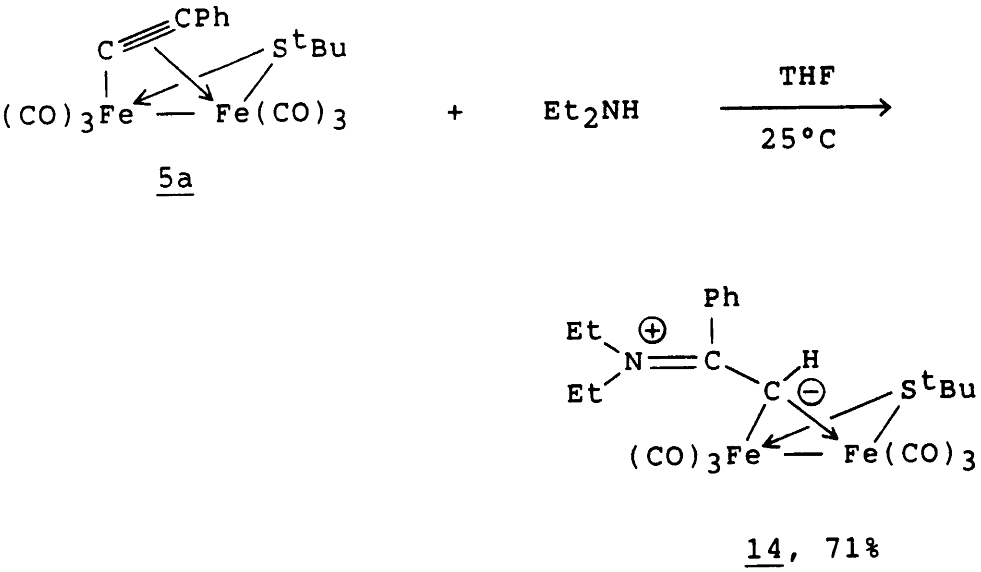


(11)

R = OMe, OEt, O^{n}Bu, Ph

this precedent, it was of interest to see if (μ-σ,π-C≡CR^1)(μ-RS)Fe$_2$(CO)$_6$, 5, would react similarly.

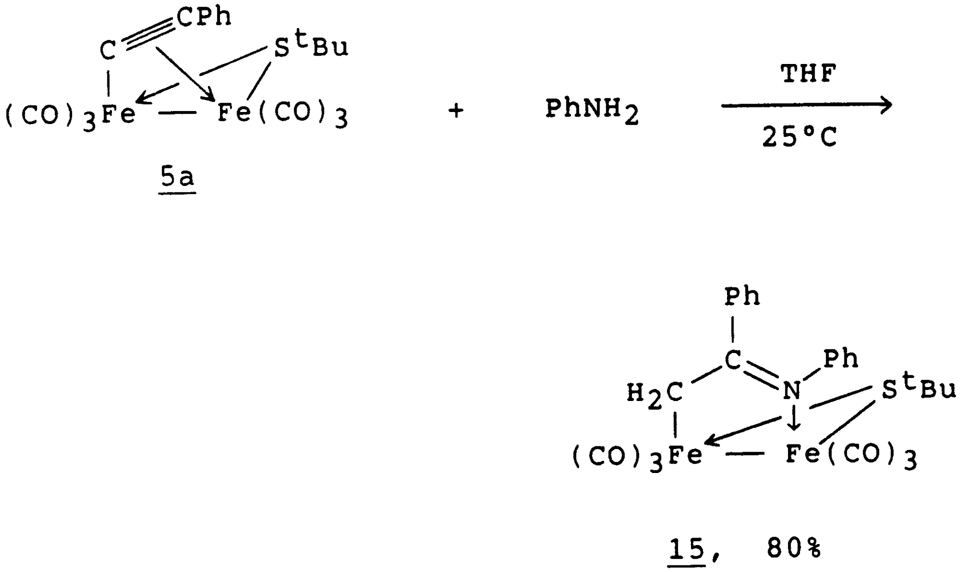
In general reaction of (μ-σ,π-C≡CPh)(μ-^{t}BuS)Fe$_2$(CO)$_6$, 5a, with amines was not as successful when compared to Carty's results. For many amines (e.g. bis(trimethylsilyl)amine, diphenylamine, methylamine, n-propylamine, dimethylamine, and diisopropylamine), reaction led to decomposition. However, diethylamine, aniline, and t-butylamine did react to yield isolable products analogous to those of type 10, 11, and 12, respectively. In the case of diethylamine, the one-carbon bridged, zwitterionic, imminium complex (μ-HC-C(Ph)=NEt$_2$)(μ-^{t}BuS)Fe$_2$(CO)$_6$, 14, was isolated in 71% yield (Eq. 12). In the reaction of aniline, the iminoethyl bridged complex, (μ-CH$_2$C(Ph)=NPh)(μ-^{t}BuS)Fe$_2$(CO)$_6$, 15 was isolated in 80% yield (Eq. 13). Finally, in the case of t-butylamine, the α,β-unsaturated acyl complex, (μ-HC(=C(Ph)NH^{t}Bu)(μ-^{t}BuS)Fe$_2$(CO)$_6$, 16, was isolated in 37% yield (Eq. 14). Since 16 has incorporated an extra (seventh) carbonyl ligand into the bridging amino framework, it was not surprising that the ubiquitous (μ-^{t}BuS)$_2$Fe$_2$(CO)$_6$, 17, was also isolated as a major byproduct



5a

14, 71%

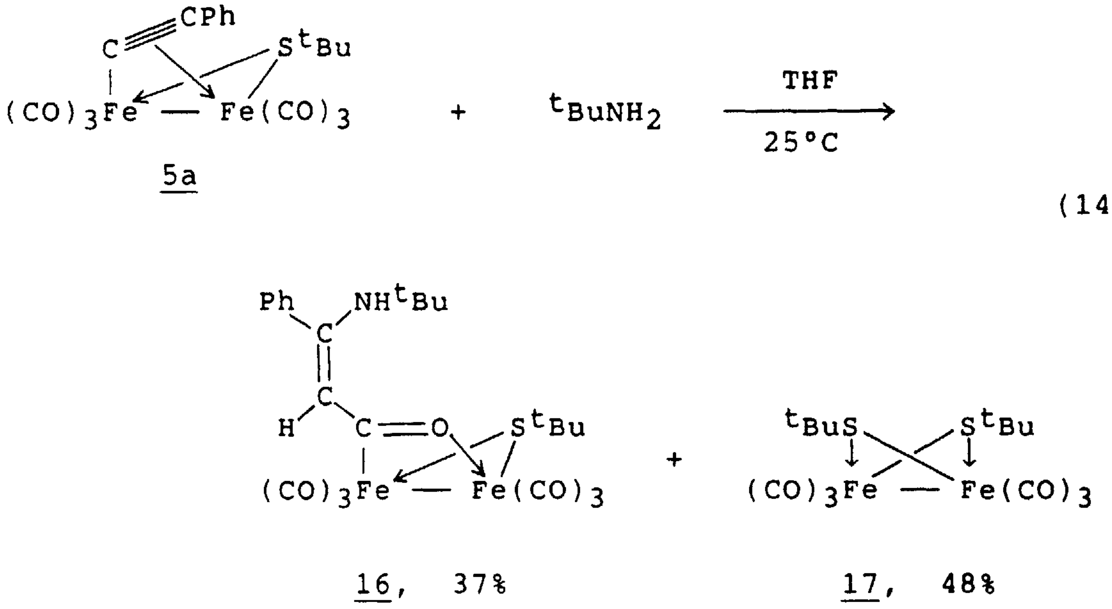
(12)



5a

15, 80%

(13)



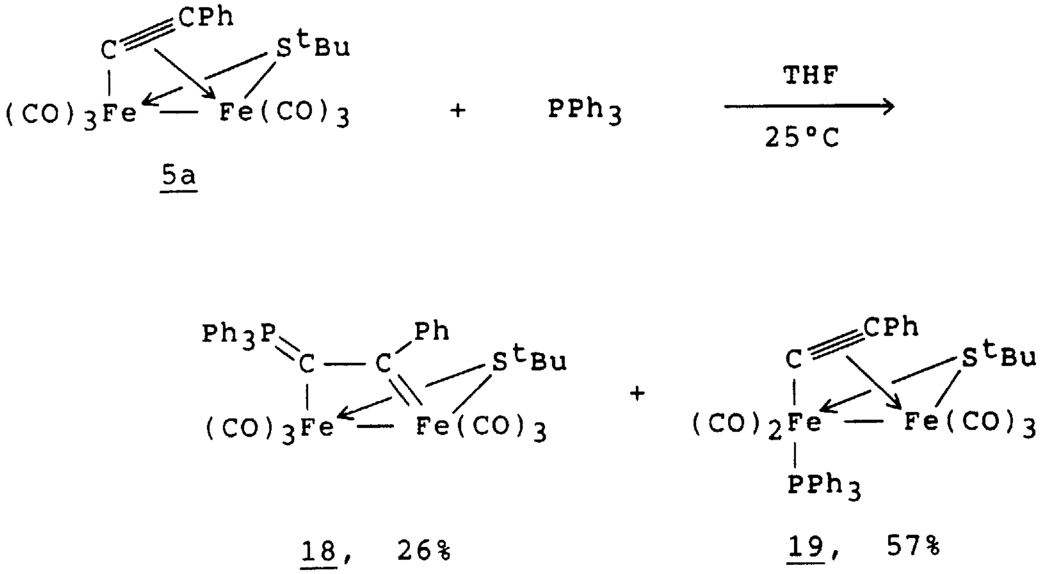
(14)

(48% yield based on sulfur). Somewhat surprisingly, however, the corresponding reactions of diethylamine with $(\mu-\sigma,\pi-C{\equiv}C^tBu)(\mu-{}^tBuS)Fe_2(CO)_6$, 5b, or $(\mu-\sigma,\pi-C{\equiv}CSiMe_3)(\mu-{}^tBuS)Fe_2(CO)_6$, 5c, only led to decomposition. Similarly, Carty has noted that nucleophilic addition of amines to $(\mu-\sigma,\pi-C{\equiv}C^tBu)(\mu-Ph_2P)Fe_2(CO)_6$, 6b, did not occur.[6e]

Products 14, 15, and 16 all gave elemental carbon/hydrogen combustion analyses, infrared, mass, and ^1H and ^{13}C NMR spectra consistent with the structures given. Furthermore, these data were consistent with the limited spectroscopic evidence presented by Carty for the related phosphido-bridged complexes, 10, 11, and 12 (Eqs. 8 - 10), whose structures were determined primarily from X-ray crystallography.[18] Furthermore, the spectroscopic data for the vinylacyl derivative, 16, were in agreement with known α,β-unsaturated diiron acyl species.[19] Finally, as illustrated in their ^1H and ^{13}C NMR specta, 14 and 16 both were isolated as a mixture of two inseparable isomers presumably resulting from either an axial (a) or equatorial (e) orientation of the organic thiolate group.

Mechanistically, formation of 14, 15, and 16 all result from initial nucleophilic attack of the amine on the β-carbon atom of the acetylide ligand of 5a. Surprisingly, this is not consistent with the assumed polarization of the triple bond. Based on the ^{13}C NMR correlations drawn by Carty and presented earlier in this discussion, the α-carbon atom of $(\mu-\sigma,\pi-C\equiv CPh)(\mu-Ph_2P)Fe_2(CO)_6$, 6a, was found to be more "electrophilic" than the β-carbon atom.[6e] Thus, nucleophilic attack should be directed at the α-carbon atom of the acetylide ligand. In fact, Carty typically did not observe this tendency (Eqs. 7 - 10), and we did not observe this orientation in the reactions of $(\mu-\sigma,\pi-C\equiv CPh)(\mu-{}^tBuS)Fe_2(CO)_6$ as well. Nevertheless, β-addition of the amine to the acetylide ligand of 5a followed by 1,3-hydrogen migration generated 14 in the case of diethylamine. In the case of t-butylamine, migration plus insertion of carbon monoxide gave 16. Finally, in the case of aniline, 1,3-hydrogen migration of both amine protons produced the iminoethyl complex 15.

In contrast to these findings, reaction of triphenylphosphine with $(\mu-\sigma,\pi-C\equiv CPh)(\mu-{}^tBuS)Fe_2(CO)_6$, 5a, generated the phosphonium, ylide-carbene complex, $(\mu-Ph_3PC{=}CPh)(\mu-{}^tBuS)Fe_2(CO)_6$, 18, resulting from α-attack of the nucleophile (Eq. 15). Based on the precedent established by Carty (Eq. 11),[6b,18e] characterization of 18 by the standard analytical and spectroscopic techniques was straightforward. However, the isolation of 18 was complicated by its rapid conversion to the substituted triphenylphosphine complex $(\mu-\sigma,\pi-C\equiv CPh)(\mu-{}^tBuS)Fe_2(CO)_5(PPh_3)$, 19. In fact, 18 decarbonylates to 19 in 88% yield at room temperature after stirring for 60 h in THF (Eq. 16). From P-C coupling data in the ^{13}C NMR spectrum of 19, it can be determined that phosphine substitution occurs at the iron bound to the α-carbon atom of the acetylide ligand. Carty has obtained similar results from the reaction of triphenylphosphine with $(\mu-\sigma,\pi-C\equiv CPh)(\mu-Ph_2P)Fe_2(CO)_6$, 6a.[6b]

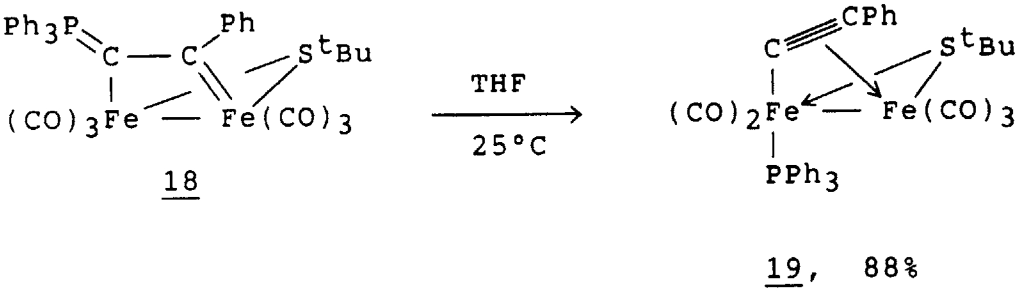


5a

18, 26%

19, 57%

(15)



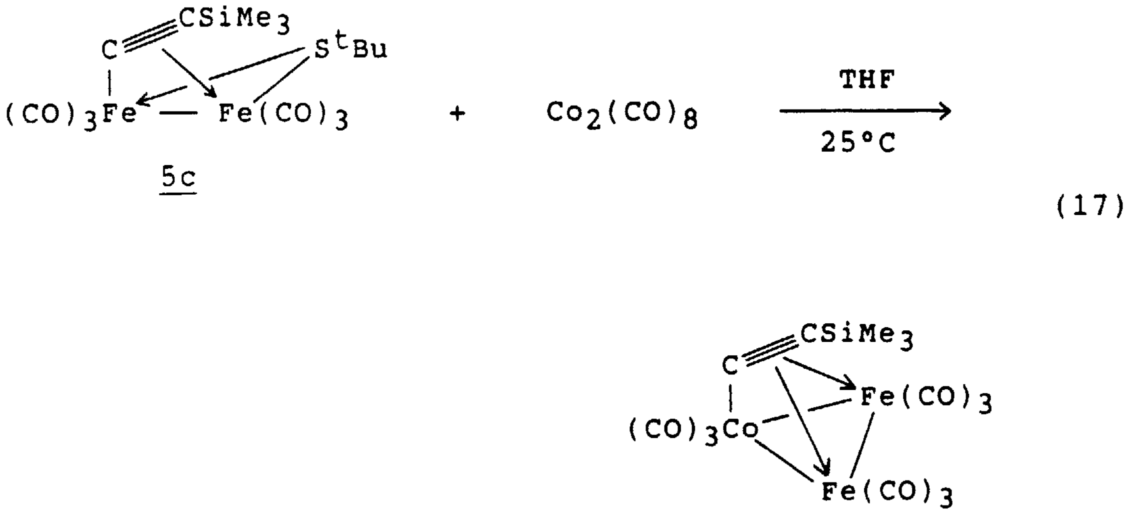
18

19, 88%

(16)

Although reaction of 5a with amines and triphenylphosphine yielded products derived from addition of the nucleophilic substrate to the acetylide ligand, of greater interest to us were the reactions of these acetylide complexes, 5, with metal carbonyls. In the past, this general synthetic approach has been successfully employed in the preparation of higher nuclearity, homo- and heterometallic acetylide clusters.[10,13,20] Thus, it was expected that reaction of 5 with dicobalt octacarbonyl and diiron nonacarbonyl, for instance, would provide a route to higher nuclearity iron and cobalt acetylide clusters. Surprisingly, the specific type of product isolated from these reactions depended not only on the added metal carbonyl ($Fe_2(CO)_9$ vs. $Co_2(CO)_8$), but also on the particular substituent (R^1) of the acetylide ligand.

Reaction of (μ-σ,π-C≡CSiMe$_3$)(μ-^{t}BuS)$Fe_2(CO)_6$, 5c, with dicobalt octacarbonyl at room temperature in THF generated the heterometallic, trinuclear acetylide complex, (μ_3,η^2-C≡CSiMe$_3$)$CoFe_2(CO)_9$, 20a, in 87% yield (Eq. 17).



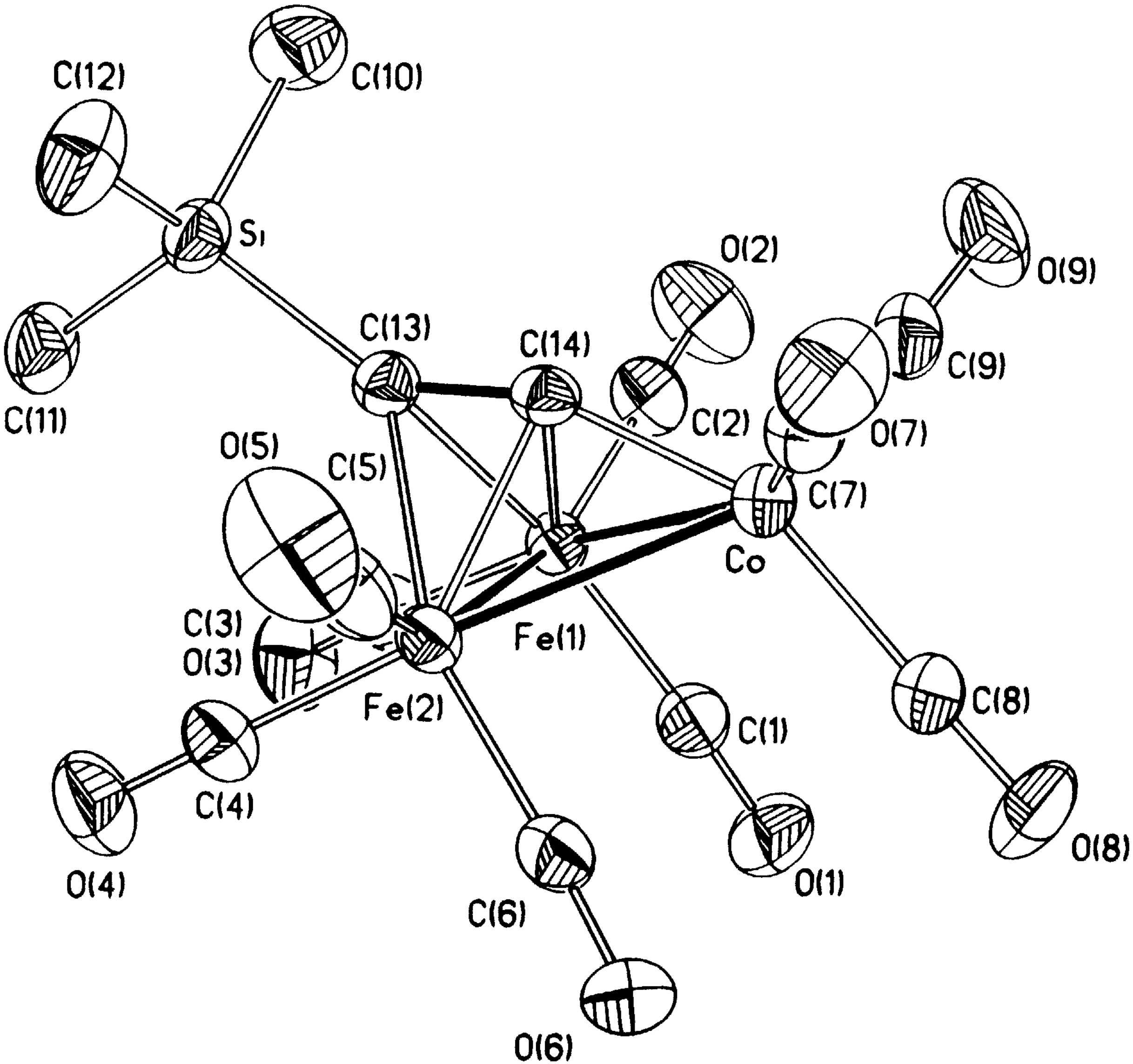
5c

(17)

20a, 87%

Unexpectedly, the thiolate ligand of 5c has been lost completely. Furthermore, whereas the acetylide ligand was σ-bound to iron in 5c, it is now σ-bound to cobalt in 20a. Subsequent bonding to the two iron atoms of the cluster then occurs through π-donation from the triple bond. The structure of 20a has been confirmed by X-ray crystallography. An ORTEP plot showing the atom labeling scheme appears in Figure 3 while pertinent bond distances and angles are given in Tables 2 and 3, respectively. The most striking feature of this molecule from a crystallographic viewpoint is the virtual plane of symmetry bisecting the Fe1-Co-Fe2 angle and containing the Co, C14, C13, and Si atoms. As expected, the C13-C14 bond distance of 1.289Å is longer than that of an uncoordinated acetylene,[21] while the corresponding Co-C14 bond distance of 1.821Å is very short or "carbene-like". Similar trends have been observed in related triiron acetylide complexes as well.[9,10,14] The "carbene-like" nature of the Co-C14 bond is aptly illustrated by the downfield shift of the C14 resonance (δ_C 202.60) in the ^{13}C NMR spectrum. Conversely, the C_β resonance occurs far upfield (δ_C 97.43) consistent with other μ_3,η^2-acetylide complexes of this general type.[6e,9,14] Finally, in the infrared spectrum, a strong band is observed at 1663 cm^{-1} which can be assigned to the carbon-carbon stretch of the coordinated triple bond, consistent with a decrease in frequency from that of a free acetylene.

Surprisingly, reaction of $(\mu-\sigma,\pi-C{\equiv}CPh)(\mu-{}^tBuS)Fe_2(CO)_6$, 5a, with dicobalt octacarbonyl did not produce the corresponding triply bridging phenylacetylide derivative of type 20, but instead generated the unusual heterometallic, tetranuclear "acetylide" complex $(\mu_4-C{\equiv}CPh)(\mu-CO)(\mu-{}^tBuS)Co_2Fe_2(CO)_{10}$, 21a, in 65% yield (Eq. 18). The structure has been confirmed by X-ray crystallography. An ORTEP plot showing the atom labeling scheme appears in Figure 4 while pertinent bond distances and angles are given in Tables 4 and 5, respectively. The



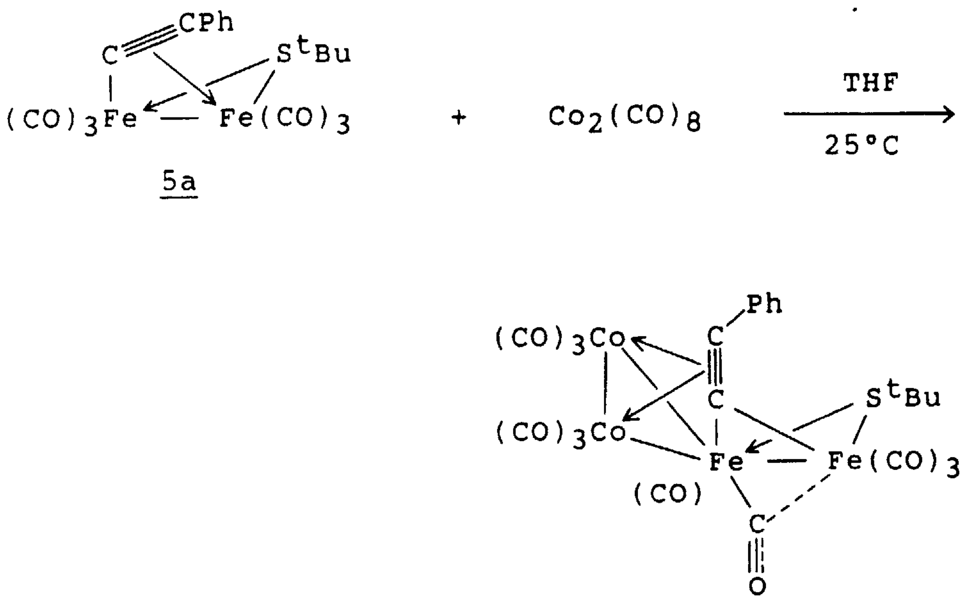
<u>Figure 3</u>: ORTEP plot of <u>20a</u>

Table 2: Relevant Bond Distances (Å) for 20a

Fe1-Fe2	2.494	Fe2-C14	2.012
Fe1-Co	2.628	Fe1-C14	2.012
Fe2-Co	2.630	Co-C14	1.821
Fe2-C13	2.133	C13-C14	1.289
Fe1-C13	2.129	C13-Si	1.862
Fe1-CO (mean)	1.796	Fe2C-O (mean)	1.135
Fe1C-O (mean)	1.132	Co-CO (mean)	1.803
Fe2-CO (mean)	1.796	CoC-O (mean)	1.121

Table 3: Relevant Bond Angles (°) for 20a

Fe2-Fe1-Co	61.7	Fe2-C13-Si	136.6
Co-Fe2-Fe1	61.6	C14-Fe2-Co	43.7
Fe2-Co-Fe1	56.6	C14-Fe1-Co	43.8
Co-C14-Fe1	86.4	C14-Fe2-C13	36.1
Co-C14-Fe2	86.5	C14-Fe1-C13	36.1
Co-C14-C13	158.8	C14-Fe1-Fe2	51.7
Fe1-C14-C13	76.9	C14-Fe2-Fe1	51.7
Fe2-C14-C13	77.1	C13-Fe1-Co	79.3
Fe1-C14-Fe2	76.6	C13-Fe2-Co	79.1
Fe1-C13-C14	67.0	C13-Fe2-Fe1	54.1
Fe2-C13-C14	66.8	C13-Fe1-Fe2	54.3
Fe1-C13-Fe2	71.6	C14-Co-Fe2	49.8
C14-C13-Si	145.6	C14-Co-Fe1	49.8
Fe1-C13-Si	136.2		



5a

(18)

21a, 65%

most striking feature of this complex is the coordination of the α-carbon atom (C13) of the "acetylide" ligand, which is within bonding distance of five atoms (Co1, Co2, Fe1, Fe2, C12). Furthermore, the cobalt atoms are electron-rich in nature while the iron atoms are electron-deficient. The electron-deficient nature of Fe1 is counteracted in three ways: 1) the bridging carbonyl ligand is semi-bridging; C8 is much closer to Fe1 than to Fe2 (1.830 vs. 2.458 Å); 2) the thiolate bridge is unsymmetrical; S is somewhat closer to Fe1 than to Fe2 (2.217 vs. 2.281 Å); and 3) the α-carbon bridge of the "acetylide" ligand is also unsymmetrical; C13 is closer to Fe1 than to Fe2 (1.912 vs. 2.022 Å). As expected, the C12-C13 bond of 1.322Å is considerably longer than in an uncoordinated acetylene.[21] The Co1-Co2 distance of 2.478Å is quite short although it is consistent with other perpendicular acetylene-dicobalt complexes.[22] Also, the C12-Co1 and C12-Co2 distances are consistent with these simpler dicobalt counterparts, although as can be seen, C12 is somewhat closer to Co1 than

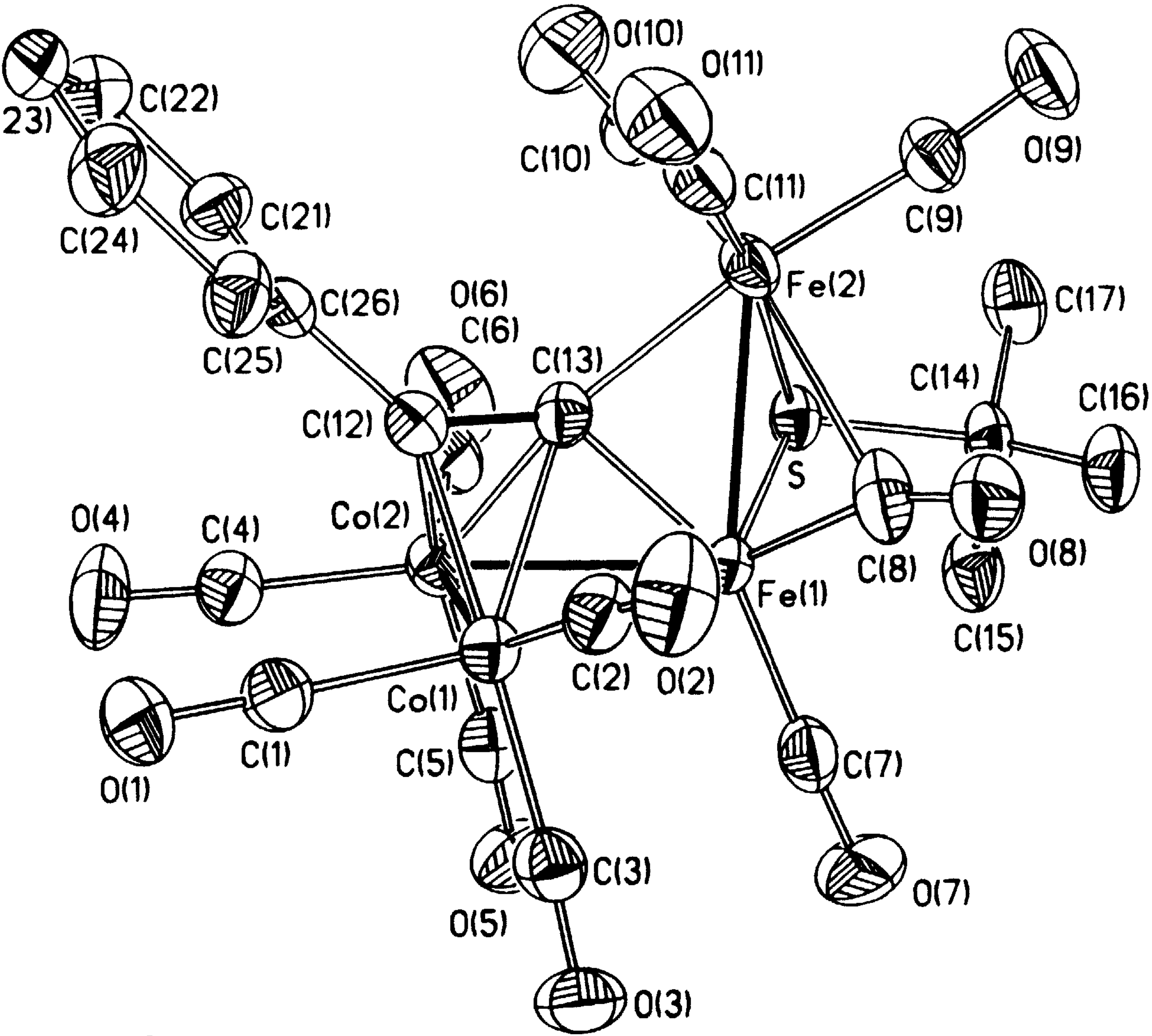


Figure 4: ORTEP plot of 21a

Table 4: Relevant Bond Distances (Å) for 21a

Col-Co2	2.478	C8-O8	1.118
Col-Fel	2.596	Fe2-C13	2.022
Co2-Fel	2.643	Fel-C13	1.912
Fel-Fe2	2.508	C12-C13	1.322
Fel-S	2.217	Col-C13	2.305
Fe2-S	2.281	Co2-C13	2.031
S-C14	1.882	Col-C12	2.015
Fel-C8	1.830	Co2-C12	2.052
Fe2-C8	2.458	C12-C26	1.472
Fel-C7	1.789	Fe2-CO (mean)	1.802
C7-O7	1.129	Fe2C-O (mean)	1.129
Co2-CO (mean)	1.797	Col-CO (mean)	1.802
Co2C-O (mean)	1.128	ColC-O (mean)	1.129

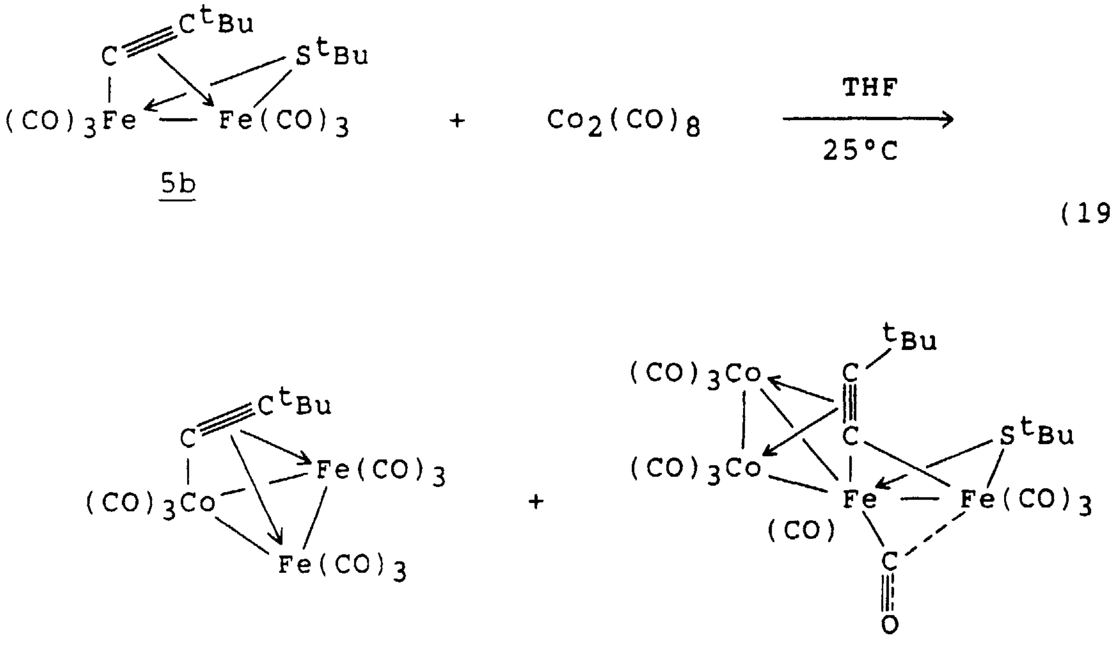
Table 5: Relevant Bond Angles (°) for 21a

Fe2-Fel-Col	105.1	C13-Col-Co2	50.1
Fe2-Fel-Co2	94.9	C13-Co2-Col	60.5
Fel-Co2-Col	60.8	Col-C13-C12	60.5
Fel-Col-Co2	62.7	Co2-C13-C12	72.0
Co2-Fel-Col	56.4	Fe2-C13-Col	139.0
S-Fel-Fe2	57.3	Fe2-C13-Co2	138.9
Fel-Fe2-S	54.9	Fe2-C13-C12	142.2
Fel-S-Fe2	67.8	C13-Col-Fel	45.4
Fel-C8-Fe2	69.8	C13-Co2-Fel	46.0
Fel-Fe2-C8	43.2	C13-Fel-S	89.5
Fe2-Fel-C8	66.9	C13-Fe2-S	85.0
Fe2-Fel-C13	52.4	C13-Fel-C8	99.4
Fel-Fe2-C13	48.5	C13-Fe2-C8	78.5
Fe2-C13-Fel	79.2	C13-C12-Col	84.7
Fel-C13-Col	75.4	C13-C12-C26	137.0
Fel-C13-Co2	84.1	Col-C12-C26	131.4
Fel-C13-C12	134.7	Co2-C12-C26	133.2
Col-C13-Co2	69.4	S-Fel-Col	145.5
C13-Fel-Col	59.2	S-Fel-Co2	93.2
C13-Fel-Co2	49.9	Fel-Col-C12	79.9
C13-Col-C12	34.8	Fel-Co2-C12	78.1
C13-Co2-C12	37.8		

to Co2. Conversely, C13 surprisingly is much closer to Co2 than to Co1 (2.031 vs. 2.305 Å). Balancing this effect, Fe1 bonds somewhat nearer to Co1 than to Co2 (2.596 vs. 2.643 Å). In general, this slightly twisted orientation of the acetylide ligand with respect to the dicobalt axis may help relieve the electron-rich nature of the cobalt atoms. Certainly, a large degree of electron delocalization over the entire cluster framework is inferred.

As revealed in the ^1H and ^{13}C NMR spectra, 21a is isolated as a mixture of two inseparable isomers which in analogy to other thiolate-bridged diiron systems, may result from either an axial or an equatorial orientation of the organic thiolate group. Furthermore, in the ^{13}C NMR spectrum, the four acetylide carbons are observed in the range of 139 - 153 ppm, while in the infrared spectrum, the coordinated triple bond gives rise to a band at 1620 cm^{-1}. The semi-bridging carbonyl ligand likewise gives rise to a strong absorption at 1850 cm^{-1}.[28]

In the corresponding reaction of $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}C^tBu)(\mu\text{-}^tBuS)Fe_2(CO)_6$, 5b, with dicobalt octacarbonyl, both products of type 20 and 21 were isolated in 44 and 30% yields, respectively (Eq. 19). As expected, the spectroscopic and



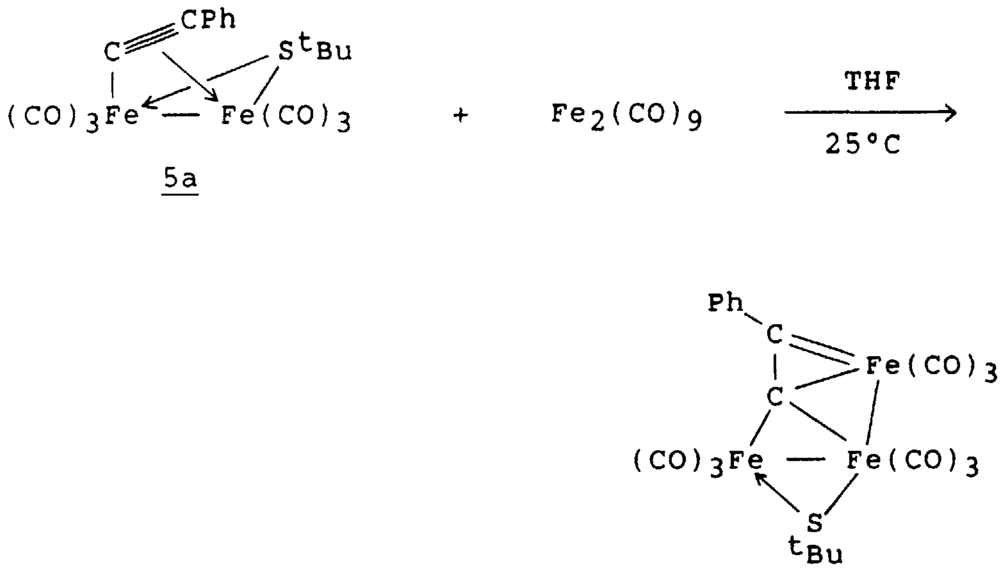
(19)

20b

21b

analytical data for these new acetylide complexes, 20b and 21b, were consistent with 20a and 21a.

Reaction of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$, 5a, with diiron nonacarbonyl generated the unusual triiron cluster, (μ_3-C≡CPh)(μ-^{t}BuS)$Fe_3(CO)_9$, 22, in 91% yield (Eq. 20).



22, 91%

(20)

The structure has been confirmed recently by X-ray crystallography. An ORTEP plot summarizing the atom labeling scheme appears in Figure 5; however, a complete discussion of the bonding will be postponed until publication. In essence, the formation of 22 can be envisioned as insertion of an $Fe(CO)_3$ unit into the eletron-rich, iron-acetylide π-bond of 5a. Whereas the α-carbon atom of the resulting "acetylide" ligand is bound to four other atoms, the β-carbon atom is bound to only three. Hence, a large degree of "carbene-like" character likely exists for the corresponding C2-Fe1 bond. Due to this unusual coordination of the alkynyl fragment, two iron atoms (Fe1 and Fe3) are not linked by a direct iron-iron bond.

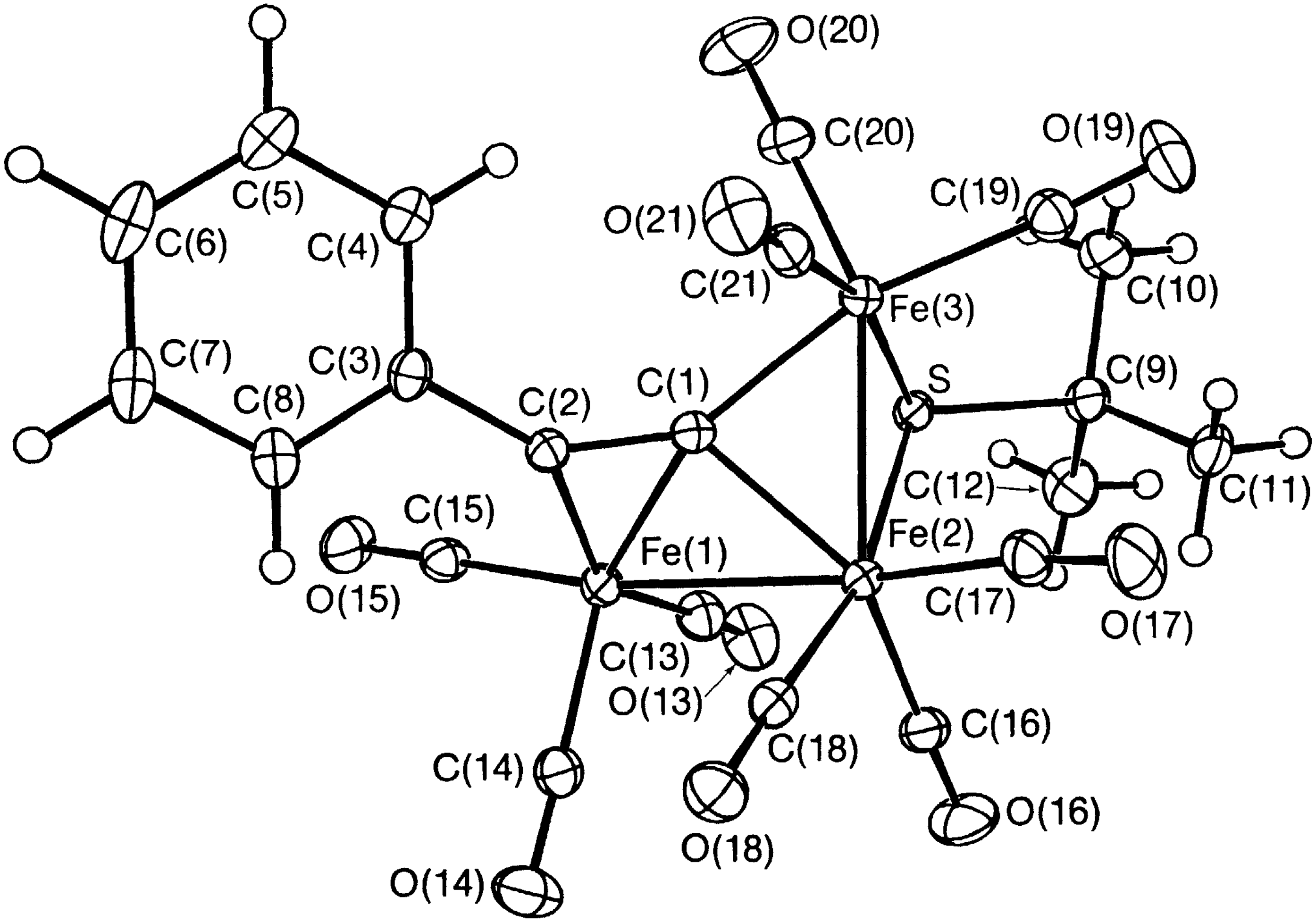
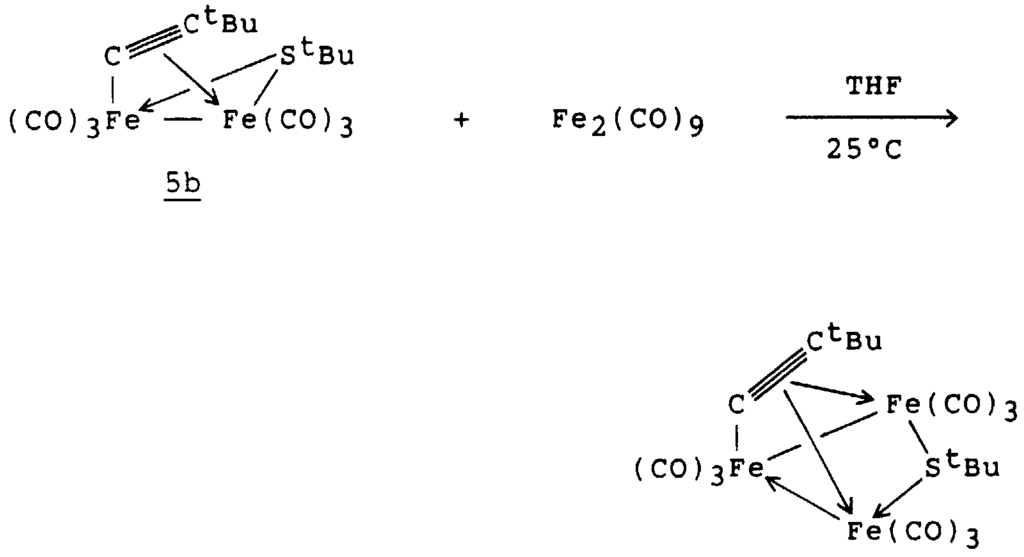


Figure 5: ORTEP plot of 22

Once again, a large degree of electron delocalization over the entire cluster framework is indicated. As illustrated in the ^1H and ^{13}C NMR spectra, 22 is isolated as a mixture of two inseparable isomers presumably resulting from an axial or equatorial orientation of the organic thiolate ligand. Furthermore, the α- and β-carbon atoms of the "acetylide" ligand are observed in the ^{13}C NMR spectrum at 201.24 and 228.61 ppm, respectively. The β-carbon is assigned the downfield shift based on the apparent "carbene-like" nature of the Fe-C_β (Fe1-C2) bond.

Reaction of $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}C^tBu)(\mu\text{-}^tBuS)Fe_2(CO)_6$, 5b, with diiron nonacarbonyl proceeded differently with the isolation of the new acetylide complex, $(\mu_3,\eta^2\text{-}C{\equiv}C^tBu)(\mu\text{-}^tBuS)Fe_3(CO)_9$, 23 (Eq. 21). Once again, the structure has



(21)

23, 51%

been confirmed recently by X-ray crystallography, but a complete discussion of the bonding will be postponed until publication. An ORTEP plot showing the atom labeling scheme appears in Figure 6. Unlike formation of 22, formation of

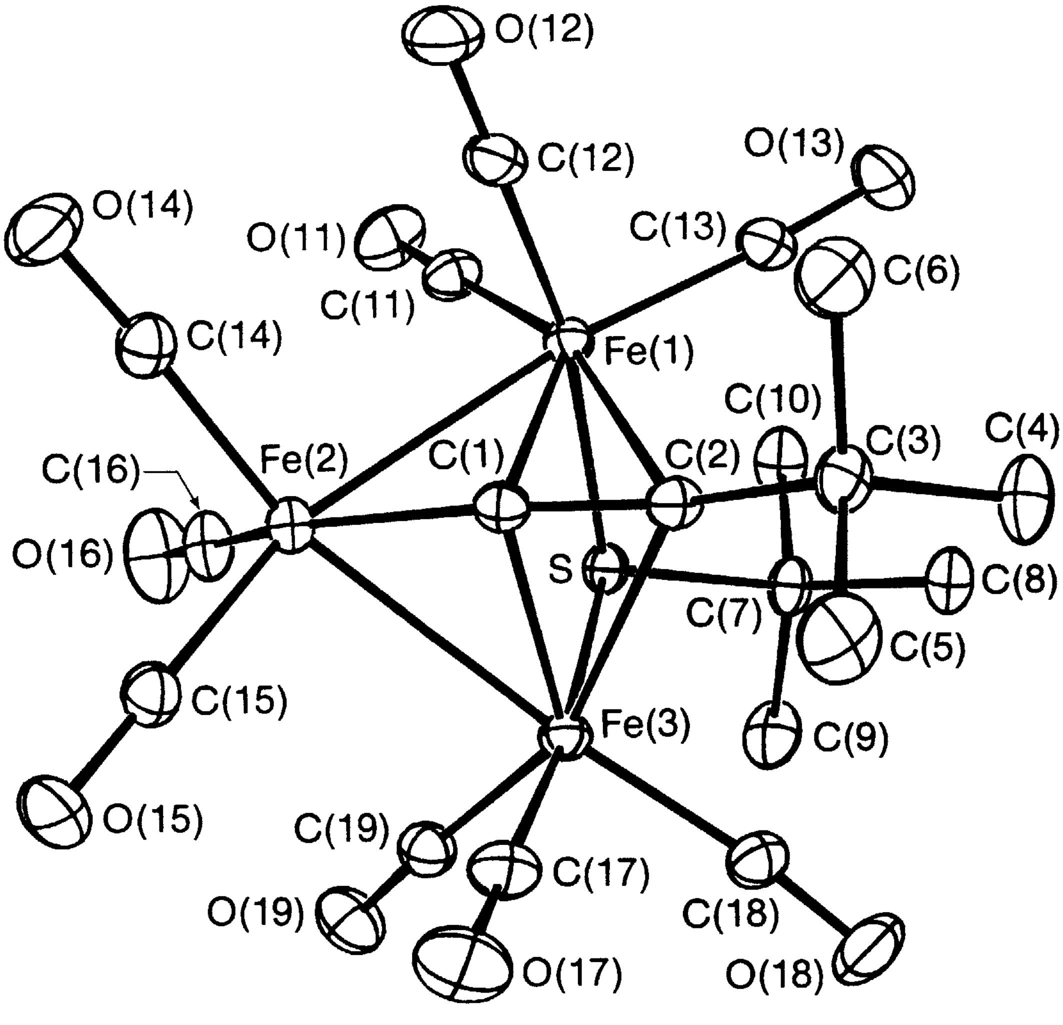
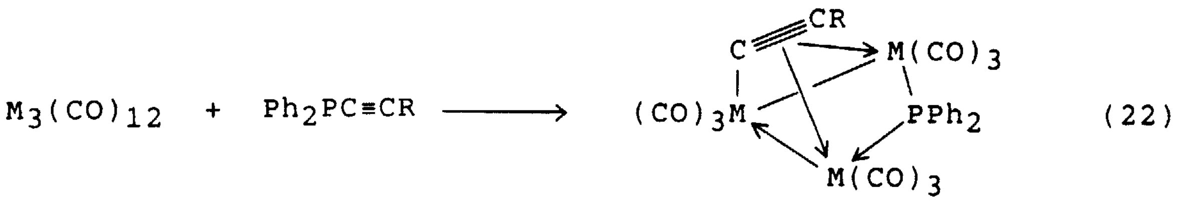


Figure 6: ORTEP plot of 23

23 can be envisioned as insertion of an $Fe(CO)_3$ unit into the electron-rich Fe-S bond of 5b with subsequent π-coordination of the acetylide ligand to this new iron center. Thus, the original μ_2,η^2-acetylide ligand has been transformed into a μ_3,η^2-acetylide ligand. In this case, the two iron atoms bridged by both the thiolate and acetylide ligands (Fe1 and Fe3) are not linked by a direct iron-iron bond. Carty has reported the synthesis and crystal structures of related phosphido and acetylide bridged triruthenium and triosmium clusters (Eq. 22).[6d,e,12b]



24

M = Ru, Os

R = Ph, ^{i}Pr, ^{t}Bu

Complex 23 is unusual in that when in solution, it appears to rearrange to the corresponding acetylide complex of type 22 (R = ^{t}Bu). Dissolving red crystals of 23 in pentane produces a deep red solution which over a period of 10 - 15 minutes becomes brownish-green. TLC shows the presence of olive-green (likely 22, R = ^{t}Bu) and red (likely 23) products. Apparently, an equilibrium is reached and complete conversion does not occur. However, when the solvent is removed in vacuo, only a red solid (23) remains. Apparently, 23 is the thermodynamic, solid-state structure whereas, in solution, both structures of type 22 and 23 may be in equilibrium. Unfortunately, this equilibrium makes the ^{13}C NMR spectrum difficult to interpret. However, it does show the presence of at least three t-butyl thiolate resonances (δ_C 30.83, 31.23, and 33.10) as well as four possible acetylide signals (δ_C 149.49, 202.40, 215.14, and 220.21) consistent with the presence of two isomers in solution. (The t-butyl resonance at 33.10 ppm is considerably more intense than the other two and therefore may result from two chemically equivalent t-butyl ligands). Likely, the ^{13}C NMR signals at 149.49 and 215.14 ppm can be assigned to the acetylide carbon atoms of the red isomer, 23, while the resonances at 202.40 and 220.21 ppm may be attributed to the corresponding green isomer of type 22 (which cannot be isolated and characterized in the solid state).

Somewhat surprisingly, (μ-σ,π-C≡CSiMe$_3$)(μ-^{t}BuS)Fe$_2$(CO)$_6$, 5c, did not react with diiron nonacarbonyl at room temperature. When the reaction mixture was heated to reflux, only decomposition was observed. Further research in extending the capabilities of (μ-σ,π-C≡CR^1)(μ-RS)Fe$_2$(CO)$_6$, 5, as a general reagent for cluster synthesis is continuing.

EXPERIMENTAL

General Comments

All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl and purged with nitrogen prior to use. Triethylamine, diethylamine, aniline, and t-butylamine were distilled under nitrogen from calcium hydride and purged with nitrogen prior to use. Triphenylphosphine was purchased from Aldrich and used as received. Ethyl, t-butyl, and phenyl mercaptans were purged with nitrogen and used without further purification. Phenylbromoacetylene ($PhC{\equiv}CBr$), trimethylsilylbromoacetylene ($Me_3SiC{\equiv}CBr$), and t-butylbromoacetylene ($^tBuC{\equiv}CBr$) all were prepared by a literature procedure[23] and purged with nitrogen prior to use. Diiron nonacarbonyl ($Fe_2(CO)_9$)[24] and triiron dodecacarbonyl ($Fe_3(CO)_{12}$)[25] were also prepared by literature methods. Dicobalt octacarbonyl was purchased from Strem Chemical Co. and was used as received.

The progress of all reactions was monitored by thin layer chromatography (Baker Flex - Silica Gel 1B-F). Purification by filtration chromatography in which the reaction products were dissolved in a suitable solvent and chromatographed on a bed of EM Science or Sigma 100-300 mesh silicic acid (ca. 200 ml) in a 350 ml glass fritted filter funnel was used in most cases. Further purification by medium pressure column chromatography was accomplished with a 300x25 mm column using Sigma 230-400 mesh silica gel. Column chromatography under nitrogen was accomplished with a 200x25 mm gravity column (solvent reservoir at the top) using Sigma 230-400 mesh silica gel (dried for several hours at ~150°C in vacuo). All chromatography was completed without exclusion of atmospheric moisture or oxygen except where specified. Solid products were recrystallized from deoxygenated solvents at -20°C.

Solution infrared spectra (NaCl windows) were obtained using a Perkin-Elmer Model 1430 double beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a JEOL FX-90Q, a Bruker WM-250, or a Varian XL-300 NMR spectrometer operating at 90, 250, or 300 MHz respectively. Carbon-13 NMR spectra were obtained using a Bruker WH-270, a Varian XL-300, or a Varian XL-400 spectrometer operating at 67.9, 75.4, or 100.5 MHz respectively. Phosphorus-31 NMR spectra were obtained using a JEOL FX-90Q spectrometer operating at 36.2 MHz. Electron impact mass spectra were obtained using a Finnigan-3200 mass spectrometer operating at 70 eV. Field desorption mass spectra were obtained using a Finnigan MAT-731 mass spectrometer operating in the positive ion mode. Masses were correlated using the following isotopes: ^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{28}Si, ^{31}P, ^{32}S, ^{56}Fe, and ^{59}Co. Melting points were determined in air on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were perfomed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

X-ray Crystallography

The crystal structures of both $(\mu_3,\eta^2\text{-}C{\equiv}CSiMe_3)CoFe_2(CO)_9$, 20a, and $(\mu_4\text{-}C{\equiv}CPh)(\mu\text{-}CO)(\mu\text{-}{}^{t}BuS)Co_2Fe_2(CO)_{10}$, 21a, were solved by Prof. Arnold Rheingold at the University of Delaware. Experimental details will be supplied in a forthcoming paper. Crystal data for 20a is summarized in Table 6, and final positional parameters are given in Table 7. Crystal data for 21a is summarized in Table 8, and final positional parameters are given in Table 9.

The crystal structures of both $(\mu_3\text{-}C{\equiv}CPh)(\mu\text{-}{}^{t}BuS)Fe_3(CO)_9$, 22, and $(\mu_3,\eta^2\text{-}C{\equiv}C^{t}Bu)(\mu\text{-}{}^{t}BuS)Fe_3(CO)_9$, 23, were solved by Dr. Allen Hunter in collaboration with Prof. Martin Cowie at the University of Edmonton, Alberta, Canada. Experimental details will be supplied in a forthcoming paper.

Table 6: Crystal Data for $(\mu_3,\eta^2\text{-}C{\equiv}CSiMe_3)CoFe_2(CO)_9$, 20a

a = 9.046	α = 101.41
b = 9.509	β = 97.58
c = 11.721	γ = 90.64

Space Group = $P\bar{1}$

R = 3.66 %

Table 7: Final Positional Parameters for 20a

ATOM	TYPE	X	Y	Z
FE1	5	.73038	.38195	.31576
FE2	5	.88764	.16998	.26872
CO	4	.65939	.14443	.38186
SI	6	.67541	.24263	-.00583
O1	3	.84552	.48305	.56295
O2	3	.44662	.52897	.31267
O3	3	.90534	.59674	.23622
O4	3	1.12529	.30193	.17250
O5	3	.91863	-.12919	.15134
O6	3	1.05621	.17301	.49909
O7	3	.62439	-.16805	.33315
O8	3	.76604	.17497	.63425
O9	3	.34934	.20913	.40191
C1	1	.79801	.43808	.46751
C2	1	.55534	.47160	.31342
C3	1	.83668	.51293	.26388
C4	1	1.03368	.25242	.20930
C5	1	.90995	-.01286	.19933
C6	1	.98642	.17212	.41103
C7	1	.63932	-.04741	.35339
C8	1	.72727	.16537	.53816
C9	1	.46912	.18421	.39799
C10	1	.47725	.29193	-.03137
C11	1	.80268	.37575	-.04144
C12	1	.70344	.05967	-.08923
C13	1	.71032	.23283	.15254
C14	1	.66451	.17978	.23524

Table 8: Crystal Data for $(\mu_4\text{-C}\equiv\text{CPh})(\mu\text{-CO})(\mu\text{-}{}^t\text{BuS})\text{Co}_2\text{Fe}_2(\text{CO})_{10}$, 21a

$a = 14.303$ $\alpha = 90.00$
$b = 11.710$ $\beta = 97.86$
$c = 16.462$ $\gamma = 90.00$

Space Group = $P2_1/c$
R = 4.64 %

Table 9: Final Positional Parameters for 21a

ATOM	TYPE	X	Y	Z
CO1	6	.39688	.55526	.68712
CO2	6	.30610	.56066	.54771
FE1	5	.33276	.75225	.63263
FE2	5	.16743	.76182	.66698
S	4	.21748	.84262	.55443
C1	1	.42296	.40503	.69461
O1	3	.43733	.31073	.69746
C2	1	.40879	.59405	.79365
O2	3	.41877	.62047	.86076
C3	1	.51256	.60024	.66700
O3	3	.58596	.62292	.65493
C4	1	.31155	.41255	.52052
O4	3	.31152	.31975	.50376
C5	1	.40193	.61365	.49851
O5	3	.46277	.64151	.46502
C6	1	.21223	.59683	.46738
O6	3	.15490	.61532	.41544
C7	1	.43802	.81861	.60802
O7	3	.50353	.86276	.59269
C8	1	.32464	.82589	.72944
O8	3	.34508	.87243	.78853
C9	1	.11470	.88782	.70378
O9	3	.07611	.96206	.72861
C10	1	.06154	.70058	.60863
O10	3	-.00372	.66212	.57227
C11	1	.15675	.68734	.76103
O11	3	.14956	.64011	.81905
C12	1	.25934	.51682	.65595
C13	1	.24874	.62786	.64339
C14	1	.22777	1.00257	.54911
C15	1	.28985	1.02052	.48073
C16	1	.27297	1.05856	.62728
C17	1	.12764	1.04546	.52080
C21	1	.12285	.38456	.62770
C22	1	.06727	.29617	.65173
C23	1	.09079	.24471	.72823
C24	1	.16990	.28166	.78069
C25	1	.22548	.37006	.75666
C26	1	.20195	.42151	.68017

Standard in-situ Preparation of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$

A 250 ml Schlenk flask equipped with a spin bar and a rubber septum was charged with 1.52 g (3.02 mmol) of triiron dodecacarbonyl and degassed by three evacuation/nitrogen-backfill cycles. The flask was then charged sequentially with 30 ml of THF, 0.42 ml (3.00 mmol) of triethylamine, and 3.00 mmol of the appropriate thiol. The resulting mixture then was stirred for 20 min at room temperature during which time slow gas evolution and a gradual color change to brown-red were observed. The $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ reagent solution subsequently was used in-situ without further purification.

Synthesis of $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ JBH-59-II

To the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ reagent solution (3.00 mmol) was added 0.37 ml (3.00 mmol) of phenylbromoacetylene by syringe at room temperature. An immediate reaction ensued with brisk gas evolution (CO), a gradual color change to cherry red, and formation of a white precipitate ($[Et_3NH][Br]$). After the reaction mixture had been stirred for 2 h at room temperature, the solvent was removed in vacuo, and the resulting cherry red tar was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Further elution with pentane yielded a dark red band which gave 1.25 g (2.65 mmol, 88%) of $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$, 5a (a mixture of two inseparable isomers), as a slightly air-sensitive red oil.

Anal. Calcd. for $C_{18}H_{14}Fe_2O_6S$: C, 45.99; H, 3.00 %. Found: C, 46.15; H, 3.14 %.

IR($CHCl_3$): 3087vw, 3070vw, 3000sh, 2965m, 2942m, 2924m, 2900w, 2883w, 1595w(Ph), 1572w(Ph), 1487m, 1472w, 1457m, 1443m, 1390vw, 1365m, 1152s, 1100vw, 1070w, 1025vw, 1000vw, 910vw, 865vw, 690vw, 611vs, 580vs, 545s, 520s cm^{-1}. Terminal carbonyl region (pentane): 2080s, 2042vs, 2018sh, 2009sh, 2002vs, 1980vw cm^{-1}.

^{1}**H NMR**(acetone-d_6; 90 MHz): δ 1.21 (s, 9H, $SC(CH_3)_3$ minor isomer), 1.38 (s, 9H, $SC(CH_3)_3$ major isomer), 7.17-7.80 (broad m, 10H, C_6H_5 both isomers). Ratio major/minor = 1.3/1.0.

^{13}**C NMR**($CDCl_3$; 67.9 MHz): δ 33.33 (q, J = 127.8 Hz, $SC(\underline{C}H_3)_3$ major isomer), 34.55 (q, J = 128.1 Hz, $SC(\underline{C}H_3)_3$ minor isomer), 47.94 (s, $S\underline{C}(CH_3)_3$ minor isomer), 48.59 (s, $S\underline{C}(CH_3)_3$ major isomer), 92.39 (s, acetylide C, minor isomer), 95.43 (s, acetylide C, major isomer), 114.46 (s, acetylide C, major isomer), 114.95 (s, acetylide C, minor isomer), 125.24 (s, ipso C_6H_5), 127.93 (d, J = 157.0 Hz, C_6H_5), 128.55 (d, J = 160.6 Hz, C_6H_5), 131.80 (d, J = 156.9 Hz, C_6H_5), 132.00 (d, J = 160.5 Hz, C_6H_5), 207.90 (s, Fe-CO minor isomer), 209.24 (s, Fe-CO major isomer).

Mass Spectrum (EI); m/z (relative intensity): 470 (M^+, 15), 442 (M^+ - CO, 12), 414 (M^+ - 2CO, 38), 386 (M^+ - 3CO, 14), 358 (M^+ - 4CO, 41), 330 (M^+ - 5CO, 40), 302 (M^+ - 6CO, 84), 246 ($HSFe_2C{\equiv}CPh$, 100), 202 ($HCSFeC{\equiv}CPh$, 10), 190 ($HSFeC{\equiv}CPh$, 7), 189 ($SFeC{\equiv}CPh$, 16), 178 (HSFeCPh, 57), 169 ($HSFeC{\equiv}C$, 12), 157 ($FeC{\equiv}CPh$, 3), 145 ($HSFe_2$, 6), 144 (SFe_2, 50), 134 ($HSC{\equiv}CPh$, 24), 102 ($HC{\equiv}CPh$, 14), 89 (FeSH, 11), 57 (^{t}Bu, 29), 56 (Fe, 18).

Synthesis of $(\mu-\sigma,\pi-C{\equiv}C^tBu)(\mu-^tBuS)Fe_2(CO)_6$ JBH-2-III

To the standard $[Et_3NH][(\mu-CO)(\mu-^tBuS)Fe_2(CO)_6]$ reagent solution (3.00 mmol) was added 0.38 ml (3.00 mmol) of t-butylbromoacetylene by syringe at room temperature. An immediate reaction ensued with brisk gas evolution (CO), a gradual color change to cherry red, and formation of a white precipitate ($[Et_3NH][Br]$). After the reaction mixture had been stirred for 2 h at room temperature, the solvent was removed in vacuo, and the resulting dark red oil was purified by filtration chromatography. Pentane eluted a dark red band which gave 1.19 g (2.65 mmol, 88%) of (μ-σ,π-$C\equiv C^tBu$)(μ-^tBuS)$Fe_2(CO)_6$, 5b (a mixture of two inseparable isomers), as a dark red, air-stable solid, mp 56.0 - 60.0°C after recrystallization from pentane.

Anal. Calcd. $C_{16}H_{18}Fe_2O_6S$: C, 42.70; H, 4.03 %. Found: C, 42.52; H, 4.13 %.

IR($CHCl_3$): 2970vs, 2942vs, 2922s, 2900s, 2867s, 1470s, 1455s, 1390m, 1360vs, 1235s, 1153vs, 1020vw, 885m, 610vs, 580vs, 535vs cm^{-1}.
Terminal carbonyl region (pentane): 2075s, 2038vs, 2000vs, 1980s, 1945w($C\equiv C$?) cm^{-1}.

^{1}H NMR($CDCl_3$; 250MHz): δ 1.17 (s, 9H, $C(CH_3)_3$ minor isomer), 1.27 (s, 9H, $C(CH_3)_3$ major isomer), 1.28 (s, 9H, $C(CH_3)_3$ major isomer), 1.34 (s, 9H, $C(CH_3)_3$ minor isomer). Ratio major/minor = 7.9/1.0

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 31.60 (q, J = 126.4 Hz, $C\equiv CC(\underline{C}H_3)_3$ major isomer), 31.92 (q, J = 127.0, $C\equiv CC(\underline{C}H_3)_3$ minor isomer), 33.30 (q, J = 127.2 Hz, $SC(\underline{C}H_3)_3$ major isomer), 34.59 (q, J = 127.0 Hz, $SC(\underline{C}H_3)_3$ minor isomer), 36.70 (s, $C\equiv C\underline{C}(CH_3)_3$), 48.16 (s, $S\underline{C}(CH_3)_3$), 102.34 (s, acetylide C), 109.60 (s, acetylide C), 208.48 (s, Fe-CO major isomer), 209.35 (s, Fe-CO minor isomer), 209.94 (s, Fe-CO minor isomer).

Mass Spectrum (EI); m/z (relative intensity): 450 (M^+, 13), 422 (M^+ - CO, 9), 394 (M^+ - 2CO, 25), 366 (M^+ - 3CO, 16), 338 (M^+ - 4CO, 42), 310 (M^+ - 5CO, 41), 282 (M^+ - 6CO, 100), 226 ($HSFe_2C\equiv C^tBu$, 95), 184 ($HSFe_2C\equiv CMe$, 10), 170 ($HSFe_2C\equiv CH$, 69), 169 ($HSFe_2C\equiv C$, 12), 168 ($SFe_2C\equiv C$, 9), 145 ($HSFe_2$, 10), 144 (SFe_2, 34), 57(^tBu, 30), 56 (Fe, 10).

Synthesis of (μ-σ,π-C≡CSiMe$_3$)(μ-^{t}BuS)Fe$_2$(CO)$_6$ DRW-41-II

To the standard [Et$_3$NH][(μ-CO)(μ-^{t}BuS)Fe$_2$(CO)$_6$] reagent solution (3.14 mmol) was added 0.43 ml (3.23 mmol) of trimethylsilylbromoacetylene by syringe at room temperature. An immediate reaction ensued with brisk gas evolution (CO), a gradual color change to cherry red, and formation of a white precipitate ([Et$_3$NH][Br]). After the reaction mixture had been stirred for 18 h at room temperature, the solvent was removed in vacuo, and the resulting cherry red tar was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Further elution with pentane yielded a dark red band which gave 1.37 g (2.94 mmol, 94%) of (μ-σ,π-C≡CSiMe$_3$)(μ-^{t}BuS)Fe$_2$(CO)$_6$, 5c (a mixture of two inseparable isomers), as an air-stable, red solid, mp 58.0 - 59.0°C after recrystallization from pentane.

Anal. Calcd. for $C_{15}H_{18}Fe_2O_6SSi$: C, 38.65; H, 3.89 %. Found: C, 38.73; H, 3.96 %.

IR(CHCl$_3$): 3025w, 2970m, 2940w, 2925w, 2900w, 1910vs(C≡C), 1473w, 1458w, 1400w, 1395w, 1365m, 1265m, 1250s, 1228w, 1205w, 1150m, 1020vw, 925vw, 845vs, 700m, 675w, 665w, 615vs, 605s, 575vs, 520w, 490w cm^{-1}. Terminal carbonyl region (pentane): 2080m, 2040s, 2017sh, 2010sh, 2002s, 1995sh, 1978vw cm^{-1}.

^{1}H NMR(CDCl$_3$; 90 MHz): δ 0.24 (s, 9H, Si(CH$_3$)$_3$ minor isomer), 0.28 (s, 9H, Si(CH$_3$)$_3$ major isomer), 1.17 (s, 9H, SC(CH$_3$)$_3$ minor isomer), 1.30 (s, 9H, SC(CH$_3$)$_3$ major isomer). Ratio major/minor = 2.3/1.0

^{13}C NMR(CDCl$_3$; 67.9 MHz): δ 0.11 (q, J = 120.1 Hz, Si(CH$_3$)$_3$ major isomer), 0.40 (q, J = 120.0 Hz, Si(CH$_3$)$_3$ minor isomer), 33.32 (q, J = 128.1 Hz, SC($\underline{C}$H$_3$)$_3$ major isomer), 34.81 (q, J = 122.5 Hz, SC($\underline{C}$H$_3$)$_3$ minor isomer), 48.55 (s, S$\underline{C}$(CH$_3$)$_3$), 90.95 (s, acetylide C minor isomer), 95.27 (s, acetylide C major isomer), 141.32 (s, acetylide C minor isomer), 143.24 (s, acetylide C major isomer), 208.16 (s, Fe-CO minor isomer), 209.48 (s, Fe-CO major isomer).

Mass Spectrum (EI); m/z (relative intensity): 466 (M^+, 7), 438 (M^+ - CO, 8), 410 (M^+ - 2CO, 18), 382 (M^+ - 3CO, 23), 354 (M^+ - 4CO, 24), 326 (M^+ - 5CO, 30), 298 (M^+ - 6CO, 85), 242 ($HSFe_2C{\equiv}CSiMe_3$, 100), 226 ($^tBuSFe_2C{\equiv}CH$, 20), 145 ($HSFe_2$, 3), 144 (SFe_2, 7), 112 (Fe_2, 4), 97 ($C{\equiv}CSiMe_3$, 6), 73 ($SiMe_3$, 41), 57 (^tBu, 49), 56 (Fe, 15).

Synthesis of (μ-σ,π-C≡CPh)(μ-EtS)$Fe_2(CO)_6$ JBH-61-II

To the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ reagent solution (3.00 mmol) was added 0.37 ml (3.00 mmol) of phenylbromoacetylene by syringe at room temperature. An immediate reaction ensued with brisk gas evolution (CO), a gradual color change to cherry red, and formation of a white precipitate ($[Et_3NH][Br]$). After the reaction mixture had been stirred for 2 h at room temperature, the solvent was removed in vacuo, and the resulting cherry red tar was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Further elution with pentane yielded a dark red band which gave 1.11 g (2.52 mmol, 84%) of (μ-σ,π-C≡CPh)(μ-EtS)$Fe_2(CO)_6$, 5d (a mixture of two inseparable isomers), as a slightly air-sensitive red oil.

Anal. Calcd. for $C_{16}H_{10}Fe_2O_6S$: C, 43.48; H, 2.28 %. Found: C, 43.55; H, 2.45 %.

IR($CHCl_3$): 3105vw, 3090vw, 3070vw, 2995w, 2977w, 2938m, 2880w, 1599w(Ph), 1575w(Ph), 1488s, 1455m, 1443m, 1435w, 1379w, 1330vw, 1310vw, 1255m, 1175vw, 1100vw, 1071w, 1046w, 1028w, 1000vw, 970w, 690s, 610vs, 580vs, 548s, 520s cm^{-1}.
Terminal carbonyl region (pentane): 2080m, 2043vs, 2005s, 2002sh cm^{-1}.

^{1}H NMR(CD_2Cl_2; 250 MHz): δ 1.11 (t, J = 7.55 Hz, 3H, $SCH_2C\underline{H}_3$ minor isomer), 1.29 (t, J = 7.55 Hz, 3H, $SCH_2C\underline{H}_3$ major isomer), 2.16 (q, J = 7.37 Hz, 2H, $SC\underline{H}_2CH_3$ minor isomer), 2.39 (q, J = 7.37 Hz, 2H, $SC\underline{H}_2CH_3$ major isomer), 7.28-7.58 (m, 10H, C_6H_5 both isomers). Ratio major/minor = 2.6/1.0

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 16.46 (q, J = 127.6 Hz, $SCH_2\underline{C}H_3$ minor isomer), 17.42 (q, J = 128.6 Hz, $SCH_2\underline{C}H_3$ major isomer), 23.46 (t, J = 140.4 Hz, $S\underline{C}H_2CH_3$ minor isomer), 34.18 (t, J = 140.9 Hz, $S\underline{C}H_2CH_3$ major isomer), 93.09 (s, acetylide C major isomer), 93.87 (s, acetylide C minor isomer), 113.21 (s, acetylide C major isomer), 119.00 (s, acetylide C minor isomer), 125.25 (s, ipso C_6H_5), 128.57 (d, J = 161.4 Hz, C_6H_5), 131.89 (d, J = 161.6 Hz, C_6H_5), 132.24 (d, J = 162.5 Hz, C_6H_5), 208.10 (s, Fe-CO minor isomer), 208.88 (s, Fe-CO major isomer).

Mass Spectrum (EI); m/z (relative intensity): 442 (M^+, 13), 414 (M^+ - CO, 12), 386 (M^+ - 2CO, 33), 358 (M^+ - 3CO, 15), 330 (M^+ - 4CO, 32), 302 (M^+ - 5CO, 33), 274 (M^+ - 6CO, 63), 246 ($HSFe_2C{\equiv}CPh$, 100), 245 ($SFe_2C{\equiv}CPh$, 34), 189 ($SFeC{\equiv}CPh$, 25), 178 (HSFeCPh, 60), 169 ($HSFe_2C{\equiv}C$, 15), 162 ($EtSC{\equiv}CPh$, 18), 157 ($FeC{\equiv}CPh$, 6), 145 ($HSFe_2$, 8), 144 (SFe_2, 48), 134 ($HSC{\equiv}CPh$, 27), 102 ($HC{\equiv}CPh$, 13), 89 (HSFe, 17), 56 (Fe, 7).

Synthesis of (μ-σ,π-$C{\equiv}C^tBu$)(μ-EtS)$Fe_2(CO)_6$ JBH-3-III

To the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ reagent solution (3.00 mmol) was added 0.38 ml (3.00 mmol) of t-butylbromoacetylene by syringe at room temperature. An immediate reaction ensued with brisk gas evolution (CO), a gradual color change to cherry red, and formation of a white precipitate ($[Et_3NH][Br]$). After the reaction mixture had been stirred for 4 h at room temperature, the solvent was removed in vacuo, and the resulting red oil was purified by filtration chromatography. Pentane eluted a dark red band which gave 0.90 g (2.14 mmol, 71%) of $(\mu\text{-}\sigma,\pi\text{-}C\equiv C^{t}Bu)(\mu\text{-}EtS)Fe_2(CO)_6$, 5e (a mixture of two inseparable isomers), as a slightly air-sensitive red oil.

Anal. Calcd. for $C_{14}H_{14}Fe_2O_6S$: C, 39.84; H, 3.34 %. Found: C, 39.64; H, 3.43 %.

IR($CHCl_3$): 2974vs, 2954s, 2933s, 2906m, 2874m, 1475m, 1456s, 1435w, 1397w, 1365s, 1258m, 1239s, 1049w, 973w, 916vw, 889m, 614vs, 518vs, 540vs cm^{-1}.
Terminal carbonyl region (pentane): 2077vs, 2044vs, 2004vs, 1994vs, 1958sh, 1932sh(C≡C ?) cm^{-1}.

^{1}H NMR($CDCl_3$; 250 MHz): δ 1.05 (t, J = 7.53 Hz, 3H, $SCH_2C\underline{H}_3$ minor isomer), 1.22 (t, J = 7.40 Hz, 3H, $SCH_2C\underline{H}_3$ major isomer), 1.28 (s, 9H, $C\equiv CC(CH_3)_3$ major isomer), 1.33 (s, 9H, $C\equiv CC(CH_3)_3$ minor isomer), 1.96 (q, J = 7.42 Hz, 2H, $SC\underline{H}_2CH_3$ minor isomer), 2.24 (q, J = 7.36 Hz, $SC\underline{H}_2CH_3$ major isomer). Ratio major/minor = 2.8/1.0

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 16.39 (q, J = 127.0 Hz, $SCH_2\underline{C}H_3$ major isomer), 17.36 (q, J = 128.2 Hz, $SCH_2\underline{C}H_3$ minor isomer), 22.64 (t, J = 142.8 Hz, $S\underline{C}H_2CH_3$ minor isomer), 31.70 (q, J = 126.4 Hz, $C\equiv CC(\underline{C}H_3)_3$), 33.40 (s, $C\equiv C\underline{C}(CH_3)_3$), 34.30 (t, J = 139.6 Hz, $S\underline{C}H_2CH_3$ major isomer), 101.50 (s, acetylide C major isomer), 105.48 (s, acetylide C minor isomer), 107.72 (s, acetylide C major isomer), 208.53 (s, Fe-CO minor isomer), 209.37 (s, Fe-CO major isomer).

Mass Spectrum (EI); m/z (relative intensity): 422 (M^+, 3), 310 (M^+ - CO, 5), 366 (M^+ - 2CO, 12), 338 (M^+ - 3CO, 8), 394 (M^+ - 4CO, 15), 282 (M^+ - 5CO, 19), 254 (M^+ - 6CO, 36), 226 ($HSFe_2C\equiv C^{t}Bu$, 41), 198 ($EtSFe_2C\equiv CH$, 5), 184 ($HSFe_2C\equiv CMe$, 5), 183 ($CH_2SFeC\equiv C^{t}Bu$, 8), 170 ($HSFe_2C\equiv CH$, 38), 145 ($HSFe_2$, 12), 144 (SFe_2, 29), 57 (^{t}Bu, 30).

Synthesis of (μ-σ,π-C≡C^{t}Bu)(μ-PhS)$Fe_2(CO)_6$ JBH-6-III

To the standard [Et_3NH][(μ-CO)(μ-PhS)$Fe_2(CO)_6$] reagent solution (1.50 mmol) was added 0.19 ml (1.50 mmol) of t-butylbromoacetylene by syringe at room temperature. An immediate reaction ensued with brisk gas evolution (CO), a gradual color change to cherry red, and formation of a white precipitate ([Et_3NH][Br]). After the reaction mixture had been stirred for 18 h at room temperature, the solvent was removed in vacuo, and the resulting red tar was dissolved in pentane and filtered through a thin pad of silicic acid. Removal of the solvent left a red oil which was purified by medium pressure chromatography. Pentane eluted three bands. The first brown-red band gave 0.14 g (0.29 mmol, 19%) of (μ-σ,π-C≡C^{t}Bu)(μ-PhS)$Fe_2(CO)_6$, 5f (a isomer only), as an air-stable, red solid, mp 99.0 - 101.0°C after recrystallization from pentane. The second cherry red band yielded 0.33 g (0.70 mmol, 47%) of (μ-σ,π-C≡C^{t}Bu)(μ-PhS)$Fe_2(CO)_6$, 5f (e isomer only), as a slightly air-sensitive red oil. The third orange band gave 0.16 g (0.33 mmol, 22% based on S) of (μ-PhS)$_2Fe_2(CO)_6$ identified by its ^{1}H NMR and mass spectra.[26] Except where specified, all data are reported for the e/a isomer mixture.

Anal. Calcd. for $C_{18}H_{14}Fe_2O_6S$: C, 45.99; H, 3.00 %.
Found (major isomer - e): C, 46.22; H, 3.19 %.
Found (minor isomer - a): C, 45.96; H, 3.11 %.

IR($CHCl_3$): 3083vw, 3071vw, 2976s, 2950m, 2932m, 2905m, 2870m, 1578m(Ph), 1473s, 1455m, 1436s, 1393w, 1363s, 1298m, 1071w, 1023w, 1002w, 888w, 697w, 685w, 613vs, 575vs, 539vs cm^{-1}.
Terminal carbonyl region (pentane): 2082s, 2042vs, 2003s, 1997sh, 1990sh cm^{-1}.

^{1}**H NMR**(CD_2Cl_2; 250 MHz): δ 0.86 (s, 9H, $C(CH_3)_3$ minor isomer), 1.34 (s, 9H, $C(CH_3)_3$ major isomer), 7.20 (s, 10H, C_6H_5 both isomers).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 30.80 (q, J = 128.0 Hz, $C(\underline{C}H_3)_3$ minor isomer), 31.71 (q, J = 127.8 Hz, $C(\underline{C}H_3)_3$ major isomer), 100.85 (s, acetylide C major isomer), 104.75 (s, acetylide C minor isomer), 108.26 (s, acetylide C major isomer), 111.01 (s, acetylide C minor isomer), 127.57 (d, J = 163.4 Hz, C_6H_5), 127.91 (d, J = 160.8 Hz, C_6H_5), 128.48 (d, J = 161.8 Hz, C_6H_5), 131.4 (d, J = 161.9 Hz, C_6H_5), 133.87 (d, J = 165.7 Hz, C_6H_5), 140.92 (s, ipso C_6H_5), 208.37 (s, Fe-CO minor isomer), 209.06 (s, Fe-CO major isomer).

Mass Spectrum (EI); m/z (relative intensity): 470 (M^+, 5), 442 (M^+ - CO, 2), 414 (M^+ - 2CO, 23), 386 (M^+ - 3CO, 7), 358 (M^+ - 4CO, 4), 330 (M^+ - 5CO, 16), 302 (M^+ - 6CO, 100), 246 ($PhSFe_2C{\equiv}CH$, 23), 221 ($PhSFe_2$, 6), 190 ($PhSC{\equiv}C^tBu$, 5), 186 (PhSPh, 8), 169 ($SFe_2C{\equiv}CH$, 5), 158 ($PhC{\equiv}C^tBu$, 26), 144 (SFe_2, 10), 143 ($PhC{\equiv}CMe_2$,84), 128 ($PhC{\equiv}CMe$, 39), 110 (PhSH, 10), 77 (Ph, 13), 57 (^tBu, 6).

Reaction of $(\mu-\sigma,\pi-C{\equiv}CPh)(\mu-^tBuS)Fe_2(CO)_6$ with Et_2NH JBH-57-VI

A 100 ml round-bottomed flask equipped with a stir-bar and a rubber septum was charged with 0.87 g (1.85 mmol) of $(\mu-\sigma,\pi-C{\equiv}CPh)(\mu-^tBuS)Fe_2(CO)_6$, 5a, and degassed by three evacuation/nitrogen-backfill cycles. The flask was then charged with 30 ml of THF and 0.21 ml (2.00 mmol) of diethylamine by syringe at room temperature. After the reaction mixture had been stirred for 20 h at room temperature, the solvent was removed in vacuo and the resulting deep red oil was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Pentane/CH_2Cl_2 (3/1 v/v) eluted a pale yellow band which was not collected and a purple band which gave 0.71 g (1.32 mmol, 71%) of $(\mu-HC-C(Ph){=}NEt_2)(\mu-^tBuS)Fe_2(CO)_6$, 14, (a mixture of two inseparable isomers), as an air-stable, deep red solid, mp 117.0 - 119.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{22}H_{25}Fe_2O_6NS$: C, 48.64; H, 4.64 %. Found: C, 48.79; H, 4.71 %.

IR($CHCl_3$): 2980m, 2965m, 2940m, 2930m, 2900w, 2880w, 1505vs(C=N), 1495s(C=N), 1472s, 1468s, 1445s, 1388s, 1370s, 1355s, 1340s, 1325s, 1265s, 1165s, 1098w, 1075m, 1030vw, 995w, 980w, 865w, 620s, 600s cm^{-1}.
Terminal carbonyl region (pentane): 2050s, 2010vs, 1970s, 1960s, 1950m cm^{-1}.

^{1}**H NMR**(CD_2Cl_2; 250 MHz): δ 0.99 (s, 9H, $SC(CH_3)_3$ minor isomer), 1.05 (t, J = 7.06 Hz, 6H, $CH_2C\underline{H}_3$ both isomers), 1.30 (t, J = 7.11 Hz, 6H, $CH_2C\underline{H}_3$ both isomers), 1.39 (s, 9H, $SC(CH_3)_3$ major isomer), 1.42 (s, 1H, Fe_2CH - endo - major isomer), 3.01 (q, J = 7.12 Hz, 4H, $C\underline{H}_2CH_3$ both isomers), 3.54 (q, J = 7.14 Hz, 4H, $C\underline{H}_2CH_3$ both isomers), 3.92 (s, 1H, Fe_2CH - endo - minor isomer), 7.23 - 7.43 (m, 10H, C_6H_5 both isomers). Ratio major/minor = 1.4/1.0

^{13}**C NMR**($CDCl_3$; 67.9 MHz): δ 11.71 (q, J = 132.0 Hz, $CH_2\underline{C}H_3$ both isomers), 13.66 (q, J = 131.8 Hz, $CH_2\underline{C}H_3$ both isomers), 32.57 (q, J = 127.4 Hz, $SC(\underline{C}H_3)_3$ minor isomer), 33.47 (q, J = 126.8 Hz, $SC(\underline{C}H_3)_3$ major isomer), 45.37 (t, J = 138.4 Hz, $\underline{C}H_2CH_3$ both isomers), 48.18 (t, J = 134.7 Hz, $\underline{C}H_2CH_3$ major isomer), 48.53 (t, J = 140.0 Hz, $\underline{C}H_2CH_3$ minor isomer), 63.78 (d, J = 133.8 Hz, Fe_2CH minor isomer), 74.95 (d, J = 134.4 Hz, Fe_2CH major isomer), 124.85 - 131.31 (m, C_6H_5), 136.31 (s, ipso C_6H_5 minor isomer), 137.37 (s, ipso C_6H_5 major isomer), 198.12 (s, $Et_2N=\underline{C}Ph$ major isomer), 200.96 (s, $Et_2N=\underline{C}Ph$ minor isomer), 214.28 and 214.71 (both s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 543 (M^+, 7), 487 (M^+ - 2CO, 7), 459 (M^+ - 3CO, 16), 431 (M^+ -

4CO, 9), 403 (M^+ - 5CO, 20), 375 (M^+ - 6CO, 100), 347 (M^+ - 6CO - C_2H_4, 6), 319 ($HSFe_2CHC(Ph)=NEt_2$, 63), 291 ($HSFe_2CHC(Ph)=NHEt$, 34), 263 ($HSFe_2CHC(Ph)=NH_2$, 7), 247 ($HSFe_2CHCPh$, 19), 221 (Fe_2SPh, 21), 185 ($SFe_2CHC=NH_2$, 20), 174 ($Et_2N=C(Ph)CH$, 27), 145 ($HSFe_2$, 16), 144 (SFe_2, 37), 105 ($PhC=NH_2$, 16), 104 (PhC=NH, 21), 103 (PhC=N, 19), 77 (Ph, 13), 57 (^{t}Bu, 37), 56 (Fe, 17).

Reaction of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$ with $PhNH_2$ JBH-62-VI

In an experiment similar to the reaction of 5a with diethylamine, a THF solution containing 0.94 g (2.00 mmol) of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$, 5a, and 0.18 ml (2.00 mmol) of aniline was stirred for 20 h at room temperature. Removal of the solvent in vacuo left a red oil which was purified by filtration chromatography. Pentane eluted a pale yellow band which was not collected. Pentane/CH_2Cl_2 (9/1 v/v) eluted a red band which gave 0.97 g (1.72 mmol, 86%) of (μ-$CH_2C(Ph)=NPh$)(μ-^{t}BuS)$Fe_2(CO)_6$, 15, as an air-stable, red solid, mp 118.0 - 121.0°C (dec) after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{24}H_{21}Fe_2O_6NS$: C, 51.18; H, 3.76 %. Found: C, 51.22; H, 3.78 %.

IR(CCl_4): 3090w, 3070w, 3035w, 3015w, 2970m, 2945m, 2930m, 2900m, 2870m, 1610m(Ph or C=N), 1595s(Ph or C=N), 1490s, 1475m, 1460m, 1445m, 1390w, 1370m, 1330vw, 1265s, 1210vw, 1160s, 1077w, 1057w, 1030m, 1000vw, 910w, 885vw, 865vw, 760vs, 615vs, 605vs, 575vs cm^{-1}.
Terminal carbonyl region (pentane): 2065s, 2025vs, 1988vs, 1967m cm^{-1}.

^{1}H NMR(CD_2Cl_2; 300 MHz): δ 1.56 (s, 9H, $SC(CH_3)_3$), 1.89 and 2.02 (AB quartet, J = 18.31 Hz, 2H, $FeCH_2$), 6.68 - 7.14 (m, 10H, C_6H_5).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 26.37 (t, J = 131.5 Hz, $FeCH_2$), 34.39 (q, J = 126.8 Hz, $SC(\underline{C}H_3)_3$), 48.18 (s, $S\underline{C}(CH_3)_3$), 121.09 - 129.77 (m, C_6H_5), 140.51 (s, ipso C_6H_5), 154.99 (s, ipso C_6H_5), 198.00 (s, C=N), 209.93, 210.99, 211.78, and 218.06 (all s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 563 (M^+, 0.3), 535 (M^+ - CO, 0.1), 507 (M^+ - 2CO, 13), 479 (M^+ - 3CO, 5), 451 (M^+ - 4CO, 2), 423 (M^+ - 5CO, 17), 395 (M^+ - 6CO, 44), 339 ($HSFe_2CH_2C(Ph)=NPh$, 75), 235 (SFe_2NPh, 12), 221 ($PhSFe_2$, 14), 195 (MeC(Ph)=NPh, 53), 180 (PhC=NPh, 100), 144 (Fe_2S, 26), 77 (Ph, 83), 57 (^tBu, 22), 56 (Fe, 14).

Reaction of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$ with ^{t}BuNH$_2$ JBH-74-VI

In an experiment similar to the reaction of 5a with diethylamine, a THF solution containing 0.97 g (2.07 mmol) of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$, 5a, and 0.32 ml (3.00 mmol) of t-butylamine was stirred for 1 h at -78°C and then 18 h at room temperature. Removal of the solvent in vacuo left a brown oil which was purified by filtration chromatography. Pentane/CH_2Cl_2 (9/1 v/v) eluted an orange band which gave 0.23 g (0.50 mmol, 48% based on S) of (μ-^{t}BuS)$_2Fe_2(CO)_6$, 17, identified by its ^1H NMR spectrum.[1] Pentane/CH_2Cl_2 (9/1 v/v) then eluted a second orange band which gave 0.44 g (0.77 mmol, 37%) of (μ-HC(=C(Ph)NH^{t}Bu)C=O)(μ-^{t}BuS)$Fe_2(CO)_6$, 16, (a mixture of two inseparable isomers) as an air-stable, red solid mp 138°C (dec) after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{23}H_{25}Fe_2O_7NS$: C, 48.36 ; H, 4.41 %. Found: C, 48.03; H, 4.56 %.

IR(CCl_4): 3240vw-br(NH), 3065vw, 2975m, 2940m, 2925m, 2900w, 2870w, 1610m(C=C), 1585sh(acyl C=O), 1573vs(acyl C=O), 1512m(Ph), 1475s, 1460s, 1445sh, 1400m, 1370s, 1308vs, 1265m, 1240m, 1200vs, 1160m, 1080s, 1037w, 1003w, 980w, 920w, 850m, 705m, 652m, 625sh, 595s, 565sh cm^{-1}. Terminal carbonyl region (pentane): 2070m, 2030vs, 2000s, 1987s, 1965m cm^{-1}.

^{1}**H NMR**(acetone-d_6; 300 MHz): 1.037 (s, 9H, $NC(CH_3)_3$ minor isomer), 1.044 (s, 9H, $NC(CH_3)_3$ major isomer), 1.47 (s, 9H, $SC(CH_3)_3$ major isomer), 1.55 (s, 9H, $SC(CH_3)_3$ minor isomer), 4.93 (s, 1H, $\underline{H}C{=}CPh$ minor isomer), 5.14 (s, 1H, $\underline{H}C{=}CPh$ major isomer), 6.96 - 7.48 (m, 10H, C_6H_5 both isomers), 9.49 (broad s, 1H, NH minor isomer), 9.55 (s, 1H, NH major isomer). Ratio major/minor = 1.5/1.0.

^{13}**C NMR**($CDCl_3$; 67.9 MHz): δ 31.36 (q, J = 126.8 Hz, $NC(\underline{C}H_3)_3$ both isomers), 34.32 (q, J = 127.8 Hz, $SC(\underline{C}H_3)_3$ both isomers), 47.45 (s, $S\underline{C}(CH_3)_3$ minor isomer), 48.67 (s, $S\underline{C}(CH_3)_3$ major isomer), 54.41 (s, $N\underline{C}(CH_3)_3$ both isomers), 113.94 (d, J = 168.2 Hz, $H\underline{C}{=}CPh$ minor isomer), 114.55 (d, J = 167.6 Hz, $H\underline{C}{=}CPh$ major isomer), 127.77 (d, J = 162.8 Hz, C_6H_5), 128.19 (d, J = 164.4 Hz, C_6H_5), 129.21 (d, J = 158.9 Hz, C_6H_5), 135.69 (s, ipso C_6H_5), 156.45 (s, $HC{=}\underline{C}Ph$ major isomer), 157.64 (s, $HC{=}\underline{C}Ph$ minor isomer), 207.32, 210.83, 211.68, 213.05, and 214.24 (all s, Fe-CO both isomers), 253.41 (s, acyl C=O minor isomer), 257.19 (s, acyl C=O major isomer).

Mass Spectrum (EI); m/z (relative intensity): 571 (M^+, 4), 543 (M^+ - CO, 4), 515 (M^+ - 2CO, 7), 487 (M^+ - 3CO, 15), 459 (M^+ - 4CO, 8), 431 (M^+ - 5CO, 17), 403 (M^+ - 6CO, 47), 375 (M^+ - 7CO, 22), 347 ($HSFe_2HC(=C(Ph)NH^tBu)C{=}O$, 100), 319 ($HSFe_2HC{=}C(Ph)NH^tBu$, 28), 291 ($HSFe_2HC(=C(Ph)NH_2)C{=}O$, 23), 263 ($HSFe_2HC{=}C(Ph)NH_2$, 55), 221 ($PhSFe_2$, 27), 202 ($HC(=C(Ph)NH^tBu)C{=}O$, 33), 185 ($HSFe_2C{=}CNH_2$, 19), 145 ($HSFe_2$, 13), 144 ($SFe_2$, 41), 104 (PhCNH, 44), 57 (^{t}Bu, 65), 56 (Fe, 16).

Reaction of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$ with PPh_3 JBH-74-IV

In an experiment similar to the reaction of 5a with diethylamine, a THF solution containing 4.42 g (9.41 mmol) of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$, 5a, and 2.53 g (9.64 mmol) of triphenylphosphine was stirred for 1 h at room temperature. Removal of the solvent in vacuo left a purple, foamy solid which was purified by filtration chromatography. Pentane eluted a pale brownish-yellow band which was not collected. Pentane/CH_2Cl_2 (4/1 v/v) eluted dark purple and purple-red bands which were collected together. Repeated filtration chromatography achieved a satisfactory separation between the two. However, the second product converted readily to the first during chromatographic workup. Subsequently, the residue from the second band was extracted with pentane to yield a purplish solution (first product) and an insoluble orange solid (second product). Ultimately, the first band yielded 3.90 g (5.54 mmol, 57%) of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_5(PPh_3)$, 19 (a mixture of two inseparable isomers), as an air-stable, purple solid, mp 145.0°C (dec) after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{35}H_{29}Fe_2O_5PS$: C, 59.68; H, 4.15 %. Found: C, 59.32; H, 4.21 %.

IR($CHCl_3$): 3070m, 2977w, 2955w, 2938w, 2908w, 2878vw, 1599m(Ph), 1576w(Ph), 1485vs, 1461m, 1435vs, 1395vw, 1368s, 1311vw, 1185vw, 1160s, 1092vs, 1072vw, 1028vw, 1001w, 630s, 619vs, 608vs, 580vs, 515vs cm^{-1}.
Terminal carbonyl region (pentane): 2050vs, 2001vs, 1992s, 1972m, 1952w cm^{-1}.

^{1}H NMR(CD_2Cl_2; 250 MHz): δ 1.04 (s, 9H, $SC(CH_3)_3$ minor isomer), 1.08 (s, 9H, $SC(CH_3)_3$ major isomer), 7.11 - 7.78 (m, 40H, C_6H_5 both isomers). Ratio major/minor = 8.5/1.0

^{13}C **NMR**(CD_2Cl_2; 67.9 MHz): δ 33.43 (q, J = 128.0 Hz, SC($\underline{C}H_3$)$_3$ major isomer), 34.14 (q, J = 125.2 Hz, SC($\underline{C}H_3$)$_3$ minor isomer), 47.87 (s, S$\underline{C}$(CH_3)$_3$), 97.13 (s, acetylide C), 125.68 - 136.80 (m, C_6H_5), 212.52, 215.59, 215.76, 216.40, and 216.57 (all s, Fe-CO).

^{31}P **NMR**(CD_2Cl_2; 36.2 MHz): δ 62.72 (s, PPh_3 major isomer), 65.41 (s, PPh_3 minor isomer).

Mass Spectrum (FD); m/z (relative intensity): 704 (M^+)

Ultimately, the second band yielded 1.86 g (2.54 mmol, 26%) of (μ-Ph_3PC=CPh)(μ-^{t}BuS)$Fe_2(CO)_6$, $\underline{18}$, as an air-stable, orange solid, mp 108.0 - 115.0°C (dec) after recrystallization from pentane/CH_2Cl_2.

IR($CHCl_3$): 3070w, 2973w, 2957w, 2937w, 2910w, 2867vw, 1599w(Ph), 1580vw(Ph), 1500vs, 1473vs, 1440vs, 1392vw, 1367w, 1320vw, 1267vw, 1185vw, 1160s, 1104s, 1073vw, 1030vw, 1002w, 895w, 640vs, 631vs, 611vs, 599vs, 510vs cm^{-1}. Terminal carbonyl region (pentane): 2085vw, 2050m, 2009vs, 1975m, 1962m, 1945w cm^{-1}.

^{1}H **NMR**(CD_2Cl_2; 90 MHz): δ 1.37 (s, 9H, SC(CH_3)$_3$), 6.72 - 7.80 (m, 20H, C_6H_5).

^{13}C **NMR**(CD_2Cl_2; 67.9 MHz): δ 33.89 (q, J = 126.7 Hz, SC($\underline{C}H_3$)$_3$), 45.80 (s, S$\underline{C}$(CH_3)$_3$), 118.72 - 136.10 (m, C_6H_5), 145.31 (d, J_{PC} = 20.4 Hz, $Ph_3P\underline{C}$=CPh), 214.30 and 214.71 (both s, Fe-CO), 292.41 (s, Ph_3PC=$\underline{C}$Ph).

^{31}P **NMR**(CD_2Cl_2; 36.2 Hz): δ 0.54 (s, PPh_3).

Mass Spectrum (FD); m/z (relative intensity): 732 (M^+).

Decarbonylation of (μ-$Ph_3PC{=}CPh$)(μ-^tBuS)$Fe_2(CO)_6$ JBH-8-V

A 100 ml round-bottomed flask equipped with a stir-bar and rubber septum was charged with 0.17 g (0.24 mmol) of (μ-$Ph_3PC{=}CPh$)(μ-^tBuS)$Fe_2(CO)_6$, 18, and degassed by three evacuation/nitrogen-backfill cycles. Subsequently, 30 ml of THF was added by syringe. After the reaction mixture had been stirred for 90 h at room temperature, the solvent was removed in vacuo, and the resulting purple tar was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Pentane/CH_2Cl_2 (5/1 v/v) eluted a dark purple band which gave 0.15 g (0.21 mmol, 88%) of (μ-σ,π-$C{\equiv}CPh$)(μ-^tBuS)$Fe_2(CO)_5PPh_3$, 19, identified by its ^1H and ^{31}P NMR spectra.

Reaction of (μ-σ,π-$C{\equiv}CSiMe_3$)(μ-^tBuS)$Fe_2(CO)_6$ with $Co_2(CO)_8$ JBH-60-VII

A 100 ml round-bottomed flask equipped with a stir-bar and rubber septum was charged with 0.68 g (1.46 mmol) of (μ-σ,π-$C{\equiv}CSiMe_3$)(μ-^tBuS)$Fe_2(CO)_6$, 5c, degassed by three evacuation/nitrogen-backfill cycles, and charged with 10 ml of THF by syringe. To the resulting red solution was added, by cannula at room temperature, a THF solution (15 ml) containing 1.01 g (2.95 mmol) of dicobalt octacarbonyl. After the reaction mixture had been stirred for 72 h at room temperature, the solvent was removed in vacuo and the resulting dark oil was purified by filtration chromatography. Hexane eluted a purplish-red band which gave 0.66 g (1.26 mmol, 87%) of (μ_3,η^2-$C{\equiv}CSiMe_3$)$CoFe_2(CO)_9$, 20a, as an air-stable, black solid, mp 116.0 - 117.0°C after recrystallization from pentane.

Anal. Calcd. for $C_{14}H_9CoFe_2O_9Si$: C, 32.34; H, 1.74 %. Found: C, 32.23; H, 1.74 %.

IR(CCl_4): 2960w, 2900vw, 1663s(C≡C), 1410w, 1268w, 1253m, 850vs, 700w, 652m, 607vs, 570s, 520s cm^{-1}.

Terminal carbonyl region (pentane): 2095w, 2055vs, 2045vs, 2020s, 2005m, 1985w cm^{-1}.

^{1}H NMR(CDCl$_3$; 300 MHz): δ 0.47 (s, Si(CH$_3$)$_3$).

^{13}C NMR(CDCl$_3$; 100.5 MHz): δ 1.05 (q, J = 120.8 Hz, Si(CH$_3$)$_3$), 97.43 (s, $C{\equiv}\underline{C}SiMe_3$), 202.60 (s, $\underline{C}{\equiv}CSiMe_3$), 209.35 and 211.34 (both s, CO).

Mass Spectrum (EI); m/z (relative intensity): 520 (M$^+$, 12), 492 (M$^+$ - CO, 13), 464 (M$^+$ - 2CO, 14), 436 (M$^+$ - 3CO, 26), 408 (M$^+$ - 4CO, 15), 380 (M$^+$ - 5CO, 100), 352 (M$^+$ - 6CO, 46), 324 (M$^+$ - 7CO, 39), 296 (M$^+$ - 8CO, 33), 268 (M$^+$ - 9CO, 75), 212 (FeCoC≡CSiMe$_3$, 12), 156 (CoC≡CSiMe$_3$, 8), 115 (FeCo, 4), 97 (C≡CSiMe$_3$, 4), 73 (SiMe$_3$, 12), 59 (Co, 19), 56 (Fe, 4).

Hexane/CH$_2$Cl$_2$ then eluted a dark purple band which was not collected.

Reaction of (μ-σ,π-C≡CPh)(μ-^{t}BuS)Fe$_2$(CO)$_6$ with Co$_2$(CO)$_8$

JBH-57-VII

In an experiment similar to the reaction of 5c with dicobalt octacarbonyl, a THF solution containing 0.68 g (1.45 mmol) of (μ-σ,π-C≡CPh)(μ-^{t}BuS)Fe$_2$(CO)$_6$, 5a, and 1.03 g (3.01 mmol) of dicobalt octacarbonyl was stirred for 22 h at room temperature. Removal of the solvent in vacuo left a black oil which was purified by filtration chromatography. Hexane eluted a brown-red band which was unstable in air and was not collected. Hexane/CH$_2$Cl$_2$ (7/1 v/v) eluted a purplish-black band which gave 0.72 g (0.98 mmol, 68%) of (μ_4-C≡CPh)(μ-^{t}BuS)(μ-CO)Co$_2$Fe$_2$(CO)$_{10}$, 21a (a mixture of two inseparable isomers), as an air-stable, black solid, mp 118°C (dec) after recrystallization from pentane/CH$_2$Cl$_2$.

Anal. Calcd. for $C_{23}H_{14}Co_2Fe_2O_{11}S$: C, 37.95; H, 1.94 %. Found: C, 38.07; H, 2.06 %.

IR(CCl_4): 3090vw, 3075vw, 3040vw, 3010w, 2980m, 2945m, 2935m, 2905m, 2870w, 1850vs(μ-CO), 1620m(C=C), 1600vw(Ph), 1580vw(Ph), 1485m, 1472m, 1460s, 1445m, 1397m, 1368s, 1330vw, 1305vw, 1155s, 692m, 610vs, 600vs cm^{-1}. Terminal carbonyl region (pentane): 2090w, 2060s, 2040vs, 2025s, 2015s, 2010w, 2000w, 1995w, 1985w, and 1885w(μ-CO) cm^{-1}.

^{1}**H NMR**(CD_2Cl_2; 250 MHz): δ 1.53 (s, 9H, $SC(CH_3)_3$ major isomer), 1.56 (s, 9H, $SC(CH_3)_3$ minor isomer), 7.46 - 7.75 (m, 10H, C_6H_5 both isomers). Ratio major/minor = 1.7/1.0

^{13}**C NMR**(CD_2Cl_2; 75.4 MHz): δ 33.25 (q, J = 127.0 Hz, $SC(\underline{C}H_3)_3$ both isomers), 47.92 (s, $S\underline{C}(CH_3)_3$ major isomer), 48.05 (s, $S\underline{C}(CH_3)_3$ minor isomer), 127.71 - 131.62 (m, C_6H_5), 133.60 (s, ipso C_6H_5), 139.23, 144.27, 148.63, and 152.21 (all s, alkynyl C), 200.38, 206.10, 208.75, 210.59, 211.19, and 219.50 (all s, CO), 232.84 (s, μ-CO).

Mass Spectrum (FD); m/z (relative intensity): 727 (M^+ - H).

Reaction of (μ-σ,π-C≡C^tBu)(μ-^tBuS)$Fe_2(CO)_6$ with $Co_2(CO)_8$

JBH-8-VIII

In an experiment similar to the reaction of 5c with dicobalt octacarbonyl, a THF solution containing 0.68 g (1.51 mmol) of (μ-σ,π-C≡C^tBu)(μ-^tBuS)$Fe_2(CO)_6$, 5b, and 1.06 g (3.10 mmol) of dicobalt octacarbonyl was stirred for 72 h at room temperature. Removal of the solvent in vacuo left a dark oil which was purified by filtration chromatography. Hexane eluted a purplish-red band which gave 0.95 g of a purple-red solid identified by its ^{1}H NMR and mass spectra to be a mixture of (μ_3-S)$Co_2Fe(CO)_9$ and (μ_3,η^2-C≡C^tBu)$CoFe_2(CO)_9$, 20b. Fractional recrystallization from pentane/CH_2Cl_2 yielded 0.33 g (0.67 mmol, 44%) of analytically pure (μ_3,η^2-C≡C^tBu)$CoFe_2(CO)_9$, 20b, as an air-stable, black solid, mp 156.0 - 157.0°C.

Anal. Calcd. for $C_{15}H_9CoFe_2O_9$: C, 35.75; H, 1.80 %. Found: C, 35.91; H, 1.90 %.

IR(CCl_4): 2970m, 2945w, 2930w, 2900w, 2862w, 1680w(C≡C), 1470m, 1460m, 1390w, 1360m, 1255w, 1230m, 885m, 680w, 608vs, 570s, 530s cm^{-1}.
Terminal carbonyl region (pentane): 2090s, 2050vs, 2040vs, 2020vs, 2000s, 1980s cm^{-1}.

^{1}H NMR($CDCl_3$; 300 MHz): δ 1.56 (s, $C(CH_3)_3$).

^{13}C NMR($CDCl_3$; 100.5 MHz): δ 33.80 (q, J = 126.6 Hz, $C(\underline{C}H_3)_3$), 36.83 (s, $\underline{C}(CH_3)_3$), 130.15 (s, C≡$\underline{C}^t$Bu), 184.11 (s, $\underline{C}$≡C^tBu), 209.51 and 211.47 (both s, CO).

Mass Spectrum (EI); m/z (relative intensity): 504 (M^+, 15), 476 (M^+ - CO, 13), 448 (M^+ - 2CO, 10), 420 (M^+ - 3CO, 25), 392 (M^+ - 4CO, 19), 364 (M^+ - 5CO, 100), 336 (M^+ - 6CO, 44), 308 (M^+ - 7CO, 39), 280 (M^+ - 8CO, 35), 252 (M^+ - 9CO, 65), 196 (Fe_2CoC≡CH, 17), 140 (CoFeC≡CH, 19), 115 (FeCo, 14), 112 (Fe_2, 5), 56 (Fe, 8).

Pentane/CH_2Cl_2 (5/1 v/v) then eluted a purple-black band which gave 0.32 g (0.45 mmol, 30%) of (μ_4-C≡C^tBu)(μ-^{t}BuS)(μ-CO)$Co_2Fe_2(CO)_{10}$, 21b, as an air-stable, black solid, mp 108.0 - 123.0°C (dec) after recrystallization from pentane.

Anal. Calcd. for $C_{21}H_{18}Co_2Fe_2O_{11}S$: C, 35.63; H, 2.56 %. Found: C, 35.77; H, 2.67 %.

IR(CCl_4): 2970m, 2930m, 2895w, 2860w, 1843vs(μ-CO), 1473m, 1458m, 1392m, 1365s, 1217w, 1153s, 872m, 640m, 616vs, 601vs, 537vs, 517vs cm^{-1}.
Terminal carbonyl region (pentane): 2080vw, 2055vs, 2035vs, 2020vs, 2010sh, 2002w, 1978w, and 1847w(μ-CO) cm^{-1}.

^1H NMR(CD_2Cl_2; 300 MHz): δ 1.49 (s, $C(CH_3)_3$, 9H minor isomer), 1.56 (s, 9H, $C(CH_3)_3$ major isomer), 1.64 (s, 9H, $C(CH_3)_3$ minor isomer), 1.72 (s, 9H, $C(CH_3)_3$ major isomer). Ratio major/minor = 19.0/1.0

^{13}C NMR(CD_2Cl_2; 67.9 MHz): δ 33.15 (q, J = 127.1 Hz, $C(\underline{C}H_3)_3$), 33.82 (q, J = 121.1 Hz, $C(\underline{C}H_3)_3$), 39.22 (s, $\underline{C}(CH_3)_3$), 48.36 (s, $S\underline{C}(CH_3)_3$), 148.22 and 151.20 (s, alkynyl C), 202.80, 206.73, 209.25, and 211.78 (all s, CO), 233.21 (s, μ-CO).

Mass Spectrum (EI); m/z (relative intensity): 708 (M^+, 1), 680 (M^+ - CO, 10), 652 (M^+ - 2CO, 22), 624 (M^+ - 3CO, 19), 596 (M^+ - 4CO, 17), 568 (M^+ - 5CO, 21), 540 (M^+ - 6CO, 37), 512 (M^+ - 7CO, 70), 484 (M^+ - 8CO, 41), 456 (M^+ - 9CO, 21), 428 (M^+ - 10CO, 11), 400 (M^+ - 11CO, 37), 344 ($HSFe_2Co_2C{\equiv}C^tBu$, 53), 288 ($HSFe_2Co_2C{\equiv}CH$, 12), 343 ($SFe_2Co_2C{\equiv}C^tBu$, 11), 287 ($SFe_2Co_2C{\equiv}CH$, 13), 81 ($C{\equiv}C^tBu$, 12), 57 (^tBu, 80), 56 (Fe, 57).

Reaction of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$ with $Fe_2(CO)_9$

JBH-19-VII

A 100 ml round-bottomed flask equipped with a stir-bar and rubber septum was charged with 0.81 g (1.73 mmol) of (μ-σ,π-C≡CPh)(μ-^{t}BuS)$Fe_2(CO)_6$, 5a, and 1.27 g (3.49 mmol) of diiron nonacarbonyl and then degassed by three evacuation/nitrogen-backfill cycles. Subsequently, 30 ml of toluene was added by syringe. An immediate reaction ensued with slow gas evolution and a gradual color change to brown-green. After the reaction mixture had been stirred for 40 h at room temperature, the solvent was removed in vacuo and the resulting dark oil was purified by column chromatography (gravity column) under nitrogen. Hexane eluted a dark green band which gave 0.96 g (1.57 mmol, 91%) of (μ_3-C≡CPh)(μ-^{t}BuS)$Fe_3(CO)_9$, 22, as a dark green, air-stable, solid, mp 88.0 - 92.0°C after recrystallization from pentane.

Anal. Calcd. for $C_{21}H_{14}Fe_3O_9S$: C, 41.35; H, 2.31 %. Found: C, 41.36; H, 2.42 %.

IR(CCl_4): 3075w, 3060w, 3000w, 2965m, 2935m, 2920m, 2895m, 2860w, 1590w(Ph), 1565m, 1475m, 1458m, 1442m, 1392w, 1365s, 1260m, 1160s, 1070w, 690s, 625vs, 605vs, 590vs cm^{-1}. Terminal carbonyl region (pentane): 2070m, 2040vs, 2025vs, 2005vs, 1995vs, 1978s, 1970m cm^{-1}.

^{1}**H NMR**(CD_2Cl_2; 300 MHz): δ 1.27 (s, 9H, $SC(CH_3)_3$ minor isomer), 1.58 (s, 9H, $SC(CH_3)_3$ major isomer), 7.63 - 8.12 (m, 10H, C_6H_5 both isomers). Ratio major/minor = 8.0/1.0

^{13}**C NMR**(CD_2Cl_2; 67.9 MHz): δ 32.76 (q, J = 127.8 Hz, $SC(\underline{C}H_3)_3$ major isomer), 33.20 (q, J = 127.5 Hz, $SC(\underline{C}H_3)_3$ minor isomer), 49.32 (s, $S\underline{C}(CH_3)_3$), 127.33 - 133.22 (m, C_6H_5), 139.23 (s, ipso C_6H_5), 201.24 (s, $Fe_3\underline{C}$≡CPh), 211.38 (s, Fe-CO), 228.61 (s, Fe_3C≡$\underline{C}$Ph).

Mass Spectrum (EI); m/z (relative intensity): 610 (M^+, 1), 582 (M^+ - CO, 7), 554 (M^+ - 2CO, 21), 526 (M^+ - 3CO, 4), 498 (M^+ - 4CO, 18), 470 (M^+ - 5CO, 43), 442 (M^+ - 6CO, 12), 414 (M^+ - 7CO, 37), 386 (M^+ - 8CO, 55), 358 (M^+ - 9CO, 16), 302 ($HSFe_3C$≡CPh, 100), 301 (SFe_3C≡CPh, 25), 246 ($HSFe_2C$≡CPh, 20), 245 (SFe_2C≡CPh, 36), 276 ($HSFe_3Ph$, 20), 224 (SFe_3C≡C, 6), 200 (SFe_3, 13), 189 (SFeC≡CPh, 14), 144 (SFe_2, 17), 102 (PhC≡CH, 15), 57 (^{t}Bu, 28), 56 (Fe, 19).

Reaction of $(\mu\text{-}\sigma,\pi\text{-C}\equiv\text{C}^t\text{Bu})(\mu\text{-}^t\text{BuS})\text{Fe}_2(\text{CO})_6$ with $\text{Fe}_2(\text{CO})_9$

JBH-27-VII

In an experiment similar to the reaction of 5a with diiron nonacarbonyl, a toluene solution containing 0.98 g (2.17 mmol) of $(\mu\text{-}\sigma,\pi\text{-C}\equiv\text{CtBu})(\mu\text{-}^t\text{BuS})\text{Fe}_2(\text{CO})_6$, 5b, and 1.57 g (4.31 mmol) of diiron nonacarbonyl was stirred for 34 h at room temperature. Removal of the solvent in vacuo left a dark oil which was purified by column chromatography under nitrogen. Hexane eluted brownish-red and dark green bands which were contiguous. The best separation possible was made. The brownish-red band was not collected while the dark green band gave 1.22 g of a greenish, oily solid. (After this greenish, oily solid had been dried in vacuo for several hours, it had changed color to red.) Recrystallization from pentane yielded 0.65 g (1.10 mmol, 51%) of $(\mu_3,\eta^2\text{-C}\equiv\text{C}^t\text{Bu})(\mu\text{-}^t\text{BuS})\text{Fe}_3(\text{CO})_9$, 23, as an air-stable, red solid, mp 91.0 - 98.0°C. When in solution, this red compound converts partially to a green product, possibly of type 22, identified by TLC. However, when the solvent is removed in vacuo, a red compound again remains. Although the solid state structure is that shown in Eq. 21, in solution both structures of type 22 and 23 may be in equilibrium. Consequently, the IR and NMR spectra reflect the presence of both of these isomers in solution.

Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{Fe}_3\text{O}_9\text{S}$: C, 38.68; H, 3.08 %. Found: C, 38.72; H, 3.03 %.

IR(CCl_4): 2970s, 2925m, 2895m, 2865m, 1710w(C≡C), 1470m, 1457m, 1392m, 1363s, 1225m, 1200w, 1155s, 872m, 610vs, 595vs, 558vs cm^{-1}.
Terminal carbonyl region (pentane): 2080m, 2045vs, 2025vs, 2010vs, 1988s, 1982sh, 1970m cm^{-1}.

^{1}H NMR(CD_2Cl_2; 300 MHz): δ 1.16 (s, 9H, $\text{C(CH}_3)_3$ first isomer), 1.52 (s, 9H, $\text{C(CH}_3)_3$ second isomer), 1.75 (s, 18H, $\text{C(CH}_3)_3$ both isomers).

^{13}C NMR(CD_2Cl_2; 67.9 MHz): δ 30.83 (q, J = 127.0 Hz, $C(\underline{C}H_3)_3$), 31.23 (q, J = 127.2 Hz, $C(\underline{C}H_3)_3$), 33.10 (q, J = 127.3 Hz, $C(\underline{C}H_3)_3$ - roughly twice the intensity of the other t-butyl resonances), 44.16 (s, $\underline{C}(CH_3)_3$), 45.95 (s, $\underline{C}(CH_3)_3$), 49.38 (s, $\underline{C}(CH_3)_3$), 149.49 (s, acetylide C), 202.40 (s, acetylide C), 211.50, 211.93, and 212.69 (all s, Fe-CO), 215.14 (s, acetylide C), 220.21 (s, acetylide C).

Mass Spectrum (EI); m/z (relative intensity): 590 (M^+, 1), 562 (M^+ - CO, 4), 534 (M^+ - 2CO, 12), 506 (M^+ - 3CO, 8), 478 (M^+ - 4CO, 7), 450 (M^+ - 5CO, 24), 422 (M^+ - 6CO, 16), 394 (M^+ - 7CO, 26), 366 (M^+ - 8CO, 38), 338 (M^+ - 9CO, 18), 282 ($HSFe_3C{\equiv}C^tBu$, 52), 226 ($HSFe_3C{\equiv}CH$, 52), 200 (SFe_3, 25), 169 ($HSFe_2C{\equiv}C$, 17), 144 (SFe_2, 15), 57 (^tBu, 50), 56 (Fe, 26).

Atempted Reaction Between (μ-σ,π-$C{\equiv}CSiMe_3$)(μ-^tBuS)$Fe_2(CO)_6$ and $Fe_2(CO)_9$ JBH-61-VII

In an experiment similar to JBH-19-VII, a toluene solution containing 0.72 g (1.56 mmol) of (μ-σ,π-$C{\equiv}CSiMe_3$)(μ-^tBuS)$Fe_2(CO)_6$, 5c, and 1.26 g (3.46 mmol) of diiron nonacarbonyl was stirred for 3 days at room temperature without any observable reaction by TLC. The reaction mixture was then heated at reflux for 1 h during which time decomposition of the reactants was observed.

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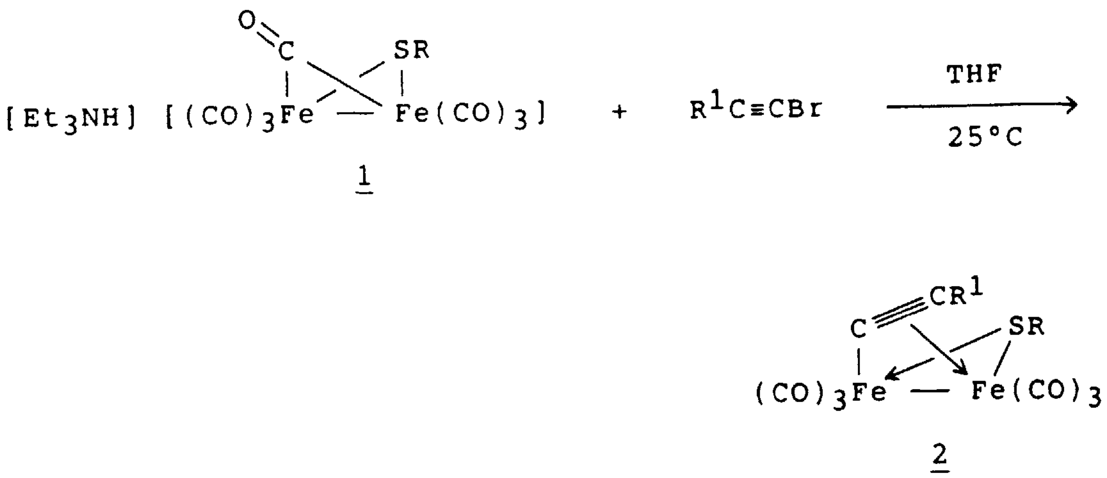
Chapter 3

"Reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with Acetylenes and α,β-Unsaturated Acid Chlorides"

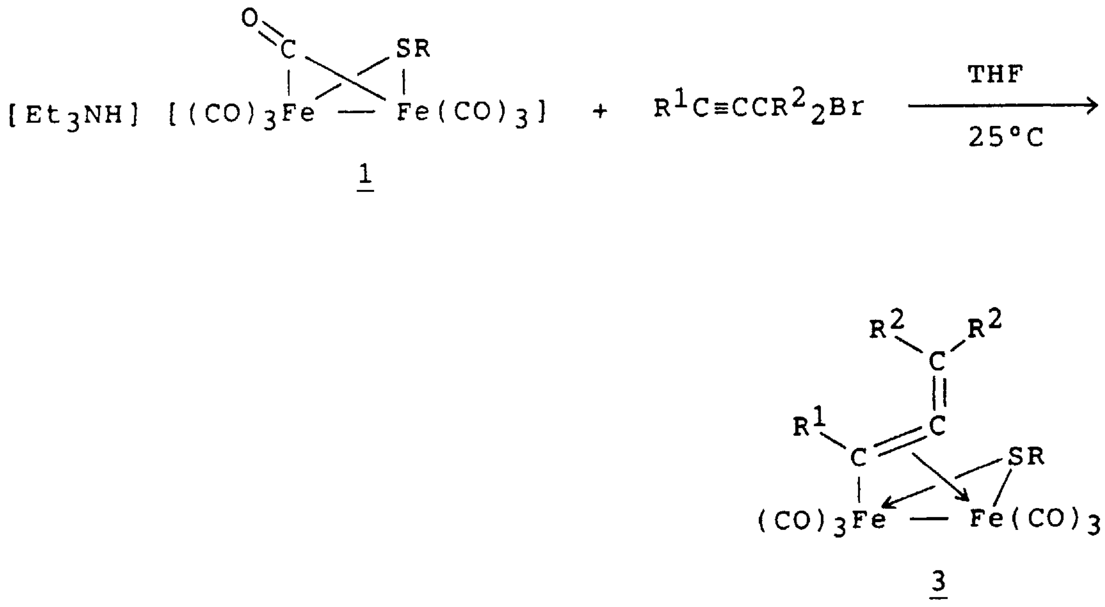
INTRODUCTION

As described in the previous chapter, reaction of α-bromoacetylenes, $R^1C{\equiv}CBr$, with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$, 1, generated, in good yields, the new bridging acetylide complexes $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR^1)(\mu\text{-}RS)Fe_2(CO)_6$, 2 (Eq. 1).



(1)

In related work, Womack has shown that reaction of propargylic halides, $R^1C{\equiv}CCR^2{}_2X$, with this salt produced bridging allenyl complexes of the type $(\mu\text{-}\sigma,\pi\text{-}R^1C{=}C{=}CR^2{}_2)(\mu\text{-}RS)Fe_2(CO)_6$, 3 (Eq. 2) also in good yields.[1] Due to our

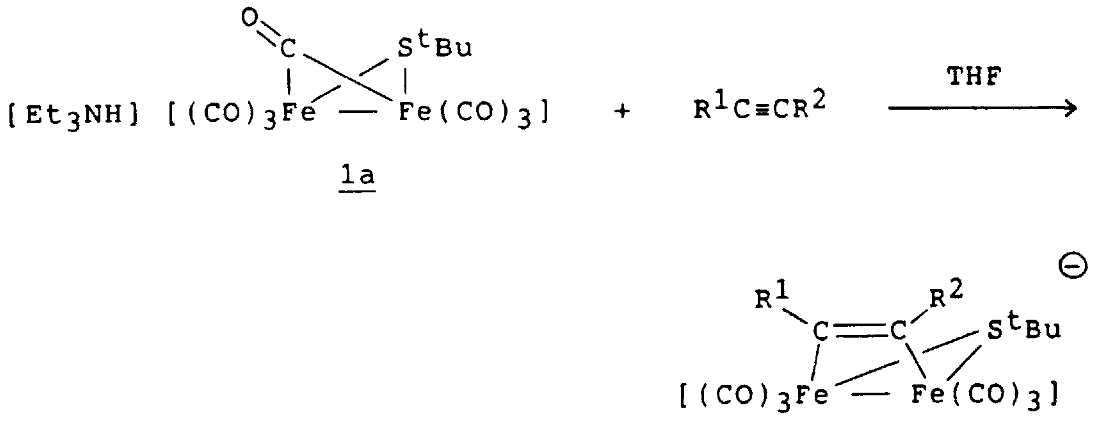


(2)

continuing emphasis on the synthesis of thiolate-bridged diiron complexes containing bridging organic ligands, it was of interest to extend the chemistry of these binuclear anions to include other acetylenes not containing reactive halide substituents. Surprisingly, the products isolated from these reactions required the presence of the triethylammonium cation of the salts.

RESULTS AND DISCUSSION

Reaction of [Et$_3$NH][(μ-CO)(μ-^{t}BuS)Fe$_2$(CO)$_6$], 1a, with alkyl- and arylacetylenes, R^{1}C≡CR^2, originally was envisioned to yield the anionic acetylene complexes [(μ-R^{1}C=CR^2)(μ-^{t}BuS)Fe$_2$(CO)$_6$]$^-$, 4, (Eq. 3). However, as

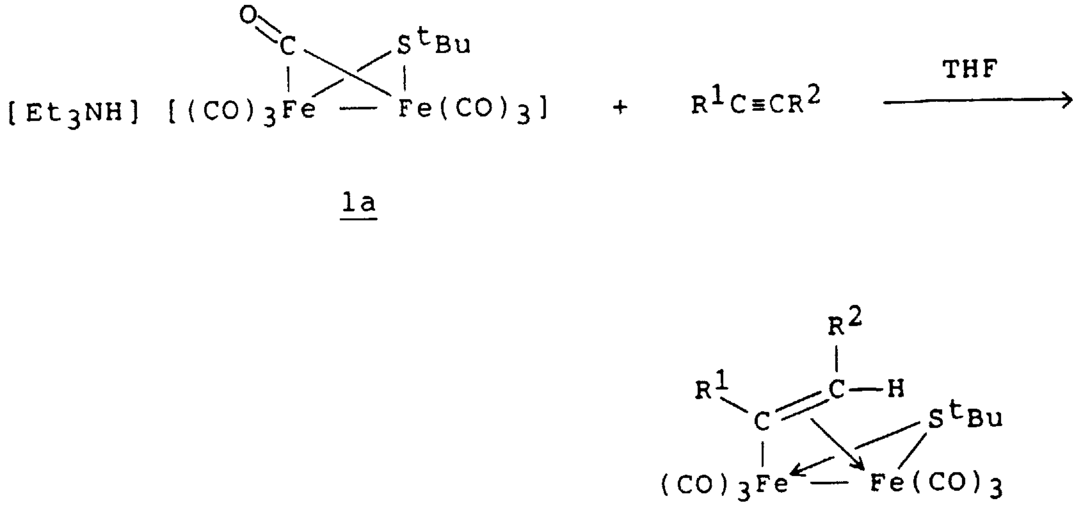


1a

4

(3)

initially discovered by Womack, these species were not obtained, but instead, neutral bridging vinyl complexes of the type (μ-σ,π-R^{1}C=C(H)R^2)(μ-^{t}BuS)Fe$_2$(CO)$_6$, 5, were isolated (Eq. 4).[16] Presumably, formation of these neutral μ-vinyl products results from the in-situ protonation of an intermediate, vinylic anion with the proton being supplied by the triethylammonium cation. In general, higher yields



1a

(4)

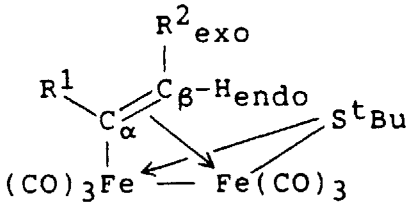
5

a	$EtOC{\equiv}CH$	R^1 = EtO	R^2 = H	84%
b	$MeO_2CC{\equiv}CCO_2Me$	R^1 = CO_2Me	R^2 = CO_2Me	67%
c	$MeC{\equiv}CCO_2Me$	R^1 = Me	R^2 = CO_2Me	60%
d	$HC{\equiv}CCO_2Me$	R^1 = H	R^2 = CO_2Me	61%
e	$HC{\equiv}CC(O)Me$	R^1 = H	R^2 = C(O)Me	28%
f	$PhC{\equiv}CPh$	R^1 = Ph	R^2 = Ph	42%
g	$HC{\equiv}CH$	R^1 = H	R^2 = H	20%

were obtained for the electrophilic acetylenes which reacted with 1a at room temperature. Conversely, reacton of diphenylacetylene and acetylene required reflux conditions under which 1 is not stable, and hence the yields of the corresponding μ-vinyl products, 5f and 5g, were somewhat lower. In the reactions of dimethyl acetylenedicarboxylate and 3-butyn-2-one, complexes of the type (μ-$R^1C{=}C(R^2)C(O)S$-$)Fe_2(CO)_6$, 6, also were isolated as unexpected by-products in 13 and 25% yields, respectively. As will be discussed in Chapter 4, formation of these species likely results from complex intramolecular rearrangements involving the thiolate, vinyl, and carbonyl ligands.

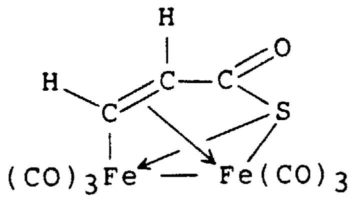
From the ^{1}H NMR data of 5 (Table 1), it has been determined that overall addition of the diiron and proton

Table 1: ^{1}H NMR Data for 5

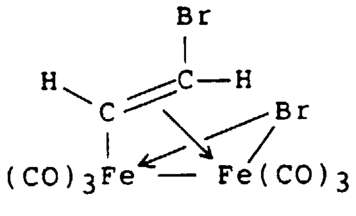


	R^1	R^2	$\delta_H(R^1)$	$\delta_H(R^2\text{-exo})$	δ_H(endo)
a	EtO	H		3.22 (d, J = 5.03 Hz)	2.02 (d, J = 5.02 Hz)
b	CO_2Me	CO_2Me			2.91 (s)
c	Me	CO_2Me			2.91 (s)
d	H	CO_2Me	8.83 (d, J = 12.2 Hz		3.45 (d, J = 12.2 Hz)
e	H	C(O)Me	8.88 (d, J = 11.7 Hz)		3.63 (d, J = 12.2 Hz)
f	Ph	Ph			4.12 (s)
g	H	H	7.77 (dd, J = 13.9 Hz, J = 9.2 Hz)	3.35 (d, J = 9.2 Hz)	3.08 (d, J = 13.9 Hz)

units to the acetylene has occurred in a *cis* fashion. Initially, the ^{1}H NMR spectrum of the parent complex *5g* ($R^1 = R^2 = H$) was instrumental in defining the characteristic chemical shifts and coupling constants associated with the three possible types of vinyl protons (H_α, H_β[endo], and H_β[exo]). Subsequent comparison of these data to the ^{1}H NMR spectra of *5a-f* then provided a tool for ascertaining the geometry of the vinyl ligand, and hence, the geometry of addition to the acetylene. In the ^{1}H NMR spectrum of *5g*, the C_α proton signal appears as a low field doublet of doublets, δ_H 7.77 (J_{trans} = 13.9 Hz and J_{cis} = 9.2 Hz), being coupled both to the *cis* and *trans* C_β protons. Correspondingly, the C_β proton signals are found upfield, δ_H(endo) 3.08 (d, J_{trans} = 13.9 Hz) and δ_H(exo) 3.35 (d, J_{cis} = 9.2 Hz). These data agree with those reported by King for other (μ-σ,π-$HC{=}CH_2$)(μ-RS)$Fe_2(CO)_6$ complexes,[2] and they are consistent with other μ-vinyl systems as well.[3] Furthermore, for two vinyl-bridged diiron complexes, (μ-σ,π-$HC{=}CHC(O)S$-)$Fe_2(CO)_6$, *7*,[4] and (μ-σ,π-$HC{=}CHBr$)(μ-Br)$Fe_2(CO)_6$, *8*,[5] (Fig. 1), in which the geometry of the vinyl ligand was determined by X-ray crystallography, *cis* (H_α/H_β[exo]) and *trans* (H_α/H_β[endo]) coupling constants of 6.7 and 10.5 Hz, respectively, were reported. In general, these values agree with known *cis* and *trans* coupling constants in free alkenes



7



8

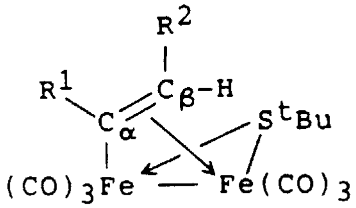
Figure 1

(J_{cis} = 6-12 Hz and J_{trans} = 12-18 Hz),[6] even though much of the double bond character is lost in bridging the iron centers.[4,5] (In fact, the infrared spectra of all the new μ-vinyl complexes 5 show no absorption in the region characteristic for free olefins).[6] Consequently, since the C_α proton signals of 5d and 5e both are observed in their ^1H NMR spectra as low field doublets with *trans* coupling constants of 12.2 and 11.7 Hz, respectively, one can determine that overall *cis*-addition of the diiron and proton units has occurred. Accordingly, the endo C_β proton resonances occur farther upfield as doublets having the corresponding *trans* coupling constants. For 5a, 5b, 5c, and 5g, the absence of any low field resonances indicates that their vinyl protons are attached only to C_β, and, as expected, the β-vinyl protons in 5a show geminal coupling of 5.02 Hz.

In the ^{13}C NMR spectra of these new σ,π-vinyl complexes, the C_α carbon signals are observed downfield, in the range of 154 - 216 ppm (Table 2). Conversely, the C_β resonances are observed farther upfield, in the range of 50 - 90 ppm. Whereas the downfield shift of C_α may be explained in terms of the "carbene-like" character associated with this carbon atom, the upfield shift of C_β may be attributed to a degree of "sp^3-like" character for this carbon atom. Similar shifts have been observed in other μ-vinyl systems.[3c,7a,b]

Like the bridging acetylide complexes described in the previous chapter, these new bridging vinyl products show fluxionality of the unsaturated ligand. This is illustrated in the variable temperature ^{13}C NMR spectra of the ethoxyvinyl derivative 5a (Fig. 2). Typical for most of the μ-vinyl products isolated, the room temperature ^{13}C NMR spectrum shows two signals (δ_C 210.24 and 211.63) in the terminal carbonyl region. (In some cases, one broad resonance was observed.) Assuming that the three CO ligands on each iron atom are locally equilibrated at room

Table 2: ^{13}C NMR Data for 5



	R^1	R^2	$\delta C\alpha$	$\delta C\beta$
a	EtO	H	216.71 (s)	50.94 (dd)
b	CO_2Me	CO_2Me	176.55 (s)	67.99 (d)
c	Me	CO_2Me	190.36 (s)	77.03 (d)
d	H	CO_2Me	161.3 (d)	76.0 (d)
e	H	C(O)Me	160.42 (d)	82.12 (d)
f	Ph	Ph	176.58 (s)	90.25 (d)
g	H	H	154.8 (d)	74.8 (dd)

temperature, then these resonances can be attributed to the two inequivalent iron tricarbonyl fragments of the unsymmetrical molecule. However, at 90°C, one observes the coalescence of these two peaks into one, indicative of a fluxional process equilibrating the two $Fe(CO)_3$ fragments on the NMR time scale. This behavior can be attributed to a flipping motion of the vinyl ligand over the face of the Fe_2S template as depicted in Figure 2. When the temperature then is lowered back to 25°C, the motion of the vinyl ligand slows on the NMR time scale, the $Fe(CO)_3$ fragments once again become inequivalent, and the single carbonyl resonance is split into the two original signals. Related fluxional behavior has been observed in other vinyl systems.[7,3c]

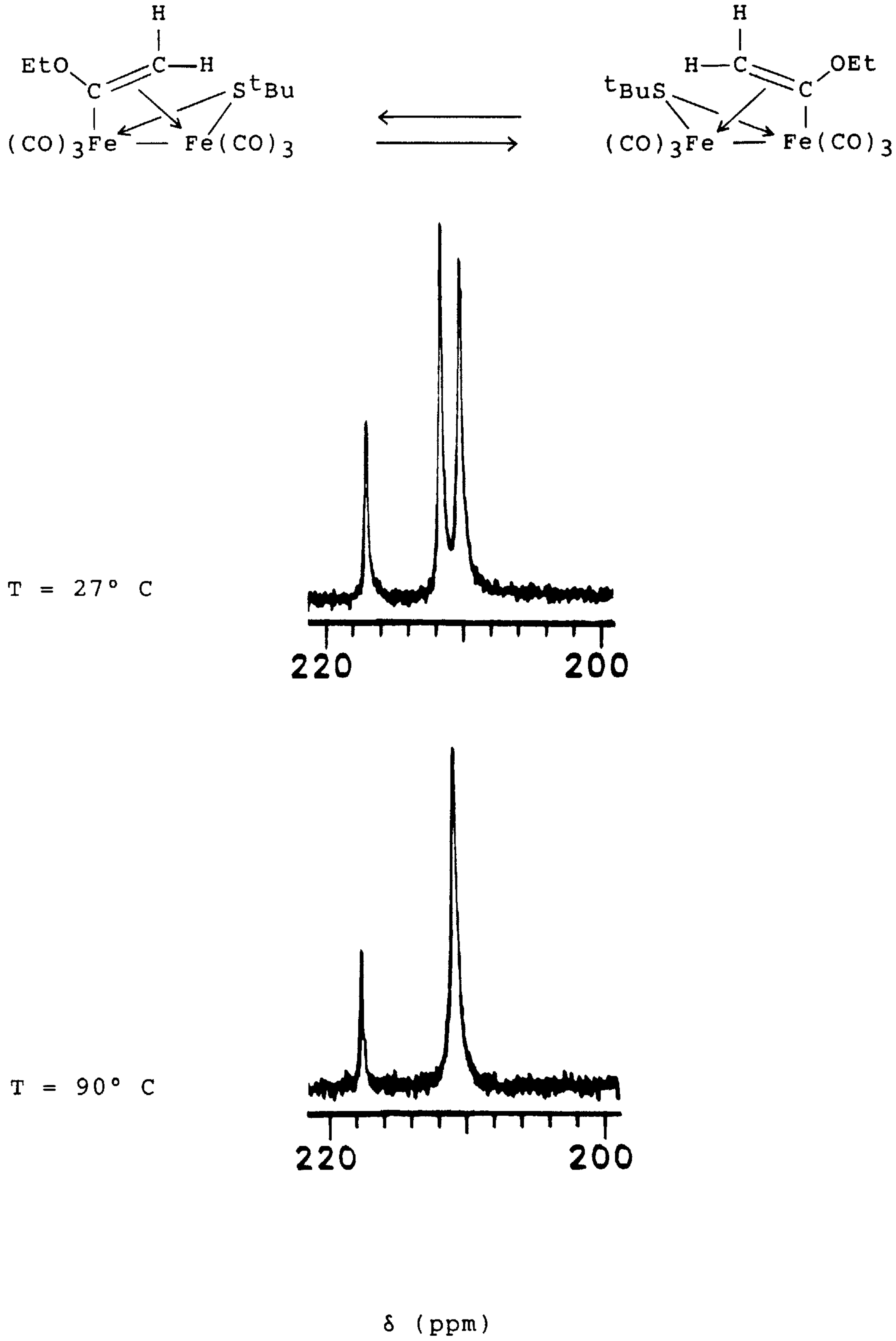
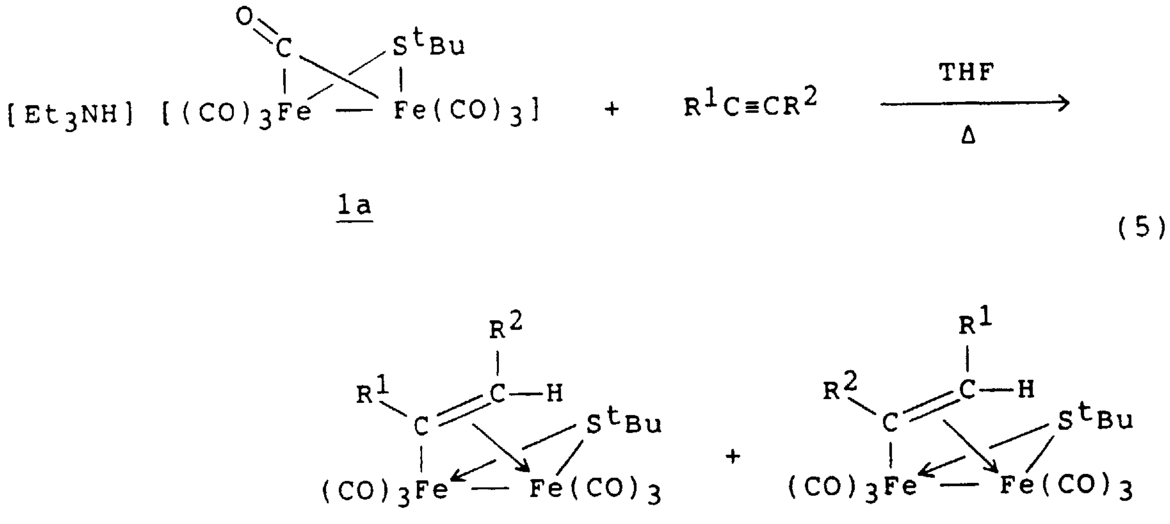

EtO
C
C—H
H
S^{t}Bu
(CO)$_3$Fe
Fe(CO)$_3$
H
H—C
C
OEt
^{t}BuS
(CO)$_3$Fe
Fe(CO)$_3$
T = 27° C
220
200
T = 90° C
220
200
δ (ppm)

Figure 2

As expected, in the reactions of electrophilic terminal acetylenes with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$, 1a, addition of the diiron and proton units was regiospecific in that only one of the two possible positional isomers of addition was formed. This observation is consistent with exclusive attack of an iron centered nucleophile at one carbon atom of the triple bond. In the case of methyl propiolate, methyl-2-butynoate, and 3-butyn-2-one, this occurs in a fashion consistent with Michael addition to the activated acetylene. In the case of ethoxyacetylene, charge distribution of the triple bond[8] directs nucleophilic attack at the α-carbon atom, consistent with Markovnikoff addition to the acetylene.

In the reactions of phenylacetylene and trimethylsilylacetylene, addition of the diiron and proton units was not regiospecific in that both possible positional isomers of addition were isolated (Eq. 5). Although



1a

(5)

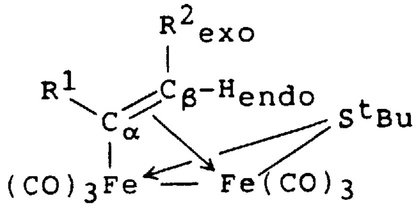
5

5'

			5	5'
h	R^1 = Ph	R^2 = H	29%	20%
i	R^1 = Me_3Si	R^2 = H	17%	17%

physical separation of the two isomers by chromatography or recrystallization was impossible, characterization of these new vinyl complexes was straightforward. As expected, assignments for vinyl proton and carbon signals could be made in the corresponding ^1H and ^{13}C NMR spectra consistent with 5a-g (Tables 3 and 4). In general, steric considerations and the ability of both the phenyl and trimethylsilyl groups to stabilize α-carbanions favors β-attack of the iron nucleophile and subsequent formation of

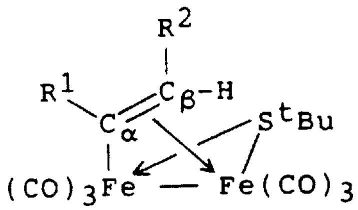
Table 3: ^1H NMR Data for 5h, 5h′, 5i, and 5i′



	R^1	R^2	$\delta_H(R^1)$	$\delta_H(R^2\text{-exo})$	$\delta_H(\text{endo})$
5h	Ph	H		3.58 (d, J = 2.5 Hz)	2.79 (d, J = 2.5 Hz)
5h′	H	Ph	8.30 (d, J = 13.7 Hz)		4.46 (d, J = 13.7 Hz)
5i	Me_3Si	H		4.05 (d, J = 3.5 Hz)	3.30 (d, J = 3.6 Hz)
5i′	H	Me_3Si	8.25 (d, J = 15.1 Hz)		3.47 (d, J = 15.2 Hz)

Table 4: ^{13}C NMR Data for

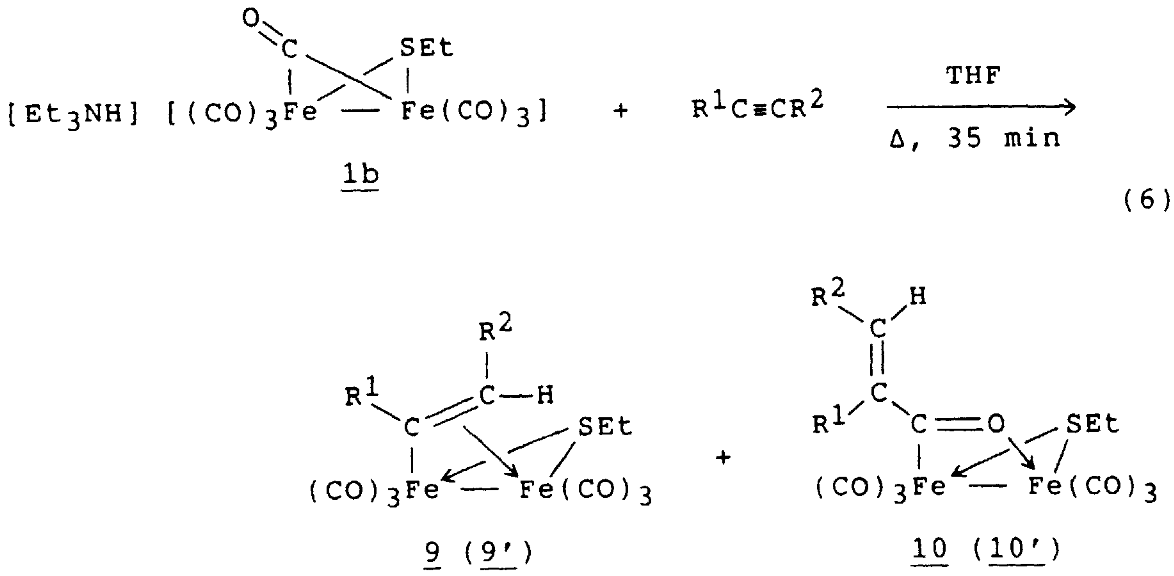
5h, 5h′, 5i, and 5i′



	R^1	R^2	δC_α	δC_β
5h	Ph	H	185.0 (s)	68.8 (dd)
5h′	H	Ph	141.5 (d)	96.6 (d)
5i	Me_3Si	H	181.19 (s)	78.19 (t)
5i′	H	Me_3Si	159.71 (d)	91.40 (d)

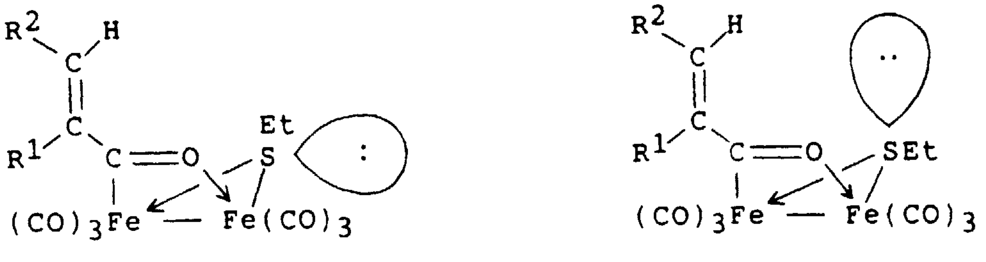
isomer 5′ upon protonation. Conversely, charge distribution in the triple bonds[8] favors α-attack of the iron nucleophile and subsequent formation of isomer 5. Neither effect predominates, and hence both isomers are formed in roughly equal amounts.

Surprisingly, reaction of the $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$, 1b, with the electron-rich, internal alkyl acetylenes 2-pentyne, 3-hexyne, and 4-octyne in refluxing THF not only yielded the expected μ-vinyl complexes, 9, but also, new α,β-unsaturated acyl complexes of the type $(\mu\text{-}R^1C(=CHR^2)C=O)(\mu\text{-}EtS)Fe_2(CO)_6$, 10 (Eq. 6). Certainly, isolation of the acyl complexes was unexpected in that insertion of carbon monoxide into an iron-vinyl bond had occurred. Typically, these μ-acyl products were obtained as a mixture of two inseparable isomers presumably resulting from either an axial (a) or equatorial (e) orientation of



(6)

a	R^1 = ^{n}Pr	R^2 = ^{n}Pr	31%	26%
b	R^1 = Et	R^2 = Et	43%	31%
c	R^1 = Me	R^2 = Et	12%	11%
	(Et)	(Me)	(8%)	(13%)

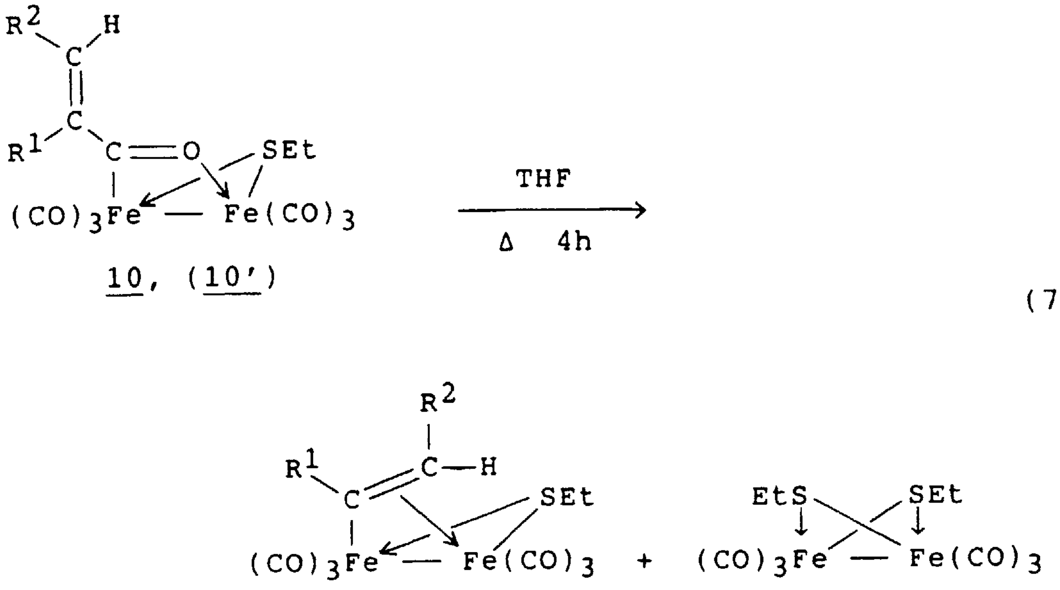


a

e

Figure 3

the organic thiolate group and lone electron pair on sulfur with respect to the Fe_2S plane (Fig. 3). For the reaction of 2-pentyne, four isomers were obtained; two (9c and 9c′) result from opposite addition to the acetylene and each of these products then exists as the e/a isomer pair. As noted in the experimental section, purification of the new μ-vinyl and μ-acyl complexes, 9 and 10, by chromatography was a problem since the common byproduct, $(\mu\text{-EtS})_2Fe_2(CO)_6$, 11, typically had similar eluting behavior. Furthermore, because 10a and 10c/10c′ were isolated as unstable oils, analytically pure samples for carbon/hydrogen combustion analysis could not be obtained. In refluxing THF (4 h), these α,β-unsaturated acyl complexes undergo decarbonylation to the respective μ-σ,π-vinyl complexes, 9, in low yield (Eq. 7). A large amount of acyl complex (21 - 35%) remained



10, (10′)

9, (9′)

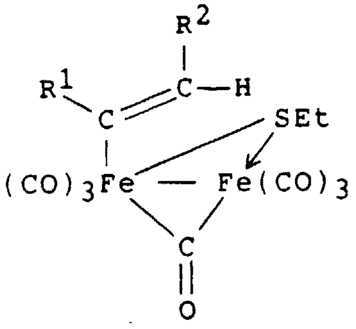
11

(7)

a	R^1 = ^{n}Pr	R^2 = ^{n}Pr	18%	36%
b	R^1 = Et	R^2 = Et	14%	42%
c	R^1 = Et	R^2 = Me	12%	18%
	(Me)	(Et)	(15%)	

unconverted, and the reaction was complicated by the isolation of large quantities of (μ-EtS)$_2$Fe$_2$(CO)$_6$, 11 (18 - 36%).

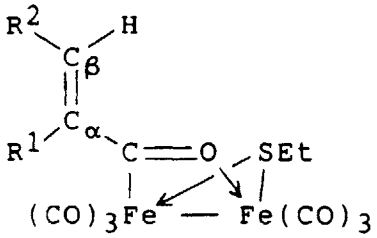
Structural characterization of the new μ-vinyl complexes, 9, was straightforward and consistent with 5a-i. However, subsequent characterization of the new α,β-unsaturated acyl complexes, 10, was difficult. In fact, it was first believed that the isomeric terminal vinyl complexes of the type ($R^1C{=}CHR^2$)(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$, 12, had been isolated (Fig. 4). Accordingly, the electron impact mass spectra all showed the correct molecular ion with subsequent loss of seven carbonyl ligands. Furthermore, assignments could be made for vinyl protons and carbons in the respective ^{1}H and ^{13}C NMR spectra (Table 5). In the ^{1}H NMR spectra, the β-proton signal of the vinyl ligand was observed downfield ($\delta_H \sim 6.6$) in the region typical for protons on uncoordinated double bonds.[6] Also, in contrast to the vinyl resonances of the μ-vinyl complexes 5 and 9, both the α- and β-vinyl carbon signals of 12 were observed downfield in the range of 145 - 156 ppm in the corresponding ^{13}C NMR spectra (compare Tables 2 and 5). The infrared spectra all showed an absorption in the region of



12

Figure 4

Table 5: ^{1}H and ^{13}C NMR Data for 10



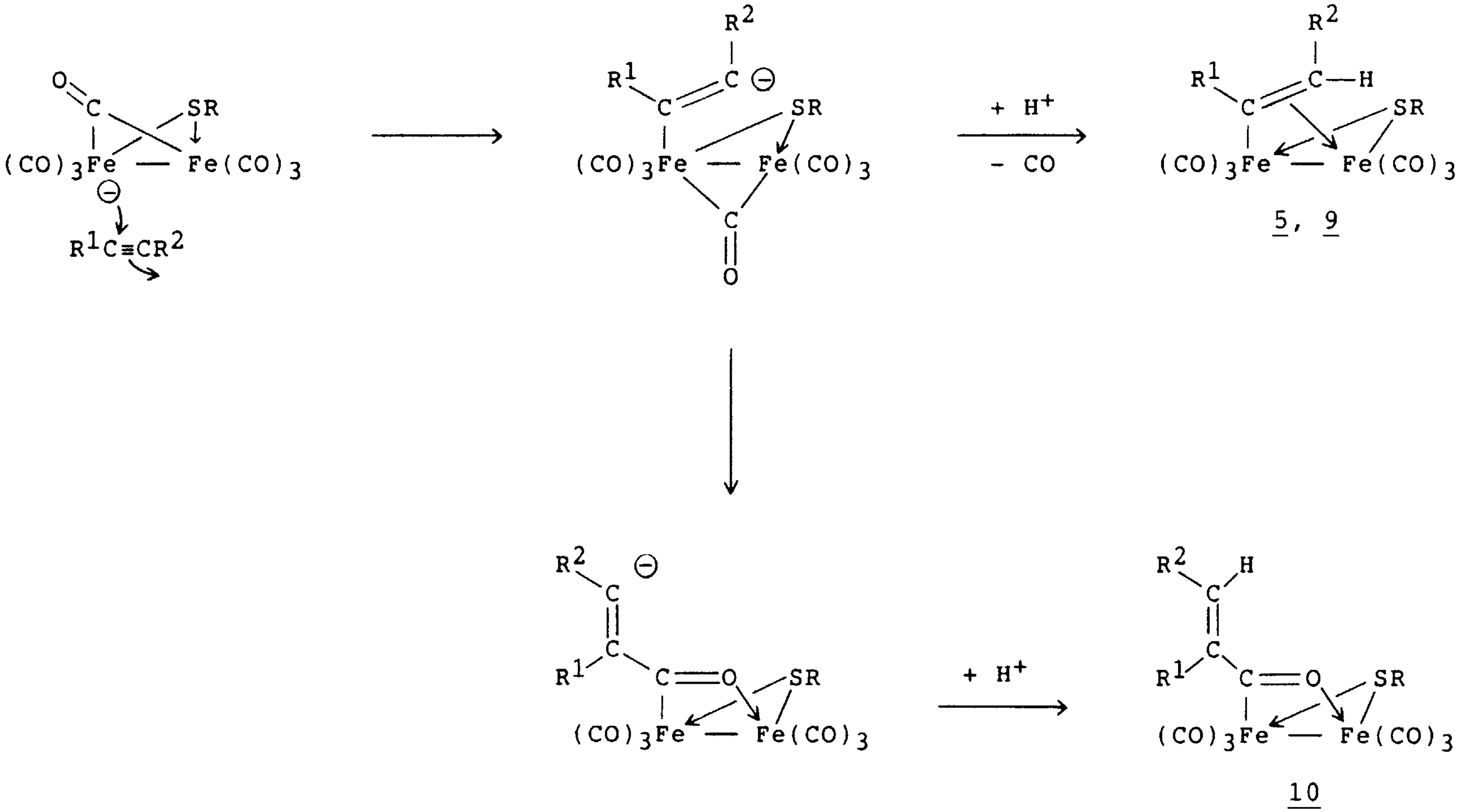
	R^1	R^2	δH_{β}	δC_{α}	δC_{β}
a	^{n}Pr	^{n}Pr	6.54 (t) 6.71 (t)	150.26 (s) 150.85 (s)	153.08 (d) 154.68 (d)
b	Et	Et	6.64 (t) 6.78 (t)	151.69 (s) 151.21 (s)	153.98 (d) 155.56 (d)
c	Me	Et	6.55 (m)	145.33*	153.49*
c′	(Et)	(Me)	6.62 (t)	147.32*	154.53*

*from $^{13}C\{^{1}H\}$ NMR spectrum

1600 cm^{-1} which could be assigned to the C-C stretch of the uncoordinated carbon-carbon double bond.[6] Curiously, though, no bridging carbonyl band was observed, and in the ^{13}C NMR spectra, a singlet was observed far downfield (δ_C ~ 288) which could not be attributed to a bridging carbonyl ligand. However, in comparison to the chemical shifts of related acyl carbon atoms in other thiolate-bridged diiron compounds, this peak could be assigned to the bridging acyl carbon of 10.[1,9] (Although shifted to lower frequency, the corresponding acyl carbonyl absorptions were observed in the IR spectra with some difficulty in the region around 1455 cm^{-1}).[1,9] On this basis the geometry of the new vinyl ligand was determined. This assignment is consistent with the analytical and spectroscopic data for the related ethoxyvinyl derivative (μ-EtOC(=CH_2)C=O)(μ-^tBuS)$Fe_2(CO)_6$, 13, which was prepared by an independent route and characterized by X-ray crystallography.[10] Other vinylacyl complexes also are known.[11,12a]

A possible mechanism incorporating the formation of both the μ-vinyl and μ-acyl products is outlined in Scheme 1. Initially, attack of the iron nucleophile at the acetylene likely generates an intermediate vinylic anion where the negative charge is localized on the β-carbon atom of the uncoordinated vinyl ligand. This vinyl ligand can then form a π-bond to the adjacent iron atom concurrent with expulsion of carbon monoxide and protonation of the β-carbon to give the μ-vinyl complexes, (μ-σ,π-R^1C=CHR^2)(μ-RS)$Fe_2(CO)_6$, 5 or 9, isolated in all cases. Alternatively, in the case of the electron-rich acetylenes, migratory insertion of CO into the iron-vinyl bond may occur, yielding an anionic acyl intermediate where the negative charge is also localized on the β-carbon of the vinyl ligand.[11b,12] Subsequent protonation at this site then gives the neutral α,β-unsaturated acyl complexes (μ-R^1C(=CHR^2)C=O)(μ-EtS)$Fe_2(CO)_6$, 10. (The exact order of protonation vs. bridging/insertion for the two separate reaction pathways cannot be determined with certainty. Protonation may occur prior to bridging or insertion.) The fact that the neutral μ-acyl derivatives decarbonylate only poorly to the corresponding μ-vinyl derivatives also suggests that they do not function as general intermediates in the synthesis of the μ-vinyl complexes.

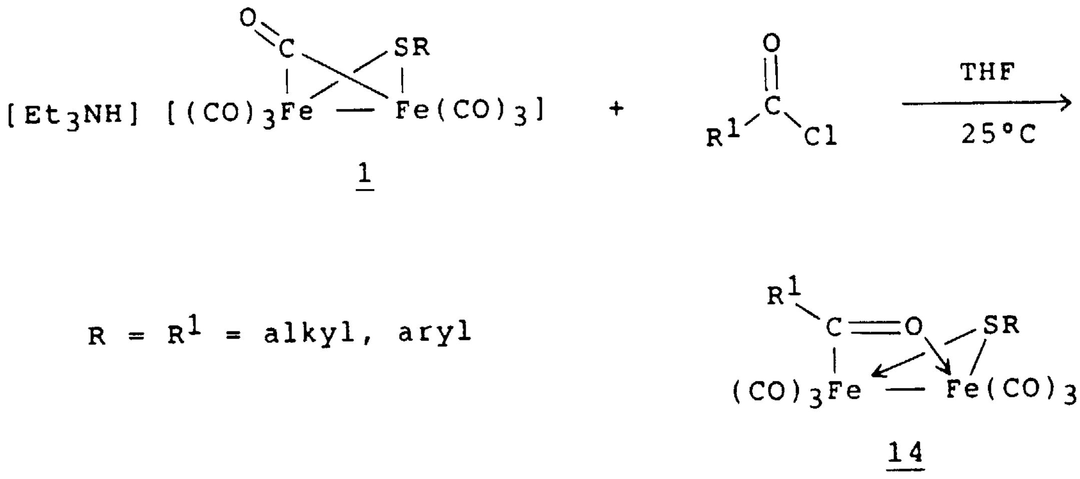
It is interesting to note that formation of the α,β-unsaturated acyl complexes 10 is not promoted by the presence of free carbon monoxide in solution. For instance, reaction of a CO saturated solution containing [Et_3NH][(μ-CO)(μ-EtS)$Fe_2(CO)_6$], 1b, with 3-hexyne yielded 9b and 10b in 47 and 34% yields, respectively. In comparison to the original reaction (Eq. 6), no increase in the production of



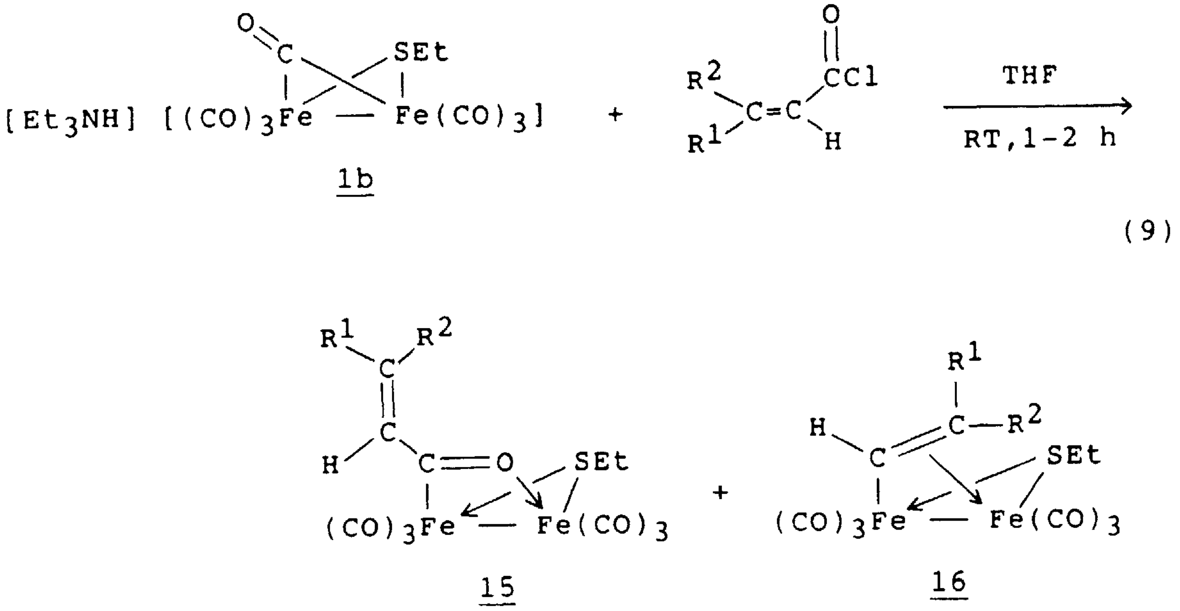
Scheme 1

the acyl complex was observed. This would indicate that formation of the acyl derivatives results entirely from an intramolecular insertion process. Since coordinative unsaturation resulting from insertion of CO can be satisfied by formation of the bridging acyl ligand, such a mechanism is entirely plausible.

In related work, Archer and Womack have shown that reaction of acid chlorides, $R^1C(O)Cl$, with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$, 1, is a general method for the synthesis of a wide variety of alkyl and aryl acyl bridged diiron complexes $(\mu\text{-}R^1C{=}O)(\mu\text{-}RS)Fe_2(CO)_6$, 14 (Eq. 8).[1,9b,9c] In light of the results just described, it was of interest to determine if reaction of α,β-unsaturated acid chlorides with 1 would proceed analogously. As expected, reaction of α,β-unsaturated acid chlorides, $R^1(R^2)C{=}CHC(O)Cl$, with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$, 1b, yielded the μ-acyl complexes $(\mu\text{-}HC({=}C(R^1)R^2)C{=}O)(\mu\text{-}EtS)Fe_2(CO)_6$, 15, in variable yield (Eq. 9). In some cases, the corresponding vinyl-bridged species, $(\mu\text{-}\sigma,\pi\text{-}HC{=}C(R^1)R^2)(\mu\text{-}EtS)Fe_2(CO)_6$, 16, also were isolated, presumably resulting from decarbonylation of the μ-acyl complexes, 15. In comparison to the acyl products prepared from the electron-rich



(8)

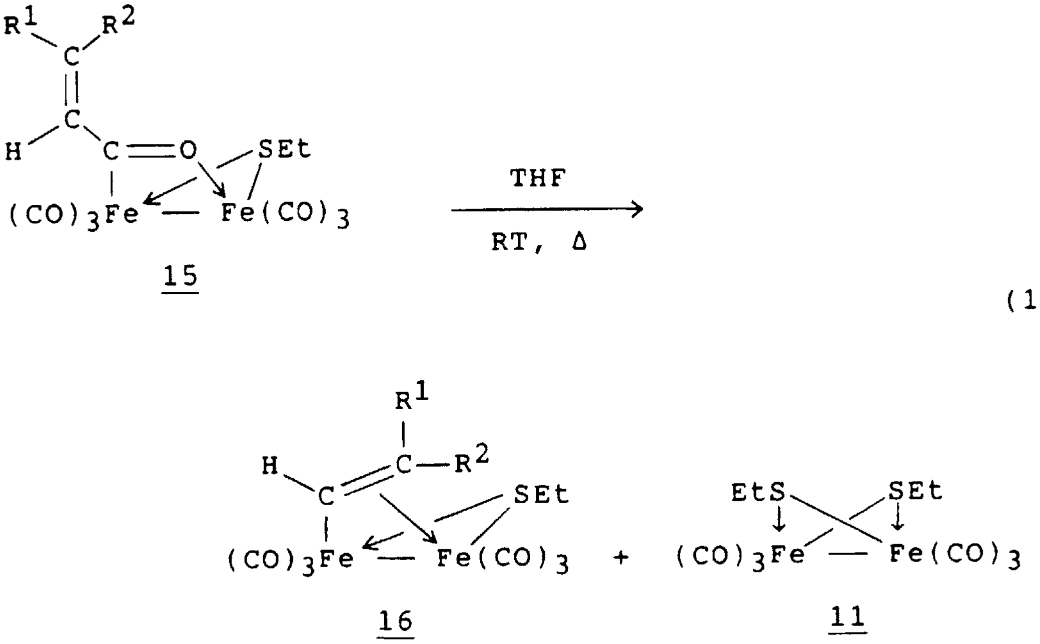


(9)

a	R^1 = H	R^2 = H	38%	51%
b	R^1 = Ph	R^2 = H	59%	38% (5h′)
c	R^1 = Me	R^2 = H	80%	13%
d	R^1 = Me	R^2 = Me	93%	-

acetylenes, subsequent structural characterization of the new acyl complexes was straightforward. Because the characteristic downfield chemical shift of the μ-acyl carbon atom (δ_C ~ 289) was easily identified, ^{13}C NMR spectroscopy was the most useful tool in determining the general structure. The corresponding ^{1}H NMR spectra also were helpful in assigning a trans geometry to the vinyl ligand. Furthermore, the acyl carbonyl stretch in the infrared spectra was typically observed in the region of 1455 cm^{-1} while the vinyl double bond stretch was observed as a strong and a weak band (two isomers!) in the range of 1600 - 1640 cm^{-1}. As in the reactions of the electron-rich acetylenes, purification of these new μ-vinyl and μ-acyl products by chromatography was at times a problem since the common byproduct, (μ-EtS)$_2$Fe$_2$(CO)$_6$, 11, had similar eluting properties.

Excluding 15d, the new acyl complexes undergo facile decarbonylation to the corresponding μ-vinyl derivatives, 16 (Eq. 10). This behavior is in contrast to the corresponding



(10)

a	R^1 = H	R^2 = H	92%	-
b	R^1 = Ph	R^2 = H	82%	-
c	R^1 = Me	R^2 = H	95%	-
d	R^1 = Me	R^2 = Me	33%	36%

poor conversions of the acetylene-derived acyls, 10, described earlier (Eq. 7). Such a difference in behavior may be ascribed to electronic effects involving the acyl bridge. Electron-donating groups are known to stabilize acyl ligands.[12a] Compounds 10a-c all contain two alkyl groups on the double bond which makes the vinyl ligand electron-rich and hence stabilizes the acyl towards decarbonylation. However, since 15a and 15c contain only a monosubstituted vinyl ligand and 15b contains an unsubstituted vinyl ligand, the acyl bridges are not as electron-rich in comparison to 10a-c and are destabilized. Subsequently, decarbonylation is much more facile as reflected in the high conversion yields (Eq. 10). In the case of 15d, steric factors probably are also involved in the low conversion yield. In addition to having a disubstituted vinyl ligand, the substitution is such that the resulting μ-vinyl ligand will contain a methyl group pointing directly at the thiolate bridge (in all the other μ-vinyl complexes prepared, a proton occupied this position). Obviously, this creates a sterically unfavorable interaction and hence the observed decarbonylation yield is quite low. Similarly, the *trans* geometry of the vinyl ligand was maintained after decarbonylation in the cases of 15b and 15c. Because of their facile decarbonylation, purification of 15a-c was a problem. Since these acyl derivatives also were isolated as slightly air-sensitive oils, analytically pure samples, and hence accurate C/H combustion analyses, could not be obtained.

EXPERIMENTAL

General Comments

All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl and purged with nitrogen prior to use. Triethylamine was distilled under nitrogen from calcium hydride and purged with nitrogen prior to use. Ethyl and t-butyl mercaptans were purged with nitrogen and used without further purification. Acryloyl, crotonyl, 3,3-dimethylacryloyl, and cinnamoyl chlorides (all purchased from Aldrich) were purged with nitrogen prior to use. Dimethyl acetylenedicarboxylate, methyl propiolate, methyl-2-butynoate, 3-butyn-2-one, and ethoxyacetylene (all purchased from Farchan Labs) were purged with nitrogen after purification by vacuum distillation (at room temperature) when necessary. Phenylacetylene (Fluka), trimethylsilylacetylene (Aldrich), 3-hexyne (Farchan), 4-octyne (Aldrich), and 2-pentyne (Aldrich) were purged with nitrogen and used without further purification. Diphenylacetylene (Aldrich) was used as obtained. Acetylene was bubbled through sulfuric acid and then passed through a column of potassium hydroxide (pellets) prior to use. Triiron dodecacarbonyl was prepared by a literature procedure.[13]

The progress of all reactions was monitered by thin-layer chromatography (Baker Flex, Silica Gel 1B-F). Purification by filtration chromatography in which the reaction products were dissolved in a suitable solvent and chromatographed on a bed of Mallinckrodt 100 mesh or Sigma 100 - 300 mesh silicic acid (ca. 200 ml) in a 350 ml glass fritted filter funnel was used in most cases. Further purification by column chromatography was accomplished with a 350x25 mm gravity column or a 450X25 mm medium pressure column using Mallinckrodt 100 mesh silicic acid or Sigma 230 - 400 mesh silica gel. All chromatography was completed without exclusion of atmospheric moisture or oxygen. Solid products were recrystallized from deoxygenated solvents at -20°C.

Solution infrared spectra (NaCl windows) were obtained using a Perkin-Elmer Model 1430 double beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a JEOL FX-90Q, a Bruker WM-250, or a Varian XL-300 spectrometer operating at 90, 250, or 300 MHz, respectively. Carbon-13 NMR spectra were recorded on either a Bruker WH-270, a Varian XL-300, or a Varian XL-400 spectrometer operating at 67.9, 75.4, or 100.5 MHz, respectively. Electron impact mass spectra were obtained using a Finnigan-3200 mass spectrometer operating at 70 eV. FAB mass spectra were obtained with a Finnigan MAT-731 mass spectrometer operating in the positive ion mode. Masses were correlated using the following isoptopes: ^{1}H, ^{12}C, ^{14}Si, ^{16}O, ^{32}S, and ^{56}Fe. Melting points were determined in air on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were perfomed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Standard in-situ Preparation of $[Et_3NH][(\mu-CO)(\mu-RS)Fe_2(CO)_6]$

A 250 ml three-necked, round-bottomed flask equipped with a reflux condenser, nitrogen inlet (gas adapter), glass stopper, stir-bar, and rubber septum was charged with 1.51 g (3.00 mmol) of $Fe_3(CO)_{12}$ and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged successively with 50 ml of THF, 3.00 mmol of the appropriate thiol, and 0.42 ml (3.00 mmol) of triethylamine by syringe. The mixture was stirred for 20 min during which time slow gas evolution and a gradual color change from green to brown-red was observed. The resulting $[Et_3NH][(\mu-CO)(\mu-RS)Fe_2(CO)_6]$ reagent solutiuon then was utilized in-situ without further purification.

Synthesis of $(\mu-\sigma,\pi\text{-EtOC=CH}_2)(\mu\text{-}^t\text{BuS})\text{Fe}_2(\text{CO})_6$ JBH-53-II

To the standard $[\text{Et}_3\text{NH}][(\mu\text{-CO})(\mu\text{-}^t\text{BuS})\text{Fe}_2(\text{CO})_6]$ reagent solution (3.00 mmol) was added 0.26 ml (3.00 mmol) of ethoxyacetylene by syringe at room temperature. An immediate reaction ensued with brisk gas evolution and gradual color change to dark red. After the reaction mixture had been stirred for 2 h at room temperature, the solvent was removed in vacuo to yield a red oil which was purified by filtration chromatography. Pentane eluted a dark red band which gave 1.11 g (2.52 mmol, 84%) of $(\mu-\sigma,\pi\text{-EtOC=CH}_2)(\mu\text{-}^t\text{BuS})\text{Fe}_2(\text{CO})_6$, 5a, as an air-stable, red solid, mp 48.0-51.0°C after recrystallization from pentane.

Anal. Calcd. for $C_{14}H_{16}Fe_2O_7S$: C, 38.21; H, 3.66 %. Found: C, 38.20; H, 3.69 %.

IR(CHCl_3): 2980m, 2941m, 2930m, 2900m, 2870m, 1471m, 1457s, 1392w, 1388w, 1365s, 1278s, 1145vs, 1085w, 1023s, 953s, 898m, 840w, 627s, 615vs, 590vs, 570vs cm^{-1}. Terminal carbonyl region (pentane): 2070s, 2035vs, 2000vs, 1988vs cm^{-1}.

^{1}H NMR(CDCl_3; 250 MHz): δ 1.25 (t, J = 6.99 Hz, 3H, $\text{OCH}_2\text{C}\underline{\text{H}}_3$), 1.36 (s, 9H, $\text{SC(CH}_3)_3$), 2.02 (d, J = 5.02 Hz, 1H, C=CH_2 endo), 3.23 (d, J = 5.03 Hz, 1H, C=CH_2 exo), 3.69 (m, 1H, $\text{OC}\underline{\text{H}}_2\text{CH}_3$ diastereotopic CH_2), 3.86 (m, 1H, $\text{OC}\underline{\text{H}}_2\text{CH}_3$ diastereotopic CH_2).

^{13}C NMR(CDCl_3; 67.9 MHz): δ 14.30 (q, J = 127.1 Hz, $\text{OCH}_2\underline{\text{C}}\text{H}_3$), 33.25 (q, J = 127.2 Hz, $\text{SC(}\underline{\text{C}}\text{H}_3)_3$), 47.68 (s, $\text{S}\underline{\text{C}}\text{(CH}_3)_3$), 50.94 (dd, J = 152.4 Hz, J = 163.4 Hz, $\text{C=}\underline{\text{C}}\text{H}_2$), 67.30 (t, J = 144.0 Hz, $\text{O}\underline{\text{C}}\text{H}_2\text{CH}_3$), 209.88 and 211.34 (both s, Fe-CO), 216.71 (s, $\text{EtO}\underline{\text{C}}\text{=CH}_2$).

Mass Spectrum (EI); m/z (relative intensity): 440 (M^+, 27), 412 (M^+ - CO, 22), 384 (M^+ - 2CO, 35), 356 (M^+ -

3CO, 46), 328 (M^+ - 4CO, 55), 300 (M^+ - 5CO, 74), 272 (M^+ - 6CO, 89), 226 ($^tBuSFe_2C=CH$, 6), 216 ($HSFe_2EtOC=CH_2$, 100), 214 ($HSFe_2EtOC=C$, 12), 190 ($HSFe_2EtO$, 56), 188 ($HSFe_2HOC=CH_2$, 60), 170 ($SFe_2C=CH_2$, 15), 159 ($SFeEtOC=CH_2$, 7), 145 ($HSFe_2$, 40), 144 (SFe_2, 50), 112 (Fe_2, 5), 57 (^tBu, 33), 56 (Fe, 12).

Synthesis of (μ-σ,π-$MeO_2CC=CHCO_2Me$)(μ-^tBuS)$Fe_2(CO)_6$ JBH-45-II

To the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}^tBuS)Fe_2(CO)_6]$ reagent solution (3.00 mmol) was added 0.37 ml (3.00 mmol) of dimethyl acetylenedicarboxylate by syringe at room temperature. An immediate reaction ensued with brisk gas evolution and gradual color change to cherry red. After the reaction mixture had been stirred for 2 h at room temperature, the solvent was removed in vacuo to yield a cherry red oil which was purified by filtration chromatography. Pentane/CH_2Cl_2 (9/1 v/v) eluted two pale orange bands which were not collected. Pentane/CH_2Cl_2 (6/4 v/v) eluted a bright red band which gave 1.22 g of a brown-orange solid identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz) to be a mixture of 1.03 g (2.00 mmol, 67%) of (μ-σ,π-$MeO_2CC=CHCO_2Me$)(μ-^tBuS)$Fe_2(CO)_6$, 5b, and 0.19 g (0.40 mmol, 13%) of (μ-σ,π-$MeO_2CC=C(CO_2Me)C(O)S-$)$Fe_2(CO)_6$, 6a.[10] Recrystallization from pentane/CH_2Cl_2 yielded analytically pure (μ-σ,π-$MeO_2CC=CHCO_2Me$)(μ-^tBuS)$Fe_2(CO)_6$, 5b, as a brown-orange, air-stable solid, mp 114.0-116.0°C.

Anal. Calcd. for $C_{16}H_{15}Fe_2O_{10}S$: C, 37.53; H, 3.15 %. Found: C, 37.73; H, 3.24 %.

IR($CHCl_3$): 3040vw, 3000sh, 2980sh, 2960m, 2937w, 2910w, 1712vs(C=O), 1475w, 1460m, 1440s, 1410s, 1398m, 1370m, 1295m, 1190s, 1181s, 1160vs, 1041m, 995m, 865w, 620m, 610s, 590vs, 550s cm^{-1}.

Terminal carbonyl region (pentane): 2088m, 2060vs, 2026s, 2019s, 2000s, 1980vw cm^{-1}.

^{1}H **NMR**($CDCl_3$; 90 MHz): δ 1.42 (s, 9H, $SC(CH_3)_3$), 2.91 (s, 1H, $C=C\underline{H}CO_2Me$), 3.69 (s, 3H, CO_2CH_3), 3.76 (s, 3H, CO_2CH_3).

^{13}C **NMR**($CDCl_3$; 67.9 MHz): δ 32.99 (q, J = 127.8 Hz, $SC(\underline{C}H_3)_3$), 51.88 (q, J = 146.8 Hz, $CO_2\underline{C}H_3$), 52.42 (q, J = 147.4 Hz, $CO_2\underline{C}H_3$), 67.99 (d, J = 168.7 Hz, $C=\underline{C}HCO_2Me$), 169.05 (s, $\underline{C}O_2Me$), 173.94 (s, $\underline{C}O_2Me$), 176.55 (s, $\underline{C}=CHCO_2Me$), 206.55 (s, Fe-CO), 208.05 (broad s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 484 (M^+ - CO, 4), 456 (M^+ - 2CO, 23), 428 (M^+ - 3CO, 12), 400 (M^+ - 4CO, 18), 372 (M^+ - 5CO, 30), 344 (M^+ - 6CO, 84), 288 ($HSFeMeO_2CC=CHCO_2Me$, 100), 260 ($HSFe_2MeO_2CC=CHOMe$, 80), 232 ($^tBuSFeMeOC=CHOMe$, 9), 230 ($SFeMeO_2CC=CCO_2Me$, 13), 227 ($SFe_2C=CCO_2Me$, 52), 202 ($^tBuSFeOC=CHO$, 12), 201 ($^tBuSFe_2$, 4), 176 ($HSFe_2OMe$, 15), 175 (SFe_2OMe, 25), 170 ($HSFe_2C=CH$, 16), 169 ($SFe_2C=CH$, 19), 168 ($SFe_2C=C$, 9), 145 ($HSFe_2$, 17), 144 (SFe_2, 23), 113 (SFeC=CH, 15), 57 (^tBu, 35), 56 (Fe, 24).

Synthesis of (μ-σ,π-MeC=$CHCO_2Me$)(μ-^tBus)$Fe_2(CO)_6$ JBH-50-II

To the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}^tBuS)Fe_2(CO)_6]$ reagent solution (3.00 mmol) was added 0.30 ml (3.00 mmol) of methyl 2-butynoate by syringe at room temperature. An immediate reaction ensued with brisk gas evolution and gradual color change to dark red. After the reaction mixture had been stirred for 4 h at room temperature, the solvent was removed in vacuo to yield a cherry red tar which was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Pentane/CH_2Cl_2 (9/1 v/v) eluted a dark red band which gave 0.85 g (1.81 mmol, 60%) of (μ-σ,π-MeC=$CHCO_2Me$)(μ-^tBuS)$Fe_2(CO)_6$, <u>5c</u>, as an air-stable, dark red solid, mp 65.0-68.0°C after recrystallization from pentane.

Anal. Calcd. for $C_{15}H_{16}Fe_2O_8S$: C, 38.49; H, 3.44 %. Found: C, 38.60; H, 3.46 %.

IR($CHCl_3$): 2970m, 2960m, 2937m, 2905m, 2875w, 1710vs(C=O), 1473w, 1460s, 1435s, 1410s, 1395m, 1368s, 1277w, 1265w, 1240vw, 1193s, 1172vs, 1155s, 1088s, 1030m, 1010m, 965w, 945w, 910m, 898w, 630s, 612s, 600vs, 590vs, 560vs cm^{-1}.
Terminal carbonyl region (pentane): 2079m, 2042vs, 2018s, 2000vs, 1988s cm^{-1}.

^{1}**H NMR**($CDCl_3$; 90 MHz): δ 1.40 (s, 9H, $SC(CH_3)_3$), 2.91 (s, 1H, $C{=}C\underline{H}CO_2Me$), 3.00 (s, 3H, $C\underline{H}_3C{=}CHCO_2Me$), 3.69 (s, 3H, CO_2CH_3).

^{13}**C NMR**($CDCl_3$; 67.9 MHz): δ 33.12 (q, J = 127.3 Hz, $SC(\underline{C}H_3)_3$), 38.09 (q, J = 128.4 Hz, $\underline{C}H_3C{=}CHCO_2Me$), 49.14 (s, $S\underline{C}(CH_3)_3$), 51.57 (q, J = 146.8 Hz, $CO_2\underline{C}H_3$), 77.03 (d, J = 165.5 Hz, $C{=}\underline{C}HCO_2Me$), 169.50 (s, $\underline{C}O_2Me$), 190.36 (s, $Me\underline{C}{=}CHCO_2Me$), 208.54 and 209.39 (both s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 468 (M^+, 8), 412 (M^+ - 2CO, 25), 384 (M^+ - 3CO, 24), 356 (M^+ - 4CO, 41), 328 (M^+ - 5CO, 34), 300 (M^+ - 6CO, 100), 272 (^{t}BuSFe$_2$MeC=CHOMe, 3), 244 (HSFe$_2$MeC=CHCO$_2$Me, 98), 216 (HSFe$_2$MeC=CHOMe, 60), 184 (^{t}BuSFeMeC=C, 29), 176 (HSFe$_2$OMe, 31), 175 (SFe$_2$OMe, 18), 145 (HSFe$_2$, 25), 144 (SFe$_2$, 34), 112 (Fe$_2$, 3), 57 (^{t}Bu, 2), 44 (CO$_2$, 5).

Synthesis of (μ-σ,π-HC=CHCO$_2$Me)(μ-^{t}BuS)Fe$_2$(CO)$_6$ JBH-39-III, GBW-XI-11

To the standard [Et$_3$NH][(μ-CO)(μ-^{t}BuS)Fe$_2$(CO)$_6$]

reagent solution (1.00 mmol) was added 0.09 ml (1.00 mmol) of methyl propiolate by syringe at room temperature. An immediate reaction ensued with brisk gas evolution and gradual color change to dark red. After the reaction mixture had been stirred for 2 h at room temperature, the solvent was removed in vacuo to yield a red oil which was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Pentane/CH_2Cl_2 (9/1 v/v) eluted a dark orange band which gave 0.28 g (0.61 mmol, 61%) of (μ-σ,π-HC=$CHCO_2Me$)(μ-^tBuS)$Fe_2(CO)_6$, 5d, as a slightly air-sensitive red oil.

Anal. Calcd. for $C_{14}H_{14}Fe_2O_8S$: C, 37.04; H, 3.11 %. Found: C, 36.57; H, 3.17 %.

IR($CHCl_3$): 3027m, 2970s, 2960s, 2950m, 2930m, 2905m, 2870w, 1708vs(C=O), 1497w, 1473m, 1460s, 1440vs, 1418s, 1398w, 1368s, 1262s, 1231vs, 1226vs, 1163vs, 1030m, 1010m, 922w, 865w, 700w, 662w, 637s, 621s, 610vs, 589vs cm^{-1}. Terminal carbonyl region (pentane): 2082m, 2048vs, 2020s, 2007m, 2000m cm^{-1}.

^{1}H NMR($CDCl_3$; 250 MHz): δ 1.37 (s, 9H, $SC(CH_3)_3$), 3.45 (d, J = 12.20 Hz, 1H, $HC=C\underline{H}CO_2Me$), 3.70 (s, 3H, CO_2CH_3), 8.83 (d, J = 12.20 Hz, 1H, $\underline{H}C=CHCO_2Me$).

^{13}C NMR(CD_2Cl_2; 67.9 MHz): δ 33.4 (q, J = 127 Hz, $SC(\underline{C}H_3)_3$), 49.0 (s, $S\underline{C}(CH_3)_3$), 52.1 (q, J = 144 Hz, $CO_2\underline{C}H_3$), 76.0 (d, J = 166 Hz, $C=\underline{C}HCO_2Me$), 161.3 (d, J = 154 Hz, $H\underline{C}=CHCO_2Me$), 169.7 (s, $\underline{C}O_2Me$), 208.7 (s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 454 (M^+, 8), 426 (M^+ - CO, 3), 398 (M^+ - 2CO, 17), 370 (M^+ - 3CO, 16), 342 (M^+ - 4CO, 34), 314 (M^+ - 5CO, 26), 286 (M^+ - 6CO, 72), 230 ($HSFe_2HC=CHCO_2Me$, 100), 202 ($HSFe_2HC=CHOMe$, 72), 176 ($HSFe_2OMe$, 45), 175 (SFe_2OMe, 21), 145 ($HSFe_2$, 31), 144 (SFe_2, 33), 86 ($H_2C=CHCO_2Me$, 7), 57 (^tBu, 43), 56 (Fe, 10).

Synthesis of (μ-σ,π-HC=CHC(O)Me)(μ-^{t}BuS)$Fe_2(CO)_6$ JBH-72-II

To the standard [Et_3NH][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (3.00 mmol) was added 0.23 ml (3.00 mmol) of 3-butyn-2-one by syringe at room temperature. An immediate reaction ensued with brisk gas evolution and gradual color change to darker red. After the reaction mixture had been stirred for 2 h at room temperature, the solvent was removed in vacuo to yield a brown-red tar. This tar was dissolved in pentane/CH_2Cl_2 (1/1 v/v), filtered through a narrow pad of silicic acid, and rotavapped down to a brown-red oil which subsequently was purified by filtration chromatography. Pentane eluted a pale orange band which gave 0.09 g (0.20 mmol, 14% based on S) of (μ-^{t}BuS)$_2Fe_2(CO)_6$, identified by its melting point and ^{1}H NMR spectrum.[14] Pentane/CH_2Cl_2 (6/4 v/v) eluted a red band which gave 0.69 g of a red solid identified by its ^{1}H NMR spectrum ($CDCl_3$; 90 MHz) to be a mixture of 0.31 g (0.76 mmol, 25%) of (μ-σ,π-HC=C(C(O)Me)C(O)S-)$Fe_2(CO)_6$, 6b,[10] and 0.37 g (0.86 mmol, 28%) of (μ-σ,π-HC=CHC(O)Me)(μ-^{t}BuS)$Fe_2(CO)_6$, 5e. Fractional recrystallization from pentane yielded analytically pure (μ-σ,π-HC=CHC(O)Me)(μ-^{t}BuS)$Fe_2(CO)_6$, 5e, as air-stable, magenta crystals, mp 53.5-57.5°C.

Anal. Calcd. for $C_{14}H_{14}Fe_2O_7S$: C, 38.39; H, 3.22 %. Found: C, 38.72; H, 3.37 %.

IR($CHCl_3$): 3008vw, 2986m, 2945m, 2927m, 2903m, 2868w, 1682vs(C=O), 1473m, 1460s, 1406vs, 1365vs, 1353s, 1245m, 1173vs, 1155vs, 1018w, 961m, 900w, 835w, 627s, 619vs, 600vs, 588vs, 553s, 550s, 503s, 575s cm^{-1}.

Terminal carbonyl region (pentane): 2073s, 2042vs, 2006s, 1998vs, 1978sh, 1968sh, 1951vw cm^{-1}.

^{1}H NMR($CDCl_3$; 90 MHz): δ 1.39 (s, 9H, $SC(CH_3)_3$), 2.26 (s, 3H, $C(O)CH_3$), 3.63 (d, J = 12.21 Hz, 1H, $HC{=}C\underline{H}C(O)Me$), 8.88 (d, J = 11.72 Hz, 1H, $\underline{H}C{=}CHC(O)Me$).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 29.41 (q, J = 127.4 Hz, $C(O)\underline{C}H_3$), 33.57 (q, J = 129.3 Hz, $SC(\underline{C}H_3)_3$), 48.59 (s, $S\underline{C}(CH_3)_3$), 82.12 (d, J = 161.0 Hz, $C{=}\underline{C}HC(O)Me$), 160.42 (d, J = 153.2 Hz, $H\underline{C}{=}CHC(O)Me$), 198.98 (s, $\underline{C}(O)Me$), 207.89 and 208.69 (both s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 438 (M^+, 4), 410 (M^+ - CO, 3), 382 (M^+ - 2CO, 15), 354 (M^+ - 3CO, 14), 326 (M^+ - 4CO, 20), 298 (M^+ - 5CO, 19), 270 (M^+ - 6CO, 43), 214 ($HSFe_2HC{=}CHC(O)Me$, 100), 196 ($SFe_2C{=}CCO$, 3), 186 ($HSFe_2HC{=}CHMe$, 6), 169 ($HSFe_2C{=}C$, 6), 145 ($HSFe_2$, 14), 144 (SFe_2, 49), 57 (^{t}Bu, 11), 56 (Fe, 3).

Synthesis of (μ-σ,π-PhC=CHPh)(μ-^{t}BuS)$Fe_2(CO)_6$ JBH-67-II

To the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ reagent solution (1.51 mmol) was added by cannula 0.27 g (1.53 mmol) of diphenylacetylene dissolved under nitrogen in a separate flask in 10 ml of THF. The reaction mixture was stirred for 45 min at reflux during which time a color change to cherry red had occurred. The solvent then was removed in vacuo yielding a red tar which was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Pentane/CH_2Cl_2 (20/1 v/v) eluted a bright red band which gave 0.34 g (1.25 mmol, 42%) of (μ-σ,π-PhC=CHPh)(μ-^{t}BuS)$Fe_2(CO)_6$, <u>5f</u>, as an air-stable, magenta solid, mp 141.0-143.0°C after recrystallization from pentane.

Anal. Calcd. for $C_{24}H_{20}Fe_2O_6S$: C, 52.59; H, 3.68 %. Found: C, 52.62; H, 3.70 %.

IR($CHCl_3$): 3097vw, 3085vw, 2950w, 2930w, 2910w, 2870w, 1600w(Ph), 1580vw(Ph), 1498s, 1479w, 1463m, 1445m, 1400w, 1371s, 1340w, 1315w, 1278vw, 1159s, 1085w, 1035vw, 1025vw, 1005w, 980w, 865w, 845w, 760m, 710m, 675w, 640m, 625s, 615vs, 605vs, 570vs, 530vs, 500vs cm^{-1}.
Terminal carbonyl region (pentane): 2060m, 2030vs, 2000s, 1989s cm^{-1}.

^1H NMR(CD_2Cl_2; 90 MHz): δ 1.49 (s, 9H, $SC(CH_3)_3$), 4.12 (s, 1H, $C{=}C\underline{H}Ph$), 6.62-7.53 (m, 10H, C_6H_5).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 33.13 (q, J = 127.1 Hz, $SC(\underline{C}H_3)_3$), 48.81 (s, $S\underline{C}(CH_3)_3$), 90.25 (d, J = 154.6 Hz, $C{=}\underline{C}HPh$), 125.13-129.80 (m, C_6H_5), 140.02 (s, ipso C_6H_5), 154.97 (s, ipso C_6H_5), 176.58 (s, $Ph\underline{C}{=}CHPh$), 210.40 (broad s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 548 (M^+, 3), 520 (M^+ - CO, 3), 492 (M^+ - 2CO, 12), 464 (M^+ - 3CO, 22), 436 (M^+ - 4CO, 9), 408 (M^+ - 5CO, 27), 380 (M^+ - 6CO, 56), 324 ($HSFe_2PhC{=}CHPh$, 100), 323 ($HSFe_2PhC{=}CPh$, 25), 322 ($SFe_2PhC{=}CPh$, 36), 309 ($Me_2CSFePhC{=}CHPh$, 8), 267 ($SFePhC{=}CHPh$, 15), 245 ($SFe_2C{=}CPh$, 9), 221 (SFe_2Ph, 34), 189 ($SFeC{=}CPh$, 5), 178 ($PhC{=}CPh$, 56), 144 (SFe_2, 40), 112 (Fe_2, 2), 89 (^tBuS, 10), 57 (^tBu, 22).

Synthesis of $(\mu\text{-}\sigma,\pi\text{-}HC{=}CH_2)(\mu\text{-}^tBuS)Fe_2(CO)_6$ GBW-X-39

Through the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}^tBuS)Fe_2(CO)_6]$ reagent solution (2.98 mmol) was bubbled acetylene for 1 h at reflux and then 1 h at room temperature. The solvent was removed in vacuo, leaving a red oil which was dissolved in pentane/CH_2Cl_2 (4/1 v/v) and filtered through a narrow pad of silicic acid. Removal of the solvent on a rotary evaporator left a red oil which was purified by filtration chromatography. Pentane eluted a red band which gave 0.22 g (0.56 mmol, 20%) of (μ-σ,π-HC=CH$_2$)(μ-^{t}BuS)Fe$_2$(CO)$_6$, 5g, as a slightly air-sensitive red oil.

Anal. Calcd. for $C_{12}H_{12}Fe_2O_6S$: C, 36.40; H, 3.05 %. Found: C, 36.57; H, 3.13 %.

IR(CHCl$_3$): 2972s, 2934s, 2910m, 2869m, 1472m, 1459s, 1396w, 1368s, 1296m, 1155s, 1019w, 984w, 616s, 595s, 499s cm^{-1}.
Terminal carbonyl region (pentane): 2068s, 2035vs, 2000vs, 1992vs cm^{-1}.

^{1}**H NMR**(C$_6$D$_6$; 250 MHz): δ 1.07 (s, 9H, SC(CH$_3$)$_3$), 3.08 (d, J = 13.9 Hz, 1H, C=CH$_2$ endo), 3.35 (d, J = 9.2 Hz, 1H, C=CH$_2$ exo), 7.77 (dd, J = 13.9 Hz, J = 9.2 Hz, 1H, $\underline{H}$C=CH$_2$).

^{13}**C NMR**(C$_6$D$_6$; 67.9 MHz): δ 33.0 (q, J = 126 Hz, SC($\underline{C}$H$_3$)$_3$), 47.8 (s, S$\underline{C}$(CH$_3$)$_3$), 74.8 (dd, J = 163 Hz, J = 157 Hz, C=$\underline{C}$H$_2$), 154.8 (d, J = 151 Hz, H$\underline{C}$=CH$_2$), 209 (s, Fe-CO), 209-211 (broad s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 397 (M$^+$, 1), 368 (M$^+$ - CO, 10), 340 (M$^+$ - 2CO, 16), 312 (M$^+$ - 3CO, 17), 284 (M$^+$ - 4CO, 29), 256 (M$^+$ - 5CO, 16), 228 (M$^+$ - 6CO, 55), 201 (^{t}BuSFe$_2$, 8), 200 (Me$_2$SFe$_2$C=CH$_2$, 63), 172 (HSFe$_2$HC=CH$_2$, 13), 171 (SFe$_2$HC=CH$_2$, 9), 169 (SFe$_2$HC=C, 5), 145 (HSFe$_2$, 35), 144 (SFe$_2$, 100), 112 (Fe$_2$, 8), 57 (^{t}Bu, 32).

Synthesis of (μ-σ,π-PhC=CH$_2$)(μ-^{t}BuS)Fe$_2$(CO)$_6$) and (μ-σ,π-HC=CHPh)(μ-^{t}BuS)Fe$_2$(CO)$_6$ GBW-X-37

To the standard $[Et_3NH][(\mu-CO)(\mu-{}^tBuS)Fe_2(CO)_6]$ reagent solution (3.00 mmol) was added 0.35 ml (3.19 mmol) of phenylacetylene by syringe at room temperature. After the reaction mixture had been stirred for 1 h at reflux and then 4 h at room temperature, the solvent was removed in vacuo to yield a red oil which was dissolved in pentane/CH_2Cl_2 (1/1 v/v) and filtered through a narrow pad of silicic acid. Removal of the solvent on a rotary evaporator left a red oil which was purified by filtration chromatography. Pentane eluted a pale yellow band which was not collected. Pentane then eluted a red band which gave, as an inseparable mixture, 0.69 g (1.46 mmol, 49%) of $(\mu-\sigma,\pi-PhC{=}CH_2)(\mu-{}^tBuS)Fe_2(CO)_6$, <u>5h</u>, and $(\mu-\sigma,\pi-HC{=}CHPh)(\mu-{}^tBuS)Fe_2(CO)_6$, <u>5h'</u>, as an air-stable, red solid, mp 85.0-90.0°C after recrystallization from pentane.

Anal. Calcd. for $C_{18}H_{16}Fe_2O_6S$: C, 45.78; H, 3.42 %. Found: C, 45.69; H, 3.51 %.

IR($CHCl_3$): 2979m, 2950m, 2935m, 2909w, 2876w, 1600w(Ph), 1496w, 1460m, 1396w, 1368w, 1310w, 1154m, 1078w, 1028w, 692m, 641m, 613s, 596s, 495m cm^{-1}.
Terminal carbonyl region (pentane): 2068s, 2036vs, 2000vs, 1993vs cm^{-1}.

^{1}H NMR($CDCl_3$; 250 MHz): δ 1.40 (s, 9H, $SC(CH_3)_3$), 1.43 (s, 9H, $SC(CH_3)_3$), 2.79 (d, J = 2.5 Hz, 1H, $C{=}CH_2$ endo), 3.58 (d, J = 2.5 Hz, 1H, $C{=}CH_2$ exo), 4.46 (d, J = 13.7 Hz, 1H, $C{=}C\underline{H}Ph$), 7.20-7.30 (m, 10H, C_6H_5 both isomers), 8.30 (d, J = 13.7 Hz, 1H, $\underline{H}C{=}CHPh$). Ratio <u>5h</u>/<u>5h'</u> = 1.4/1.0.

^{13}C NMR($CDCl_3$, 67.9 MHz): δ 33.0 (q, J = 128 Hz, $SC(\underline{C}H_3)_3$), 33.3 (q, J = 128 Hz, $SC(\underline{C}H_3)_3$), 48.1 (s, $S\underline{C}(CH_3)_3$), 48.3 (s, $S\underline{C}(CH_3)_3$), 68.8 (dd, J = 155 Hz, J = 163 Hz, $C{=}\underline{C}H_2$), 96.6 (d, J = 158 Hz, $C{=}\underline{C}HPh$), 124.8-130.5 (m, C_6H_5), 139.3 (s, ipso C_6H_5), 141.5 (d, J = 145 Hz, $H\underline{C}{=}CHPh$), 156.9 (s, ipso C_6H_5), 185.0 (s, $Ph\underline{C}=CH_2$), 208.1, 210.0, and 212.2 (all s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 472 (M^+, 6), 444 (M^+ - CO, 27), 416 (M^+ - 2CO, 9), 388 (M^+ - 3CO, 24), 360 (M^+ - 4CO, 10), 332 (M^+ - 5CO, 19), 304 (M^+ - 6CO, 56), 248 ($HSFe_2PhC=CH_2$, 100), 144 (SFe_2, 69), 56 (Fe, 19).

Synthesis of (μ-σ,π-$Me_3SiC=CH_2$)(μ-^tBuS)$Fe_2(CO)_6$ and (μ-σ,π-$HC=CHSiMe_3$)(μ-^tBuS)$Fe_2(CO)_6$ JBH-49-II

To the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}^tBuS)Fe_2(CO)_6]$ reagent solution (3.00 mmol) was added 0.42 ml (3.00 mmol) of trimethylsilylacetylene by syringe at room temperature. After the reaction mixture had been stirred for 1 h at room temperature and then 2 h at reflux, the solvent was removed in vacuo to yield a red tar which was purified by filtration chromatography. Pentane eluted an orange band which gave, as an inseparable mixture, 0.48 g (1.02 mmol, 34%) of (μ-σ,π-$Me_3SiC=CH_2$)(μ-^tBuS)$Fe_2(CO)_6$, <u>5i</u>, and (μ-σ,π-$HC=CHSiMe_3$)(μ-^tBuS)$Fe_2(CO)_6$, <u>5i'</u>, as a slightly air-sensitive red oil.

Anal. Calcd. for $C_{15}H_{20}Fe_2O_6SSi$: C, 38.48; H, 4.30 %. Found: C, 38.45; H, 4.41 %.

IR($CHCl_3$): 2965s, 2950s, 2930s, 2905s, 2865m, 1472m, 1458s, 1405w, 1395m, 1365s, 1353s, 1262s, 1249vs, 1155s, 1100m, 1020m, 860vs, 840vs, 611vs, 590vs, 555vs, 500s cm^{-1}. Terminal carbonyl region (pentane): 2070m, 2035vs, 2000vs, 1992vs, 1980s cm^{-1}.

^{1}H NMR($CDCl_3$; 250 MHz): δ 0.11 (s, 9H, $Si(CH_3)_3$), 0.25 (s, 9H, $Si(CH_3)_3$), 1.36 (s, 9H, $SC(CH_3)_3$), 1.40 (s, 9H, $SC(CH_3)_3$), 3.30 (d, J = 3.57 Hz, 1H, $C=CH_2$ endo), 3.47 (d, J

= 15.19 Hz, 1H, HC=C<u>H</u>SiMe$_3$), 4.05 (d, J = 3.53 Hz, 1H, C=CH$_2$ exo), 8.25 (d, J = 15.10 Hz, 1H, <u>H</u>C=CHSiMe$_3$). Ratio <u>5i</u>/<u>5i'</u> = 1.0/1.0

^{13}C **NMR**(CDCl$_3$; 67.9 MHz): δ -0.56 (q, J = 119.4 Hz, Si(CH$_3$)$_3$), 2.24 (q, J = 119.0 Hz, Si(CH$_3$)$_3$), 33.30 (q, J = 126.4 Hz, SC(<u>C</u>H$_3$)$_3$), 32.89 (q, J = 127.3 Hz, SC(<u>C</u>H$_3$)$_3$), 48.04 (s, S<u>C</u>(CH$_3$)$_3$), 48.54 (s, S<u>C</u>(CH$_3$)$_3$), 78.19 (t, J = 158.2 Hz, C=<u>C</u>H$_2$), 91.40 (d, J = 141.1 Hz, C=<u>C</u>HSiMe$_3$), 159.71 (d, J = 147.8 Hz, H<u>C</u>=CHSiMe$_3$), 181.19 (s, Me$_3$Si<u>C</u>=CH$_2$), 207.96 (s, Fe-CO), 209.82 (broad s, Fe-CO), 212.06 (s, Fe-CO).

Mass Spectrum (FAB); m/z: 468 (M$^+$)

<u>Synthesis of (μ-σ,π-^{n}PrC=CH^{n}Pr)(μ-EtS)Fe$_2$(CO)$_6$ and (μ-^{n}PrC(=CH^{n}Pr)C=O)(μ-EtS)Fe$_2$(CO)$_6$</u> JBH-75A-VII

To the standard [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] reagent solution (3.21 mmol) was added 0.51 ml (3.50 mmol) of 4-octyne by syringe at room temperature. After the reaction mixture had been stirred for 35 min at reflux, the solvent was removed in vacuo to yield a red oil which was dissolved in pentane/CH$_2$Cl$_2$ (4/1 v/v) and filtered through a thin pad of silicic acid. Removal of the solvent on a rotary evaporator left a red oil which was purified by medium pressure chromatography. Pentane eluted three red bands. The first two contiguous bands were difficult to separate and were collected together. Removal of the solvent on a rotary evaporator left a red oil which was subjected to repeated medium pressure chromatography. Ultimately, the first band yielded 0.45 g (1.00 mmol, 31%) of (μ-σ,π-^{n}PrC=CH^{n}Pr)(μ-EtS)Fe$_2$(CO)$_6$, <u>9a</u>, as a slightly air-sensitive red oil.

Anal. Calcd. for $C_{16}H_{20}Fe_2O_6S$: C, 42.51; H, 4.46 %. Found: C, 42.94; H, 4.57 %.

IR(CCl_4): 2955vs, 2925s, 2865s, 2820w, 1470m, 1453s, 1433w, 1380m, 1338w, 1290w, 1255m, 1220w, 1130w, 1083w, 1045w, 965w, 933w, 880w, 660w, 630sh, 618vs, 600vs, 565vs cm^{-1}.
Terminal carbonyl region (pentane): 2060m, 2025vs, 1990vs-br, 1977s, 1970sh cm^{-1}.

^{1}**H NMR**($CDCl_3$; 250 MHz): δ 0.96 (t, J = 7.40 Hz, 3H, $CH_2CH_2C\underline{H}_3$), 1.02 (t, J = 7.25 Hz, 3H, $CH_2CH_2C\underline{H}_3$), 1.32 (t, J = 7.45 Hz, 3H, $SCH_2C\underline{H}_3$), 1.54, 1.75, 2.02, and 2.37 (all very broad s, 8H, CH_2), 2.63 (t, J = 7.74 Hz, 2H, $CH_3CH_2C\underline{H}_2C{=}CH^nPr$), 2.91 (t, J = 6.01 Hz, 1H, $C{=}C\underline{H}CH_2CH_2CH_3$).

^{13}**C NMR**(CD_2Cl_2; 75.4 MHz): δ 14.55 (q, J = 124.3 Hz, $CH_2CH_2\underline{C}H_3$), 14.99 (q, J = 126.6 Hz, $CH_2CH_2\underline{C}H_3$), 18.36 (q, J = 127.6 Hz, $SCH_2\underline{C}H_3$), 24.37 (t, J = 125.7 Hz, $CH_2\underline{C}H_2CH_3$), 28.93 (t, J = 127.5 Hz, $CH_2\underline{C}H_2CH_3$), 34.90 (t, J = 137.7 Hz, $S\underline{C}H_2CH_3$), 36.18 (t, J = 125.6 Hz, $\underline{C}H_2CH_2CH_3$), 52.53 (t, J = 125.4 Hz, $\underline{C}H_2CH_2CH_3$), 96.94 (d, J = 154.0 Hz, $C{=}\underline{C}H^nPr$), 187.27 (s, $^nPr\underline{C}{=}CH^nPr$), 209.16 and 211.76 (both s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 452 (M^+, 12), 424 (M^+ - CO, 12), 396 (M^+ - 2CO, 17), 368 (M^+ - 3CO, 43), 340 (M^+ - 4CO, 59), 312 (M^+ - 5CO, 59), 284 (M^+ - 6CO, 100), 256 ($HSFe_2{}^nPrC{=}CH^nPr$, 50), 254 ($SFe_2{}^nPrC{=}C^nPr$, 47), 226 ($SFe_2CH_2C{=}CH^nPr$, 24), 212 ($SFe_2C{=}CH^nPr$, 27), 198 ($HSFe_2C{=}CHCH_2CH_2$, 13), 184 ($HSFe_2C{=}CHCH_2$, 19), 170 ($HSFe_2C{=}CH$, 25), 145 ($HSFe_2$, 50), 144 (SFe_2, 85), 112 (Fe_2, 7), 56 (Fe, 10).

The second band yielded 0.06 g (0.16 mmol, 10% based on S) of (μ-EtS)$_2$Fe$_2$(CO)$_6$, 11, identified by its ^{1}H NMR spectrum.[15] The third red band eluting in pentane gave 0.40 g (0.83 mmol, 26%) of (μ-^{n}PrC(=CH^{n}Pr)C=O)(μ-EtS)Fe$_2$(CO)$_6$, 10a (an inseparable mixture of two isomers), as a slightly air-sensitive red oil. Analytically pure 10a for carbon/hydrogen combustion analysis could not be obtained.

IR(CCl$_4$): 2980vs, 2925s, 2905sh, 2875m, 1625m(C=C), 1455vs-br(acyl C=O), 1438s, 1378m, 1255m, 1188m, 1075s, 1035m, 907m, 888m, 703w, 678m, 620s, 608s, 580vs cm^{-1}. Terminal carbonyl region (pentane): 2065s, 2025vs, 2000vs, 1990vs, 1965s cm^{-1}.

^{1}H NMR(CDCl$_3$; 250 MHz): δ 0.68 (t, J = 7.23 Hz, 3H, CH$_2$CH$_2$C$\underline{H}_3$ major isomer), 0.74 (t, J = 6.64 Hz, 3H, CH$_2$CH$_2$C$\underline{H}_3$ minor isomer), 0.95 (t, J = 7.34 Hz, 3H, CH$_2$CH$_2$C$\underline{H}_3$ major isomer), 0.97 (t, J = 7.39 Hz, 3H, CH$_2$CH$_2$C$\underline{H}_3$ minor isomer), 1.29 (t, J = 7.42 Hz, 2H, CH$_3$CH$_2$C$\underline{H}_2$C=CH^{n}Pr minor isomer), 1.30 (t, J = 7.36 Hz, 3H, SCH$_2$C$\underline{H}_3$ minor isomer), 1.51 (t, J = 7.48 Hz, 3H, SCH$_2$C$\underline{H}_3$ major isomer), 1.54 (t, J = 7.58 Hz, 2H, CH$_3$CH$_2$C$\underline{H}_2$C=CH^{n}Pr major isomer), 1.77, 2.06, 2.22 (all m, 12H, CH$_2$ both isomers), 2.41 and 2.59 (both m, 4H, SC$\underline{H}_2$CH$_3$ both isomers), 6.54 (t, J = 7.36 Hz, 1H, C=C$\underline{H}$CH$_2$CH$_2$CH$_3$ major isomer), 6.71 (t, J = 7.34 Hz, 1H, C=C$\underline{H}$CH$_2$CH$_2$CH$_3$ minor isomer). Ratio major/minor = 3.8/1.0.

^{13}C NMR(CDCl$_3$; 67.9 MHz): δ 13.72 (q, J = 123.6 Hz, CH$_2$CH$_2\underline{C}$H$_3$ both isomers), 17.71 (q, J = 128.0 Hz, SCH$_2\underline{C}$H$_3$ minor isomer), 18.26 (q, J = 127.5 Hz, SCH$_2\underline{C}$H$_3$ major isomer), 22.04 (t, J = 126.1 Hz, CH$_2$), 26.10 (t, J = 125.2 Hz, CH$_2$), 27.38 (t, J = 126.4 Hz, CH$_2$), 27.56 (t, J = 125.7 Hz, CH$_2$), 29.65 (t, J = 124.9 Hz, CH$_2$), 31.20 (t, J = 124.8 Hz, CH$_2$), 32.93 (t, J = 140.9 Hz, S$\underline{C}$H$_2$CH$_3$ both isomers), 150.26 (s, ^{n}Pr$\underline{C}$=CH^{n}Pr minor isomer), 150.85 (s, ^{n}Pr$\underline{C}$=CH^{n}Pr major isomer), 153.08 (d, J = 150.0 Hz, C=$\underline{C}$H^{n}Pr major isomer), 154.68 (d, J = 151.4 Hz, C=<u>C</u>H^{n}Pr minor isomer), 208.02, 208.80, 209.63, 209.75, 210.82, 211.37, 212.12, and 212.69 (all s, Fe-CO), 287.14 (s, acyl C=O major isomer), 288.64 (s, acyl C=O minor isomer).

Mass Spectrum (EI); m/z (relative intensity): 480 (M^+, 4), 452 (M^+ - CO, 6), 424 (M^+ - 2CO, 11), 396 (M^+ - 3CO, 22), 368 (M^+ - 4CO, 24), 340 (M^+ - 5CO, 41), 312 (M^+ - 6CO, 61), 284 (M^+ - 7CO, 58), 256 ($HSFe_2{}^nPrC{=}CH^nPr$, 33), 254 ($SFe_2{}^nPrC{=}C^nPr$, 27), 226 ($HSFe_2CH_2CH_2C{=}CHCH_2CH_2$, 19), 224 ($SFe_2CH_2CH_2C{=}CCH_2CH_2$, 17), 212 ($HSFe_2CH_2CH_2C{=}CHCH_2$, 22), 198 ($HSFe_2CH_2C{=}CHCH_2$, 10), 184 ($HSFe_2C{=}CHCH_2$, 16), 170 ($HSFe_2C{=}CH$, 21), 145 ($HSFe_2$, 63), 144 ($SFe_2$, 100), 112 ($Fe_2$, 11), 56 (Fe, 32).

<u>Synthesis of (μ-σ,π-EtC=CHEt)(μ-EtS)$Fe_2(CO)_6$ and (μ-EtC(=CHEt)C=O)(μ-EtS)$Fe_2(CO)_6$</u> JBH-50-VII, GBW-X-22

To the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ reagent solution (2.95 mmol) was added 0.68 ml (6.00 mmol) of 3-hexyne by syringe at room temperature. After the reaction mixture had been stirred for 30 min at reflux, the solvent was removed in vacuo to yield a red oil which was dissolved in pentane and filtered through a thin pad of silicic acid. Removal of the solvent on a rotary evaporator left a red oil which was purified by filtration chromatography. Pentane eluted an orange band which gave 0.54 g (1.28 mmol, 43%) of (μ-σ,π-EtC=CHEt)(μ-EtS)$Fe_2(CO)_6$, <u>9b</u>, as an air-stable, red solid mp 58.0-60.0°C after recrystallization from pentane.

Anal. Calcd. for $C_{14}H_{16}Fe_2O_6S$: C, 39.66; H, 3.80 %. Found: C, 39.64; H, 3.85 %.

IR($CHCl_3$): 2991s, 2943s, 2882m, 1478w, 1457m, 1437w, 1380m, 1314m, 1260m, 1134m, 1058w, 976m, 871m, 844m, 640m, 620s, 600s, 575s, 500s cm^{-1}.

Terminal carbonyl region (pentane): 2079m, 2068s, 2036vs, 1994vs, 1984s cm^{-1}.

^{1}H NMR($CDCl_3$; 250 MHz): δ 1.14 (t, J = 7.4 Hz, 3H, CH_3), 1.28 (t, J = 7.4 Hz, 3H, CH_3), 1.33 (t, J = 7.4 Hz, 3H, $SCH_2C\underline{H}_3$), 1.88, 2.13, 2.40, and 2.68 (all m, 6H, CH_2), 2.84 (t, J = 6.0 Hz, 1H, $C{=}C\underline{H}Et$).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 14.7 (q, J = 131 Hz, CH_3), 17.9 (q, J = 128 Hz, CH_3), 18.6 (q, J = 131 Hz, CH_3), 26.2 (t, J = 128 Hz, CH_2), 34.2 (t, J = 141 Hz, $S\underline{C}H_2CH_3$), 42.5 (t, J = 127 Hz, CH_2), 97.7 (d, J = 161 Hz, $EtC{=}\underline{C}HEt$), 183.3 (s, $Et\underline{C}{=}CHEt$), 210.8 (broad s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 424 (M^+, 22), 396 (M^+ - CO, 24), 368 (M^+ - 2CO, 30), 340 (M^+ - 3CO, 31), 312 (M^+ - 4CO, 58), 284 (M^+ - 5CO, 44), 256 (M^+ - 6CO, 100), 228 ($HSFe_2EtC{=}CHEt$, 30), 144 (SFe_2, 51), 56 (Fe, 5).

Further elution with pentane yielded a second orange band which gave 0.42 g (0.92 mmol, 31%) of (μ-EtC(=CHEt)C=O)(μ-EtS)$Fe_2(CO)_6$, <u>10b</u> (an inseparable mixture of two isomers), as an air-stable, red solid mp 57.0-58.0°C after recrystallization from pentane.

Anal. Calcd. for $C_{15}H_{16}Fe_2O_7S$: C, 39.86; H, 3.57 %. Found: C, 39.97; H, 3.61 %.

IR(CCl_4): 2970s, 2930m, 2875m, 1628m(C=C), 1460sh, 1452vs(acyl C=O), 1440vs, 1377m, 1317w, 1291w, 1255m, 1200s, 1115w, 1075s, 1058vs, 985m, 978m, 680m, 625s, 610vs, 580 vs cm^{-1}.
Terminal carbonyl region (pentane): 2070m, 2025vs, 2005s, 1995vs, 1968m cm^{-1}.

^{1}H NMR(acetone-d_6; 250 MHz): δ 0.62 (t, J = 7.42 Hz, 3H, CH_3 major isomer), 0.70 (t, J = 7.42 Hz, 3H, CH_3 minor isomer), 1.12 (t, J = 7.50 Hz, 3H, CH_3 major isomer), 1.28 (t, J = 7.42 Hz, 6H, CH_3 and $SCH_2C\underline{H}_3$ minor isomers), 1.50 (t, J = 7.43 Hz, 3H, $SCH_2C\underline{H}_3$ major isomer), 1.86 (q, J = 7.33 Hz, 2H, CH_2 major isomer), 1.87 (q, J = 7.48 Hz, 2H, CH_2 minor isomer), 2.33 and 2.72 (both m, 6H, CH_2 both isomers), 2.52 (q, J = 7.31 Hz, 2H, $SC\underline{H}_2CH_3$ minor isomer), 6.64 (t, J = 7.40 Hz, 1H, $C{=}C\underline{H}CH_2CH_3$ major isomer), 6.78 (t, J = 7.42 Hz, $C{=}C\underline{H}CH_2CH_3$ minor isomer). Ratio major/minor = 3.7/1.0.

^{13}C NMR($CDCl_3$; 75.4 MHz): δ 13.10 (q, J = 127.8 Hz, CH_3 both isomers), 13.61 (q, J = 127.0 Hz, CH_3 both isomers), 18.21 (q, J = 123.9 Hz, $SCH_2\underline{C}H_3$ both isomers), 19.04 (t, J = 122.4 Hz, CH_2 both isomers), 22.30 (t, J = 126.7 Hz, CH_2 both isomers), 32.91 (t, J = 141.1 Hz, $S\underline{C}H_2CH_3$ major isomer), 151.21 (s, $Et\underline{C}{=}CHEt$ minor isomer), 151.69 (s, $Et\underline{C}{=}CHEt$ major isomer) 153.98 (d, J = 153.0 Hz, $EtC{=}\underline{C}HEt$ major isomer), 155.56 (d, J = 154.2 Hz, $EtC{=}\underline{C}HEt$ minor isomer), 208.10, 208.85, 209.14, 209.73, 212.09, 212.28, and 212.66 (all s, Fe-CO both isomers), 287.20 (s, acyl C=O major isomer), 287.31 (s, acyl C=O minor isomer).

Mass Spectrum (EI); m/z (relative intensity): 452 (M^+, 20), 424 (M^+ - CO, 21), 396 (M^+ - 2CO, 37), 368 (M^+ - 3CO, 43), 340 (M^+ - 4CO, 42), 312 (M^+ - 5CO, 73), 284 (M^+ - 6CO, 100), 256 (M^+ - 7CO, 48), 144 (SFe_2, 40), 56 (Fe, 5).

Synthesis of (μ-σ,π-MeC=CHEt)(μ-EtS)$Fe_2(CO)_6$, (μ-σ,π-EtC=CHMe)(μ-EtS)$Fe_2(CO)_6$, (μ-EtC(=CHMe)C=O)(μ-EtS)$Fe_2(CO)_6$, and (μ-MeC(=CHEt)C=O)(μ-EtS)$Fe_2(CO)_6$ JBH-1-VIII

To the standard [Et_3NH][(μ-CO)(μ-EtS)$Fe_2(CO)_6$] reagent solution (3.13 mmol) was added 0.34 ml (3.50 mmol) of 2-pentyne by syringe at room temperature. After the reaction mixture had been stirred for 45 min at reflux, the solvent was removed in vacuo to yield a red oil which was dissolved in pentane and filtered through a thin pad of silicic acid. Removal of the solvent on a rotary evaporator left a red oil which was purified by medium pressure chromatography. Pentane eluted three red bands. The first two contiguous bands were difficult to separate and were collected together. Removal of the solvent on a rotary evaporator left a red oil which was subjected to repeated medium pressure chromatography. Ultimately, the first band yielded, as an inseparable mixture, 0.26 g (0.64 mmol, 20%) of (μ-σ,π-EtC=CHMe)(μ-EtS)$Fe_2(CO)_6$, 9c′, and (μ-σ,π-MeC=CHEt)(μ-EtS)$Fe_2(CO)_6$, 9c, as a slightly air-sensitive red oil.

Anal. Calcd. for $C_{13}H_{14}Fe_2O_6S$: C, 38.08; H, 3.44 %. Found: C, 38.58; H, 3.54 %.

IR(CCl_4): 2965s, 2925s, 2900sh, 2870m, 2850sh, 1475sh, 1455s, 1433m, 1378m, 1370m, 1308w, 1290w, 1255m, 1130w, 1058w, 1045w, 1025w, 1008w, 965w, 940w, 875w, 660w, 638s, 615vs, 600vs, 565vs cm^{-1}.
Terminal carbonyl region (pentane): 2060m, 2025vs, 1993s, 1988s, 1978m cm^{-1}.

^{1}H NMR($CDCl_3$; 250 MHz): δ 1.12 (t, J = 7.74 Hz, 3H, $CH_2C\underline{H}_3$), 1.25 (t, J = 7.24 Hz, 3H, $CH_2C\underline{H}_3$), 1.32 (t, J = 7.65 Hz, 3H, $SCH_2C\underline{H}_3$), 1.68 (d, J = 5.65 Hz, 3H, $EtC{=}CHC\underline{H}_3$), 1.95 (m, 2H, $MeC{=}CHC\underline{H}_2CH_3$), 2.34 (q, J = 7.29 Hz, 2H, $SC\underline{H}_2CH_3$ both isomers), 2.56 (s, 3H, $C\underline{H}_3C{=}CHEt$), 2.73 (q, J = 7.04 Hz, 2H, $CH_3C\underline{H}_2C{=}CHMe$), 2.93 (q, J = 5.58 Hz, 1H, $EtC{=}C\underline{H}CH_3$), 2.94 (t, J = 5.58 Hz, 1H, $MeC{=}C\underline{H}CH_2CH_3$). Ratio 9c/9c′ = 1.45/1.0

^{13}C NMR(CD_2Cl_2; 67.9 MHz): δ 14.69 (q, J = 127.4 Hz, CH_3), 18.29 (q, J = 129.1 Hz, CH_3), 18.49 (q, J = 128.6 Hz,

CH_3), 27.42 (t, J = 126.8 Hz, $MeC{=}CH\underline{C}H_2CH_3$), 34.52 (t, J = 140.2 Hz, $S\underline{C}H_2CH_3$), 34.64 (t, J = 140.5 Hz, $S\underline{C}H_2CH_3$), 35.45 (q, J = 126.2 Hz, $\underline{C}H_3C{=}CHEt$), 42.81 (t, J = 130.2 Hz, $CH_3\underline{C}H_2C{=}CHMe$), 89.06 (d, J = 155.5 Hz, $C{=}\underline{C}HMe$), 97.76 (d, J = 148.4 Hz, $C{=}\underline{C}HEt$), 176.20 (s, $Me\underline{C}{=}CHEt$), 184.40 (s, $Et\underline{C}{=}CHMe$), 211.22 (s, Fe-CO both isomers).

Mass Spectrum (EI); m/z (relative intensity): 410 (M^+, 3), 382 (M^+ - CO, 8), 354 (M^+ - 2CO, 15), 326 (M^+ - 3CO, 15), 298 (M^+ - 4CO, 20), 270 (M^+ - 5CO, 21), 242 (M^+ - 6CO, 56), 214 ($HSFe_2EtC{=}CHMe$, 26), 212 ($SFe_2EtC{=}CMe$, 29), 186 ($HSFe_2HC{=}CHMe$, 8), 185 ($SFe_2HC{=}CHMe$, 12), 184 ($SFe_2C{=}CHMe$, 29), 183 ($SFe_2C{=}CMe$, 8), 145 ($HSFe_2$, 46), 144 (SFe_2, 100), 112 (Fe_2, 12), 69 (EtC=CHMe, 43), 56 (Fe, 39).

The second band gave 0.07 g (0.17 mmol, 11% based on S) of $(\mu\text{-}EtS)_2Fe_2(CO)_6$, 11, identified by its ^1H NMR spectrum.[15] The third band gave, as an inseparable mixture, 0.32 g (0.74 mmol, 24%) of $(\mu\text{-}EtC({=}CHMe)C{=}O)(\mu\text{-}EtS)Fe_2(CO)_6$, 10c′ (also an inseparable mixture of two isomers), and $(\mu\text{-}MeC({=}CHEt)C{=}O)(\mu\text{-}EtS)Fe_2(CO)_6$, 10c (also an inseparable mixture of two isomers), as a slightly air-sensitive red oil. Analytically pure 10c/10c′ could not be obtained for a carbon/hydrogen combustion analysis.

IR(CCl_4): 2960s, 2920s, 2865m, 2845m, 1630m(C=C), 1450vs-br(acyl C=O), 1375m, 1343vw, 1295vw, 1253m, 1203m, 1070m, 1055m, 1043m, 1003m, 965w, 850w, 688m, 660m, 620s, 608s, 580vs-br cm^{-1}.

Terminal carbonyl region (pentane): 2068m, 2028vs, 2000s, 1993s, 1965m cm^{-1}.

^1H NMR($CDCl_3$; 300 MHz): δ 0.61 (t, J = 7.61 Hz, 3H, $CH_2C\underline{H}_3$ major isomer), 0.66 (t, J = 8.03 Hz, 3H, $CH_2C\underline{H}_3$ minor isomer), 1.09 (t, J = 7.62 Hz, 3H, $CH_2C\underline{H}_3$ major isomer), 1.10 (t, J = 7.45 Hz, 3H, $CH_2C\underline{H}_3$ minor isomer), 1.30 (t, J = 7.33 Hz, 3H, $SCH_2C\underline{H}_3$ minor isomer), 1.33 (s, 3H, $C\underline{H}_3C{=}CHEt$ major isomer), 1.35 (t, J = 7.22 Hz, 3H, $SCH_2C\underline{H}_3$ minor isomer), 1.40 (s, 3H, $C\underline{H}_3C{=}CHEt$ minor isomer), 1.48 (t, J = 7.24 Hz, 6H, $SCH_2C\underline{H}_3$ major isomers $\underline{c}$ and $\underline{c'}$), 1.87 (d, J = 6.62 Hz, 3H, $EtC{=}CHC\underline{H}_3$ major isomer), 1.92 (d, J = 7.54 Hz, 3H, $EtC{=}CHC\underline{H}_3$ minor isomer), 1.85, 2.05, and 2.21 (all m, 8H, $C\underline{H}_2CH_3$ major and minor isomers $\underline{c}$ and $\underline{c'}$), 2.41 and 2.59 (both m, 8H, $SC\underline{H}_2CH_3$ major and minor isomers $\underline{c}$ and $\underline{c'}$), 6.55 (m, 2H, $MeC{=}C\underline{H}Et$ minor isomer and $EtC{=}C\underline{H}Me$ major isomer), 6.62 (t, J = 6.85 Hz, 1H, $MeC{=}C\underline{H}CH_2CH_3$ major isomer), 6.76 (q, J = 7.33 Hz, 1H, $EtC{=}C\underline{H}CH_3$ minor isomer). Ratio $\underline{10c'}/\underline{10c}$ = 1.1/1.0. Ratio $\underline{10c}$(major)/$\underline{10c}$(minor) = 2.0/1.0. Ratio $\underline{10c'}$(major)/$\underline{10c'}$(minor) = 2.5/1.0.

$^{13}C\{^1H\}$ **NMR**($CDCl_3$; 67.9 MHz): δ 11.01, 11.30, 12.81, 13.22, 14.17, 14.80, 17.91, 18.44, 18.81, 22.74, 26.48, 29.78, 31.31, 31.94, and 33.20 (CH_2 and CH_3); 145.33, 147.32, and 148.61 ($R^1\underline{C}{=}CHR^2$); 153.49 and 154.53 ($R^1C{=}\underline{C}HR^2$); 208.16, 209.76, 210.82, 211.12, 212.11 and 212.72 (Fe-CO); 286.42, 286.74, and 288.21 (acyl C=O).

Mass Spectrum (EI); m/z (relative intensity): 438 (M^+, 12), 410 (M^+ - CO, 17), 382 (M^+ - 2CO, 32), 354 (M^+ - 3CO, 48), 326 (M^+ - 4CO, 48), 298 (M^+ - 5CO, 76), 270 (M^+ - 6CO, 100), 242 (M^+ - 7CO, 99), 214 ($HSFe_2EtC{=}CHMe$, 68), 212 ($SFe_2EtC{=}CMe$, 76), 186 ($HSFe_2HC{=}CHMe$, 18), 185 ($SFe_2HC{=}CHMe$, 20), 184 ($SFe_2C{=}CHMe$, 57), 183 ($SFe_2C{=}CMe$, 14), 159 (SFe_2Me, 15), 145 ($HSFe_2$, 95), 144 (SFe_2, 100), 112 (Fe_2, 7), 69 (EtC=CHMe, 12), 56 (Fe, 3).

Decarbonylation of (μ-^{n}PrC(=CH^{n}Pr)C=O)(μ-EtS)$Fe_2(CO)_6$ JBH-5-VIII

A 100 ml three necked, round bottomed flask equipped with a reflux condenser and nitrogen inlet (gas adapter), glass stopper, stir-bar, and rubber septum was charged with 0.18 g (0.38 mmol) of $(\mu\text{-}^{n}PrC(=CH^{n}Pr)C=O)(\mu\text{-}EtS)Fe_2(CO)_6$, 10a, and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 30 ml of THF. After the reaction mixture had been stirred for 20 h at room temperature and then 4 h at reflux, the solvent was removed in vacuo to yield a dark oil which was purified by medium pressure column chromatography. Pentane eluted two contiguous bands which were collected together and which yielded a red oil identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz) to be a mixture of 0.03 g (0.07 mmol, 18%) of $(\mu\text{-}\sigma,\pi\text{-}^{n}PrC=CH^{n}Pr)(\mu\text{-}EtS)Fe_2(CO)_6$, 9a, and 0.03 g (0.07 mmol, 36% based on S) of $(\mu\text{-}EtS)_2Fe_2(CO)_6$, 11.[15] Pentane then eluted two contiguous orange bands which were collected together and which gave 0.06 g (0.13 mmol, 35%) of starting material (10a - mixture of two inseparable isomers) identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz).

Decarbonylation of $(\mu\text{-}EtC(=CHEt)C=O)(\mu\text{-}EtS)Fe_2(CO)_6$ JBH-4-VIII

In an experiment similar to the decarbonylation of 10a, a THF solution containing 0.16 g (0.34 mmol) of $(\mu\text{-}EtC(=CHEt)C=O)(\mu\text{-}EtS)Fe_2(CO)_6$, 10b, was heated at reflux for 4 h. Subsequently, the solvent was removed in vacuo and the resulting brown-black oil was purified by medium pressure chromatography. Pentane eluted two contiguous orange bands which were collected together and which yielded 0.05 g of a red oil identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz) to be a mixture of 0.02 g (0.05 mmol, 14%) of $(\mu\text{-}\sigma,\pi\text{-}EtC=CHEt)(\mu\text{-}EtS)Fe_2(CO)_6$, 9b, and 0.03 g (0.07 mmol, 42% based on S) of $(\mu\text{-}EtS)_2Fe_2(CO)_6$, 11.[15] Pentane then eluted a third orange band which gave 0.03 g (0.07 mmol, 21%) of starting material (10b - mixture of two inseparable isomers) identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz).

Decarbonylation of (μ-EtC(=CHMe)C=O)(μ-EtS)$Fe_2(CO)_6$ and (μ-MeC(=CHEt)C=O)(μ-EtS)$Fe_2(CO)_6$ JBH-6-VIII

In an experiment similar to the decarbonylation of 10a, a THF solution containing 0.19 g (0.43 mmol) of (μ-EtC(=CHMe)C=O)(μ-EtS)$Fe_2(CO)_6$, 10c, and (μ-MeC(=CHEt)C=O)(μ-EtS)$Fe_2(CO)_6$, 10c′, as an inseparable mixture was heated at reflux for 4 h. Subsequently, the solvent was removed in vacuo and the resulting brown-black oil was purified by medium pressure chromatography. Pentane eluted an orange band which yielded 0.06 g of a red oil identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz) to be a mixture of 0.05 g (0.12 mmol, 27%) of (μ-σ,π-EtC=CHMe)(μ-EtS)$Fe_2(CO)_6$, 9c, and (μ-σ,π-MeC=CHEt)(μ-EtS)$Fe_2(CO)_6$, 9c′, and 0.02 g (0.04 mmol, 18% based on S) of (μ-EtS)$_2Fe_2(CO)_6$, 11.[15] Pentane then eluted a second orange band which gave 0.06 g (0.13 mmol, 31%) of starting material (10c/10c′ - mixture of four inseparable isomers) identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz).

Synthesis of (μ-EtC(=CHEt)C=O)(μ-EtS)$Fe_2(CO)_6$ under CO JBH-53-VII

The standard [Et_3NH][(μ-CO)(μ-EtS)$Fe_2(CO)_6$] reagent solution was prepared (1.66 mmol) and purged with a stream of carbon monoxide for 30 min. Subsequently, 0.34 ml (3.00 mmol) of 3-hexyne was added by syringe at room temperature, and the reaction mixture was then heated at reflux for 35 min with continuous CO purge. The solvent was removed in vacuo, and the resulting red oil was purified by filtration chromatography. Pentane eluted a dark orange band which gave 0.33 g (0.78 mmol, 47%) of (μ-σ,π-EtC=CHEt)(μ-EtS)$Fe_2(CO)_6$, 9b, identified by its ^1H NMR spectrum (acetone-d_6; 250 MHz). Pentane then eluted a light orange band which gave 0.25 g (0.56 mmol, 34%) of (μ-EtC(=CHEt)C=O)(μ-EtS)$Fe_2(CO)_6$, 10b, also identified by its ^1H NMR spectrum (acetone-d_6; 250 MHz).

Synthesis of (μ-HC(=CH$_2$)C=O)(μ-EtS)Fe$_2$(CO)$_6$ JBH-73-VII

To the standard [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] reagent solution (3.21 mmol) was added 0.26 ml (3.21 mmol) of acryloyl chloride by syringe at room temperature. An immediate reaction ensued with brisk gas evolution, a gradual color change to bright red, and formation of a white precipitate ([Et$_3$NH][Cl]). After the reaction mixture had been stirred for 1 h at room temperature, the solvent was removed in vacuo to yield a red oily solid which was purified by filtration chromatography. Pentane eluted two orange bands. The first band gave a red oil which when subjected to repeated purification by medium pressure chromatography yielded 0.53 g (1.44 mmol, 45%) of (μ-σ,π-HC=CH$_2$)(μ-EtS)Fe$_2$(CO)$_6$, 16a,[9a] and 0.04 g (0.10 mmol, 6% based on S) of (μ-EtS)$_2$Fe$_2$(CO)$_6$, 11,[15] both as slightly air-sensitive red oils, and both identified by their respective ^{1}H NMR spectra. The second band gave 0.56 g of a slightly air-sensitive red oil identified by its ^{1}H NMR spectrum (CDCl$_3$; 300 MHz) to be a mixture of 0.07g (0.19 mmol, 6%) of the decarbonylation product (μ-σ,π-HC=CH$_2$)(μ-EtS)Fe$_2$(CO)$_6$, 16a,[9a] and 0.48 g (1.76 mmol, 38%) of (μ-HC(=CH$_2$)C=O)(μ-EtS)Fe$_2$(CO)$_6$, 15a (itself a mixture of two inseparable isomers). Due to the facile loss of carbon monoxide, analytically pure (μ-HC(=CH$_2$)C=O)(μ-EtS)Fe$_2$(CO)$_6$, 15a, could not be obtained.

IR(CCl$_4$): 3015vw, 2985sh, 2983m, 2928m, 2870w, 1619vw(C=C), 1603w(C=C), 1462vs-br(acyl C=O), 1435m, 1400m, 1380m, 1293vw, 1275vw, 1258m, 1162s, 1070vw, 1050vw, 1005s, 985m, 975m, 962s, 942s, 623s, 610vs, 590vs cm^{-1}.
Terminal carbonyl region (pentane): 2078s, 2040vs, 2010vs, 1998vs, 1975s cm^{-1}.

^{1}**H NMR**(CDCl$_3$; 300 MHz): δ 1.33 (t, J = 7.23 Hz, 3H, SCH$_2$C$\underline{H}_3$ minor isomer), 1.49 (t, J = 7.44 Hz, 3H, SCH$_2$C$\underline{H}_3$ major isomer), 2.08, 2.26, and 2.67 (all m, 4H, SC$\underline{H}_2$CH$_3$ both isomers), 5.69-6.22 (m, 6H, vinylic protons both isomers). Ratio major/minor = 2.5/1.0.

^{13}C **NMR**($CDCl_3$; 100.5 MHz): δ 18.35 (q, J = 128.4 Hz, $SCH_2\underline{C}H_3$ both isomers), 25.91 (t, J = 139.0 Hz, $S\underline{C}H_2CH_3$ minor isomer), 32.97 (t, J = 138.0 Hz, $S\underline{C}H_2CH_3$ major isomer) 128.34 (t, J = 159.0 Hz, $HC{=}\underline{C}H_2$ major isomer), 129.40 (t, J = 159.8 Hz, $HC{=}\underline{C}H_2$ minor isomer), 143.76 (d, J = 154.7 Hz, $H\underline{C}{=}CH_2$ major isomer), 144.21 (d, J = 158.7 Hz, $H\underline{C}{=}CH_2$ minor isomer), 207.54, 209.34, 209.80, 210.16, 211.01, and 211.66 (all s, Fe-CO both isomers), 289.39 (s, acyl C=O major isomer), 291.88 (s, acyl C=O minor isomer).

Mass Spectrum (EI); m/z (relative intensity): 396 (M^+, 0.1), 368 (M^+ - CO, 3), 340 (M^+ - 2CO, 6), 312 (M^+ - 3CO, 8), 284 (M^+ - 4CO, 7), 256 (M^+ - 5CO, 9), 228 (M^+ - 6CO, 16), 200 (M^+ - 7CO, 17), 198 ($EtSFe_2C{=}CH$, 10), 172 ($HSFe_2HC{=}CH_2$, 9), 145 ($HSFe_2$, 23), 144 (SFe_2, 44), 112 (Fe_2, 6), 111 ($FeH_2C{=}CHCO$, 15), 97 (FeCCO, 25), 56 (Fe, 23), 55 ($H_2C{=}CHCO$, 52).

Synthesis of (μ-HC(=CHPh)C=O)(μ-EtS)$Fe_2(CO)_6$ JBH-2-VIII

To the standard [Et_3NH][(μ-CO)(μ-EtS)$Fe_2(CO)_6$] reagent solution (3.02 mmol) was added by cannula 0.50 g (3.01 mmol) of cinnamoyl chloride dissolved under nitrogen in a separate flask in 30 ml of THF. An immediate reaction ensued with brisk gas evolution, a gradual color change to bright red, and formation of a white precipitate ([Et_3NH][Cl]). After the reaction mixture had been stirred for 45 min at room temperature, the solvent was removed in vacuo to yield a red oily solid which was purified by filtration chromatography. Pentane eluted a very pale orange band which was not collected. Pentane/CH_2Cl_2 (20/1 v/v) eluted an orange band which gave 0.45 g (1.00 mmol, 33%) of (μ-σ,π-HC=CHPh)(μ-EtS)$Fe_2(CO)_6$, 16b (5h′), as an air-stable, red solid identified by its ^{1}H NMR spectrum ($CDCl_3$; 300 MHz). Pentane then eluted a red band which gave 0.89 g of a slightly air-sensitive red oil identified by its ^{1}H NMR spectrum ($CDCl_3$; 250 MHZ) to be a mixture of 0.06g (0.15 mmol, 5%) of the decarbonylation product (μ-σ,π-HC=CHPh)(μ-EtS)$Fe_2(CO)_6$, <u>16b</u> (<u>5h'</u>), and 0.83 g (1.76 mmol, 59%) of (μ-HC(=CHPh)C=O)(μ-EtS)$Fe_2(CO)_6$, <u>15b</u> (itself an inseparable mixture of two isomers). Due to the facile loss of carbon monoxide, analytically pure (μ-HC(=CHPh)C=O)(μ-EtS)$Fe_2(CO)_6$, <u>15b</u>, could not be obtained.

IR(CCl_4): 3075vw, 3055vw, 3025vw, 2960w, 2920w, 2865w, 1618m(C=C), 1605s(C=C), 1573w(Ph), 1495w(Ph), 1448vs-br(acyl C=O), 1375w, 1323w, 1298w, 1273w, 1253w, 1207w, 1180w, 1157w, 1135s, 1050s, 1000w, 968m, 878w, 858w, 685m, 663w, 645w, 620m, 603s, 580s-br cm^{-1}.
Terminal carbonyl region (pentane): 2070m, 2030vs, 2000s, 1993s, 1970m cm^{-1}.

^{1}**H NMR**($CDCl_3$; 250 MHz): δ 1.34 (t, J = 7.48 Hz, 3H, $SCH_2C\underline{H}_3$ minor isomer), 1.50 (t, J = 7.42 Hz, 3H, $SCH_2C\underline{H}_3$ major isomer), 2.13, 2.37, 2.63 (all m, 4H, $SC\underline{H}_2CH_3$ both isomers), 6.55 (d, J = 15.85 Hz, 1H, $\underline{H}$C=CHPh major isomer), 6.87 (d, J = 15.74 Hz, 1H, $\underline{H}$C=CHPh minor isomer), 7.10 (d, J = 15.82 Hz, 1H, HC=C$\underline{H}$Ph major isomer), 7.13 (d, J = 15.81 Hz, 1H, HC=C$\underline{H}$Ph minor isomer), 7.26-7.53 (m, 10H, C_6H_5 both isomers). Ratio major/minor = 2.3/1.0.

^{13}**C NMR**($CDCl_3$; 67.9 MHz): δ 17.80 (q, J = 129.7 Hz, $SCH_2\underline{C}H_3$ minor isomer), 18.28 (q, J = 128.7 Hz, $SCH_2\underline{C}H_3$ major isomer), 25.95 (t, J = 139.8 Hz, $S\underline{C}H_2CH_3$ minor isomer), 32.95 (t, J = 141.7 Hz, $S\underline{C}H_2CH_3$ major isomer), 125.80 (d, J = 152.4 Hz, HC=$\underline{C}$HPh minor isomer), 128.86 (d, J = 158.5 Hz, C_6H_5), 131.14 (d, J = 150.4 Hz, HC=$\underline{C}$HPh major isomer), 134.07 (s, ipso C_6H_5), 134.36 (d, J = 158.6 Hz, C_6H_5), 134.72 (d, J = 158.6 Hz, C_6H_5), 142.48 (d, J = 154.8 Hz, H$\underline{C}$=CHPh minor isomer), 143.50 (d, J = 154.1 Hz, H$\underline{C}$=CHPh major isomer), 207.66, 209.42, 210.23, 210.59, 211.38, 212.04 (all s, Fe-CO both isomers), 284.31 (s, acyl C=O major isomer), 287.02 (s, acyl C=O minor isomer).

Mass Spectrum (EI); m/z (relative intensity): 472 (M^+, 0.2), 444 (M^+ - CO, 7), 416 (M^+ - 2CO, 7), 388 (M^+ - 3CO, 12), 360 (M^+ - 4CO, 16), 332 (M^+ - 5CO, 11), 304 (M^+ - 6CO, 23), 276 (M^+ - 7CO, 83), 248 ($HSFe_2HC=CHPh$, 53), 247 ($SFe_2HC=CHPh$, 19), 246 ($SFe_2C=CHPh$, 12), 245 ($SFe_2C=CPh$, 7), 221 (SFe_2Ph, 43), 169 ($HSFe_2C=C$, 19), 145 ($HSFe_2$, 31), 144 (SFe_2, 100), 77 (Ph, 12), 56 (Fe, 27).

Synthesis of (μ-σ-π-HC=CHMe)(μ-EtS)$Fe_2(CO)_6$ and (μ-HC(=CHMe)C=O)(μ-EtS)$Fe_2(CO)_6$ JBH-69-VII

To the standard [Et_3NH][(μ-CO)(μ-EtS)$Fe_2(CO)_6$] reagent solution (3.12 mmol) was added 0.30 ml (3.12 mmol) of crotonyl chloride by syringe at room temperature. An immediate reaction ensued with brisk gas evolution, a gradual color change to bright red, and formation of a white precipitate ([Et_3NH][Cl]). After the reaction mixture had been stirred for 1.5 h at room temperature, the solvent was removed in vacuo to yield a red oily solid which was purified by filtration chromatography. Pentane and pentane/CH_2Cl_2 (20/1 v/v) eluted two orange bands. The first gave a red oil which when subjected to repeated purification by medium pressure chromatography yielded 0.05 g (0.13 mmol, 8% based on S) of (μ-EtS)$_2Fe_2(CO)_6$, 11 (a red oil identified by its ^1H NMR spectrum),[15] and 0.12 g (0.34 mmol, 10%) of (μ-σ,π-HC=CHMe)(μ-EtS)$Fe_2(CO)_6$, 16c (also a slightly air-sensitive red oil).

Anal. Calcd. for $C_{11}H_{10}Fe_2O_6S$: C, 34.59; H, 2.64 %. Found: C, 34.92; H, 2.72 %.

IR(CCl_4): 2990sh, 2970m, 2930s, 2910m, 2870w, 2860w, 1469m, 1456m, 1445w, 1438w, 1378m, 1258m, 1238w, 1050w,

1030w, 990m, 980w, 920w, 842w, 675m, 625sh, 615vs, 600vs, 570s, 500s cm^{-1}.
Terminal carbonyl region (pentane): 2068s, 2040vs, 2005vs, 1999vs, 1958vw cm^{-1}.

^1H NMR($CDCl_3$; 250 MHz): δ 1.28 (t, J = 7.39 Hz, 3H, $SCH_2C\underline{H}_3$), 1.72 (d, J = 5.82 Hz, 3H, $C{=}CHC\underline{H}_3$), 2.30 (q, J = 7.36 Hz, 2H, $SC\underline{H}_2CH_3$), 3.57 (m, 1H, $HC{=}C\underline{H}CH_3$), 7.56 (d, J = 13.06 Hz, 1H, $\underline{H}C{=}CHMe$).

^{13}C NMR($CDCl_3$; 100.5 MHz): δ 17.95 (q, J = 128.6 Hz, $SCH_2\underline{C}H_3$), 24.86 (q, J = 127.3 Hz, $C{=}CH\underline{C}H_3$), 33.71 (t, J = 140.5 Hz, $S\underline{C}H_2CH_3$), 93.49 (d, J = 158.7 Hz, $C{=}\underline{C}HMe$), 151.47 (d, J = 146.5 Hz, $H\underline{C}{=}CHMe$), 208.85 and 209.85 (both s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 382 (M^+, 4), 354 (M^+ - CO, 11), 326 (M^+ - 2CO, 12), 298 (M^+ - 3CO, 13), 270 (M^+ - 4CO, 16), 242 (M^+ - 5CO, 17), 214 (M^+ - 6CO, 46), 212 ($EtSFe_2C{=}CMe$, 18), 186 ($HSFe_2HC{=}CHMe$, 32), 185 ($HSFe_2C{=}CHMe$, 9), 184 ($HSFe_2C{=}CMe$, 9), 183 ($SFe_2C{=}CMe$, 5), 145 ($HSFe_2$, 34), 144 (SFe_2, 100), 112 (Fe_2, 8), 95 (FeC=CMe, 6), 56 (Fe, 21).

The second band gave, as an inseparable mixture of two isomers, 1.03 g (2.51 mmol, 80%) of (μ-HC(=CHMe)C=O)(μ-EtS)$Fe_2(CO)_6$, 15c, as a slightly air-sensitive red oil. Due to facile loss of carbon monxide, analytically pure (μ-HC(=CHMe)C=O)(μ-EtS)$Fe_2(CO)_6$ could not be obtained.

IR(CCl_4): 3040vw, 2990sh, 2970s, 2930s, 2870w, 2855w, 1640s(C=C), 1628s(C=C), 1460vs-br(acyl C=O), 1440sh, 1380m, 1287m, 1260m, 1160vs, 1118m, 1095m, 1070s, 1052m, 1030w, 965s, 932s, 910s, 640s, 625vs, 609vs, 590vs, 570sh cm^{-1}.
Terminal carbonyl region (pentane): 2078s, 2040vs, 2010vs, 1998vs, 1973s cm^{-1}.

^{1}H NMR($CDCl_3$; 300 MHz): δ 1.34 (t, J = 7.24 Hz, 3H, $SCH_2C\underline{H}_3$ minor isomer), 1.49 (t, J = 7.76 Hz, 3H, $SCH_2C\underline{H}_3$ major isomer), 1.85 (m, 6H, $C{=}CHC\underline{H}_3$ both isomers), 2.11, 2.32, and 2.64 (all m, 4H, $SC\underline{H}_2CH_3$ both isomers), 5.96 (dd, J = 15.49Hz, J = 1.47 Hz, 1H, $\underline{H}C{=}CHMe$ major isomer), 6.07 (dd, J = 14.95 Hz, J = 2.30 Hz, 1H, $\underline{H}C{=}CHMe$ minor isomer), 6.57 (m, 2H, $HC{=}C\underline{H}Me$ both isomers). Ratio major/minor = 2.0/1.0.

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 17.70 (q, J = 128.1 Hz, $HC{=}CH\underline{C}H_3$ both isomers), 18.18 (q, J = 128.4 Hz, $SCH_2\underline{C}H_3$ both isomers), 25.86 (t, J = 142.9 Hz, $S\underline{C}H_2CH_3$ minor isomer), 32.87 (t, J = 141.8 Hz, $S\underline{C}H_2CH_3$ major isomer), 140.83 (d, J = 158.8 Hz, $HC{=}\underline{C}HMe$ major isomer), 141.33 (d, J = 160.4 Hz, $HC{=}\underline{C}HMe$ minor isomer), 143.91 (d, J = 154.3 Hz, $H\underline{C}{=}CHMe$ minor isomer), 145.03 (d, J = 154.9 Hz, $H\underline{C}{=}CHMe$ major isomer), 207.65, 209.45, 209.81, 210.14, 211.36, and 212.02 (all s, Fe-CO), 284.94 (s, acyl C=O major isomer), 287.74 (s, acyl C=O minor isomer).

Mass Spectrum (EI); m/z (relative intensity): 410 (M^+, 5), 382 (M^+ - CO, 27), 354 (M^+ - 2CO, 32), 326 (M^+ - 3CO, 50), 298 (M^+ - 4CO, 34), 270 (M^+ - 5CO, 67), 242 (M^+ - 6CO, 100), 214 (M^+ - 7CO, 50), 186 ($HSFe_2HC{=}CHMe$, 29), 145 ($HSFe_2$, 27), 144 (SFe_2, 66), 112 (Fe_2, 3), 56 (Fe, 19).

Synthesis of (μ-HC(=CMe_2)C=O)(μ-EtS)$Fe_2(CO)_6$ JBH-65-VII

To the standard [Et_3NH][(μ-CO)(μ-EtS)$Fe_2(CO)_6$] reagent solution (2.98 mmol) was added 0.33 ml (2.98 mmol) of 3,3-dimethyl acryloylchloride by syringe at room temperature. An immediate reaction ensued with gas evolution, a gradual color change to bright red, and formation of a white precipitate ([Et_3NH][Cl]). After the reaction mixture had been stirred for 2 h at room temperature, the solvent was removed in vacuo to yield a red oily solid which was purified by filtration chromatography. Pentane/CH_2Cl_2 (20/1 v/v) eluted a red band which gave 1.18 g (2.77 mmol, 93%) of (μ-HC(=CMe_2)C=O)(μ-EtS)$Fe_2(CO)_6$, 15d, identified by its ^{1}H NMR spectrum ($CDCl_3$; 300 MHz).[11a]

Decarbonylation of (μ-HC(=CMe_2)C=O)(μ-EtS)$Fe_2(CO)_6$ JBH-67-VII

A 100 ml three necked, round bottomed flask equipped with a reflux condenser and nitrogen inlet (gas adapter), glass stopper, stir-bar, and rubber septum was charged with 0.73 g (1.72 mmol) of (μ-HC(=CMe_2)C=O)(μ-EtS)$Fe_2(CO)_6$, 15d, and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 30 ml of THF. After the reaction mixture had been stirred for 15 h at room temperature and then 4 h at reflux, the solvent was removed in vacuo to yield a red oil which was dissolved in pentane/CH_2Cl_2 (4/1 v/v) and filtered through a thin pad of silicic acid. Removal of solvent left a red oil which was purified by filtration chromatography. Pentane eluted two red bands. The first gave a red oil identified by its ^{1}H NMR spectrum to be a mixture of several products. The second band gave 0.13 g (0.30 mmol, 17%) of starting material, 15d, identified by its ^{1}H NMR spectrum ($CDCl_3$; 250 MHz). Repurification of the first fraction by medium pressure chromatography yielded two bands eluting in pentane. The first gave a red oil identified by its ^{1}H NMR spectrum ($CDCl_3$; 250 MHz) to be a mixture of 0.22 g (0.57 mmol, 33%) of (μ-σ,π-HC=CMe_2)(μ-EtS)$Fe_2(CO)_6$, 16d, and 0.12 g (0.31 mmol, 36% based on S) of (μ-EtS)$_2Fe_2(CO)_6$, 11.[15] The second gave 0.08 g (0.18 mmol, 11%) of starting material, 15d, identified by its ^{1}H NMR spectrum ($CDCl_3$; 250 MHz). Analytically pure (μ-σ,π-HC=CMe_2)(μ-EtS)$Fe_2(CO)_6$, 16d (a slightly air-sensitive red oil), could be obtained by repeated medium pressure chromatography of the first fraction (fractionation of the leading edge).

Anal. Calcd. for $C_{12}H_{12}Fe_2O_6S$: C, 36.40; H, 3.05 %. Found: C, 36.80; H, 3.14 %.

IR(CCl_4): 3010sh, 2960s, 2930vs, 2910sh, 2870s 2855s, 1465m, 1452m, 1392w, 1378m, 1370m, 1300w, 1257m, 1135w, 1100w, 1060m, 1045w, 1010w, 968w, 920w, 665w, 615vs, 600vs-br, 555s cm^{-1}.
Terminal carbonyl region (pentane): 2070s, 2035vs, 1992vs-br, 1952vw cm^{-1}.

^{1}H NMR($CDCl_3$; 250 MHz): δ 1.29 (t, J = 7.37 Hz, 3H, $SCH_2C\underline{H}_3$), 1.66 (s, 3H, $HC{=}C(C\underline{H}_3)_2$ endo), 1.77 (s, 3H, $HC{=}C(C\underline{H}_3)_2$ exo), 2.30 (q, J = 7.36 Hz, 2H, $SC\underline{H}_2CH_3$), 7.57 (s, 1H, $\underline{H}C{=}CMe_2$).

^{13}C NMR($CDCl_3$; 100.5 MHz): δ 17.88 (q, J = 128.9 Hz, $SCH_2\underline{C}H_3$), 24.76 (q, J = 128.1 Hz, $HC{=}C(\underline{C}H_3)_2$ exo), 35.41 (t, J = 142.2 Hz, $S\underline{C}H_2CH_3$), 36.10 (q, J = 128.6 Hz, $HC{=}C(\underline{C}H_3)_2$ endo), 114.91 (s, $HC{=}\underline{C}Me_2$), 153.31 (d, J = 143.5 Hz, $H\underline{C}{=}CMe_2$), 208.86 and 210.09 (both s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 396 (M^+, 5), 368 (M^+ - CO, 5), 340 (M^+ - 2CO, 15), 312 (M^+ - 3CO, 11), 284 (M^+ - 4CO, 17), 256 (M^+ - 5CO, 29), 228 (M^+ - 6CO, 38), 200 ($HSFe_2HC{=}CMe_2$, 100), 159 ($HSFe_2CH_2$, 14), 145 ($HSFe_2$, 31), 144 (SFe_2, 89), 56 (Fe, 15), 43 ($HC{=}CMe_2$, 24).

Decarbonylation of (μ-HC(=CH_2)C=O)(μ-EtS)$Fe_2(CO)_6$ JBH-74-VII

In an experiment similar to the decarbonylation of 15d, a THF solution containing 0.39 g (0.99 mmol) of (μ-HC(=CH_2)C=O)(μ-EtS)$Fe_2(CO)_6$, 15a, was stirred for 48 h at room temperature. Subsequently, the solvent was removed in vacuo, and the resulting red oil was purified by filtration chromatography. Pentane eluted an orange band which gave

0.34 g (0.91 mmol, 92%) of (μ-σ,π-HC=CH$_2$)(μ-EtS)Fe$_2$(CO)$_6$, 16a,[9a] identified by its ^{1}H NMR spectrum (CDCl$_3$; 300 MHz).

Decarbonylation of (μ-HC(=CHPh)C=O)(μ-EtS)Fe$_2$(CO)$_6$ JBH-17-VIII

In an experiment similar to the decarbonylation of 15d, a THF solution containing 0.09 g (0.20 mmol) of (μ-HC(=CHPh)C=O)(μ-EtS)Fe$_2$(CO)$_6$, 15b, was stirred for 40 h at room temperature and then 1.5 h at reflux. Subsequently, the solvent was removed in vacuo and the resulting red oil was purified by filtration chromatography. Pentane eluted a pale yellow band which was not collected. Pentane then eluted a red band which gave 0.07 g (0.16 mmol, 82%) of (μ-σ,π-HC=CHPh)(μ-EtS)Fe$_2$(CO)$_6$, 16b (5h'), identified by its ^{1}H NMR spectrum (CDCl$_3$; 300 MHz).

Decarbonylation of (μ-HC(=CHMe)C=O)(μ-EtS)Fe$_2$(CO)$_6$ JBH-71-VII

In an experiment similar to the decarbonylation of 15d, a THF solution containing 0.44 g (1.07 mmol) of (μ-HC(=CHMe)C=O)(μ-EtS)Fe$_2$(CO)$_6$, 15c, was stirred for 17 h at room temperature, 1.5 h at reflux, and then 4 more hours at room temperature. Subsequently, the solvent was removed in vacuo, and the resulting red oil was purified by filtration chromatography. Pentane eluted an orange band which gave 0.40 g (1.04 mmol, 98%) of (μ-σ,π-HC=CHMe)(μ-EtS)Fe$_2$(CO)$_6$, 16c, identified by its ^{1}H NMR spectrum (CDCl$_3$; 300 MHz).

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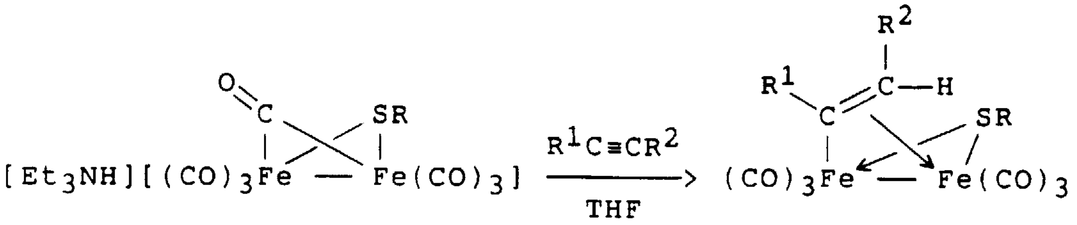
Chapter 4

"Reactions of $[Li][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with Acetylenes"

INTRODUCTION

As reported in the previous chapter, the reaction of alkyl and aryl acetylenes with the triethylammonium salts of $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anions, 1, in general, yields as major products the new thiolate and vinyl bridged diiron complexes $(\mu\text{-}\sigma,\pi\text{-}R^1C{=}C(H)R^2)(\mu\text{-RS})Fe_2(CO)_6$, 2 (Eq. 1). The



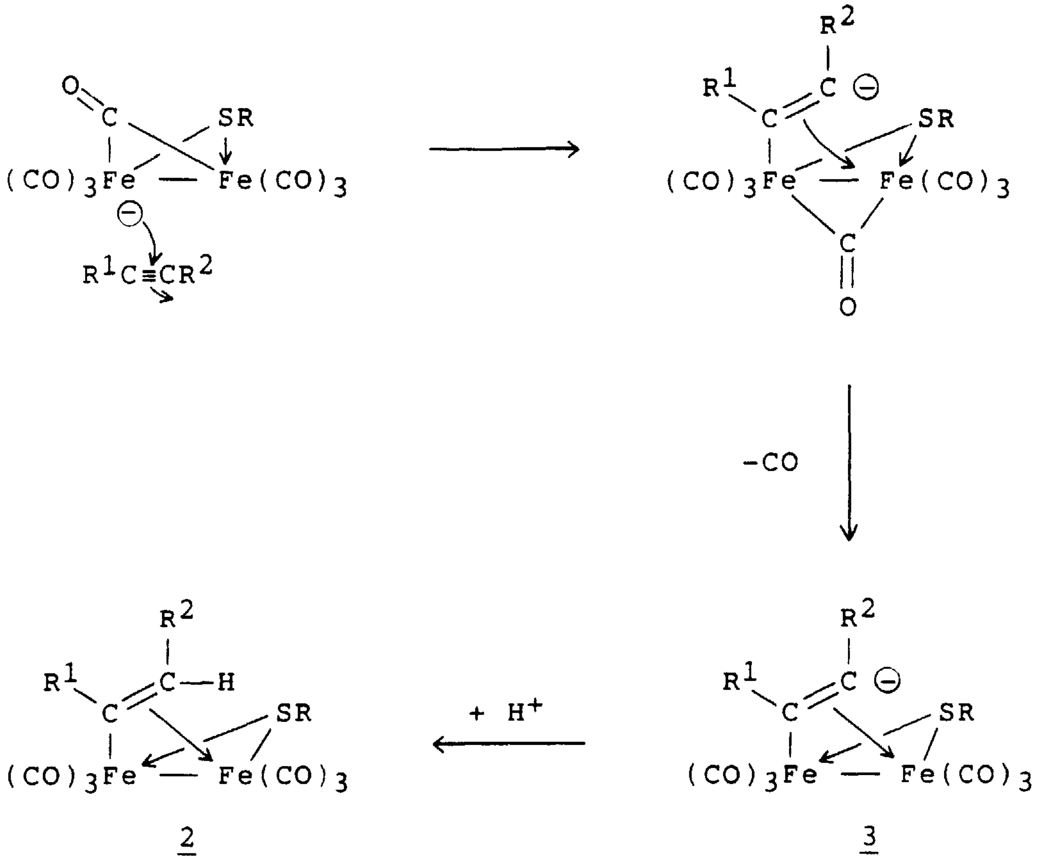
(1)

1a

2

$R^1 = R^2 =$ alkyl, aryl
$R = {}^tBu$, Et

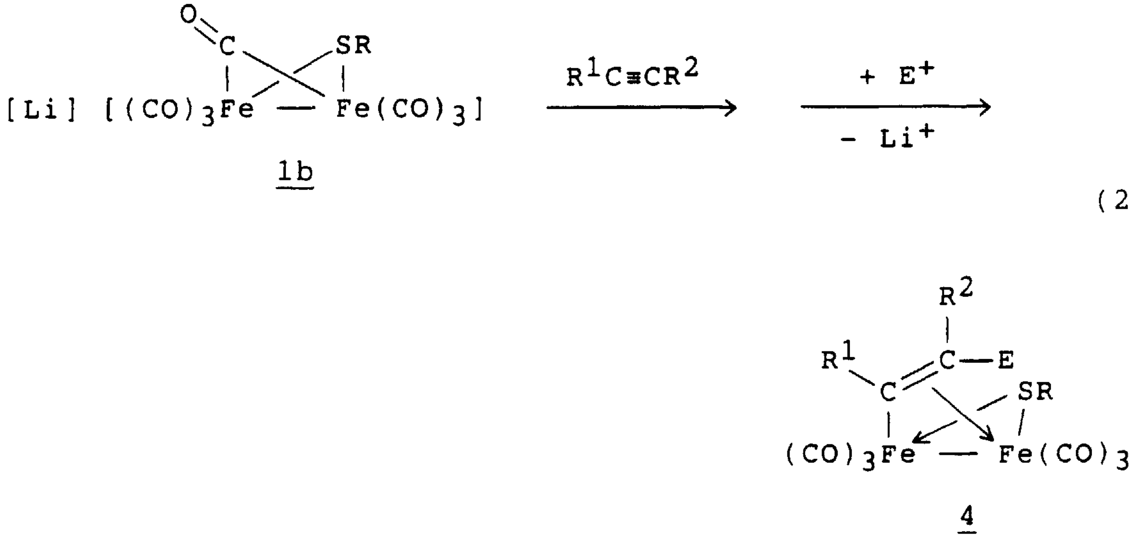
isolation of neutral μ-σ,π-vinyl rather than anionic acetylene (or vinyl) complexes apparently results from the facile *in-situ* protonation of the presumed intermediate vinylic anion $[(\mu\text{-}\sigma,\pi\text{-}R^1C{=}CR^2)(\mu\text{-RS})Fe_2(CO)_6]^-$, 3, by the weakly acidic triethylammonium cation (Scheme 1). It might be expected that in the absence of the triethylammonium cation, this transient vinylic anion, 3, would be long-lived enough to undergo attack by a variety of electrophilic reagents (E^+) yielding the substituted μ-vinyl complexes $(\mu\text{-}\sigma,\pi\text{-}R^1C{=}C(E)R^2)(\mu\text{-RS})Fe_2(CO)_6$, 4 (Eq. 2). Surprisingly, however, reaction of the corresponding lithium salts of anions of type 1 with electrophilic acetylenes followed by reaction of the anionic intermediate with an electrophile did not yield simple vinyl substitution derivatives. Instead, products derived from complex intramolecular rearrangement chemistry involving vinyl, carbonyl, and thiolate ligands were isolated. Furthermore, the specific



2

3

Scheme 1



1b

4

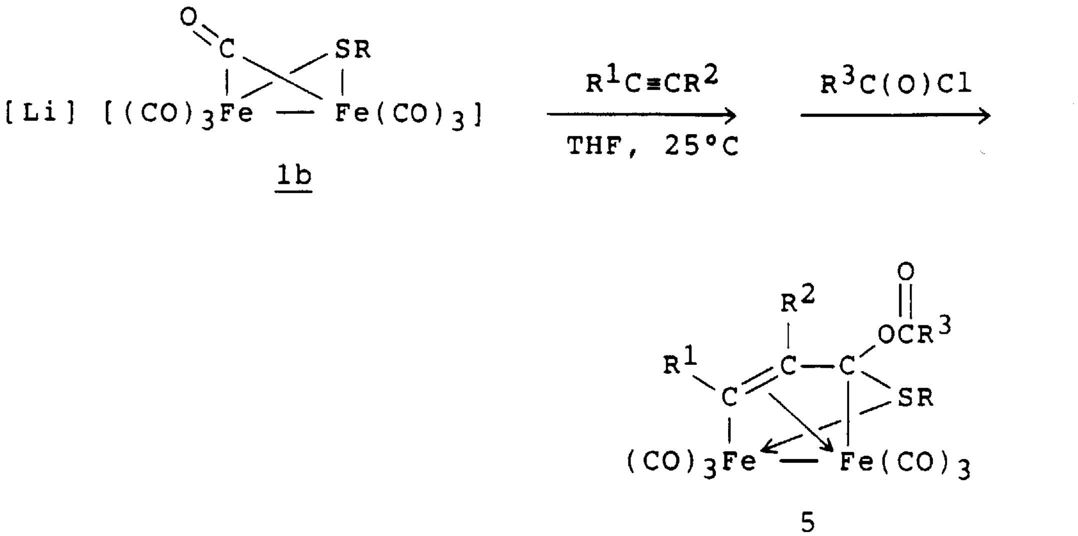
(2)

type of product obtained depended not only on the cation (Et_3NH^+ vs. Li^+), but also on the organic group of the RS ligand, the substituents on the acetylene, the reaction temperature, and the added electrophile as well. As a consequence, chemistry originally envisioned to be straightforward turned out to be quite complex, and in general, new diiron complexes containing unexpected μ-vinyl, μ-vinylcarbene, and μ-vinylacyl bridges were obtained in these reactions.

RESULTS AND DISCUSSION

Reaction of $[Li][(\mu-CO)(\mu-RS)Fe_2(CO)_6]$, <u>1b</u>, with the electrophilic, carbonyl activated acetylenes dimethyl acetylenedicarboxylate, methyl propiolate, and 3-butyn-2-one at room temperature, followed by reaction of the anionic intermediate with an acid chloride, $R^3C(O)Cl$ (R^3 = Me, ^tBu, Ph), gave in generally high yields the new μ-vinythioketal complexes, $(\mu-\sigma,\pi-R^1C=C(R^2)C(OC(O)R^3)SR-)Fe_2(CO)_6$, <u>5</u> (Eq. 3). These new μ-vinyl products are unusual in that: (1) a carbonyl ligand has been incorporated into the organic framework through bridging between the vinyl and thiolate ligands while retaining a bond to its parent metal center; (2) the once symmetrical thiolate bridge has been cleaved in the process and only a dative S→Fe bond is retained to one iron center; and (3) a new anion <u>6</u> (Fig. 1), in which the negative charge is localized on the oxygen atom of the inserted carbonyl fragment likely has been generated. In general, acylation of this anion at oxygen to produce <u>5</u> required long reaction times at room temperature (in the case of <u>3e</u>, even reflux conditions were required) for the less nucleophilic anions of type <u>6</u> (where $R^1 = R^2 = CO_2Me$ and R = Et, Ph) and the less reactive acid chlorides (R^3 = Ph, ^tBu).

Structure proof of compounds <u>5a-g</u> by the standard analytical and spectroscopic techniques was not

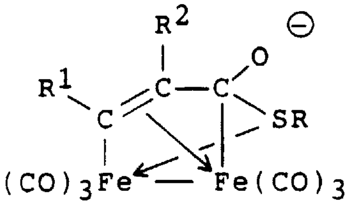


1b

(3)

5

a	$R^1 = R^2 = CO_2Me$		$R^3 = Me$	$R = {}^tBu$	87%
b	$R^1 = R^2 = CO_2Me$		$R^3 = Me$	$R = Et$	77%
c	$R^1 = R^2 = CO_2Me$		$R^3 = Me$	$R = Ph$	60%
d	$R^1 = R^2 = CO_2Me$		$R^3 = Ph$	$R = {}^tBu$	90%
e	$R^1 = R^2 = CO_2Me$		$R^3 = {}^tBu$	$R = {}^tBu$	52%
f	$R^1 = H$	$R^2 = CO_2Me$	$R^3 = Me$	$R = {}^tBu$	65%
g	$R^1 = H$	$R^2 = C(O)Me$	$R^3 = Me$	$R = {}^tBu$	68%



6

Figure 1

straightforward. In fact, it was first believed that the vinyl-substitution derivatives 4 (Eq. 2) had been isolated. Initially this conclusion was supported by the carbon/hydrogen combustion analyses, electron impact mass spectra, and the ^{1}H NMR spectra. Furthermore, assignments could be made for α- and β-vinyl carbons and protons in the ^{13}C and ^{1}H NMR spectra which were consistent with other μ-σ,π systems.[1,2,4b,e,g] In general, the α-carbon atom of the vinyl ligands was observed at much lower field ($\delta_C \sim 160$) than the β-carbon atom ($\delta_C \sim 100$) in the ^{13}C NMR spectra. Similarly, the α-protons in 5f and 5g appeared as low field singlets in the corresponding ^{1}H NMR spectra. However, the ^{13}C NMR spectra also revealed an additional tertiary carbon resonance ($\delta_C \sim 86$) which should be absent in the simple vinyl substitution derivatives. Furthermore, the IR spectra showed an absorption (ca. 1730-1775 cm^{-1}) assignable to an ester instead of the expected ketone moiety in 4. To resolve these discrepancies and determine the exact geometry of the vinyl ligand, a complete X-ray crystallographic analysis was conducted on 5g. An ORTEP plot showing 30% probability thermal ellipsoids and the atom labeling scheme appears in Figure 2. Pertinent bond distances and angles appear in Tables 1 and 2, respectively.

The basic structure of 5g consists of two inequivalent Fe(CO)$_3$ fragments linked via an iron-iron single bond and the unusual vinylthioketal bridge. The Fe1-Fe2 distance of 2.627(1)Å is well within the range of iron-iron single bonds surveyed by Churchill (2.43 - 2.88 Å),[3] but is somewhat longer than in related, but simpler, diiron vinyl systems (2.438(3) - 2.550(1) Å).[4] This lenghthening likely results from the inherent size and complexity of the vinylthioketal bridge. Nevertheless, the vinyl portion of this complex ligand is similar to these related vinyl systems. The C31-C32 bond distance of 1.408(6)Å indicates the expected lengthening of typical π-complexed carbon-carbon double bonds (1.363(9) - 1.402(5)

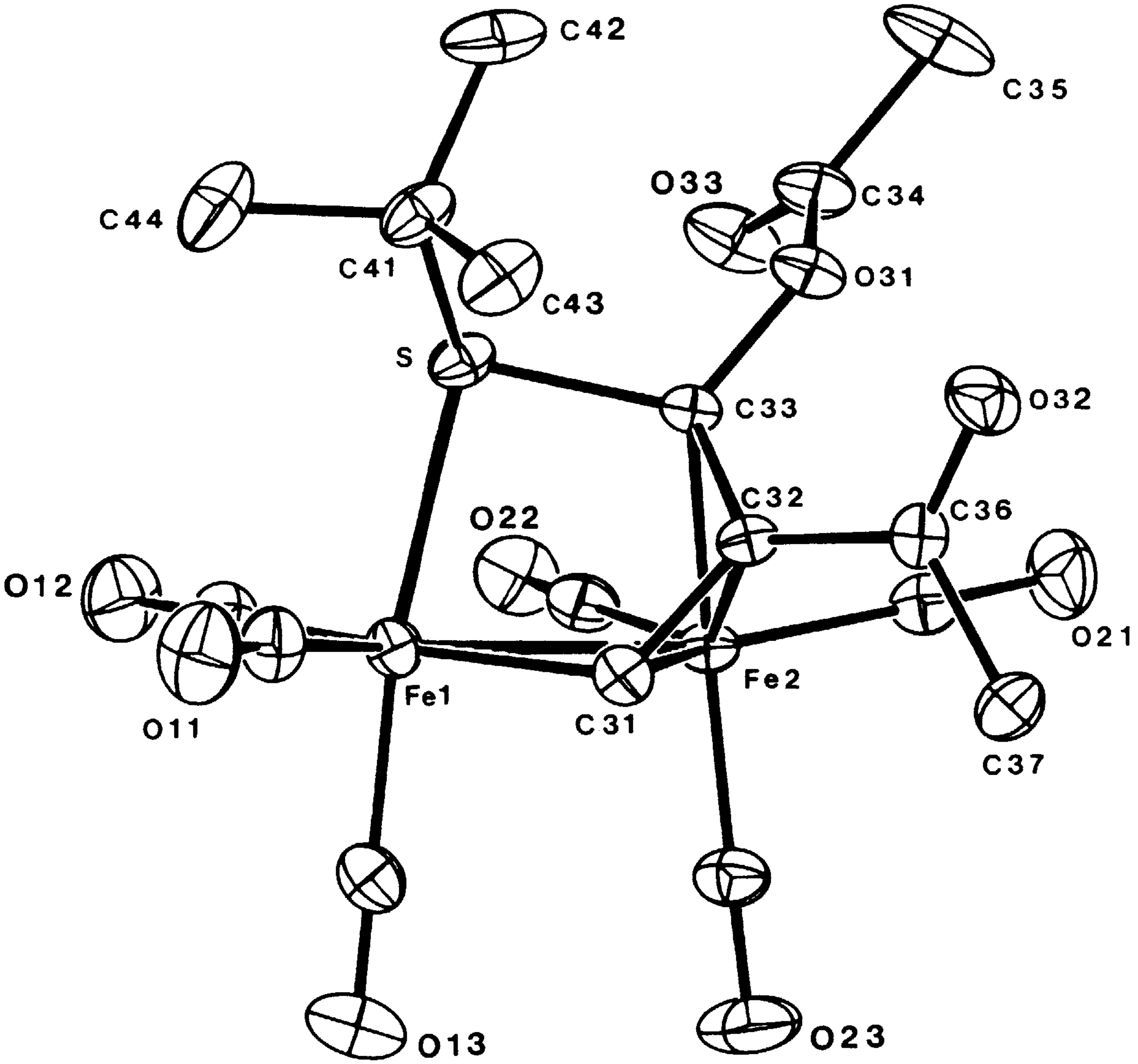


Figure 2: ORTEP of 5g showing 30% probability thermal ellipsoids

Table 1: Relevant Bond Distances (Å) for 5g

Fel-S	2.291(1)	C33-O31	1.408(5)
Fe2-S	3.017(1)	O31-C34	1.380(5)
Fel-C31	1.945(4)	C34-C35	1.502(7)
Fe2-C31	2.065(4)	C34-O33	1.188(6)
Fe2-C32	2.055(4)	C33-S	1.767(5)
Fe2-C33	2.060(4)	C41-S	1.874(5)
Fel-C33	2.916	C41-CH_3 (mean)	1.545
Fel-C32	2.903	Fel-CO (mean)	1.799
C31-C32	1.408(6)	FelC-O (mean)	1.137
C32-C33	1.449(6)	Fe2-CO (mean)	1.791
C32-C36	1.489(6)	Fe2C-O (mean)	1.140
C36-C37	1.522(7)	Fel-Fe2	2.627(1)
C36-O32	1.212(6)		

Table 2: Relevant Bond Angles (°) for 5g

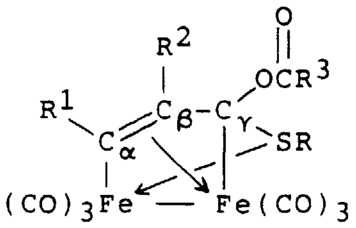
S-Fel-Fe2	75.3(0)	C33-O31-C34	119.8(4)
S-Fel-C31	87.0(1)	O31-C34-C35	108.6(4)
Fel-Fe2-C31	47.1(1)	O31-C34-O33	122.9(5)
Fel-C31-Fe2	81.8(2)	O31-C33-S	166.8(3)
C31-Fel-Fe2	51.1(4)	C33-S-Fel	91.0(1)
Fel-C31-C32	119.1(3)	C33-S-C41	106.5(2)
C31-C32-C33	111.4(4)	C41-S-Fel	117.6(2)
C31-C32-C36	124.4(4)	O33-C34-C35	128.4(5)
C31-C32-Fe2	70.4(2)	C33-C32-Fe2	69.6(2)
C32-C36-C37	118.6(4)	C33-C32-C36	124.2(4)
C32-C36-O32	121.0(4)	O32-C36-C37	120.4(4)
C32-C33-S	117.0(3)	S-C33-Fe2	103.8(2)
C32-C33-O31	116.1(4)	C32-Fel-Fe2	75.5(1)
C32-C33-Fe2	69.2(2)	C33-Fe2-Fel	75.9(1)
C32-C31-Fe2	69.6(2)	C33-Fe2-C31	69.8(2)
C32-Fe2-C31	40.0(2)	C33-Fe2-C32	41.3(2)
C36-C32-Fe2	125.5(3)	O31-C33-Fe2	125.5(3)

Å),[4,6] and the Fe1-C31, Fe2-C31 and Fe2-C32 distances of 1.945(4), 2.065(4) and 2.055(4) Å, respectively, also are comparable to these vinyl counterparts.[4] Bond angles about the vinyl component deviate slightly from idealized sp^2 hybridization, but this is likewise consistent with π-complexation of carbon-carbon double bonds.[4,6]

Although the vinyl double bond shows the expected lengthening from that of a simple carbon-carbon double bond (1.337(6)Å),[5] the C32-C33 distance of 1.449(6)Å adjacent to this vinyl moiety shows considerable shortening from that of a simple carbon-carbon single bond (1.53(1)Å).[5] Although this C32-C33 bond distance is somewhat longer than its C31-C32 counterpart, electron delocalization over the entire C31-C32-C33 fragment is considerable and approaches that of an η^3-allyl ligand in the limit.[23] In fact, as can be seen in Table 2, Fe2 is bonded equidistantly to C31, C32, and C33 (2.065(4), 2.055(4), 2.060(4) Å, respectively), and the bond angles around this "allyl" moiety deviate only slightly from those of true sp^2 hybridization.

Once the exact geometry of these new acylated vinylthioketal complexes was determined, a re-analysis of the spectroscopic and analytical data clearly explains the observed ambiguities. The carbonyl absorptions (ca. 1730 - 1775 cm^{-1}) in the infrared spectra can be attributed to the ester moiety derived from acylation of the likely oxygen-centered anion 6.[13] Furthermore, the singlet (δ_C ~ 86) observed in the carbon-13 NMR spectra can be attributed to the tertiary vinylthioketal carbon atom (consistent with organic thioketals[7]) derived from the "inserted" carbon monoxide ligand (Table 3). As discussed previously, assignments for vinyl carbons and protons in the ^{13}C and ^1H NMR spectra are consistent with the proven vinyl framework (Table 3). Finally, as expected, the carbon/hydrogen combustion analyses do agree with the proven structure, and although the electron impact mass spectra did not show a molecular ion for these species (in fact, 28 amu less),

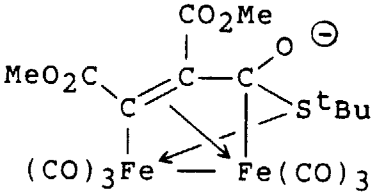
Table 3: ^{13}C and ^{1}H NMR Data for 5



	δC_α	δC_β	δC_γ	δH_α
a	174.27	99.53	84.25	
b	174.30	98.50	86.40	
c	174.37	99.07	86.94	
d	174.69	97.83	85.29	
e	174.73	100.37	85.82	
f	153.34	95.63	88.84	8.72
g	153.56	101.96	88.28	8.76

representative field desorption mass spectra of 5b and 5d did indeed confirm the actual molecular weights.

In addition to elucidating the nature of the vinylthioketal framework, the ^{13}C and ^{1}H NMR spectra also revealed a useful correlation concerning the bonding of the thiolate group. In the simple vinyl and thiolate bridged diiron complexes described in Chapter 3, (μ-σ,π-$R^1C{=}C(H)R^2$)(μ-RS)$Fe_2(CO)_6$, 2, the methyl resonances of the t-butyl thiolate ligand are observed in the ^{13}C NMR spectra at ~33 ppm and in the ^{1}H NMR spectra at ~ 1.3 ppm. However, in the new vinylthioketal complexes, 5, which do not contain a thiolate bridge, these methyl resonances are observed at ~ 27 and 1.1 ppm respectively. In general, an upfield shift is observed in both the ^{13}C and ^{1}H NMR spectra corresponding to an "unbridging" of the thiolate ligand. Cautious use of this correlation likely will be useful in determining the bridging nature of thiolate groups in other related diiron systems as well.

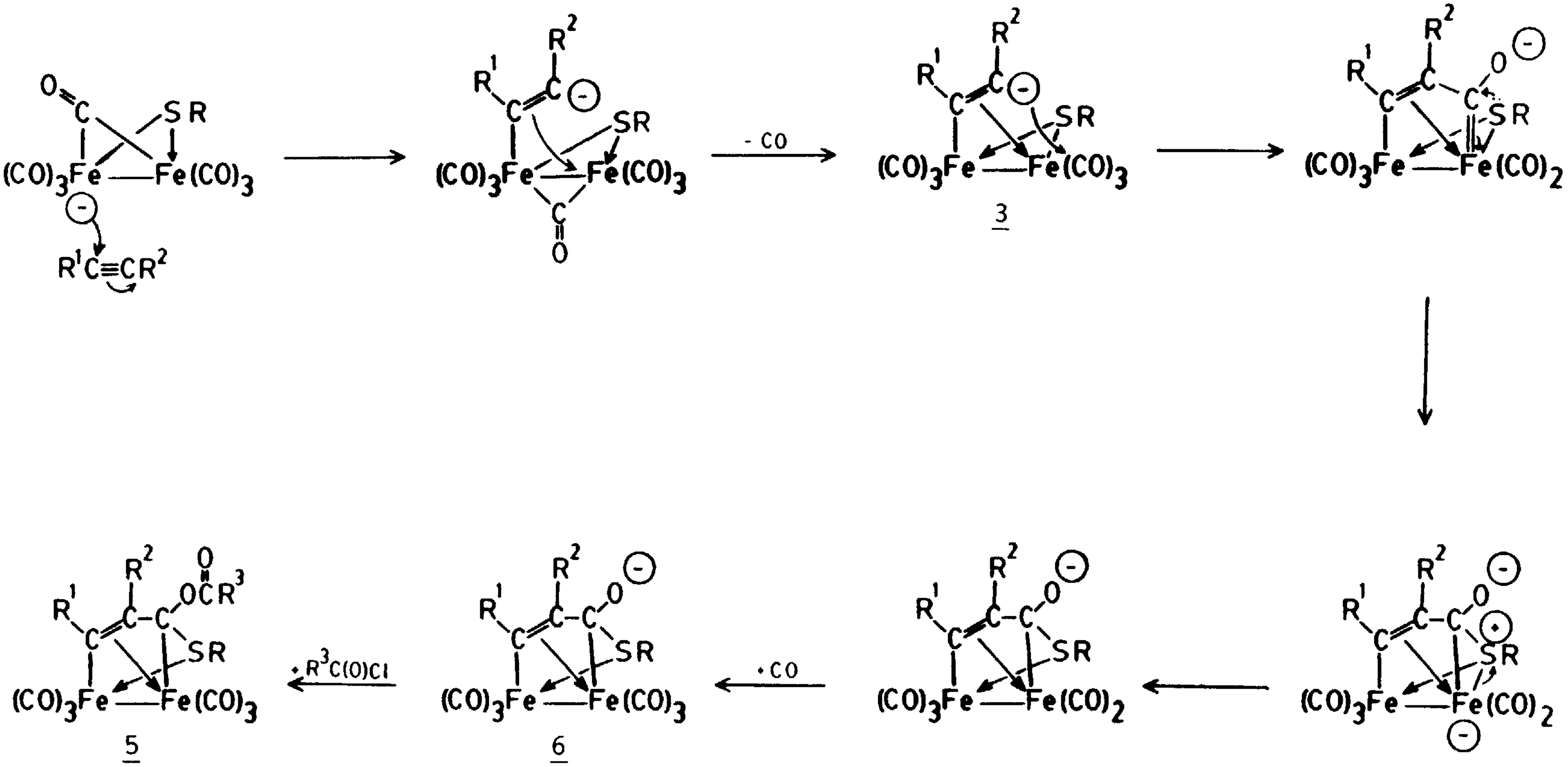


7

Figure 3

As alluded to earlier, the overall generation of an oxygen-centered anionic intermediate, 6 (Fig. 1), has likely occurred. This, upon acylation, generates the observed vinylthioketal products. In an attempt to prove this hypothesis, we have isolated what we believe to be the anionic intermediate 7 ($R = {}^tBu$, $R^1 = R^2 = CO_2Me$), from the crude reaction mixture as the Li^+/12-crown-4 salt (Fig. 3). In the ^{13}C NMR spectrum of 7, the methyl resonance of the t-butyl substituent appears at δ_C 28.24 which, as discussed above, is indicative of a thiolate group datively bound to one iron center but not bridging two centers. Furthermore, singlets appear at δ_C 68.23 and 142.33 which can be assigned to the thioketal and β-vinyl carbon atoms of the new ligand. A slight downfield shift of the terminal carbonyl resonances is also observed which is consistent with an increase of electron density on the iron centers.[8] In the ^1H NMR spectrum, two t-butyl resonances are observed at 1.21 and 1.39 ppm. This indicates that, at least in solution, this anion exists as a mixture of two isomers. The presence of two isomers is no doubt due to the two possible orientations of the t-butyl group and the lone electron pair on sulfur. (In the neutral acylated complexes, 5, only one isomer was observed by ^1H NMR spectroscopy. This would indicate that acylation of 6 to produce 5 increases the steric bulk of the molecule to the extent that isomerization is sterically unfavorable.) We are currently awaiting results of a X-ray crystallographic study on 7 to confirm its structure.

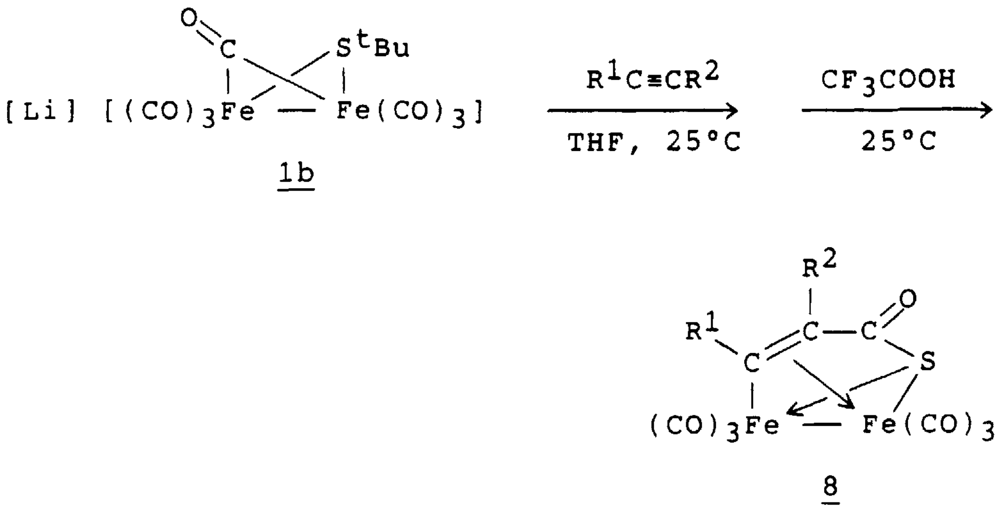
A possible mechanism describing the complex intramolecular rearrangements which may lead to the formation of this type of anion and subsequently the neutral vinylthioketal species, 5, is outlined in Scheme 2. The initial step, Michael addition of the iron-centered anion 1 to the activated acetylene, leads to the formation of a σ-bonded vinyl ligand which subsequently forms a bridging π-bond to the other iron atom with expulsion of carbon monoxide (consistent with the observation of gas evolution). The resulting vinyllithium intermediate, 3, in analogy to known alkyl- and aryllithium reactivity,[9] attacks a terminal carbonyl ligand on the adjacent iron center, yielding a dinuclear analog of the well-known Fischer acylmetalates. (An intramolecular mechanism is postulated since preparation of 5a under an atmosphere of carbon-13 carbon monoxide does not lead to ^{13}CO incorporation into the vinylthioketal unit.) The electrophilic carbene carbon atom thus formed undergoes nucleophilic attack by the neighboring bridging sulfur atom, thereby generating an unstable, dipolar, cyclic metallasulfonium species. (This step would appear especially likely with the sulfur lone pair occupying an axial position on the thiolate bridge.) Sulfonium salts are quite common in organosulfur chemistry and are known to exercise considerable stabilizing influence on adjacent carbanions.[10] However, in this instance, ring opening as indicated and readdition of CO gives anion 6 whose reaction with $R^3C(O)Cl$ produces 5. (Note that a drastically reduced product yield was obtained when CO was purged from the reaction mixture. For instance, when the $[Li][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$/dimethyl acetylenedicarboxylate reaction mixture was bubbled with nitrogen for 20 h prior to acylation with acetyl chloride, 5a was obtained in only 49% yield. However, when the $[Li][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$/dimethyl acetylenedicarboxylate reaction



Scheme 2

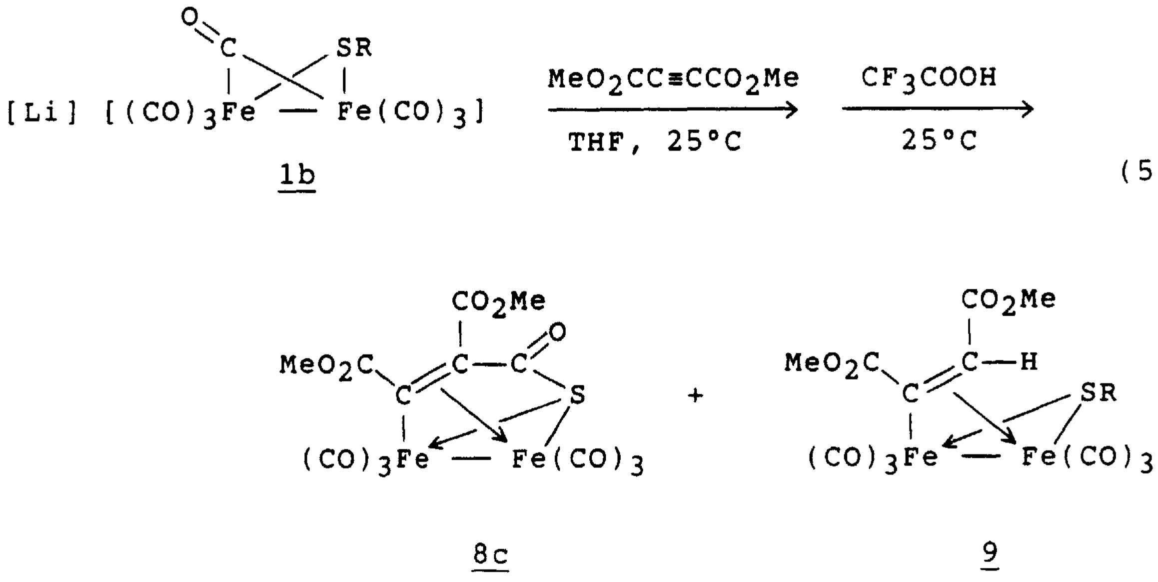
mixture was purged with carbon monoxide for 20 h prior to acylation with acetyl chloride, 5a was obtained in 90% yield.)

Attempted interception of anion 6 by protonation rather than acylation led to unexpected results. Although the vinylthioketal complexes, 5, were isolated when the $[Li][\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$/acetylene mixtures were treated with an acid chloride, isolable hemithioketal analogs were not generated when these mixtures were similarly treated with trifluoroacetic acid. As originally anticipated, bridging vinyl complexes were indeed isolated, although their exact structure depended intimately on the specific thiolate bridged anion employed. When R of the μ-RS ligand was t-butyl, μ-vinylthioester complexes of the type $(\mu\text{-}\sigma,\pi\text{-}R^1C{=}C(R^2)C(O)S\text{-})Fe_2(CO)_6$, 8, were isolated in good yield (Eq. 4). However, when R of the μ-RS ligand was either ethyl, benzyl, or phenyl, only minor quantities of 8 were formed while the simple μ-vinyl compounds, $(\mu\text{-}\sigma,\pi\text{-}R^1C{=}C(H)R^2)(\mu\text{-}RS)Fe_2(CO)_6$, 9, were isolated as the major products (Eq. 5). As mentioned previously in Chapter 3, the t-butyl thiolate analogs of 9 had been synthesized by the *in-situ* reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ with the appropriate activated acetylene (Eq. 1). The subsequent characterization of 9 by the standard analytical and spectroscopic techniques was therefore straightforward although their isolation under these conditions was rather mysterious. Similarly, the isolation of the new μ-vinylthioester complexes 8 was completely unexpected. Although they do show marked similarities to their acylated counterparts, 5, they are unusual in that: (1) a carbon monoxide ligand has been incorporated into the organic framework through bridging the vinyl and thiolate moieties without retaining any bond to its original iron center; and (2) the original organic substituent has been cleaved from sulfur with substitution by the new acryloyl ligand thereby allowing the sulfur atom to maintain a bridge between the two iron centers.



(4)

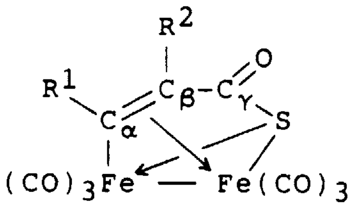
a	R^1 = H	R^2 = C(O)Me	51%
b	R^1 = H	R^2 = CO_2Me	69%
c	R^1 = R^2 = CO_2Me		66%



(5)

R = Et	9%	a	34%
R = CH_2Ph	6%	b	40%
R = Ph	-	c	40%

Table 4: ^{13}C and ^{1}H NMR Data for 8



	δC_α	δC_β	δC_γ	δH_α
a	170.07	95.91	185.22	9.49
b	168.51	89.26	182.44	9.42
c	178.11	86.71	187.88	

Derivatives 8a-c all had elemental carbon/hydrogen combustion analyses, mass, IR, ^{1}H NMR, and ^{13}C NMR spectra consistent with the structure given. Assignments for α- and β-vinyl protons and carbons were readily made in the corresponding ^{1}H and ^{13}C NMR spectra as described previously (Table 4). Organic thiolate resonances (either ethyl, t-butyl, or benzyl) were conspicuously absent in these spectra, while in the ^{13}C NMR spectra, a new organic carbonyl resonance was observed $\delta_C \sim 184$ (Table 4). In all cases, the electron impact mass spectra revealed similar fragmentation patterns including the presence of a molecular ion and subsequent loss of six terminal carbonyl ligands. These analytical and spectroscopic data, however, were insufficient in determining the exact geometry of the vinyl ligand, particularly the relative location of the incorporated carbonyl ligand with regard to the vinyl and sulfur substituents. Consequently, a complete X-ray crystallographic analysis was conducted on 8a. An ORTEP plot showing 30% probability thermal ellipsoids and the atom labeling scheme appears in Figure 4. Pertinent bond

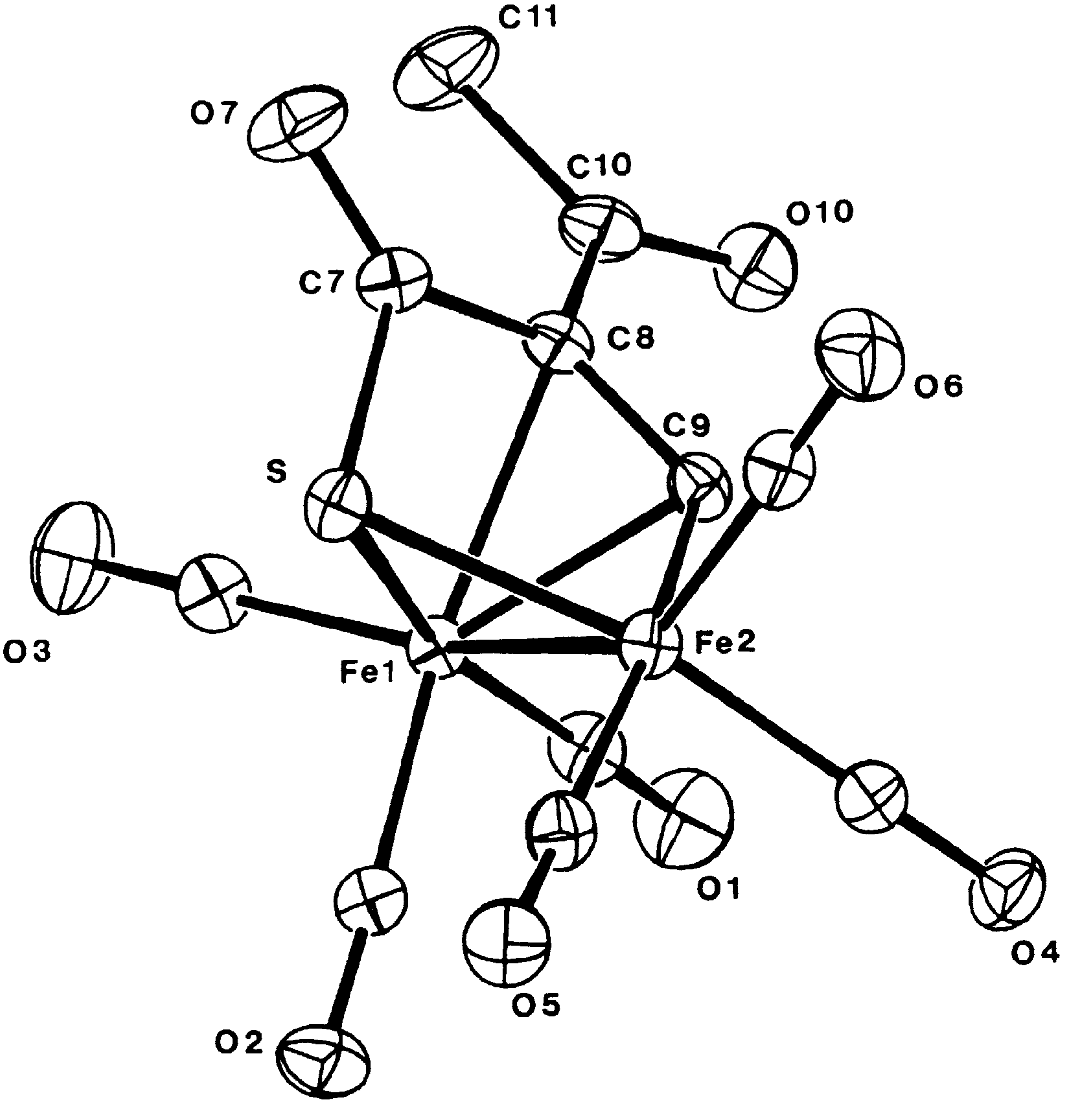


Figure 4: ORTEP of 8a showing 30% probability thermal ellipsoids

Table 5: Relevant Bond Distances (Å) for 8a

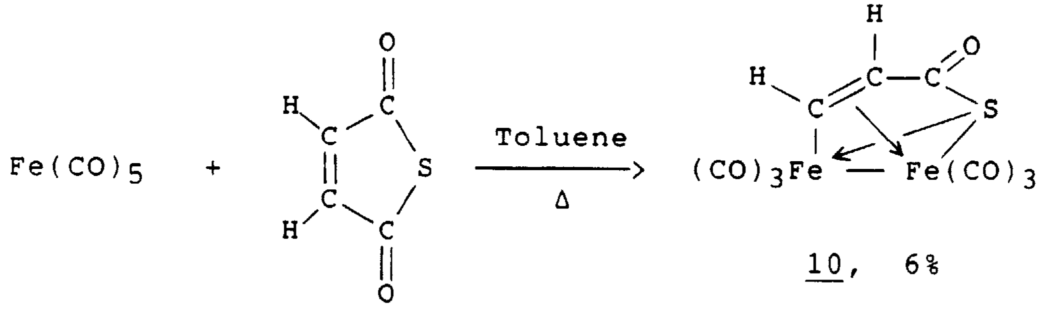
Fe1-Fe1	2.539(1)	C8-C7	1.476(7)
Fe1-S	2.294(1)	C7-O7	1.207(6)
Fe2-S	2.240(1)	C7-S	1.824(5)
Fe2-C9	1.925(5)	Fe1-C7	2.599(5)
Fe1-C9	2.075(5)	Fe2-C7	3.125(5)
Fe1-C8	2.137(5)	Fe1-CO (mean)	1.801
C9-C8	1.411(7)	Fe1C-O (mean)	1.131
C8-C10	1.518(7)	Fe2-CO (mean)	1.814
C10-O10	1.208(7)	Fe2C-O (mean)	1.120
C10-C11	1.528(8)		

Table 6: Relevant Bond Angles (°) for 8a

S-Fe1-Fe2	54.9(0)	C9-C8-C10	120.4(5)
S-Fe2-Fe1	57.0(0)	C8-C10-C11	118.9(5)
S-Fe1-C9	79.1(1)	C8-C10-O10	118.8(5)
S-Fe1-C8	73.3(1)	C11-C10-O10	122.3(5)
S-Fe2-C9	83.6(0)	C10-C8-C7	122.1(4)
Fe2-S-Fe1	68.1(0)	C8-C7-O7	129.9(5)
Fe2-Fe1-C9	48.0(1)	C8-C7-S	106.2(3)
Fe2-Fe1-C8	77.1(1)	O7-C7-S	123.5(4)
Fe2-C9-Fe1	78.7(2)	Fe1-C8-C7	90.1(3)
Fe1-Fe2-C9	53.3(1)	Fe1-C9-C8	72.8(3)
Fe2-C9-C8	122.1(4)	Fe1-C8-C9	68.1(3)
C9-C8-C7	166.3(4)	C9-Fe1-C8	39.1(1)

distances and angles are given in Tables 5 and 6, respectively.

The basic structure of 8a consists of two inequivalent Fe(CO)$_3$ fragments linked by an iron-iron single bond and the complex vinylthioester bridge. The parent compound of this class ($R^1 = R^2 = H$), 10, was prepared some years ago by Hoffmann and Weiss by the reaction of thiomaleic anhydride and iron pentacarbonyl (Eq. 6), and its



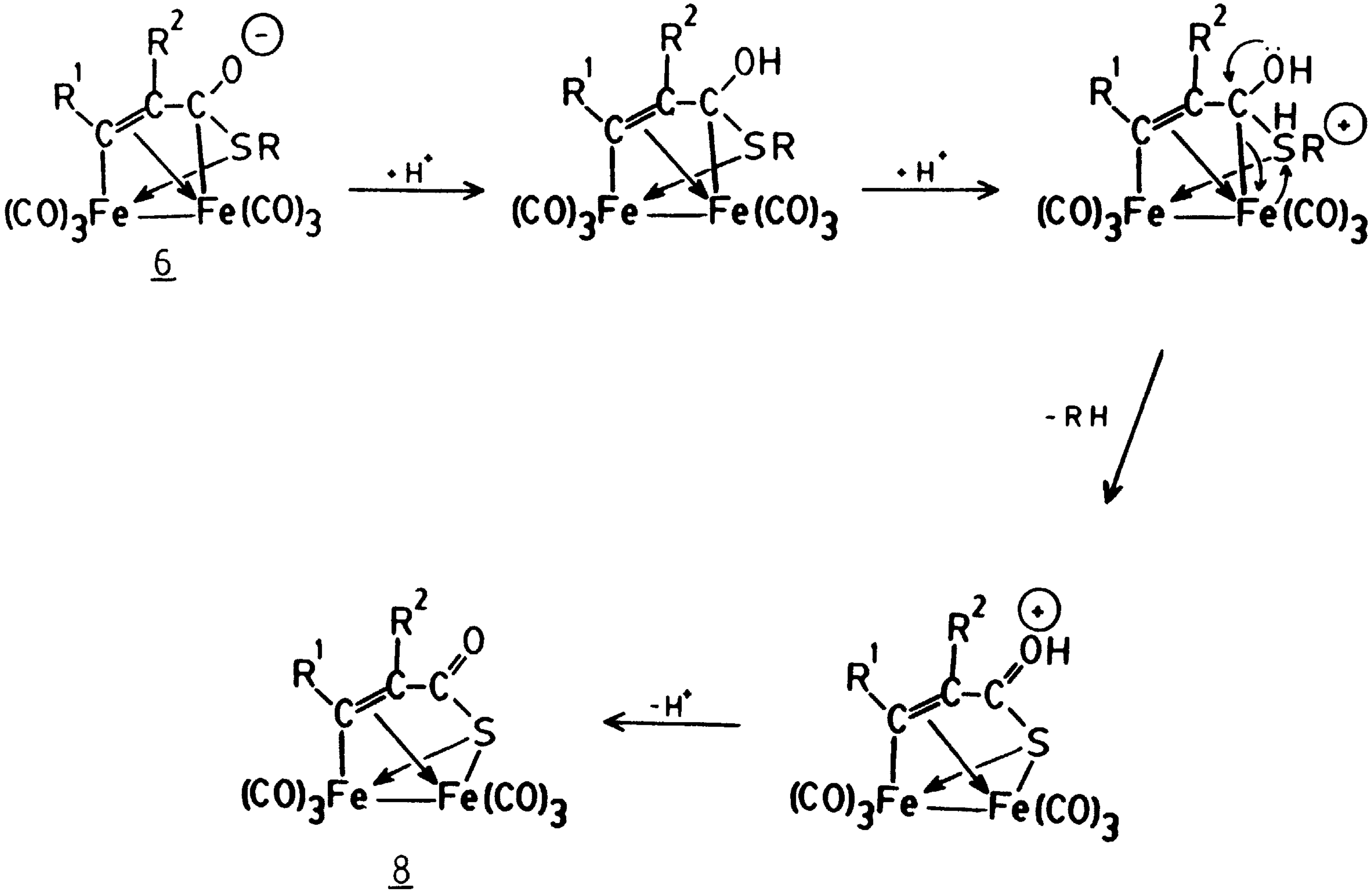
10, 6%

(6)

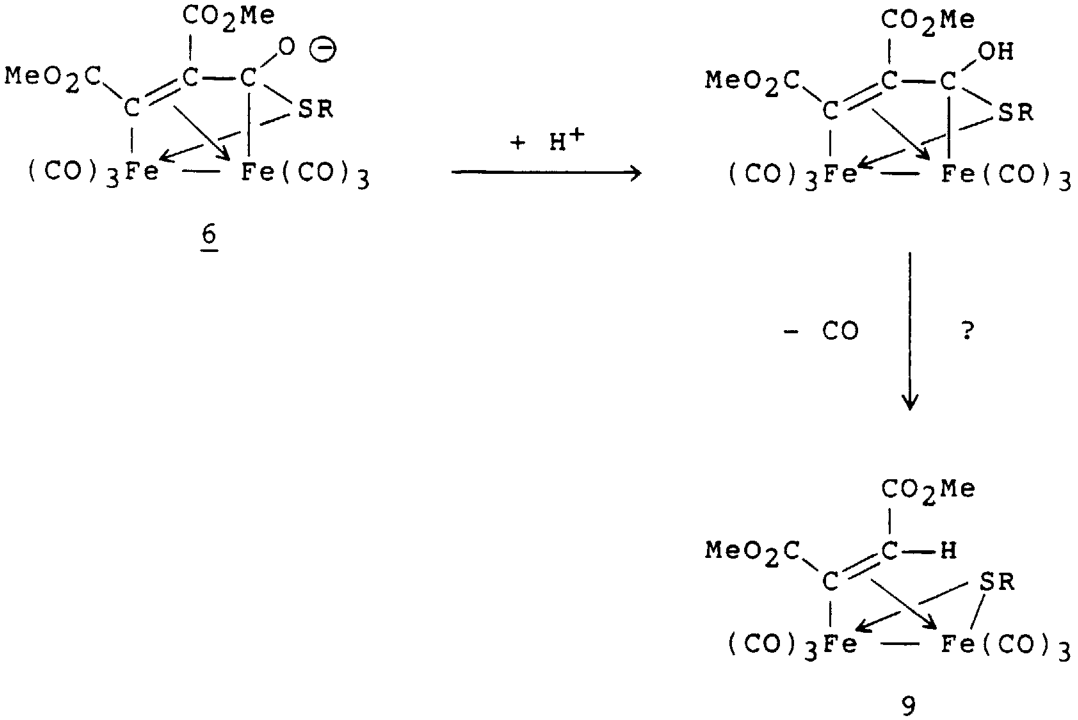
structure was determined by means of X-ray crystallography.[4g] Accordingly, the crystal structures of both complexes compare favorably, in general, indicating broad electron delocalization over the organic fragment. The bonding of the vinyl ligand in 8a is likewise similar to that in (μ-σ,π-MeO$_2$CC=C(CO$_2$Me)C(OC(O)Me)S^{t}Bu-)Fe$_2$(CO)$_6$, 5g, and, therefore, is comparable to that in other diiron vinyl systems as well.[4] Furthermore, the iron-sulfur bond distances of 2.294(1)Å (Fe1-S) and 2.240(1)Å (Fe2-S) are comparable to those in other thiolate bridged diiron complexes,[4b,c,f] although the asymmetry of the bridge is more pronounced than in 10. Surprisingly, the iron-iron bond of 2.539(1)Å is nearly 0.1Å shorter than in 5g. This likely results from the smaller "bite" of the vinylthioester ligand which does not contain any direct Fe-C7 interaction (Fe1-C7 and Fe2-C7 are 2.599(5) and 3.125(5) Å respectively.)

A possible mechanism accounting for the formation of these new vinylthioester derivatives is outlined in Scheme 3, starting with the anionic intermediate [(μ-σ,π-$R^1C{=}C(R^2)C(O^-)RS$-)$Fe_2(CO)_6$], 6, posulated in Scheme 2. Reaction with trifluoroacetic acid presumably yields the neutral O-protonated hemithioketal which may then spontaneously undergo an acid-catalyzed, metal-assisted intramolecular oxidation to give the observed product. In analogy to the known acid-catalyzed oxidation of organic hemimercaptals,[11] further protonation at sulfur would take place yielding an unstable, metallasulfonium species. Unable to eliminate thiol (RSH) as would occur in the acid-catalyzed oxidation of hemimercaptals, this intermediate may undergo a metal-assisted oxidation to a protonated oxonium species with concomitant formation of an Fe-S bond and elimination of alkane (RH). Subsequent loss of a proton then yields the neutral product, 8. The fact that these new vinyl complexes are isolated as major products only when the organo-thio group involved is tertiary supports the hypothesis that loss of RH is some type of free-radical- or carbonium-ion-like process which may be assisted by the metal-sulfur interaction. Furthermore, the isolation of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(O)S$-)$Fe_2(CO)_6$, 8c (albeit in a small amount), in the reaction involving the benzyl thiolate bridged 1 eliminates the possibility that loss of RH by β-hydride elimination is occurring. Finally, in the case where the organo-thio substituent is not tertiary (either ethyl, benzyl, or phenyl), an alternate, obscure rearrangement of the transient vinylhemithioketal intermediate must occur, ultimately yielding the simple bridging vinyl complexes (μ-σ,π-$MeO_2CC{=}C(H)CO_2Me$)(μ-RS)$Fe_2(CO)_6$, 9, in only moderate yield (Scheme 4).

It is interesting to note that although complexes of type 9 were isolated as the major products from the in-situ reaction of [Et_3NH][(μ-CO)(μ-RS)$Fe_2(CO)_6$], 1a, with alkyl and aryl acetylenes, 8a and 8c were generated as by-products



Scheme 3


6

9

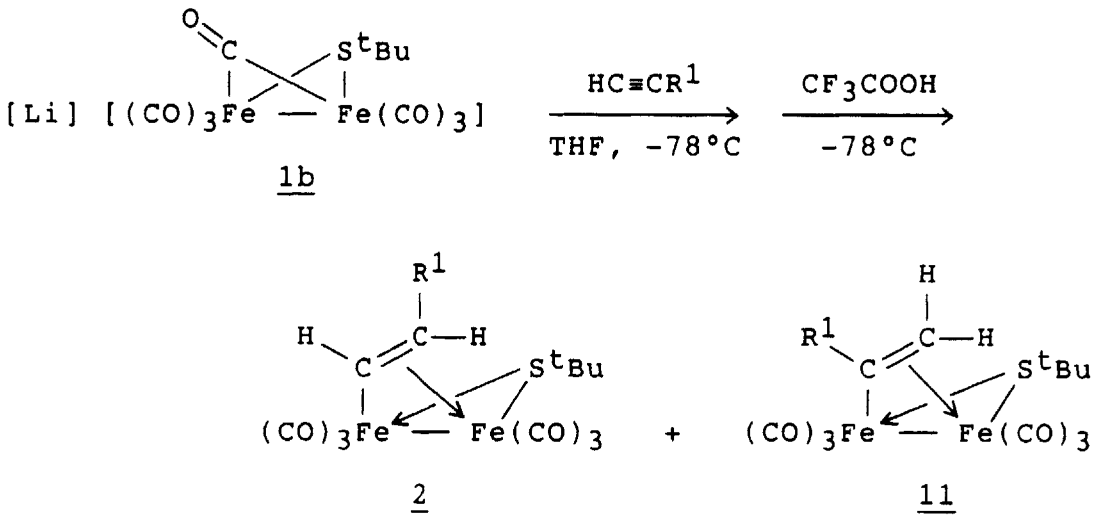
Scheme 4

in the corresponding reactions of 3-butyn-2-one (25%) and dimethyl acetylenedicarboxylate (9%), respectively (Chapter 3). Apparently, protonation was slow enough in these cases to allow the intramolecular rearrangements of Schemes 2 and 3 to occur. Othewise, the in-situ protonation inherent in that system was fast enough to limit formation to products of type $(\mu\text{-}\sigma,\pi\text{-}R^1C{=}C(H)R^2)(\mu\text{-}RS)Fe_2(CO)_6$, 2.

Certainly, the chemistry of the Li[1]/activated acetylene system is dominated by complex rearrangement mechanisms operating at room temperature. However, at lower temperature, this complex chemistry is considerably retarded. Even when R in the RS ligand is t-butyl, products of type $(\mu\text{-}\sigma,\pi\text{-}R^1C{=}C(H)R^2)(\mu\text{-}RS)Fe_2(CO)_6$,2, are obtained when 1b (R = ^{t}Bu)is treated with the electrophilic acetylenes at -78°C and the subsequent anionic intermediate is likewise reacted with trifluoroacetic acid at -78°C.

Formation of these complexes is believed to occur by the direct protonation at the β-vinyl carbon atom of the intermediate $[(\mu\text{-}\sigma,\pi\text{-}R^1C{=}CR^2)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$, 3 (R = ^{t}Bu), in the absence of rearrangement (see Scheme 1). For instance, reaction of $[Li][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ with dimethyl acetylenedicarboxylate at -78°C for 1 h followed by addition of trifluoroacetic acid to the reaction mixture, also at -78°C, yielded $(\mu\text{-}\sigma,\pi\text{-}MeO_2CC{=}C(H)CO_2Me)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$, 2c, in 71% yield and $(\mu\text{-}\sigma,\pi\text{-}MeO_2CC{=}C(CO_2Me)C(O)S\text{-})Fe_2(CO)_6$, 8c, in only 10% yield.

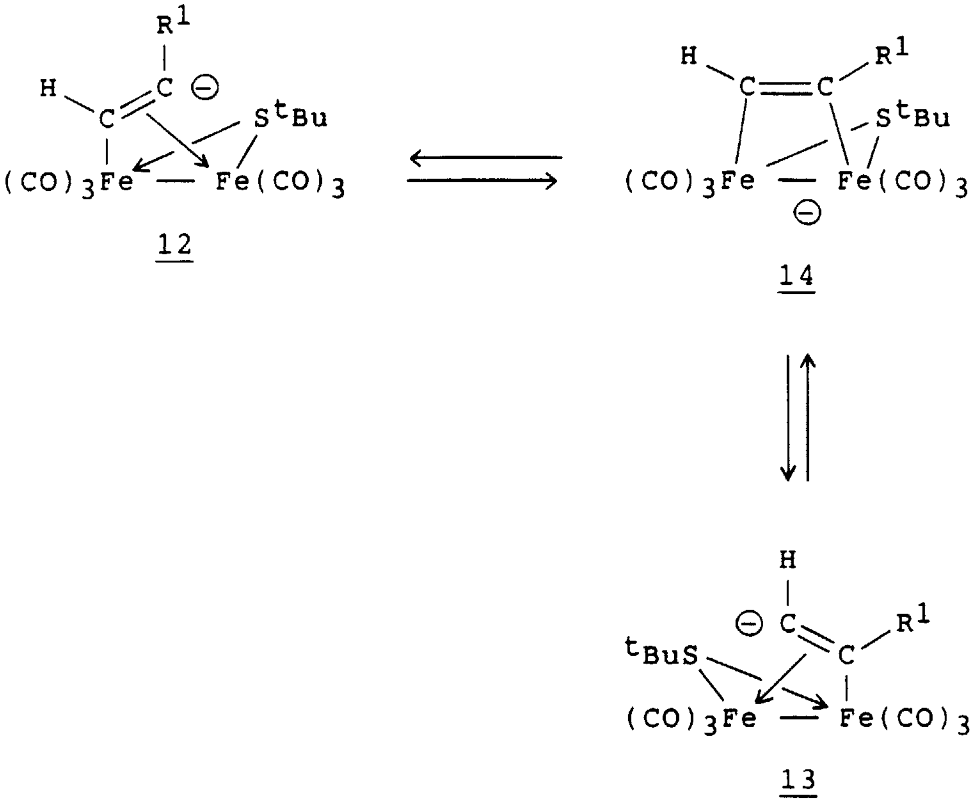
The corresponding reaction of methyl propiolate not only gave the new, rearranged vinylthioester product, $(\mu\text{-}\sigma,\pi\text{-}HC{=}C(CO_2Me)C(O)S\text{-})Fe_2(CO)_6$, 8b, in 30 % yield, but also $(\mu\text{-}\sigma,\pi\text{-}HC{=}C(H)CO_2Me)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$, 2a (23%) and its isomer of addition, $(\mu\text{-}\sigma,\pi\text{-}MeO_2CC{=}CH_2)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$, 11a (23%) (Eq. 7). Formation of 11a was unexpected since 2a,



(7)

a	$R^1 = CO_2Me$	23%	23%
b	$R^1 = C(O)Me$	24%	24%

the product derived from Michael addition to the conjugated acetylene, was the only product isolated from the in-situ reaction of [Et_3NH][(μ-CO)(μ-${}^tBuS$)$Fe_2(CO)_6$] with methyl propiolate at room temperature (Chapter 3). At -78°C, initial Michael addition to the acetylene may occur; in the absence of an in-situ protonation reagent, however, the resulting vinylic anion, 12, may isomerize reversibly to the new vinylic anion, 13, possibly via the intermediate, 14 (Scheme 5). (Bridging of the vinyl ligand likely occurs before isomerization and protonation as evidenced by the observation of very slow gas evolution after acetylene addition.) In support of this hypothesis, reaction of [Et_3NH][(μ-CO)(μ-${}^tBuS$)$Fe_2(CO)_6$], 1a (R = ${}^tBu$), with methyl propiolate at -78°C yielded only 2a in 64% yield. In this



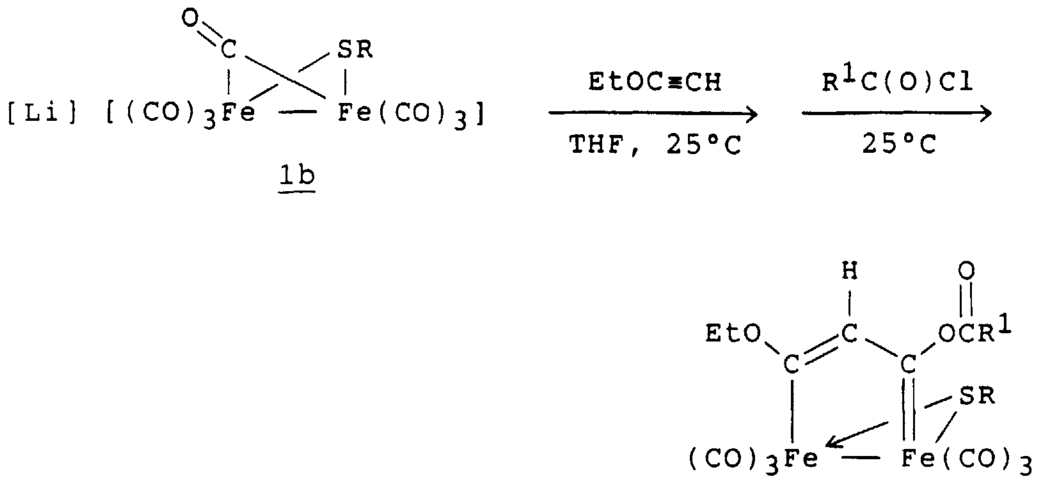
Scheme 5

instance, the intermediate vinylic anion has no time to isomerize (or rearrange!) before protonation by the weakly acidic triethylammonium cation.

Reaction of 3-butyn-2-one with $[Li][(\mu\text{-}CO)(\mu\text{-}{}^{t}BuS)Fe_2(CO)_6]$, 1b (R = ^{t}Bu), at -78°C revealed behavior similar to that observed for methyl propiolate. After reaction of the subsequent vinylic intermediate at -78°C with trifluoroacetic acid, $(\mu\text{-}\sigma,\pi\text{-}HC{=}C(H)C(O)Me)(\mu\text{-}tBuS)Fe_2(CO)_6$, 2b (24%), and its isomer of addition, $(\mu\text{-}\sigma,\pi\text{-}MeC(O)C{=}CH_2)(\mu\text{-}{}^{t}BuS)Fe_2(CO)_6$, 11b (24%), were isolated (Eq. 7). Furthermore, reaction of 3-butyn-2-one with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^{t}BuS)Fe_2(CO)_6]$ at -78°C yielded 2b and 8a in 36% and 19% yields respectively. Isomer 11b was not observed.

As a whole, the reaction of dimethyl acetylenedicarboxylate, methyl propiolate, and 3-butyn-2-one with $[Li][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$, 1b, was similar, depending on the R group of the thiolate ligand, the added electrophile, and the reaction temperature. In general, unusual μ-σ,π-vinylthioketal and μ-σ,π-vinylthioester complexes were isolated. Presumably these species arise from complex intramolecular rearrangement chemistry involving vinyl, carbonyl, and thiolate ligands prior to reaction with a suitable electrophile, either an acid chloride or trifluoroacetic acid respectively. (In contrast to protonation which, presumably, was instantaneous, acylation required long reaction times.) In extending the chemistry of 1b to ethoxyacetylene, however, we discovered rearrangement chemistry similar to that observed in the activated acetylene system but which ultimately yielded new and unexpected products.

Reaction of 1b with ethoxyacetylene at room temperature followed by reaction of the anionic intermediate with an acid chloride, $R^1C(O)Cl$ (R^1 = Me, Ph), did not yield vinylthioketal analogs of 5, but instead new bridging vinylcarbene complexes, 15, were formed in high yield (Eq. 8). In this reaction, a carbonyl ligand has once again been



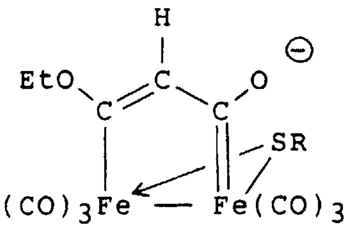
1b

15

(8)

	R	R^1	
a	R = ^{t}Bu	R^1 = Me	79%
b	R = ^{t}Bu	R^1 = Ph	71%
c	R = Et	R^1 = Me	75%

incorporated into the acetylenic framework. However, in contrast to what had been observed for the carbonyl activated acetylenes, further reaction with the thiolate bridge has not occurred. Instead, direct acylation of the presumed vinylic acylmetalate, 16, has resulted (Fig. 5).



16

Figure 5

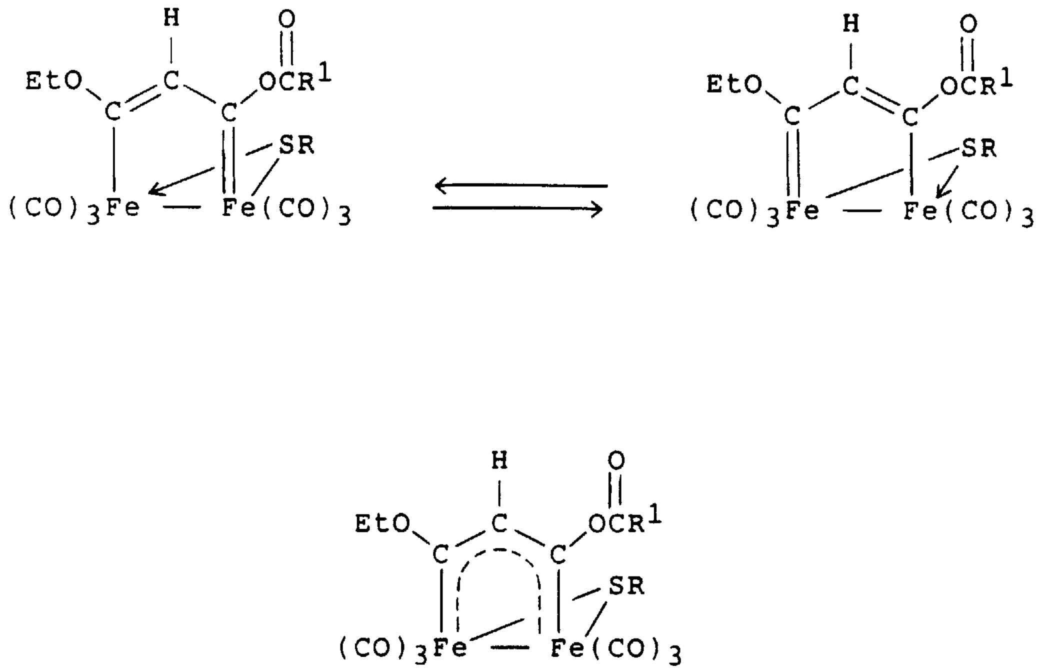
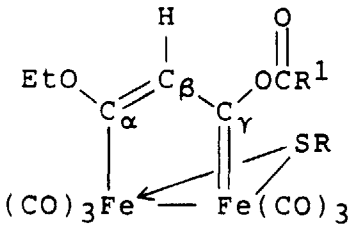


Figure 6

Complexes of type 15 are structurally interesting in that two distinct resonance forms can be drawn for the vinylcarbene bridge (Fig 6). A more accurate description of these species, therefore may be that of a novel π-delocalized vinylcarbene system. In general, the far downfield shift of the two "carbene" atom singlets in the ^{13}C NMR spectra (δ_C ~ 267 and 284) corroborates these findings (Table 7).[12] The carbon and proton resonances of the methine unit (δ_C ~ 136 and δ_H ~ 6.8) are likewise in agreement with this interpretation. In addition, the IR spectra all showed a strong carbonyl absorption (ca. 1748 - 1780 cm^{-1}) which can be assigned to the ester moiety derived from acylation of the oxygen-centered anion 16.[13] Finally, as discussed earlier in this chapter, the methyl resonances of the t-butyl group in the ^1H and ^{13}C NMR spectra of 15a and 15b (δ_H ~ 1.4 and δ_C ~ 34.0) indicate that the thiolate

Table 7: ^{13}C and ^{1}H NMR Data for 15



	δC_α	δC_β	δC_γ	δH_β
a	284.82	136.06(d)	267.43	6.85
b	284.14	136.16(d)	267.15	6.99
c	283.76	136.28(d)	266.07	6.81

group indeed bridges the two iron atoms and therefore does not interact with the vinylcarbene bridge.

Desiring to confirm unambiguously the presence of the μ-vinylcarbene bridge, a complete X-ray crystallographic analysis was conducted on 15a. An ORTEP plot showing 20% probability thermal ellipsoids and the atom labeling scheme appears in Figure 7. Pertinent bond distances and angles appear in Tables 8 and 9, respectively.

As expected, the basic structure of 15a consists of a diiron hexacarbonyl core linked in a butterfly arrangement by the thiolate and delocalized vinylcarbene bridges. The thiolate bridge itself is nearly perfectly symmetrical as evidenced by the Fe1-S and Fe2-S distances of 2.252(2) and 2.256(3) Å as well as the Fe2-Fe1-S and Fe1-Fe2-S angles of 55.4(1) and 54.3(1)° respectively. The t-butyl group occupies an equatorial (as opposed to an axial) position on the bridging sulfur atom, thereby minimizing steric interactions with the neighboring vinylcarbene bridge. While the iron-sulfur distances are standard for thiolate bridged diiron complexes,[4f,14] the C31-S bond of 1.875(9)Å

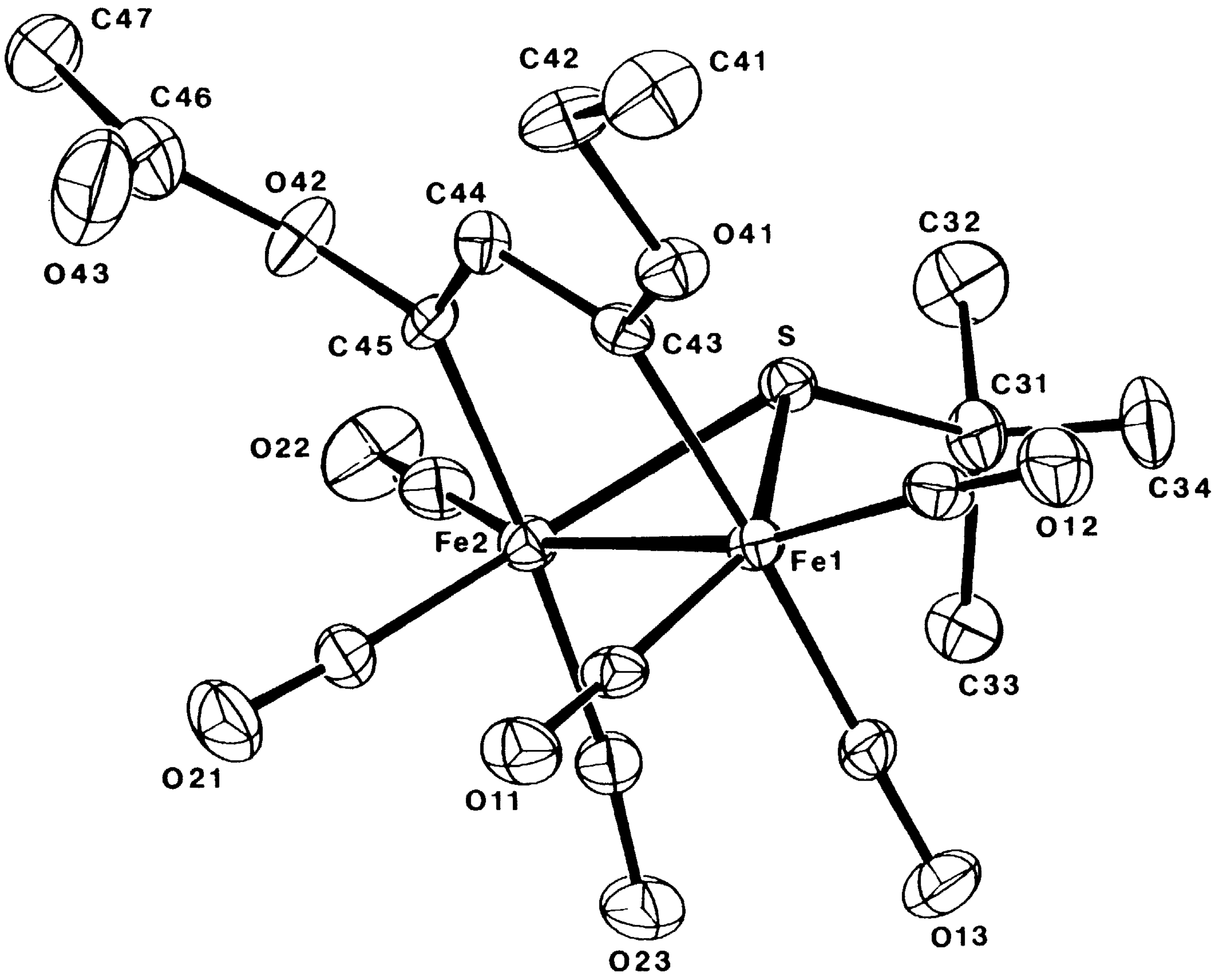


Figure 7: ORTEP of 15a showing 20% probability thermal ellipsoids

Table 8: Relevant Bond Distances (Å) for 15a

Fe1-Fe2	2.638(2)	C42-C41	1.515(13)
Fe1-S	2.252(2)	C45-O42	1.363(9)
Fe2-S	2.256(3)	O42-C46	1.319(14)
Fe1-C43	1.976(8)	C46-C47	1.477(16)
Fe2-C45	1.967(8)	C46-O43	1.223(14)
C43-C44	1.392(11)	S-C31	1.875(9)
C44-C45	1.365(11)	C31-CH_3 (mean)	1.558
Fe1-C44	3.010	Fe1-CO (mean)	1.781
Fe2-C44	2.997	Fe1C-O (mean)	1.140
Fe2-C43	3.169	Fe2-CO (mean)	1.787
Fe1-C45	3.157	Fe2C-O (mean)	1.136
C43-O41	1.318(9)	O41-C42	1.501(11)

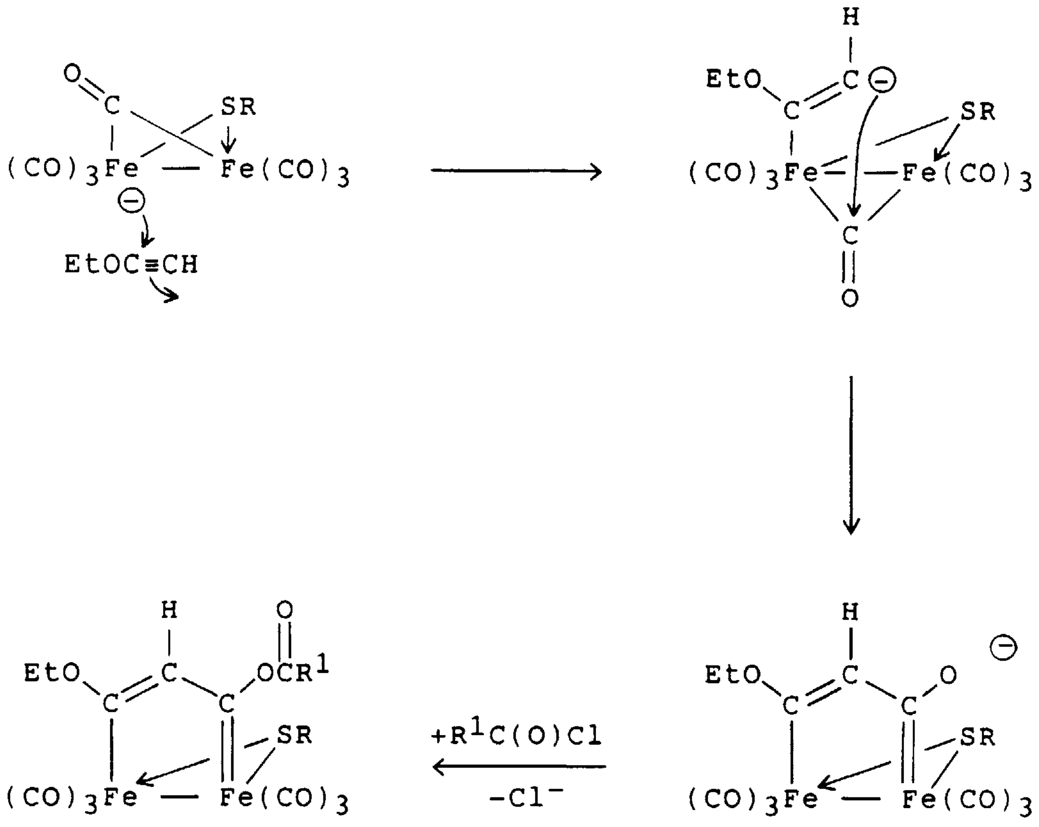
Table 9: Relevant Bond Angles (°) for 15a

S-Fe1-Fe2	55.4(1)	O42-C46-C47	115.6(12)
Fe2-S-Fe1	71.3(1)	O43-C46-C46	124.6(14)
Fe1-Fe2-S	54.3(1)	O42-C45-C44	118.4(8)
S-Fe1-C43	84.9(3)	C45-C44-C43	115.4(8)
S-Fe2-C45	82.3(3)	C44-C43-Fe1	125.8(6)
Fe1-S-C31	120.2(3)	C44-C43-O41	119.0(8)
Fe2-S-C31	120.9(3)	C43-O41-C42	119.8(7)
Fe2-C45-C44	127.3(6)	O41-C42-C41	105.0(8)
Fe2-C45-O42	114.3(6)	O41-C43-Fe1	115.2(6)
C45-O42-C46	128.5(9)	C43-Fe1-Fe2	85.8(2)
O42-C46-O43	119.5(13)	C45-Fe2-Fe1	85.5(3)

is slightly longer than typical carbon-sulfur single bonds of 1.815(1)Å[5] and therefore indicates some delocalization of electron density out of the thiolate bridge into the diiron core.

Delocalization of electron density throughout the vinylcarbene bridge is likewise evident. The similar C43-C44 and C44-C45 bonding distances of 1.392(11) and 1.365(11) Å, respectively, are considerably shorter than typical carbon-carbon single bonds of 1.541(3)Å,[5] but conversely, slightly longer than typical carbon-carbon double bonds of 1.337(6)Å.[5] Likewise, the nearly equivalent Fe2-C45 and Fe1-C43 distances of 1.967(8) and 1.976(8) Å are in the range of known, related iron carbene or carbene-like (i.e. μ-vinyl, μ-acetylide, μ-acyl) systems.[4,15] Furthermore, the symmetry of the vinylcarbene-diiron ring with respect to an orthogonal plane bisecting the angle C43-C44-C45 is easily seen in the Fe2-C45-C44 and Fe1-C43-C44 angles of 127.3(6) and 125.8(6)° as well as the C45-Fe2-Fe1 and C43-Fe1-Fe2 angles of 85.5(3) and 85.8(2)°, respectively. In fact, the electron delocalization in the ring is so pronounced that the largest deviation from a plane defined by Fe1, Fe2, C43, C44, and C45 is only 0.0346(1)Å for C43. Inclusion of O41 and O42 with these five ring atoms defines a plane with a largest deviation of 0.0799(1)Å, and therefore, double bond character extends to these adjacent atoms as well. Related Fischer alkoxy and acyloxy carbenes are known to display considerable carbon-oxygen double bond character,[9a,b,c,15a] which is also in agreement with the observed C45-O42 and C43-O41 bond distances of 1.363(9) and 1.318(9)Å, respectively.

A possible mechanism accounting for the formation of 15a-c is outlined in Scheme 6. Initially, addition of the iron-centered anion 1 to the α-carbon atom of the acetylene leads to the formation of a reactive, electron-rich vinylic anion (Li^+ cation). In analogy to known RLi reactivity,[9] this vinyl anion readily and rapidly attacks a coordinated



15

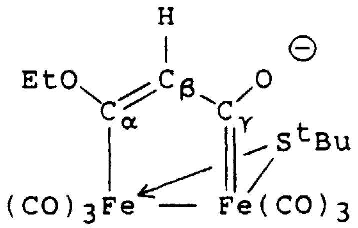
16

Scheme 6

(either bridging or terminal) carbon monoxide ligand on the adjacent iron center (compare Scheme 2 of the vinylthioketal case where bridging of the less nucleophilic vinyl ligand likely occurs prior to attack on carbon monoxide). Due to the electron-rich and resonance-stabilized nature of the resulting Fischer-type, anionic oxy-carbene species, 16, bridging of the vinyl ligand and further reaction with the nucleophilic thiolate bridge does not occur (compare Scheme 2). Instead, direct acylation of oxygen with $R^1C(O)Cl$ produces 15. (In contrast to acylation of the vinylthioketal anions, 6, described earlier in this chapter, acylation of the more nucleophilic vinylcarbene anions, 16, is much more rapid at room temperature.)

In an effort to prove the validity of this reaction mechanism, we have isolated what we believe to be the anionic intermediate, 16 (R = ^{t}Bu), from the crude reaction mixture as the Li^+/12-crown-4 salt. We are currently awaiting the results of an X-ray crystallographic analysis. In comparison to the neutral complexes (μ-EtOC=C(H)C(OC(O)R^3)=)(μ-RS)$Fe_2(CO)_6$, 15, the IR spectrum of 16 shows the terminal carbonyl absorptions shifted somewhat to lower wavenumbers which is consistent with an increase of electron density on the iron centers. This phenomenon is likewise evident in the ^{13}C NMR spectrum where the terminal carbonyl resonances are shifted slightly downfield as compared to those observed in 15. For the same reason, the carbon-13 NMR resonances of the vinylcarbene bridge are conversely shifted upfield (compare tables 7 and 10). As expected, the greatest effect is observed for C_γ, the carbene atom adjacent to the negatively charged oxygen atom, which is shifted approximately 35 ppm upfield (δ_C ~ 267 in 15 vs. 231.6 in 16). Due to this increase of electron

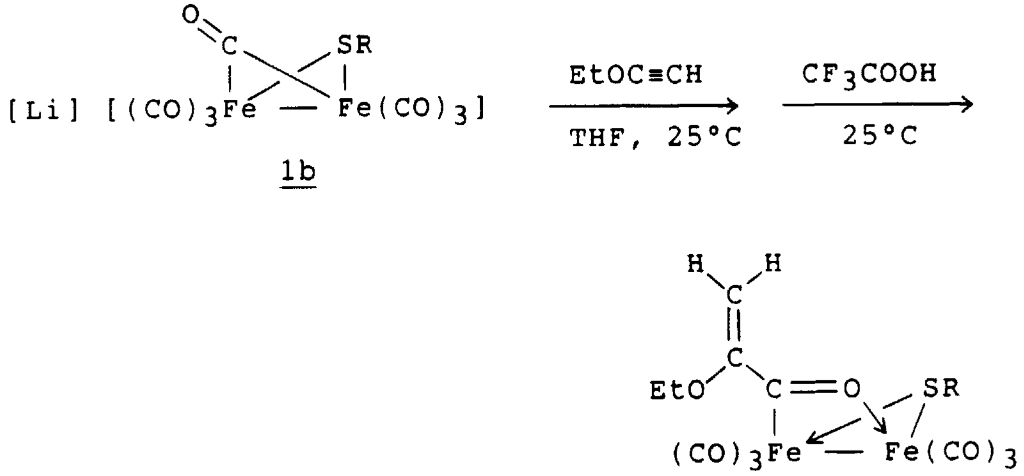
Table 10: ^{13}C and ^{1}H NMR Data for 16



δC_α	δC_β	δC_γ	δH_β
259.78	125.52(d)	231.63	5.27

density in the ring ligand, C_α and C_β are similarly shifted upfield relative to 15 by approximately 24 and 11 ppm, respectively. (An upfield shift is likewise observed for the proton attached to C_β in the corresponding ^1H NMR spectrum.) Finally, delocalization of electron density onto the thiolate bridge is observed in the upfield shift of the ipso t-butyl carbon atom resonance from ~ 50 ppm in 15a-b to 34.57 ppm in 16.

Attempted interception of anion 16 by protonation rather than acylation once again led to unexpected results. Addition of an equimolar amount of trifluoroacetic acid at room temperature to the Li[1]/ethoxyacetylene reaction mixture (with stirring for 30 min) did not yield stable hydroxy vinylcarbene analogs of 15, but instead, the α,β-unsaturated bridging acyl species ($(\mu\text{-EtOC(=CH}_2\text{)C=O)(}\mu\text{-RS)Fe}_2\text{(CO)}_6$), 17, in good yields (Eq. 9). While hydroxy-



1b

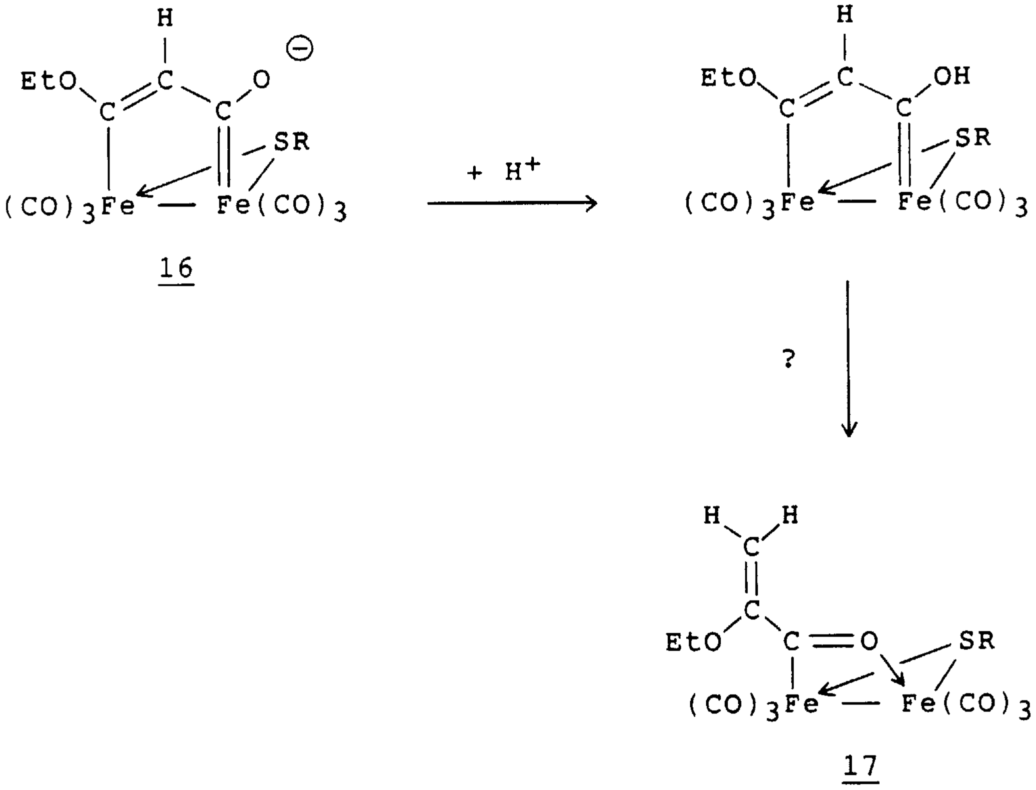
(9)

17

a R = ^{t}Bu 76%

b R = Et 52%

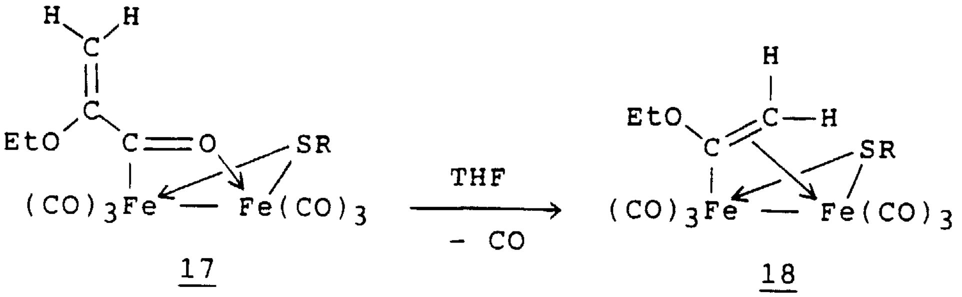
vinylcarbene species may be implicated as reactive intermediates, a complex, secondary rearrangement must occur which ultimately yields the new bridging acyl products (Scheme 7). These μ-acyl complexes are rather unstable



Scheme 7

towards decarbonylation, readily converting to the simple μ-vinyl species (μ-σ,π-EtOC=CH$_2$)(μ-RS)Fe$_2$(CO)$_6$, 18 (see Chapter 3), in nearly quantitative yield at room temperature in THF (Eq. 10).

Because of their quite unexpected isolation, structure proof of (μ-EtOC(=CH$_2$)C=O)(μ-^{t}BuS)Fe$_2$(CO)$_6$, 17, proved to be somewhat ambiguous. In fact, the more logical formation of the isomeric unbridged vinyl compounds, (EtOC=CH$_2$)(μ-CO)(μ-^{t}BuS)Fe$_2$(CO)$_6$, 19, was at first



(10)

a	R	=	^{t}Bu	92%
b	R	=	Et	95%

considered a possibility. As a result, a single crystal X-ray diffraction study of 17a was undertaken. An ORTEP plot showing 30% probability thermal ellipsoids and the atom labeling scheme is shown in Figure 8. Pertinent bond distances and angles are shown in Tables 11 and 12, respectively. Here also, a carbonyl ligand has been incorporated into the organic framework, however, functioning in this instance as a μ-acyl. The acetylenic portion of the ligand is no longer bound to iron as in 15 but is now attached by the same α-carbon atom to the acyl bridge. Net protonation at the β-carbon atom of the acetylenic moiety thus gives rise to the pendant vinyl substituent. Typically, these acyl products were isolated as inseparable mixtures of two isomers, presumably resulting from either an axial(a) or equatorial(e) orientation of the organic group on the symmetrical thiolate bridge (Fig. 9). X-ray crystallography confirmed the structure of the axial isomer of 17a only.

Surprisingly, the X-ray structure of 17a shows little electron delocalization over the vinyl portion of the acyl bridge. The C15-C16 bond of 1.504(4)Å is typical for carbon-carbon single bonds adjacent to a carbonyl unit (1.516(5)Å),[5] and the C16-C17 bond of 1.337(4)Å shows no shortening from that of a typical carbon-carbon double bond

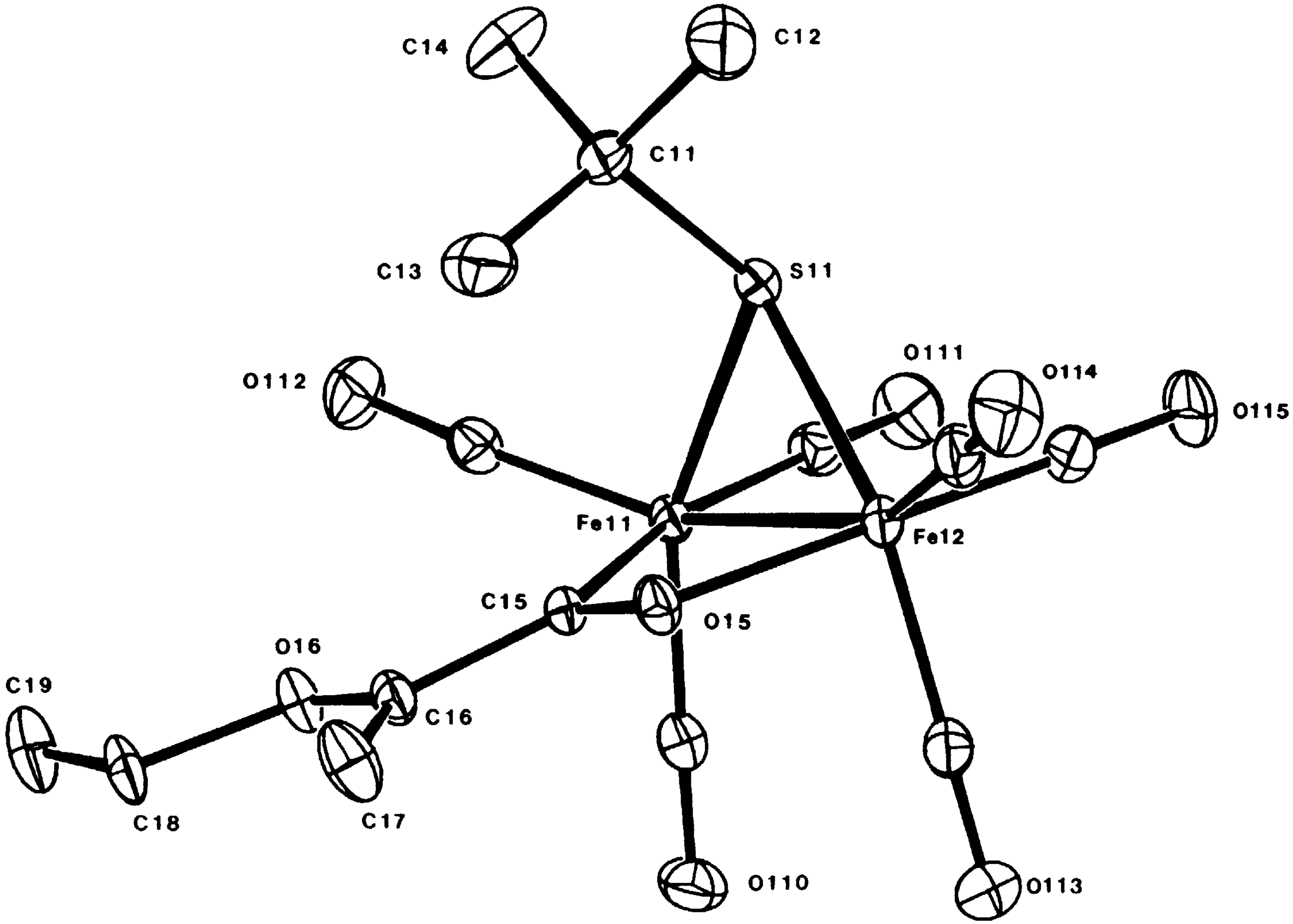


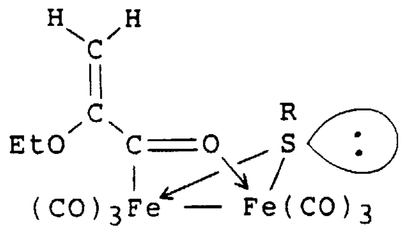
Figure 8: ORTEP of 17a showing 30% probability thermal ellipsoids

Table 11: Relevant Bond Distances (Å) for 17a

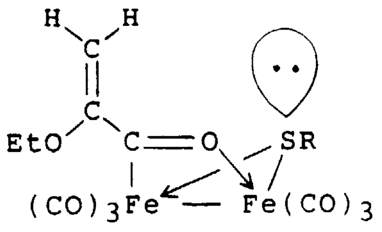
Fe11-Fe12	2.565(1)	C18-C19	1.518(6)
Fe11-C15	1.930(3)	Fe11-S11	2.253(1)
Fe11-O15	2.704	Fe12-S11	2.243(1)
Fe12-O15	1.976(2)	S11-C11	1.865(4)
Fe12-C15	2.586(3)	C11-CH_3 (mean)	1.532
C15-O15	1.248(4)	Fe11-CO (mean)	1.806
C15-C16	1.504(4)	Fe11C-O (mean)	1.143
C16-C17	1.337(5)	Fe12-CO (mean)	1.803
C16-O16	1.351(4)	Fe12C-O (mean)	1.137
O16-C18	1.449(4)		

Table 12: Relevant Bond Angles (°) for 17a

Fe11-Fe12-O15	71.8(1)	O16-C18-C19	108.0(3)
Fe12-Fe11-C15	68.6(1)	C16-O16-C18	115.3(3)
Fe11-C15-O15	115.0(2)	Fe11-S11-Fe12	69.6(0)
Fe11-C15-C16	130.2(3)	Fe12-Fe11-S	55.0(0)
Fe12-O15-C15	104.4(2)	Fe11-Fe12-S	55.4(0)
C15-C16-C17	120.4(3)	O15-Fe12-S11	90.2(1)
C15-C16-O16	112.6(3)	C15-Fe11-S11	90.2(1)
O15-C15-C16	114.7(3)	Fe11-S11-C11	120.9(1)
O16-C16-C17	127.0(3)	Fe12-S11-C11	119.7(1)



a



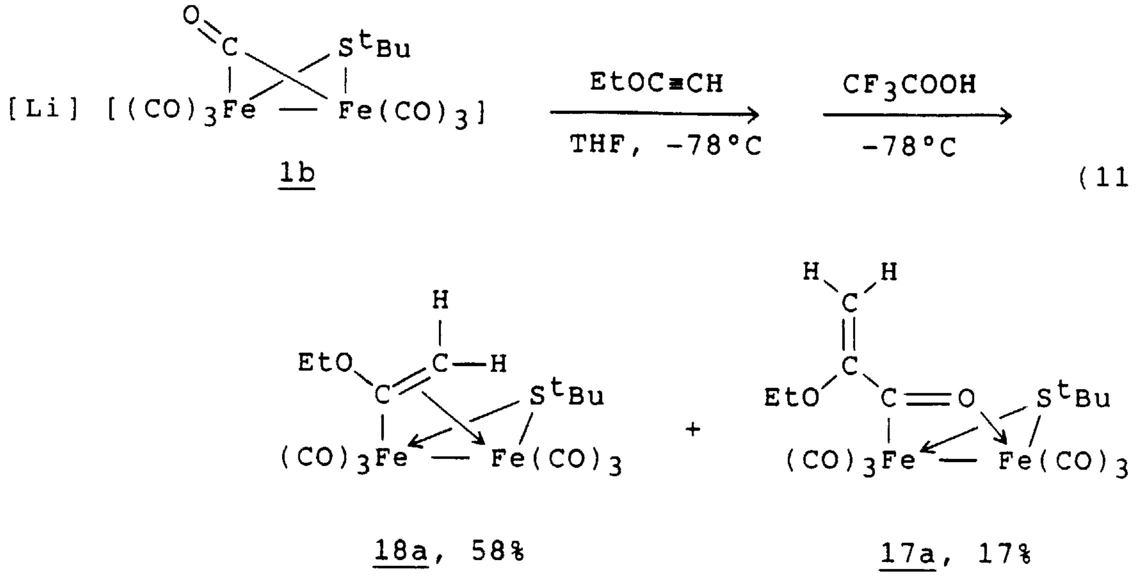
e

Figure 9

(1.337(6)Å).[5] The C16-O16 distance of 1.351(4)Å does show some shortening from that of a simple carbon-oxygen single bond (1.43(1)Å),[5] but remarkably, the C18-O16 bond of 1.449(4)Å remains largely unaffected. In contrast to these findings, Carty has reported the crystal structure of a related complex (μ-HC(=C(Ph)NHPh)C=O)(μ-Ph_2P)$Fe_2(CO)_6$, 20, which was found to have considerable electron delocalization over the entire α,β-unsaturated acyl bridge.[16b] As expected, however, electron delocalization in the bridging acyl fragment of 17a is indicated. The C15-O15 distance of 1.248(4)Å is longer than that of a typical conjugated, carbon-oxygen double bond,[5] although it is somewhat shorter than in related acyl bridged complexes.[15b,16] Conversely, the short Fe11-C15 bond of 1.930(3)Å is consistent with known μ-acyl or related "carbene-like" ligands (i.e. μ-thioacyl, μ-vinyl, μ-acetylide).[4,15,17]

Once the structure of these new α,β-unsaturated acyl species was determined with certainty, a re-analysis of the analytical and spectroscopic data harmonized with this result. In general, a very strong band at 1480cm^{-1} is observed in the infrared spectra of these complexes, which in comparison to known thiolate and acyl bridged diiron systems, can be assigned to the carbonyl absorptions of the bridging acyl ligands.[18] The free vinyl ligand is likewise identified in the IR spectra as a medium band at 1600 cm^{-1},[13] as well as in the ^1H and ^{13}C NMR spectra as appropriate vinyl resonances. In the ^{13}C NMR spectra, the acyl moiety gives rise to a pair of singlets (two isomers!) far downfield ($\delta_C \sim 285$) in the region typically reported for related acyl and thioacyl bridged clusters.[16,17,18] Finally, although 17a could be isolated as a red, crystalline solid, 17b was isolated as a slightly air sensitive, red oil, which when coupled with its tendency to undergo facile decarbonylation, could not be purified sufficiently to give an accurate C/H combustion analysis.

Certainly, the chemistry of the Li[1]/ethoxyacetylene system is dominated by complex rearrangement mechanisms operating at room temperature. As with the reactions of 1b with the electrophilic acetylenes dimethyl acetylenedicarboxylate, methyl propiolate, and 3-butyn-2-one, these intramolecular rearrangements resulting in carbon monoxide incorporation are disfavored at low temperature. For instance, reaction of $[Li][(\mu\text{-}CO)(\mu\text{-}^tBuS)Fe_2(CO)_6]$, 1b (R= ^{t}Bu), with ethoxyacetylene at -78°C followed by reaction of the anionic intermediate with trifluoroacetic acid at -78°C gave $(\mu\text{-}EtOC(=CH_2)C=O)(\mu\text{-}^tBuS)Fe_2(CO)_6$, 17a, in only 17% yield with the major product being $(\mu\text{-}\sigma,\pi\text{-}EtOC=CH_2)(\mu\text{-}^tBuS)Fe_2(CO)_6$, 18a, in 58% yield (Eq. 11). Furthermore, in contrast to what had been observed for the electrophilic, unsymmetrical acetylenes methyl propiolate and 3-butyn-2-one, isomeric vinyl complexes derived from addition of 1b to either carbon atom of the triple bond of ethoxyacetylene were not isolated. Presumably, only 18a arises in this instance via the direct protonation at the β-position of the assumed intermediate vinylic anion $[(\mu\text{-}\sigma,\pi\text{-}EtOC=CH)(\mu\text{-}^tBuS)Fe_2(CO)_6]^-$, 21, in the absence of rearrangement (see Scheme 1). Analogously, we have prepared 18a as the sole product from the *in-situ* reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}^tBuS)Fe_2(CO)_6]$, 1a (R = ^{t}Bu), with ethoxyacetylene at room temperature (Chapter 3). Finally, as expected for a likely



(11)

intramolecular rearrangement process (see Scheme 7), formation of products of type 17 is not promoted by the presence of free carbon monoxide in solution. For example, reaction of ethoxyacetylene with a carbon monoxide saturated solution of $[Li][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ at -78°C followed by reaction of the anionic intermediate with trifluoroacetic acid also at -78°C gives 17a in only 11% yield with the major product being $(\mu\text{-}\sigma,\pi\text{-}EtOC{=}CH_2)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$, 18a (71%).

EXPERIMENTAL

General Comments

All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl and purged with nitrogen prior to use. Triethylamine was distilled under nitrogen from calcium hydride and purged with nitrogen prior to use. Ethyl, t-butyl, phenyl, and benzyl mercaptans were purged with nitrogen and used without further purification. Acetyl, benzoyl, and pivaloyl chlorides were all freshly distilled and purged with nitrogen prior to use. 12-Crown-4 (Aldrich) was purged with nitrogen and used without further purification. Trifluoroacetic acid was purified by vacuum distillation (at room temperature) and purged with nitrogen prior to use. Dimethyl acetylenedicarboxylate, methyl propiolate, 3-butyne-2-one, and ethoxyacetylene (all purchased from Farchan Labs) were purged with nitrogen after purification by vacuum distillation (at room temperature) when necessary. Triiron dodecacarbonyl was prepared by a literature procedure[19] and n-butyllithium (2.4 M in hexane) was purchased from Alfa and used as received.

The progress of all reactions was monitored by thin layer chromatography (Baker-Flex Silica Gel, 1B-F). Purification by filtration chromatography in which the reaction products were dissolved in a suitable solvent and chromatographed on a bed of EM Science or Sigma 100-300 mesh silicic acid (ca. 200 ml) in a 350 ml glass fritted filter funnel was used in most cases. Further purification by medium pressure column chromatography was accomplished with a 300x25 mm or a 450x25 mm column using Sigma 230-400 mesh silica gel. All chromatography was completed without exclusion of atmospheric moisture or oxygen. Solid products were recrystallized from deoxygenated solvents at -20°C.

Solution infrared spectra (NaCl windows) were obtained using a Perkin-Elmer Model 1430 double beam grating infrared spectrophotometer. Proton NMR were recorded on either a JEOL FX-90Q, a Bruker WM-250, or a Varian XL-300 NMR spectrometer operating at 90, 250, or 300 MHz respectively. Carbon-13 NMR were obtained using a Bruker WH-270 or Varian XL-300 spectrometer operating at 67.9 or 75.4 MHz respectively. Electron impact mass spectra were obtained using a Finnigan-3200 mass spectrometer operating at 70 eV. Field desorption mass spectra were obtained with a Finnigan MAT-731 mass spectrometer operating in the positive ion mode. FAB mass spectra were obtained with a Finnigan MAT-731 mass spectrometer operating in the negative ion mode. All masses were correlated using the following isotopes: ^{1}H, ^{7}Li, ^{12}C, ^{16}O, ^{32}S, and ^{56}Fe. Melting points were determined in air on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were perfomed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

X-Ray Crystallography

The following crystal structures were solved by Dr. John C. Dewan, crystallographer, Department of Chemistry, the Massachusetts Institute of Technology:

$(\mu\text{-}\sigma,\pi\text{-}HC{=}C(C(O)Me)C(OC(O)Me)S^{t}Bu\text{-})Fe_2(CO)_6$, 5g:

Data in the range $3° \leq 2\theta \leq 55°$ were collected using Mo Kα radiation on an Enraf-Nonius CAD4F-11 diffractometer. Data collection, reduction, and refinement procedures have been detailed elsewhere.[20] Hydrogen atoms were ignored while all other atoms were refined anisotropically. Final $R_1 = 0.049$ and $R_2 = 0.064$ for 3634 observed reflections ($\pm h, \pm k, +l$) $[I_o > 2\sigma(I_o)]$ and 262 variables. The largest peak on the difference-Fourier map was 0.77 e$Å^{-3}$. Crystal data are summarized in Table 13 and final positional parameters appear in Table 14.

Table 13: Crystal Data for $(\mu-\sigma,\pi-HC=C(C(O)Me)C(OC(O)Me)S^{t}Bu-)Fe_2(CO)_6$, 5g

a = 9.810(1) Å

b = 15.629(1) Å

c = 7.438(1) Å

V = 1056.0 $Å^3$

Z = 2

Space group = $P\bar{1}$

α = 96.66(1)°

β = 111.18(1)°

γ = 86.65(1)°

μ = 14.7 cm^{-1} *

ρ(calcd) = 1.598 g cm^{-1}

*A semi-empirical absorption correction was applied

Table 14: Final Positional Parameters for 5g

ATOM	X	Y	Z
Fe1	0.77021(7)	0.62454(4)	0.10115(10)
Fe2	0.59560(7)	0.73988(4)	0.19618(9)
S	0.92278(12)	0.71196(8)	0.35370(17)
C11	0.8810(6)	0.5974(4)	-0.0412(8)
O11	0.9441(5)	0.5800(3)	-0.1448(7)
C12	0.8163(6)	0.5383(3)	0.2636(8)
O12	0.8424(5)	0.4865(3)	0.3635(7)
C13	0.6247(6)	0.5641(3)	-0.0746(8)
O13	0.5330(5)	0.5255(3)	-0.1902(7)
C21	0.5093(5)	0.8306(3)	0.2834(7)
O21	0.4560(5)	0.8888(3)	0.3408(7)
C22	0.6226(5)	0.6732(3)	0.3883(7)
O22	0.6316(5)	0.6354(3)	0.5137(6)
C23	0.4264(6)	0.6974(4)	0.0285(8)
O23	0.3169(5)	0.6713(3)	-0.0786(7)
C31	0.6856(5)	0.7291(3)	-0.0174(6)
C32	0.7194(5)	0.8092(3)	0.0948(6)
C33	0.7956(5)	0.7987(3)	0.2982(6)
C34	0.8373(6)	0.8760(3)	0.6129(7)
C35	0.8883(9)	0.9628(4)	0.7184(9)
C36	0.6770(5)	0.8941(3)	0.0159(7)
C37	0.5367(6)	0.9009(4)	-0.1587(8)
O31	0.8312(4)	0.8751(2)	0.4244(5)
O32	0.7539(4)	0.9564(2)	0.0860(5)
O33	0.8048(5)	0.8160(3)	0.6726(5)
C41	1.0938(5)	0.7478(4)	0.3296(8)
C42	1.1641(6)	0.8120(5)	0.5117(9)
C43	1.0650(6)	0.7898(4)	0.1436(8)
C44	1.1891(6)	0.6642(4)	0.3373(11)

$(\mu\text{-}\sigma,\pi\text{-}HC{=}C(C(O)Me)C(O)S\text{-})Fe_2(CO)_6$, 8a:

Data in the range 3° $\leq 2\theta \leq$ 55° were collected at -7°C using Mo Kα radiation on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid nitrogen low temperature device. Data collection, reduction, and refinement procedures have been detailed elsewhere.[20] Hydrogen atoms were ignored while all other atoms were refined anisotropically. Final $R_1 = 0.049$ and $R_2 = 0.060$ for 2406 observed reflections (±h,±k,+l) $[F_o > 6\sigma(F_o)]$ and 199 variables. A final difference-Fourier map showed no significant features. Crystal data are summarized in Table 15 and final positional parameters appear in Table 16.

$(\mu\text{-}EtOC{=}C(H)C(OC(O)Me){=})(\mu\text{-}{}^tBuS)Fe_2(CO)_6$, 15a:

Data in the range 3° $\leq 2\theta \leq$ 55° were collected using Mo Kα radiation on an Enraf-Nonius CAD4F-11 diffractometer. Data collection, reduction, and refinement procedures have been detailed elsewhere.[20] Hydrogen atoms were ignored while all other atoms were refined anisotropically. Final $R_1 = 0.069$ and $R_2 = 0.073$ for 2360 observed reflections (+h,+k,±l) $[I_o > 2\sigma(I_o)]$ and 262 variables. The largest peak on the difference-Fourier map was 0.68 $eÅ^{-3}$. Crystal data are summarized in Table 17 and final positional parameters appear in Table 18.

$(\mu\text{-}EtOC({=}CH_2)C{=}O)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$, 17a:

Data in the range 3° $\leq 2\theta \leq$ 55° were collected at -65°C using Mo Kα radiation on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid nitrogen low temperature device. Data collection, reduction, and refinement procedures have been detailed elsewhere.[20] Hydrogen atoms were ignored while all other atoms were refined anisotropically. Final $R_1 = 0.044$ and $R_2 = 0.060$ for 3769 observed reflections (±h,±k,+l) $[I_o > 2\sigma(I_o)]$

Table 15: Crystal Data for $(\mu\text{-}\sigma,\pi\text{-HC=C(C(O)Me)C(O)S-)Fe}_2\text{(CO)}_6$, 8a

a = 8.939(4) Å

α = 93.89(2)°

b = 12.275(2) Å

β = 100.44(3)°

c = 6.934(3) Å

γ = 108.72(3)°

V = 702.15 $Å^3$

μ = 22.1 cm^{-1} *

Z = 2

ρ(calcd) = 1.929 g cm^{-3}

Space group = $P\bar{1}$

*An empirical absorption correction was applied

Table 16: Final Positional Parameters for 8a

ATOM	X	Y	Z
Fe1	0.75451(8)	0.29278(6)	0.37088(10)
Fe2	0.90572(8)	0.18065(6)	0.21302(10)
S	0.92843(14)	0.36367(10)	0.1672(2)
C1	0.6153(6)	0.1990(5)	0.4954(8)
O1	0.5320(5)	0.1381(4)	0.5773(7)
C2	0.9200(6)	0.3201(4)	0.5781(8)
O2	1.0224(5)	0.3407(4)	0.7118(6)
C3	0.6984(6)	0.4196(5)	0.4244(8)
O3	0.6621(6)	0.4980(4)	0.4557(8)
C4	0.8575(6)	0.0461(5)	0.3187(8)
O4	0.8217(5)	-0.0366(3)	0.3859(6)
C5	1.1226(6)	0.2254(4)	0.3319(8)
O5	1.2544(5)	0.2531(4)	0.4020(7)
C6	0.9136(6)	0.1193(5)	-0.0244(9)
O6	0.9133(6)	0.0819(4)	-0.1762(7)
C7	0.7309(6)	0.3393(4)	0.0088(8)
O7	0.7060(5)	0.4025(4)	-0.1095(7)
C8	0.6160(6)	0.2403(4)	0.0742(7)
C9	0.6773(6)	0.1547(4)	0.1447(7)
C10	0.4351(6)	0.2176(5)	0.0285(8)
O10	0.3456(4)	0.1262(4)	0.0588(7)
C11	0.3729(7)	0.3112(6)	-0.0528(11)

Table 17: Crystal Data for
(μ-EtOC=CHC(OC(O)Me)=)(μ-^{t}BuS)$Fe_2(CO)_6$, 15a

a = 9.583(2) Å
b = 14.176(3) Å
c = 16.206(2) Å
V = 2197.8 $Å^3$
Space group = $P2_1/n$

β = 93.37(1)°
ρ(calcd) = 1.541 g cm^{-3}
μ = 14.2 cm^{-1} *
Z = 4

*A semi-empirical absorption correction was applied

Table 18: Final Positional Parameters for 15a

ATOM	X	Y	Z
Fe1	-0.01635(12)	0.25952(8)	-0.10122(7)
Fe2	0.03455(13)	0.26530(9)	0.05980(7)
S	0.1649(2)	0.18949(15)	-0.03083(14)
C11	-0.1821(10)	0.3143(6)	-0.1003(6)
O11	-0.2895(7)	0.3479(5)	-0.0986(5)
C12	-0.0078(10)	0.2308(6)	-0.2075(6)
O12	-0.0045(9)	0.2171(5)	-0.2765(4)
C13	0.0656(10)	0.3709(7)	-0.1198(6)
O13	0.1111(8)	0.4427(5)	-0.1366(5)
C21	-0.1284(11)	0.3128(7)	0.0861(6)
O21	-0.2328(8)	0.3394(6)	0.1041(5)
C22	0.1227(11)	0.2447(7)	0.1578(7)
O22	0.1759(9)	0.2309(6)	0.2221(5)
C23	0.1057(11)	0.3832(7)	0.0552(6)
O23	0.1403(9)	0.4596(5)	0.0572(5)
C31	0.3485(9)	0.2280(7)	-0.0471(6)
C32	0.4411(11)	0.1555(9)	0.0060(8)
C33	0.3830(10)	0.3309(7)	-0.0162(7)
C34	0.3676(12)	0.2209(9)	-0.1396(7)
C41	-0.3445(14)	0.0023(8)	-0.2226(7)
C42	-0.2791(12)	0.0209(7)	-0.1368(6)
O41	-0.1840(7)	0.1037(4)	-0.1466(4)
C43	-0.1173(9)	0.1410(6)	-0.0810(5)
C44	-0.1251(9)	0.0964(6)	-0.0049(5)
C45	-0.0621(9)	0.1429(6)	0.0610(5)
O42	-0.0590(7)	0.1007(5)	0.1366(4)
C46	-0.1601(15)	0.0549(10)	0.1713(9)
O43	-0.2801(12)	0.0615(8)	0.1419(7)
C47	-0.1190(14)	0.0061(8)	0.2495(7)

and 235 variables. The largest peak on the difference-Fourier map was 0.69 $e\text{Å}^{-3}$. The structure solution proved difficult and was initially obtained in space group P1 and then transformed to $P\bar{1}$. Crystal data are summarized in Table 19 and final positional parameters are given in Table 20.

Standard in-situ Preparation of $[Li][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$

A 250 ml Schlenk flask (one necked, round bottomed) equipped with a stir-bar and rubber septum was charged with 1.51 g (3.00 mmol) of $Fe_3(CO)_{12}$ and degassed via three evacuation/nitrogen-backfill cycles. The flask was then charged with 30 ml of THF by syringe, and the resulting deep green solution was cooled to -78°C by immersing the flask in a dry ice/acetone slush bath. Subsequently, 3.00 mmol of the appropriate thiol was added by syringe followed by the slow addition of 3.00 mmol of n-butyllithium also by syringe. The mixture was stirred for 10 min at -78°C and then warmed to room temperature during which time a green to brown-red color change was observed. The $[Li][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ reagent solution was stirred an additonal 15 min at room temperature and subsequently used in-situ without further purification.

Synthesis of $(\mu\text{-}\sigma,\pi\text{-}MeO_2CC{=}C(CO_2Me)C(OC(O)Me)S^tBu\text{-})Fe_2(CO)_6$ JBH-59-III

To the standard $[Li][(\mu\text{-}CO)(\mu\text{-}^tBuS)Fe_2(CO)_6]$ reagent solution (1.00 mmol) was added 0.12 ml (1.00 mmol) of dimethyl acetylenedicarboxylate by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and a color change to brighter red. After the reaction mixture had been stirred for 20 min at room temperature, 0.11 ml (1.50 mmol) of acetyl chloride was added by syringe. After the mixture had been stirred for an

Table 19: Crystal Data for $(\mu\text{-EtOC}(=\text{CH}_2)\text{C=O})(\mu\text{-}^t\text{BuS})\text{Fe}_2(\text{CO})_6$, 17a

a = 11.125(3) Å　　α = 100.88(2)°
b = 11.400(2) Å　　β = 91.57(2)°
c = 7.820(3) Å　　γ = 85.37(2)°
V = 970.7 $Å^3$　　μ = 16.0 cm^{-1} *
Z = 2　　ρ(calcd) = 1.601 g cm^{-3}
Space group = $P\bar{1}$

*A semi-empirical absorption correction was applied

Table 20: Final Positional Parameters for 17a

ATOM	X	Y	Z
Fe11	0.21557(4)	0.29484(4)	0.19319(6)
Fe12	0.12703(4)	0.23214(4)	0.45879(6)
S11	0.16614(7)	0.10862(7)	0.20394(11)
O15	0.3016(2)	0.2468(2)	0.5015(3)
O16	0.4969(2)	0.3618(2)	0.2453(3)
O110	0.2109(3)	0.5546(2)	0.3104(4)
O111	-0.0101(3)	0.3230(3)	-0.0131(4)
O112	0.3810(3)	0.2482(3)	-0.1033(4)
O113	0.0856(3)	0.4716(3)	0.6767(4)
O114	0.1059(3)	0.0691(3)	0.7083(5)
O115	-0.1259(2)	0.2317(3)	0.3501(5)
C11	0.2845(3)	-0.0180(3)	0.1938(5)
C12	0.2201(5)	-0.1162(4)	0.2566(8)
C13	0.3997(4)	0.0104(4)	0.3003(8)
C14	0.3137(5)	-0.0558(4)	0.0005(6)
C15	0.3362(3)	0.2847(3)	0.3729(4)
C16	0.4634(3)	0.3217(3)	0.3874(5)
C17	0.5303(4)	0.3131(5)	0.5298(6)
C18	0.6215(3)	0.3904(4)	0.2453(6)
C19	0.6456(4)	0.4240(5)	0.0712(7)
C110	0.2135(3)	0.4531(3)	0.2627(5)
C111	0.0767(3)	0.3101(3)	0.0647(5)
C112	0.3182(3)	0.2689(3)	0.0135(5)
C113	0.1010(3)	0.3786(4)	0.5931(5)
C114	0.1139(3)	0.1319(4)	0.6140(5)
C115	-0.0269(3)	0.2325(3)	0.3931(5)

additional 30 h, the solvent was removed in vacuo to yield a red, oily solid which was purified by filtration chromatography. Pentane eluted a very pale orange band which was not collected. Methylene chloride eluted a red band which gave 0.51 g (0.87 mmol, 87%) of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(OC(O)Me)S^tBu$-)$Fe_2(CO)_6$, 5a, as an air-stable, red-orange solid, mp 180.0-202.0°C (dec - the sample gradually darkened from 180°C upwards and eventually decomposed with gas evolution) after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{19}H_{18}Fe_2O_{12}S$: C, 39.20; H, 3.17 %. Found: C, 39.15; H, 3.23 %.

IR($CHCl_3$): 3035w, 3018w, 2983vw, 2950w, 2922w, 2900vw, 2863vw, 1763s(C=O), 1720vs(C=O), 1690sh(C=O), 1515m, 1469m, 1451m, 1431s, 1391m, 1365s, 1332w, 1200vs-br, 1150s, 1080s, 1039m, 1019vs, 978m, 921m, 871w, 845w, 780vs-br, 740vs-br, 665vs, 608s, 595s, 579s, 550s cm^{-1}.
Terminal carbonyl region (pentane): 2075s, 2033vs, 2010s, 2000sh, 1994s, 1981m cm^{-1}.

^{1}H NMR($CDCl_3$; 90 MHz): δ 1.15 (s, 9H, $SC(CH_3)_3$), 2.08 (s, 3H, $OC(O)CH_3$), 3.85 (s, 3H, CO_2CH_3), 3.87 (s, 3H, CO_2CH_3).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 20.65 (q, J = 130.8 Hz, $OC(O)\underline{C}H_3$), 26.79 (q, J = 128.0 Hz, $SC(\underline{C}H_3)_3$), 52.34 (q, J = 147.2 Hz, $CO_2\underline{C}H_3$), 52.78 (q, J = 148.0 Hz, $CO_2\underline{C}H_3$), 54.62 (s, $S\underline{C}(CH_3)_3$), 84.25 (s, $\underline{C}OC(O)Me$), 99.53 (s, $MeO_2CC{=}\underline{C}$), 155.04 (s, $\underline{C}O_2Me$), 165.50 (s, $\underline{C}O_2Me$), 167.47 (s, $O\underline{C}(O)Me$), 174.27 (s, $MeO_2C\underline{C}{=}C$), 207.08, 208.72, and 208.99 (all s, Fe-CO).

Synthesis of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(OC(O)Me)SEt$-)$Fe_2(CO)_6$

JBH-75-V

To the standard [Li][(μ-CO)(μ-EtS)$Fe_2(CO)_6$] reagent solution (3.21 mmol) was added 0.39 ml (3.21 mmol) of dimethyl acetylenedicarboxylate by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and a color change to brighter red. After the reaction mixture had been stirred for 30 min at room temperature, 0.43 ml (6.00 mmol) of acetyl chloride was added by syringe. After the mixture had been stirred for an additional 5 days, the solvent was removed in vacuo to yield a red oil which was purified by filtration chromatography. Pentane/CH_2Cl_2 (6/4 v/v) eluted a yellow-brown band which was not collected. Acetone/CH_2Cl_2 (1/20 v/v) eluted a dark orange band which gave 1.37 g (2.47 mmol, 77%) of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(OC(O)Me)SEt$-)$Fe_2(CO)_6$, 5b, as an air-stable, red-orange solid, mp 107.0-109.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{17}H_{14}Fe_2O_{12}S$: C, 36.85; H, 2.55 %. Found: C, 36.95; H, 2.58 %.

IR(CCl_4): 2990w, 2950s, 2900w, 2870w, 2840vw, 1775vs(C=O), 1725vs(C=O), 1710sh(C=O), 1453sh, 1435vs, 1398s, 1390s, 1370s, 1340m, 1200vs-br, 1083s, 1021vs, 983s, 915m, 875w, 863w, 705m, 680m, 643m, 610vs, 598vs, 560vs, 493s cm^{-1}.
Terminal carbonyl region (pentane): 2075s, 2035vs, 2010sh, 2000m, 1998sh cm^{-1}.

^1H NMR($CDCl_3$; 300 MHz): δ 1.16 (t, J = 7.22 Hz, 3H, $SCH_2C\underline{H}_3$), 2.10 (s, 3H, $OC(O)CH_3$), 2.45 (m, 2H, $SC\underline{H}_2CH_3$), 3.86 (s, 3H, CO_2CH_3), 3.87 (s, 3H, CO_2CH_3).

^{13}C NMR($CDCl_3$; 75.4 MHz): δ 12.48 (q, J = 129.3 Hz, $SCH_2\underline{C}H_3$), 20.77 (q, J = 129.8 Hz, $OC(O)\underline{C}H_3$), 44.20 (t, J =

142.8 Hz, S$\underline{C}H_2CH_3$), 52.67 (q, J = 147.0 Hz, $CO_2\underline{C}H_3$), 53.14 (q, J = 147.0 Hz, $CO_2\underline{C}H_3$), 86.40 (s, $\underline{C}OC(O)Me$), 98.50 (s, $MeO_2CC=\underline{C}$), 156.05 (s, $\underline{C}O_2Me$), 165.98 (s, $\underline{C}O_2Me$), 168.31 (s ,O$\underline{C}$(O)Me), 174.30 (s, $MeO_2C\underline{C}=C$), 207.09, 207.22, and 209.10 (all s, Fe-CO).

Mass Spectrum (FD); m/z: 554 (M^+)

Synthesis of (μ-σ,π-$MeO_2CC=C(CO_2Me)C(OC(O)Me)SPh$-)$Fe_2(CO)_6$

JBH-55-VI

To the standard [Li][(μ-CO)(μ-PhS)$Fe_2(CO)_6$] reagent solution (3.31 mmol) was added 0.41 ml (3.31 mmol) of dimethyl acetylenedicarboxylate by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and a color change to brighter red. After the reaction mixture had been stirred for 30 min at room temperature, 0.36 ml (5.00 mmol) of acetyl chloride was added by syringe. After the mixture had been stirred for an additional 11 days, the solvent was removed in vacuo to yield a red tar which was purified by filtration chromatography. Pentane eluted a brown-orange band which was not collected. Acetone/CH_2Cl_2 (1/20 v/v) eluted a red band which gave 1.32 g of a red tar identified by its ^1H NMR spectrum (CD_2Cl_2; 300 MHz) to be a mixture of 1.18 g (1.97 mmol, 60%) of (μ-σ,π-$MeO_2CC=C(CO_2Me)C(OC(O)Me)SPh$-)$Fe_2(CO)_6$, 5c, and 0.13 g (0.25 mmol, 7%) of (μ-σ,π-$MeO_2CC=C(H)CO_2Me$)(μ-PhS)$Fe_2(CO)_6$, 9c. Recrystallization from pentane/CH_2Cl_2 yielded analytically pure (μ-σ,π-$MeO_2CC=C(CO_2Me)C(OC(O)Me)SPh$-)$Fe_2(CO)_6$, 5c, as an air-stable, red solid, mp 137.0-139.5°C.

Anal. Calcd. for $C_{21}H_{14}Fe_2O_{12}S$: C, 41.89; H, 2.34 %. Found: C, 41.93; H, 2.41 %.

IR(CCl_4): 3065w, 3000w, 2950m, 2900vw, 2840vw, 1780vs(C=O), 1730vs(C=O), 1710sh(C=O), 1580w(Ph), 1480m, 1440vs, 1400m, 1370s, 1340m, 1305w, 1250sh, 1215vs, 1190vs, 1090s, 1027vs, 987s, 980s, 915m, 860w, 705m, 688s, 612vs, 600vs, 560vs cm^{-1}.
Terminal carbonyl region (pentane): 2080s, 2060w, 2045vs, 2015s, 1995sh cm^{-1}.

^{1}**H NMR**(CD_2Cl_2; 300 MHz): δ 2.03 (s, 3H, $C(O)CH_3$), 3.87 (s, 3H, CO_2CH_3), 3.91 (s, 3H, CO_2CH_3), 7.33-7.47 (m, 5H, C_6H_5).

^{13}**C NMR**($CDCl_3$; 75.4 MHz): δ 19.83 (q, J = 131.3 Hz, $C(O)\underline{C}H_3$), 52.54 (q, J = 147.1 Hz, $CO_2\underline{C}H_3$), 52.98 (q, J = 147.9 Hz, $CO_2\underline{C}H_3$), 86.94 (s, $\underline{C}OC(O)Me$), 99.07 (s, $MeO_2CC{=}\underline{C}$), 127.94 (d, J = 163.1 Hz, C_6H_5), 129.36 (d, J = 163.6 Hz, C_6H_5), 130.65 (d, J = 163.6 Hz, C_6H_5), 135.13 (s, ipso C_6H_5), 156.71 (s, $\underline{C}O_2Me$), 165.83 (s, $\underline{C}O_2Me$), 167.82 (s, $O\underline{C}(O)Me$), 174.37 (s, $MeO_2C\underline{C}{=}C$), 207.03 and 209.04 (both s, Fe-CO).

Synthesis of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(OC(O)Ph)S^tBu$-)$Fe_2(CO)_6$

JBH-71-V

To the standard $[Li][(\mu\text{-}CO)(\mu\text{-}^tBuS)Fe_2(CO)_6]$ reagent solution (1.54 mmol) was added 0.19 ml (1.54 mmol) of dimethyl acetylenedicarboxylate by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and a color change to brighter red. After the reaction mixture had been stirred for 30 min at room temperature, 0.35 ml (3.00 mmol) of benzoyl chloride was added by syringe. After the mixture had been stirred for an additional 8 days, the solvent was removed in vacuo to yield a red oil which was purified by filtration chromatography. Pentane/CH_2Cl_2 (7/3 v/v) eluted a pale yellow band which was not collected. Acetone/CH_2Cl_2 (1/20 v/v) eluted an orange band which gave 0.90 g (1.39 mmol, 90%) of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(OC(O)Ph)S^tBu$-)$Fe_2(CO)_6$, 5d, as an air-stable, red solid, mp 181.0-184.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{24}H_{20}Fe_2O_{12}S$: C, 44.75; H, 3.13 %. Found: C, 44.77; H, 3.19 %.

IR($CHCl_3$): 3030w, 2983w, 2948w, 2920w, 2897vw, 2860vw, 1730vs(C=O), 1712vs(C=O), 1690s(C=O), 1595w(Ph), 1580vw(Ph), 1468w, 1451m, 1447m, 1431s, 1391m, 1362m, 1255vs, 1220vs-br, 1175s, 1100m, 1081s, 1052vs, 1029vs, 1002w, 996m, 982m, 921m, 871m, 842m, 780vs-br, 680vs-br, 660vs, 605s cm^{-1}.
Terminal carbonyl region (pentane): 2075s, 2033vs, 2007s, 1998s, 1995sh, 1982m cm^{-1}.

^{1}H **NMR**(CD_2Cl_2; 90 MHz): δ 1.14 (s, 9H, $S(CH_3)_3$), 3.89 (s, 6H, CO_2CH_3), 7.31-8.12 (m, 5H, C_6H_5).

^{13}C **NMR**($CDCl_3$; 67.9 MHz): δ 26.99 (q, J = 128.1 Hz, $SC(\underline{C}H_3)_3$), 52.48 (q, J = 147.8 Hz, $CO_2\underline{C}H_3$), 52.90 (q, J = 147.9 Hz, $CO_2\underline{C}H_3$), 54.77 (s, $S\underline{C}(CH_3)_3$), 85.29 (s, $\underline{C}OC(O)Ph$), 97.83 (s, $MeO_2CC{=}\underline{C}$), 128.49 (d, J = 162.6 Hz, C_6H_5), 129.57 (d, J = 162.8 Hz, C_6H_5), 133.84 (d, J = 160.5 Hz, C_6H_5), 156.71 (s, $\underline{C}O_2Me$), 163.52 (s, $\underline{C}O_2Me$), 165.78 (s, $O\underline{C}(O)Ph$), 174.69 (s, $MeO_2C\underline{C}{=}C$), 207.26, 208.86, and 209.15 (all s, Fe-CO).

Mass Spectrum (FD); m/z: 644 (M^+)

Synthesis of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(OC(O)^tBu)S^tBu$-)$Fe_2(CO)_6$ JBH-20-VII

To the standard [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (2.04 mmol) was added 0.25 ml (2.04 mmol) of dimethyl acetylenedicarboxylate by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and a color change to brighter red. After the reaction mixture had been stirred for 24 h at room temperature, 0.50 ml (4.08 mmol) of pivaloyl chloride was added by syringe. After the mixture had been stirred for an additional 48 h at reflux, the solvent was removed in vacuo to yield a red-brown tar which was purified by filtration chromatography. Pentane/CH_2Cl_2 (8/2 v/v) eluted a pale orange-brown band which was not collected. Acetone/CH_2Cl_2 (1/20 v/v) eluted a red band which gave 0.66 g (1.05 mmol, 52%) of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(OC(O)^tBu)S^tBu$-)$Fe_2(CO)_6$, <u>5e</u>, as an air-stable, brown-red solid, mp 150.0-152.5°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{22}H_{24}Fe_2O_{12}S$: C, 42.33; H, 3.88 %. Found: C, 42.50; H, 3.86 %.

IR(CCl_4): 2970s, 2955s, 2930m, 2905m, 2875w, 1760vs(C=O), 1730vs(C=O), 1705vs(C=O), 1480s, 1460s, 1440s, 1400s, 1370s, 1270m, 1215vs, 1385s, 1360s, 1105vs, 1085vs, 1035s, 1015s, 995s, 980s, 940w, 710w, 680m, 610vs, 600vs cm^{-1}.
Terminal carbonyl region (pentane): 2080s, 2040vs, 2015s, 2000m, 1988m cm^{-1}.

^{1}H NMR(CD_2Cl_2; 300 MHz): δ 1.17 (s, 9H, $SC(CH_3)_3$), 1.18 (s, 9H, $C(O)C(CH_3)_3$), 3.85 (s, 3H, CO_2CH_3), 3.87 (s, 3H, CO_2CH_3).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 26.85 (q, J = 127.4 Hz, $SC(\underline{C}H_3)_3$), 27.30 (q, J = 128.1 Hz, $CC(\underline{C}H_3)_3$), 30.14 (s, $C\underline{C}(CH_3)_3$), 52.66 (q, J = 147.8 Hz, $CO_2\underline{C}H_3$), 53.00 (q, J = 147.8 Hz, CO_2CH_3), 55.00 (s, $S\underline{C}(CH_3)_3$), 85.82 (s, $\underline{C}OC(O)^tBu$), 100.37 (s, $MeO_2CC{=}\underline{C}$), 154.38 (s, $\underline{C}O_2Me$), 166.04 (s, $\underline{C}O_2Me$), 174.73 (s, $O\underline{C}(O)^tBu$), 175.60 (s, $MeO_2C\underline{C}{=}C$), 208.98, 209.43, and 207.47 (all s, Fe-CO).

Synthesis of (μ-σ,π-HC=C(CO_2Me)C(OC(O)Me)S^tBu-)$Fe_2(CO)_6$

JBH-6-IV

To the standard [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (3.00 mmol) was added 0.27 ml (3.00 mmol) of methyl propiolate by syringe at room temperature. An immediate reaction ensued with moderate gas evolution. After the reaction mixture had been stirred for 30 min at room temperature, 0.25 ml (3.50 mmol) of acetyl chloride was added by syringe. After the mixture had been stirred for an additional 17 h, the solvent was removed in vacuo to yield a red oil which was purified by filtration chromatography. Pentane/CH_2Cl_2 (9/1 v/v) eluted a pale orange band which was not collected. Pentane/CH_2Cl_2 (1/1 v/v) eluted a dark orange band which gave 1.02 g (1.94 mmol, 65%) of (μ-σ,π-HC=C(CO_2Me)C(OC(O)Me)S^tBu-)$Fe_2(CO)_6$, 5f, as an air-stable, brown-orange solid, mp 131.0-133.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{17}H_{16}Fe_2O_{10}S$: C, 38.96; H, 3.08 %. Found: C, 38.90; H, 3.07 %.

IR(CCl_4): 2980m, 2947s, 2920m, 2890m, 2860w, 1770vs(C=O), 1720vs(C=O), 1602vw, 1469w, 1452s, 1432s, 1390m, 1365vs, 1200vs, 1145vs, 1060vs, 1000s, 985s, 912m, 895m, 862w, 710vw, 670m, 635s, 610vs, 595vs, 560s, 500s cm^{-1}.

Terminal carbonyl region (pentane): 2070s, 2025vs, 2010vs, 1995m, 1980m cm^{-1}.

^{1}H NMR($CDCl_3$; 90 MHz): δ 1.09 (s, 9H, $SC(CH_3)_3$), 2.12 (s, 3H, $OC(O)CH_3$), 3.84 (s, 3H, CO_2CH_3), 8.72 (s, 1H, HC=C).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 21.05 (q, J = 130.2 Hz, $OC(O)\underline{C}H_3$), 27.06 (q, J = 128.1 Hz, $SC(\underline{C}H_3)_3$), 52.48 (q, J = 147.4 Hz, $CO_2\underline{C}H_3$), 53.57 (s, $S\underline{C}(CH_3)_3$), 88.84 (d, J = 13.8

Hz, $\underline{C}$OC(O)Me), 95.63 (s, HC=$\underline{C}$), 153.34 (d, J = 162.7 Hz, H$\underline{C}$=C), 166.56 (s, $\underline{C}O_2Me$), 167.74 (s, O$\underline{C}$(O)Me), 209.23 and 209.93 (both broad s, Fe-CO).

Synthesis of (μ-σ,π-HC=C(C(O)Me)C(OC(O)Me)S^{t}Bu-)$Fe_2(CO)_6$

JBH-4-IV

To the standard [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (3.00 mmol) was added 0.23 ml (3.00 mmol) of 3-butyne-2-one by syringe at room temperature. An immediate reaction ensued with moderate gas evolution. After the reaction mixture had been stirred for 20 min at room temperature, 0.24 ml (3.50 mmol) of acetyl chloride was added by syringe. After the mixture had been stirred for an additional 36 h, the solvent was removed in vacuo to yield a red tar which was purified by filtration chromatography. Pentane/CH_2Cl_2 (9/1 v/v) eluted a pale orange band which was not collected. Pentane/CH_2Cl_2 (3/2 v/v) eluted a pale red band which was not collected. Pentane/CH_2Cl_2 (1/4 v/v) eluted a dark orange band which gave 1.03 g (2.04 mmol, 68%) of (μ-σ,π-HC=C(C(O)Me)C(OC(O)Me)S^{t}Bu-)$Fe_2(CO)_6$, $\underline{5g}$, as an air-stable, brown-orange solid, mp 134.0-137.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{17}H_{16}Fe_2O_9S$: C, 40.19; H, 3.17 %. Found: C, 40.26; H, 3.22 %.

IR(CCl_4): 2958vs, 2920vs, 2865s, 2860sh, 1770vs(C=O), 1690vs(C=O), 1457m, 1428w, 1393m, 1369vs, 1347m, 1258vw, 1195vs, 1185vs, 1145vs, 1055vs, 1015w, 895m, 685w, 669w, 635m, 610vs, 600vs, 555s, 500m cm^{-1}.
Terminal carbonyl region (pentane): 2070s, 2025vs, 2010vs, 1992s, 1980s cm^{-1}.

^{1}**H NMR**($CDCl_3$; 90 MHz): δ 1.08 (s, 9H, $SC(CH_3)_3$), 2.11 (s, 3H, $OC(O)CH_3$), 2.46 (s, 3H, $C(O)CH_3$), 8.76 (s, 1H, HC=C).

^{13}C **NMR**($CDCl_3$; 67.9 MHz): δ 21.14 (q, J = 131.0 Hz, $OC(O)\underline{C}H_3$), 27.06 (q, J = 127.8 Hz, $SC(\underline{C}H_3)_3$), 27.98 (q, J = 128.2 Hz, $C(O)\underline{C}H_3$), 53.66 (s, $S\underline{C}(CH_3)_3$), 88.28 (s, J = 13.8 Hz, $\underline{C}OC(O)Me$), 101.96 (s, $HC{=}\underline{C}$), 153.56 (d, J = 160.8 Hz, $H\underline{C}{=}C$), 167.64 (s, $O\underline{C}(O)Me$), 197.48 (s, $\underline{C}(O)Me$), 209.04 and 210.08 (both broad s, Fe-CO).

Synthesis of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(O)S{-}$)$Fe_2(CO)_6$ JBH-23-VII

To the standard [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (1.49 mmol) was added 0.18 ml (1.49 mmol) of dimethyl acetylenedicarboxylate by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and gradual color change to brighter red. After the reaction mixture had been stirred for 72 h at room temperature, 0.11 ml (1.49 mmol) of trifluoroacetic acid was added by syringe. After the mixture had been stirred for an additional 1 h, the solvent was removed in vacuo to yield a brown-red tar which was purified by filtration chromatography. Pentane/CH_2Cl_2 (9/1 v/v) eluted a pale orange band which was not collected. Methylene chloride eluted a dark orange band which gave 0.48 g (0.99 mmol, 66%) of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(O)S{-}$)$Fe_2(CO)_6$, 8c, as an air-stable, orange solid, mp 148.0°C (dec) after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{13}H_6Fe_2O_{11}S$: C, 32.40; H, 1.25 %. Found: C, 32.23; H, 1.34 %.

IR($CHCl_3$): 3030w, 3005vw, 2960m, 2750vw, 1745vs-br(C=O), 1720vs-br(C=O), 1435vs, 1370vs, 1275vs, 1230s, 1190m, 1150m, 1032m, 972m, 908vw, 860vw, 650w, 625m, 600vs, 575vs, 555vs cm^{-1}.
Terminal carbonyl region (pentane): 2100s, 2070vs, 2045s, 2025vs cm^{-1}.

^{1}**H NMR**($CDCl_3$; 90 MHz): δ 3.81 (s, 3H, CO_2CH_3), 3.84 (s, 3H, CO_2CH_3).

^{13}**C NMR**($CDCl_3$; 67.9 MHz): δ 53.05 (q, J = 147.9 Hz, $\underline{C}O_2\underline{C}H_3$), 86.71 (s, $MeO_2CC{=}\underline{C}$), 165.00 (s, $\underline{C}O_2Me$), 174.57 (s, $\underline{C}O_2Me$), 178.11 (s, $MeO_2C\underline{C}{=}C$), 187.88 (s, $\underline{C}(O)S$), 202.99 and 204.54 (both s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 482 (M^+, 18), 454 (M^+ - CO, 33), 426 (M^+ - 2CO, 8), 398 (M^+ - 3CO, 32), 370 (M^+ - 4CO, 39), 342 (M^+ - 5CO, 39), 314 (M^+ - 6CO, 100), 286 (M^+ - 7CO, 29), 258 (M^+ - 8CO, 49), 230 (M^+ - 9CO, 5), 228 (M^+ - 8CO-2CH_3, 27), 200 (M^+ - 9CO-2CH_3, 24), 170 ($MeO_2CC{=}CCO_2MeCO$, 22), 168 ($SFe_2C{=}C$, 20), 144 (SFe_2, 20), 143 ($MeO_2CC{=}CCOS$, 21), 112 (Fe_2, 12), 111 ($MeO_2CC{=}CCO$, 17), 59 (CO_2Me, 15), 56 (Fe, 12).

Synthesis of (μ-σ,π-HC=C(CO_2Me)C(O)S-)$Fe_2(CO)_6$ JBH-10-IV

To the standard [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (1.00 mmol) was added 0.09 ml (1.00 mmol) of methyl propiolate by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and slight color change to brighter red. After the reaction mixture had been stirred for 15 min at room temperature, 0.08 ml (1.00 mmol) of trifluoroacetic acid was added by syringe. After the mixture had been stirred for an additional 24 h, the solvent was removed in vacuo to yield a cherry red oil which was purified by filtration chromatography. Pentane and pentane/CH_2Cl_2 (4/1 v/v) eluted very pale orange bands which were not collected. Pentane/CH_2Cl_2 (3/7 v/v) eluted a dark orange band which gave 0.29 g (0.69 mmol, 69%) of (μ-σ,π-HC=C(CO_2Me)C(O)S-)$Fe_2(CO)_6$, 8b, as an air-stable, red solid, mp 96.0-98.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{11}H_4Fe_2O_9S$: C, 31.17; H, 0.94 %. Found: C, 31.19; H, 0.96 %.

IR($CHCl_3$): 3070m, 3033vw, 2988m, 2878vw, 1763vs-vbr(C=O), 1455s, 1380vs, 1316m, 1297m, 1253vs, 1238m, 1098m, 983s, 868w, 787m, 763m, 678s, 658s, 637s, 626vs, 597vs, 565vs cm^{-1}.
Terminal carbonyl region (pentane): 2100m, 2065vs, 2038s, 2025vs, 2015m cm^{-1}.

^{1}**H NMR**($CDCl_3$; 90 MHz): δ 3.83 (s, 3H, CO_2CH_3), 9.42 (s, 1H, HC=C).

^{13}**C NMR**($CDCl_3$; 67.9 MHz): δ 52.74 (q, J = 148.1 Hz, $CO_2\underline{C}H_3$), 89.26 (s, HC=$\underline{C}$), 164.89 (s, $\underline{C}O_2Me$), 168.51 (d, J = 160.8 Hz, H$\underline{C}$=C), 182.44 (d, J = 11.5 Hz, C(O)S), 202.96, 205.29, and 206.59 (all s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 424 (M^+, 26), 396 (M^+ - CO, 24), 368 (M^+ - 2CO, 23), 340 (M^+ - 3CO, 34), 312 (M^+ - 4CO, 22), 284 (M^+ - 5CO, 44), 256 (M^+ - 6CO, 91), 228 (M^+ - 7CO, 63), 200 (M^+ - 8CO, 22), 170 ($SFe_2HC=CH$, 58), 169 ($SFe_2HC=C$, 45), 168 ($SFe_2C=C$, 32), 144 (SFe_2, 60), 112 (Fe_2, 14), 84 ($HC=CCO_2Me$, 8), 81 (FeHC=C, 14), 56 (Fe, 28), 53 (HC=CCO, 100).

Synthesis of (μ-σ,π-HC=C(C(O)Me)C(O)S-)$Fe_2(CO)_6$ JBH-24-VII

To the standard [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (1.51 mmol) was added 0.12 ml (1.51 mmol) of 3-butyne-2-one by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and slight color change to brighter red. After the reaction mixture had been stirred for 20 min at room temperature, 0.12 ml (1.51 mmol) of trifluoroacetic acid was added by syringe. After the mixture had been stirred for an additional 16 h, the solvent was removed in vacuo to yield a red tar which was purified by filtration chromatography. Pentane/CH_2Cl_2 (9/1 v/v) eluted a pale yellow-brown band which was not collected. Pentane/CH_2Cl_2 (3/7 v/v) eluted a dark orange band which gave 0.31 g (0.76 mmol, 51%) of (μ-σ,π-HC=C(C(O)Me)C(O)S-)$Fe_2(CO)_6$, 8a, as an air-stable, red solid, mp 125.0-128.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{11}H_4Fe_2O_8S$: C, 32.39; H, 0.99 %. Found: C, 32.44; H, 1.13 %.

IR($CHCl_3$): 2958m, 2923m, 2867w, 1715vs(C=O), 1690s(C=O), 1455w, 1410w, 1364s, 1335s, 1260vw, 1192m, 1017w, 920vw, 900vw, 711w, 685w, 620m, 610s, 585s, 552m cm^{-1}.
Terminal carbonyl region (pentane): 2090m, 2059vs, 2030s, 2020vs, 2010s cm^{-1}.

^1H NMR($CDCl_3$; 250 MHz): δ 2.54 (s, 3H, C(O)CH_3), 9.49 (s, 1H, HC=C).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 28.60 (q, J = 128.8 Hz, C(O)$\underline{C}H_3$), 95.91 (s, HC=$\underline{C}$), 170.07 (d, J = 162.0 Hz, H$\underline{C}$=C), 185.22 (d, J = 11.8 Hz, C(O)S), 196.16 (s, $\underline{C}$(O)Me), 202.97, 205.33, and 206.38 (all s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 408 (M^+, 37), 380 (M^+ - CO, 47), 352 (M^+ - 2CO, 42), 324 (M^+ - 3CO, 27), 296 (M^+ - 4CO, 25), 268 (M^+ - 5CO, 56), 240 (M^+ - 6CO, 100), 212 (SFe_2HC=CCOMe, 63), 184 (SFe_2HC=CMe, 37), 169 (SFe_2HC=C, 57), 144 (SFe_2, 61), 113 (FeHC=CS, 11), 112 (Fe_2, 10), 68 (HC=CCOMe, 14).

Reaction of [Li][(μ-CO)(μ-EtS)$Fe_2(CO)_6$] with $MeO_2CC{\equiv}CCO_2Me$ and CF_3COOH JBH-46-III

To the standard [Li][(μ-CO)(μ-EtS)$Fe_2(CO)_6$] reagent solution (2.00 mmol) was added 0.25 ml (2.00 mmol) of dimethyl acetylenedicarboxylate by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and gradual color change to brighter red. After the reaction mixture had been stirred for 42 h at room temperature, 0.15 ml (2.00 mmol) of trifluoroacetic acid was added by syringe. After the mixture had been stirred for an additional 2 h, the solvent was removed in vacuo to yield a brown-red tar which was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Pentane/CH_2Cl_2 (1/4 v/v) eluted a dark red band which gave 0.40 g of a red oily solid identified by its ^1H NMR spectrum ($CDCl_3$; 90 MHz) to be a mixture of 0.32 g (0.65 mmol, 34%) of (μ-σ,π-$MeO_2CC{=}C(H)CO_2Me$)(μ-EtS)$Fe_2(CO)_6$, 9a, and 0.08 g (0.18 mmol, 9%) of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(O)S$-)$Fe_2(CO)_6$, 8c. Medium pressure column chromatography yielded pure (μ-σ,π-$MeO_2CC{=}C(H)CO_2Me$)(μ-EtS)$Fe_2(CO)_6$, 9a, (first red band) as an air-stable, red solid, mp 112.5-114.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{14}H_{12}Fe_2O_{10}S$: C, 34.74; H, 2.50 %. Found: C, 34.81; H, 2.51 %.

IR($CHCl_3$): 3007vw, 2970m, 2940s, 2865m, 1717s(C=O), 1457m, 1443s, 1414m, 1381w, 1300m, 1210m, 1194s, 1186m, 1167s, 1035w, 996m, 889vw, 867vw, 827vw, 697w, 622m, 610s, 595s, 550s cm^{-1}.
Terminal carbonyl region (pentane): 2090w, 2060vs, 2033s, 2019s, 2003s cm^{-1}.

^{1}H NMR($CDCl_3$; 250 MHz): δ 1.37 (t, J = 7.48 Hz, 3H, $SCH_2C\underline{H}_3$), 2.41 (m, 2H, $SC\underline{H}_2CH_3$), 2.62 (s, 1H, $C{=}C(\underline{H})CO_2Me$), 3.70 (s, 3H, CO_2CH_3), 3.77 (s, 3H, CO_2CH_3).

^{13}C **NMR**($CDCl_3$; 67.9 MHz): δ 17.59 (q, J = 128.8 Hz, $SCH_2\underline{C}H_3$), 33.75 (t, J = 140.3 Hz, $S\underline{C}H_2CH_3$), 51.80 (q, J = 147.2 Hz, $CO_2\underline{C}H_3$), 52.33 (q, J = 147.0 Hz, $CO_2\underline{C}H_3$), 66.43 (d, J = 168.3 Hz, $C{=}\underline{C}(H)CO_2Me$), 169.05 (s, $\underline{C}O_2Me$), 175.80 (s, $\underline{C}O_2Me$), 176.14 (s, $MeO_2C\underline{C}{=}C$), 206.27 and 207.03 (both s, Fe–CO).

Mass Spectrum (EI); m/z (relative intensity): 484 (M^+, 2), 456 (M^+ - CO, 9), 428 (M^+ - 2CO, 23), 400 (M^+ - 3CO, 15), 372 (M^+ - 4CO, 20), 344 (M^+ - 5CO, 33), 316 (M^+ - 6CO, 64), 288 (M^+ - 7CO, 100), 260 (M^+ - 8CO, 65), 227 ($SFe_2MeO_2CC{=}C$, 30), 175 (HSFeMeOC=COMe, 37), 169 ($HSFe_2C{=}C$, 27), 145 ($HSFe_2$, 22), 144 (SFe_2, 24), 112 (Fe_2, 11), 57 (HSC=C, 28), 56 (Fe, 18), 43 (COMe, 22).

Reaction of $[Li][(\mu\text{-}CO)(\mu\text{-}PhS)Fe_2(CO)_6]$ with $MeO_2CC{\equiv}CCO_2Me$ and CF_3COOH JBH-47-III

To the standard $[Li][(\mu\text{-}CO)(\mu\text{-}PhS)Fe_2(CO)_6]$ reagent solution (2.00 mmol) was added 0.25 ml (2.00 mmol) of dimethyl acetylenedicarboxylate by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and gradual color change to brighter red. After the reaction mixture had been stirred for 46 h at room temperature, 0.15 ml (2.00 mmol) of trifluoroacetic acid was added by syringe. After the mixture had been stirred for an additional 15 h, the solvent was removed in vacuo to yield a red tar which was purified by filtration chromatography. Pentane eluted an orange band which gave 0.20 g (0.40 mmol, 40% based on S) of $(\mu\text{-}PhS)_2Fe_2(CO)_6$ identified by its ^{1}H NMR spectrum and melting point.[21] Pentane/CH_2Cl_2 (1/4 v/v) eluted a red band which gave 0.33 g (0.80 mmol, 40%) of $(\mu\text{-}\sigma,\pi\text{-}MeO_2CC{=}C(H)CO_2Me)(\mu\text{-}PhS)Fe_2(CO)_6$, 9c, as an air-stable, red solid, mp 135.0-137.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{18}H_{12}Fe_2O_{10}S$: C, 40.64; H, 2.27 %. Found: C, 40.91; H, 2.39 %.

IR($CHCl_3$): 3095w, 3042w, 3017w, 2962w, 2843w, 1713vs(C=O), 1582w(Ph), 1578w(Ph), 1480w, 1440vs, 1412m, 1300m, 1267m, 1197s, 1185s, 1165s, 1071w, 1033m, 1025w, 1000m, 993m, 867w, 699m, 690m, 620s, 609s, 593s, 551s cm^{-1}. Terminal carbonyl region (pentane): 2090m, 2060vs, 2032s, 2017vs, 1997w cm^{-1}.

^{1}**H NMR**($CDCl_3$; 250 MHz): δ 2.81 (s, 1H, C=C($\underline{H}$)CO_2Me), 3.73 (s, 3H, CO_2CH_3), 3.79 (s, 3H, CO_2CH_3), 7.25-7.32 (m, 5H, C_6H_5).

^{13}**C NMR**($CDCl_3$; 67.9 MHz): δ 52.00 (q, J = 147.6 Hz, $CO_2\underline{C}H_3$), 52.50 (q, J = 147.7 Hz, $CO_2\underline{C}H_3$), 66.31 (d, J = 168.5 Hz, C=$\underline{C}$(H)CO_2Me), 128.59 (d, J = 162.8 Hz, C_6H_5), 129.08 (d, J = 164.0 Hz, C_6H_5), 131.28 (d, J = 161.5 Hz, C_6H_5), 136.38 (s, ipso C_6H_5), 169.13 (s, $\underline{C}O_2Me$), 175.59 (s, $\underline{C}O_2Me$), 176.32 (s, $MeO_2C\underline{C}$=C), 205.86 and 206.62 (both s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 532 (M^+, 0.3), 504 (M^+ - CO, 5), 476 (M^+ - 2CO, 32), 448 (M^+ - 3CO, 7), 420 (M^+ - 4CO, 6), 392 (M^+ - 5CO, 34), 364 (M^+ - 6CO, 100), 336 (M^+ - 7CO, 45), 308 (M^+ - 8CO, 21), 278 ($PhSFe_2OC$=CHO, 36), 252 (PhS(CO_2Me)C=$CHCO_2Me$, 37), 246 ($PhSFe_2C$=CH, 57), 221 ($PhSFe_2$, 36), 193 (MeO_2CC(SPh)=CH, 21), 192 (MeO_2CC(SPh)=C, 20), 169 ($HSFe_2C$=C, 15), 161 (PhSC=CCO, 45), 144 (SFe_2, 46), 134 (PhSC=CH, 28), 109 (SPh, 17), 77 (Ph, 14).

Reaction of [Li][(μ-CO)(μ-$PhCH_2S$)$Fe_2(CO)_6$] with $MeO_2CC{\equiv}CCO_2Me$ and CF_3COOH DRW-50-II

To the standard [Li][(μ-CO)(μ-$PhCH_2S$)$Fe_2(CO)_6$]

reagent solution (1.40 mmol) was added 0.18 ml (1.40 mmol) of dimethyl acetylenedicarboxylate by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and gradual color change to brighter red. After the reaction mixture had been stirred for 46 h at room temperature, 0.11 ml (1.40 mmol) of trifluoroacetic acid was added by syringe. After the mixture had been stirred for an additional 2 h, the solvent was removed in vacuo to yield a brown-red tar which was purified by filtration chromatography. Pentane and pentane/CH_2Cl_2 (7/3 v/v) eluted pale orange bands which were not collected. Methylene chloride eluted a dark orange band which gave 0.35 g of a red, oily solid identified by its ^1H NMR spectrum (CD_2Cl_2; 90 MHz) to be a mixture of 0.31 g (0.57 mmol, 40%) of (μ-σ,π-$MeO_2CC{=}C(H)CO_2Me$)(μ-$PhCH_2S$)$Fe_2(CO)_6$, <u>9b</u>, and 0.04 g (0.08 mmol, 6%) of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(O)S$-)$Fe_2(CO)_6$, <u>8c</u>. Medium pressure column chromatography yielded pure (μ-σ,π-$MeO_2CC{=}C(H)CO_2Me$)(μ-$PhCH_2S$)$Fe_2(CO)_6$, <u>9b</u>, (major orange band) as an air-stable, red solid, mp 115.0-118.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{19}H_{14}Fe_2O_{10}S$: C, 41.79; H, 2.58 %. Found: C, 41.82; H, 2.71 %.

IR($CHCl_3$): 3085vw, 3063w, 3030w, 2995w, 2870vw, 1720vs(C=O), 1600vw(Ph), 1495w, 1455m, 1438s, 1410s, 1380sh, 1295m, 1205vs, 1185sh, 1160vs, 1070w, 1030m, 998m, 910vw, 870w, 698s, 630s, 609s, 595s, 555s cm^{-1}.
Terminal carbonyl region (pentane): 2083w, 2055vs, 2030m, 2010s, 2000s, 1980vw cm^{-1}.

^{1}H NMR(CD_2Cl_2; 250 MHz): δ 2.54 (s, 1H, $C{=}C(\underline{H})CO_2Me$), 3.34 (d, J = 12.85 Hz, 1H, $SC\underline{H}_2Ph$ diastereotopic CH_2), 3.63 (s, 3H, CO_2CH_3), 3.73 (s, 3H, CO_2CH_3), 3.84 (d, J = 12.86 Hz, 1H, $SC\underline{H}_2Ph$ diastereotopic CH_2), 7.28-7.44 (m, 5H, C_6H_5).

^{13}C **NMR**($CDCl_3$; 67.9 MHz): δ 43.49 (t, J = 142.4 Hz, S$\underline{C}H_2$Ph), 51.86 (q, J = 147.4 Hz, $CO_2\underline{C}H_3$), 52.46 (q, J = 147.1 Hz, $CO_2\underline{C}H_3$), 66.31 (d, J = 168.8 Hz, C=$\underline{C}$(H)CO_2Me), 128.37 (d, J = 158.7 Hz, C_6H_5), 129.06 (d, J = 159.7 Hz, C_6H_5), 138.34 (s, ipso C_6H_5), 169.12 (s, $\underline{C}O_2$Me), 175.80 (s, $\underline{C}O_2$Me), 176.28 (s, $MeO_2C\underline{C}$=C), 204.54 and 206.49 (both s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 546 (M^+, 0.3), 518 (M^+ - CO, 0.4), 490 (M^+ - 2CO, 9), 462 (M^+ - 3CO, 22), 434 (M^+ - 4CO, 19), 406 (M^+ - 5CO, 30), 378 (M^+ - 6CO, 100), 350 (M^+ - 7CO, 59), 322 (M^+ - 8CO, 5), 287 ($SFe_2MeO_2CC{=}CHCO_2Me$, 73), 260 ($HSFe_2MeO_2CC{=}CHOMe$, 19), 259 ($SFe_2MeO_2CC{=}CHOMe$, 18), 227 ($Fe_2MeO_2CC{=}CHOMe$, 48), 175 (HSFeMeOC=COMe, 30), 169 ($HSFe_2C{=}C$, 24), 145 ($HSFe_2$, 14), 144 (SFe_2, 32), 91 (CH_2Ph, 81), 56 (Fe, 5).

Reaction of [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] with HC≡CCO_2Me and CF_3COOH at -78°C JBH-18-IV

To the standard [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (4.00 mmol) cooled to -78°C was added 0.36 ml (4.00 mmol) of methyl propiolate. After the reaction mixture had been stirred for 1 h at -78°C, 0.31 ml (4.00 mmol) of trifluoroacetic acid was added by syringe. After the mixture had been warmed slowly to room temperature over a period of several hours and subsequently stirred for an additional 16 h at room temperature, the solvent was removed in vacuo to yield a brown-red tar which was purified by filtration chromatography. Pentane/CH_2Cl_2 (7/3 v/v) eluted a red band which gave 0.85 g of a red oil identified by its ^{1}H NMR spectrum ($CDCl_3$; 250 MHz) to be a mixture of 0.43 g (0.94 mmol, 23%) of (μ-σ,π-HC=C(H)CO_2Me)(μ-^{t}BuS)$Fe_2(CO)_6$, 2a,[1] and 0.43 g (0.94 mmol, 23%) of (μ-σ,π-$MeO_2CC{=}CH_2$)(μ-^{t}BuS)$Fe_2(CO)_6$, 11a. Medium pressure chromatography (pentane/CH_2Cl_2 - 8/2 v/v) yielded pure (μ-σ,π-

$MeO_2CC{=}CH_2)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$, 11a, (first orange band) as an air-stable, orange solid, mp 89.0-91.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{14}H_{14}Fe_2O_8S$: C, 37.04; H, 3.11 %. Found: C, 37.10; H, 3.12 %.

IR(CCl_4): 2965m, 2945m, 2925m, 2898w, 2862w, 2835vw, 1713s(C=O), 1473w, 1458m, 1435m, 1410vw, 1397vw, 1368m, 1290m, 1205vs, 1155s, 1095vs, 1017w, 983w, 930vw, 860vw, 703m, 640s, 613s, 600s, 563s, 498m cm^{-1}.
Terminal carbonyl region (pentane): 2075m, 2045vs, 2003s, 1993s, 1973vw cm^{-1}.

^{1}**H NMR**($CDCl_3$; 90 MHz): δ 1.38 (s, 9H, $SC(CH_3)_3$), 2.93 (d, J = 2.93 Hz, 1H, $C{=}CH_2$ endo, diastereotopic CH_2), 3.74 (s, 3H, CO_2CH_3), 3.94 (d, J = 2.93 Hz, 1H, $C{=}CH_2$ exo, diastereotopic CH_2).

^{13}**C NMR**($CDCl_3$; 67.9 MHz): δ 32.94 (q, J = 127.6 Hz, $SC(\underline{C}H_3)_3$), 48.17 (s, $S\underline{C}(CH_3)_3$), 52.16 (q, J = 147.6 Hz, $CO_2\underline{C}H_3$), 71.95 (t, J = 162.02 Hz, $C{=}\underline{C}H_2$), 166.20 (s, $\underline{C}O_2Me$), 178.13 (s, $MeO_2C\underline{C}{=}CH_2$), 207.94 and 210.00 (both s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 454 (M^+, 4), 426 (M^+ - CO, 10), 398 (M^+ - 2CO, 13), 370 (M^+ - 3CO, 36), 342 (M^+ - 4CO, 30), 314 (M^+ - 5CO, 17), 286 (M^+ - 6CO, 95), 258 (M^+ - 7CO, 2), 230 ($HSFe_2MeO_2CC{=}CH_2$, 100), 202 ($HSFe_2MeOC{=}CH_2$, 66), 145 ($HSFe_2$, 43), 144 (SFe_2, 42), 112 (Fe_2, 3), 57 (^{t}Bu, 22), 56 (Fe, 4).

Further elution with pentane/CH_2Cl_2 (3/7 v/v) yielded an orange band which gave 0.51 g (1.20 mmol, 30%) of (μ-σ,π-$HC{=}C(CO_2Me)C(O)S)Fe_2(CO)_6$, 8b, identified by its ^{1}H NMR spectrum.

Reaction of [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] with HC≡CC(O)Me and CF_3COOH at -78°C JBH-16-IV

To the standard [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (3.00 mmol) cooled to -78°C was added 0.23 ml (3.00 mmol) of 3-butyne-2-one. After the reaction mixture had been stirred for 1 h at -78°C, 0.23 ml (3.00 mmol) of trifluoroacetic acid was added by syringe. After the mixture had been warmed slowly to room temperature over a period of several hours and subsequently stirred for an additional 60 h at room temperature, the solvent was removed in vacuo to yield a brown-red tar which was purified by filtration chromatography. Pentane eluted an orange band which gave 0.17 g (0.37 mmol, 24% based on S) of (μ-^{t}BuS)$_2$$Fe_2(CO)_6$ identified by its ^{1}H NMR spectrum.[22] Pentane/CH_2Cl_2 (1/1 v/v) eluted a red band which gave 0.62 g of a red oil identified by its ^{1}H NMR spectrum ($CDCl_3$; 250 MHz) to be a mixture of 0.31 g (0.71 mmol, 24%) of (μ-σ,π-HC=C(H)C(O)Me)(μ-^{t}BuS)$Fe_2(CO)_6$, 2b,[1] and 0.31 g (0.71 mmol, 24%) of (μ-σ,π-MeC(O)C=CH_2)(μ-^{t}BuS)$Fe_2(CO)_6$, 11b. Medium pressure chromatography (pentane/CH_2Cl_2 - 3/1 v/v) yielded pure (μ-σ,π-MeC(O)C=CH_2)(μ-^{t}BuS)$Fe_2(CO)_6$, 11b, (the first orange band) as a slightly air sensitive red oil.

Anal. Calcd. for $C_{14}H_{14}Fe_2O_7S$: C, 38.39; H, 3.22 %. Found: C, 38.44; H, 3.26 %.

IR(CCl_4): 2965s, 2930s, 2900m, 2880m, 1690s(C=O), 1475m, 1460m, 1415w, 1398w, 1370m, 1352w, 1300w, 1260vw, 1188w, 1155s, 1120w, 1084m, 1020w, 960w, 700vw, 660m, 615s, 590vs cm^{-1}.
Terminal carbonyl region (pentane): 2083w, 2050vs, 2040w, 2020m, 2000m cm^{-1}.

^{1}H NMR($CDCl_3$; 250 MHz): δ 1.39 (s, 9H, $SC(CH_3)_3$), 2.40 (s, 3H, $C(O)CH_3$), 2.78 (d, J = 3.24 Hz, 1H, C=CH_2 endo - diastereotopic CH_2), 3.39 (d, J = 3.18 Hz, 1H, C=CH_2 exo - diastereotopic CH_2).

^{13}C **NMR**(CDCl$_3$; 67.9 MHz): δ 29.87 (q, J = 128.1 Hz, $C(O)\underline{C}H_3$), 32.99 (q, J = 127.7 Hz, $SC(\underline{C}H_3)_3$), 48.12 (s, $S\underline{C}(CH_3)_3$), 63.30 (dd, J = 155.9 Hz, J = 166.6 Hz, $C{=}\underline{C}H_2$), 184.17 (s, $\underline{C}(O)Me$), 208.12 and 209.80 (both s, Fe-CO).

Mass Spectrum (EI); m/z (relative intensity): 438 (M^+, 2), 410 (M^+ - CO, 6), 382 (M^+ - 2CO, 10), 354 (M^+ - 3CO, 20), 326 (M^+ - 4CO, 17), 298 (M^+ - 5CO, 11), 270 (M^+ - 6CO, 56), 214 ($HSFe_2MeC(O)C{=}CH_2$, 100), 145 ($HSFe_2$, 19), 144 (SFe_2, 58), 112 (Fe_2, 2), 57 (^{t}Bu, 2), 56 (Fe, 4), 43 (MeCO, 14).

Reaction of $[Li][(\mu\text{-}CO)(\mu\text{-}^tBuS)Fe_2(CO)_6]$ with $MeO_2CC{\equiv}CCO_2Me$ and CF_3COOH at -78°C JBH-30-III

To the standard $[Li][(\mu\text{-}CO)(\mu\text{-}^tBuS)Fe_2(CO)_6]$ reagent solution (1.50 mmol) cooled to -78°C was added 0.18 ml (1.50 mmol) of dimethyl acetylenedicarboxylate. After the reaction mixture had been stirred for 3 h at -78°C, 0.12 ml (1.50 mmol) of trifluoroacetic acid was added by syringe. After the mixture had been warmed slowly to room temperature over a period of 1 h and subsequently stirred for an additional 2 h at room temperature, the solvent was removed in vacuo to yield a red-brown tar which was purified by filtration chromatography. Pentane/CH_2Cl_2 (3/7 v/v) eluted a red band which gave 0.62 g of an orange-red solid identified by its ^{1}H NMR spectrum (CDCl$_3$; 250 MHz) to be a mixture of 0.55 g (1.07 mmol, 71%) of $(\mu\text{-}\sigma,\pi\text{-}MeO_2CC{=}C(H)CO_2Me)(\mu\text{-}^tBuS)Fe_2(CO)_6$, 2c,[1] and 0.07 g (0.14 mmol, 10%) of$(\mu\text{-}\sigma,\pi\text{-}MeO_2CC{=}C(CO_2Me)C(O)S)Fe_2(CO)_6$, 8c.

Standard in-situ Preparation of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}^tBuS)Fe_2(CO)_6]$

A 250 ml Schlenk flask equipped with a stir-bar and rubber septum was charged with 1.51 g (3.00 mmol) of

$Fe_3(CO)_{12}$ and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged successively with 30 ml of THF, 0.33 ml (3.00 mmol) of t-butyl mercaptan, and 0.42 ml (3.00 mmol) of triethylamine by syringe. The mixture was stirred for 30 min at room temperature during which time slow gas evolution and a color change from green to brown-red was observed. The resulting $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ reagent solution subsequently was used *in-situ* without further purification.

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ with $HC{\equiv}CCO_2Me$ at -78°C **JBH-23-IV**

To the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ reagent solution (1.00 mmol) cooled to -78°C was added 0.09 ml (1.00 mmol) of methyl propiolate by syringe. After the reaction mixture had been warmed slowly to room temperature over a period of several hours and stirred for an additional 14 h at room temperature, the solvent was removed in vacuo to yield a red oil which was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Pentane/CH_2Cl_2 (3/2 v/v) eluted a dark orange band which gave 0.29 g (0.64 mmol, 64%) of $(\mu\text{-}\sigma,\pi\text{-}HC{=}C(H)CO_2Me)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$, 2a,[1] identified by its ^1H NMR spectrum.

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ with $HC{\equiv}CC(O)Me$ at -78°C **JBH-24-IV**

To the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ reagent solution (1.00 mmol) cooled to -78°C was added 0.08 ml (1.00 mmol) of 3-butyn-2-one by syringe. After the reaction mixture had been slowly warmed to room temperature over a period of several hours and stirred for an additional 16 h at room temperature, the solvent was removed in vacuo to yield a red tar which was purified by filtration chromatography. Pentane eluted pale green and pale yellow bands which were not collected. Pentane/CH_2Cl_2 (1/1 v/v) eluted a red band which gave 0.24 g of a red-brown solid identified by its ^1H NMR spectrum ($CDCl_3$; 90MHz) to be a mixture of 0.16 g (0.36 mmol, 36%) of (μ-HC=C(H)C(O)Me)(μ-$^tBuS)Fe_2(CO)_6$, <u>2b</u>,[1] and 0.08 g (0.19 mmol, 19%) of (μ-HC=C(C(O)Me)C(O)S-)$Fe_2(CO)_6$, <u>8a</u>.

Isolation of [Li(12-crown-4)][(μ-σ,π-$MeO_2CC=C(CO_2Me)C(O)$-S^tBu-)$Fe_2(CO)_6$ JBH-19-VIII

To the standard [Li][(μ-CO)(μ-$^tBuS)Fe_2(CO)_6$] reagent solution (3.02 mmol) was added 0.43 ml (3.50 mmol) of dimethyl acetylenedicarboxylate. An immediate reaction ensued with moderate gas evolution and a color change to brighter red. After the reaction mixture had been stirred for 48 h at room temperature, the solvent was removed in vacuo. The resulting brown-red, foamy solid was dissolved in Et_2O/CH_2Cl_2 (3/1 v/v) and filtered under nitrogen into a 250 ml Schlenk flask equipped with a spin bar. To the resulting brown-red solution was added 0.49 ml (3.02 mmol) of 12-crown-4 by syringe. After the resulting reaction mixture had been stirred for 3 h at room temperature, the solvent was removed in vacuo to yield a brown-red, foamy solid. This was dissolved in CH_2Cl_2/Et_2O/hexane (6ml/ 4ml/ 3ml) and cannulated under nitrogen into a 50 ml Schlenk tube. Subsequent crystallization at -20°C yielded 0.85 g (1.18 mmol, 39%) of [Li(12-crown-4)][(μ-σ,π-$MeO_2CC=C(CO_2Me)C(O)S^tBu$-)$Fe_2(CO)_6$], <u>7</u>.

Anal. Calcd. for $C_{25}H_{31}Fe_2O_{15}SLi$: C, 41.58; H, 4.33 %. Found: C, 41.11; H, 4.77 %.

^1H NMR($CDCl_3$; 300 MHz): δ 1.21 (s, 9H, $SC(CH_3)_3$ major isomer), 1.39 (s, 9H, $SC(CH_3)_3$ minor isomer), 3.66 (s, 16H, CH_2 crown ether), 3.70 (s, 6H, CO_2CH_3 both isomers), 3.72 (s, 6H, CO_2CH_3 both isomers). Ratio major/minor = 2.9/1.0

^{13}C NMR(acetone-d_6; 67.9 MHz): δ 28.24 (q, J = 127.2 Hz, $SC(\underline{C}H_3)_3$), 51.52 (q, J = 145.9 Hz, $CO_2\underline{C}H_3$), 52.45 (q, J = 147.0 Hz, $CO_2\underline{C}H_3$), 53.54 (s, $S\underline{C}(CH_3)_3$ major isomer), 54.73 (s, $S\underline{C}(CH_3)_3$ minor isomer), 68.23 (s, $C\text{-}O^-$), 69.40 (t, J = 142.4 Hz, CH_2 crown ether), 142.33 (s, $MeO_2CC{=}\underline{C}$), 163.84 (s, $\underline{C}O_2Me$), 172.58 (s, $\underline{C}O_2Me$), 178.34 (s, $MeO_2C\underline{C}{=}C$), 213.20, and 219.47 (both s, Fe-CO).

Mass Spectrum (FAB); m/z: 539 (M^- anion)

Synthesis of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(OC(O)Me)S^tBu$-)$Fe_2(CO)_6$ under ^{13}CO JBH-20-VIII

The standard $[Li][(\mu\text{-}CO)(\mu\text{-}^tBuS)Fe_2(CO)_6]$ reagent solution (2.96 mmol) was prepared in a 250 ml three necked, round bottomed flask equipped with a stir-bar, glass stopper, rubber septum, and gas inlet tube connected to a rubber balloon. (The flask was attached to a Schlenk line via a needle through the rubber septum.) Subsequently, 0.36 ml (2.96 mmol) of dimethyl acetylenedicarboxylate was added by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and a gradual color change to brighter red. After the reaction mixture had been stirred for 30 min at room temperature, the flask was partially evacuated, cooled back down to -78°C, detached from the Schlenk line, and then backfilled with carbon-13 enriched carbon monoxide (Cambridge Isotope Labs) until the balloon was partially inflated (ensuring that the reaction mixture was under a positive pressure of ^{13}CO). The reaction flask was then warmed to room temperature. After the mixture had been stirred for 6 h, 0.36 ml (5.00 mmol) of acetyl chloride was added by syringe. The mixture was stirred for an additional 60 h (balloon still inflated) at room temperature. Subsequently, the solvent was removed in vacuo and the resulting red tar was purified by filtration chromatography. Pentane/CH_2Cl_2 (7/3 v/v) eluted a very pale orange band which was not collected. Acetone/CH_2Cl_2 (1/20 v/v) eluted a dark orange band which gave 1.56 g (2.68 mmol, 91%) of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(OC(O)Me)S^tBu$-)$Fe_2(CO)_6$, 5a. The ^{13}C NMR spectrum of 5a showed signal enhancement of the terminal carbonyl region only.

$^{13}C\{^1H\}$ NMR($CDCl_3$; 67.9 MHz): δ 20.50 ($OC(O)\underline{C}H_3$), 26.74 ($SC(\underline{C}H_3)_3$), 52.17 ($CO_2\underline{C}H_3$), 52.62 ($CO_2\underline{C}H_3$), 54.54 ($S\underline{C}(CH_3)_3$), 85.27 ($\underline{C}OC(O)Me$), 99.67 ($MeO_2CC{=}\underline{C}$), 155.05 ($\underline{C}O_2Me$), 165.37 ($\underline{C}O_2Me$), 167.22 ($O\underline{C}(O)Me$), 174.13 ($MeO_2C\underline{C}{=}C$), 204.26, 207.05, and 208.96 (Fe-*CO).

Synthesis of (μ-σ,π-$MeO_2CC{=}C(CO_2Me)C(OC(O)Me)S^tBu$-)$Fe_2(CO)_6$ with N_2 Purge JBH-37-VII

To the standard [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (1.78 mmol) was added 0.22 ml (1.78 mmol) of dimethyl acetylenedicarboxylate by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and a color change to brighter red. After the reaction mixture had been stirred for 1 h at room temperature, it was purged with a stream of nitrogen for 20 h. As the solvent slowly evaporated, THF was periodically added by syringe. Subsequently, 0.36 ml (5.00 mmol) of acetyl chloride was added by syringe at room temperature. After the mixture had been stirred for an additional 40 h, the solvent was removed in vacuo to yield a red oil which was purified by filtration chromatography. Pentane/CH_2Cl_2 (9/1 v/v) eluted a very pale orange band which was not collected. Methylene chloride/acetone (20/1 v/v) eluted a dark orange band which gave 0.85 g of a red, oily solid identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz) to be a mixture of 0.34 g (0.67 mmol, 38%) of (μ-σ,π-

$MeO_2CC{=}C(H)CO_2Me)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$, 2c,[1] and 0.50 g (0.87 mmol, 49%) of $(\mu\text{-}\sigma,\pi\text{-}MeO_2CC{=}C(CO_2Me)C(OC(O)Me)S^tBu\text{-})Fe_2(CO)_6$, 5a.

Synthesis of $(\mu\text{-}\sigma,\pi\text{-}MeO_2CC{=}C(CO_2Me)C(OC(O)Me)S^tBu\text{-})Fe_2(CO)_6$ with CO Purge JBH-38-VII

To the standard $[Li][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ reagent solution (1.83 mmol) was added 0.22 ml (1.83 mmol) of dimethyl acetylenedicarboxylate by syringe at room temperature. An immediate reaction ensued with moderate gas evolution and a color change to brighter red. After the reaction mixture had been stirred for 1 h at room temperature, it was purged with a stream of carbon monoxide for 20 h. As the solvent slowly evaporated, THF was periodically added by syringe. Subsequently, 0.36 ml (5.00 mmol) of acetyl chloride was added by syringe at room temperature. After the mixture had been stirred for an additional 40 h, the solvent was removed in vacuo to yield an orange, oily solid which was purified by filtration chromatography. Pentane/CH_2Cl_2 (9/1 v/v) eluted a very pale yellow band which was not collected. Methylene chloride/acetone (20/1 v/v) eluted a dark orange band which gave 0.96 g (1.65 mmol, 90%) of $(\mu\text{-}\sigma,\pi\text{-}MeO_2CC{=}C(CO_2Me)C(OC(O)Me)S^tBu\text{-})Fe_2(CO)_6$, 5a, identified by its ^1H NMR spectrum.

Synthesis of $(\mu\text{-}EtOC{=}C(H)C(OC(O)Me){=})(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ JBH-13-IV

To the standard $[Li][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ reagent solution (1.00 mmol) was added 0.09 ml (1.00 mmol) of ethoxyacetylene by syringe at room temperature. After the reaction mixture had been stirred for 30 min at room temperature, 0.11 ml (1.50 mmol) of acetyl chloride was added by syringe. Within minutes, a color change to cherry red had occurred. After the mixture had been stirred for an additional 3.5 h, the solvent was removed in vacuo to yield a red solid which was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Pentane/CH_2Cl_2 (3/2 v/v) eluted a dark orange band which gave 0.41 g (0.79 mmol, 79%) of (μ-EtOC=C(H)C(OC(O)Me)=)(μ-^{t}BuS)$Fe_2(CO)_6$, 15a, as an air-stable, red solid, mp 111.0-113.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{17}H_{18}Fe_2O_9S$: C, 40.03; H, 3.56 %. Found: C, 40.03; H, 3.55 %.

IR(CCl_4): 2960w, 2940w, 2890w, 2860vw, 1778s(C=O), 1475m, 1455s, 1383m, 1368m, 1200vs, 1155vs, 1108w, 1048sh, 1020vs, 850w, 630m, 610s, 590m, 490w cm^{-1}.
Terminal carbonyl region (pentane): 2065vs, 2025vs, 2000vs, 1990vs, 1978m, 1968sh, 1948vw cm^{-1}.

^{1}**H NMR**($CDCl_3$; 250 MHz): δ 1.39 (s, 9H, $SC(CH_3)_3$), 1.42 (t, J = 6.89 Hz, 3H, $OCH_2C\underline{H}_3$), 2.25 (s, 3H, $C(O)CH_3$), 4.07 (m, 2H, $OC\underline{H}_2CH_3$), 6.85 (s, 1H, EtOC=C$\underline{H}$).

^{13}**C NMR**($CDCl_3$; 67.9 MHz): δ 14.06 (q, J = 128.1 Hz, $OCH_2\underline{C}H_3$), 21.64 (q, J = 130.0 Hz, $C(O)\underline{C}H_3$), 33.88 (q, J = 127.0 Hz, $SC(\underline{C}H_3)_3$), 50.47 (s, $S\underline{C}(CH_3)_3$), 71.56 (t, J = 148.0 Hz, $O\underline{C}H_2CH_3$), 136.06 (d, J = 159.5 Hz, EtOC=$\underline{C}$H), 165.37 (s, $\underline{C}$(O)Me), 207.99, 210.12, and 214.20 (all s, Fe-CO), 267.43 (s, MeC(O)O$\underline{C}$-CH), 284.82 (s, EtO$\underline{C}$=CH).

Synthesis of (μ-EtOC=C(H)C(OC(O)Ph)=)(μ-^{t}BuS)$Fe_2(CO)_6$ JBH-52-VI

To the standard [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (3.06 mmol) was added 0.27 ml (3.06 mmol) of ethoxyacetylene by syringe at room temperature. After the reaction mixture had been stirred for 1 h at room temperature, 0.37 ml (3.20 mmol) of benzoyl chloride was added by syringe. Over a period of several hours, a gradual color change to cherry red had occurred. After the mixture had been stirred for a total of 18 h, the solvent was removed in vacuo to yield a red oil which was purified by filtration chromatography. Pentane eluted a pale orange band which was not collected. Pentane/CH_2Cl_2 (3/2 v/v) eluted a dark orange band which gave 1.24 g (2.17 mmol, 71%) of (μ-EtOC=C(H)C(OC(O)Ph)=)(μ-^{t}BuS)$Fe_2(CO)_6$, 15b, as an air-stable, red solid, mp 115.0-118.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{22}H_{20}Fe_2O_9S$: C, 46.18; H, 3.52 %. Found: C, 46.32; H, 3.55 %.

IR(CCl_4): 2975m, 2940w, 2930w, 2900w, 2870w, 1748vs(C=O), 1605w(Ph), 1586w(Ph), 1495m, 1475s, 1405vs, 1385s, 1368m, 1310w, 1225vs, 1200vs, 1190s, 1160s, 1110m, 1078m, 1040vs, 1032vs, 1000vs, 980s, 935w, 850w, 705s, 687w, 657w, 632m, 610vs, 500m cm^{-1}.
Terminal carbonyl region (pentane): 2065vs, 2025vs, 2000vs, 1990vs, 1980s, 1975sh, 1950vw cm^{-1}.

^{1}H NMR(CD_2Cl_2; 300 MHz): δ 1.44 (s, 9H, $SC(CH_3)_3$), 1.44 (t, J = 7.52 Hz, 3H, $OCH_2C\underline{H}_3$), 4.12 (m, 2H, $OC\underline{H}_2CH_3$), 6.99 (s, 1H, EtOC=C$\underline{H}$), 7.51-8.18 (m, 5H, C_6H_5).

^{13}C NMR($CDCl_3$; 75.4 MHz): δ 14.18 (q, J = 127.8 Hz, $OCH_2\underline{C}H_3$), 33.98 (q, J = 129.1 Hz, $SC(\underline{C}H_3)_3$), 50.64 (s, $S\underline{C}(CH_3)_3$), 71.69 (t, J = 147.7 Hz, $O\underline{C}H_2CH_3$), 127.55-134.99 (m, C_6H_5), 136.16 (d, J = 159.8 Hz, EtOC=$\underline{C}$H), 161.34 (s, $\underline{C}$(O)Ph), 208.01, 208.20, 209.98, 210.10, 214.06, and 214.19 (all s, Fe-CO), 267.15 (s, PhC(O)O$\underline{C}$-CH), 284.14 (s, EtO$\underline{C}$=CH).

Synthesis of (μ-EtOC=C(H)C(OC(O)Me)=)(μ-EtS)$Fe_2(CO)_6$ **JBH-47-VI**

To the standard [Li][(μ-CO)(μ-EtS)$Fe_2(CO)_6$] reagent solution (2.73 mmol) was added 0.24 ml (2.73 mmol) of ethoxyacetylene by syringe at room temperature. After the reaction mixture had been stirred for 1 h at room temperature, 0.28 ml (4.00 mmol) of acetyl chloride was added by syringe. Within minutes, a color change to cherry red had occurred. After the mixture had been stirred for an additional 16 h, the solvent was removed in vacuo to yield a red oil which was purified by filtration chromatography. Pentane/CH_2Cl_2 (9/1 v/v) eluted two pale orange bands which were not collected. Pentane/CH_2Cl_2 (1/1 v/v) eluted a dark orange band which gave 0.98 g (2.04 mmol, 75%) of (μ-EtOC=C(H)C(OC(O)Me)=)(μ-EtS)$Fe_2(CO)_6$, 15c, as an air-stable, red solid, mp 108.0-110.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{15}H_{14}Fe_2O_9S$: C, 37.38; H, 2.93 %. Found: C, 37.52; H, 2.94 %.

IR(CCl_4): 2990w, 2975w, 2935w, 2875vw, 1780vs(C=O), 1478s, 1455vs, 1385s, 1370s, 1278w, 1255w, 1205vs, 1160vs, 1110m, 1095w, 1050s, 1025vs, 850m, 650w, 630s, 610vs, 585s, 500m cm^{-1}.
Terminal carbonyl region (pentane): 2070vs, 2030vs, 2005vs, 1995vs, 1982m, 1975m, 1952vw cm^{-1}.

^{1}H NMR(CD_2Cl_2; 300 MHz): δ 1.41 (t, J = 7.32 Hz, 3H, $SCH_2\underline{H}_3$), 1.42 (t, J = 6.98 Hz, 3H, $OCH_2C\underline{H}_3$), 2.25 (s, 3H, $C(O)CH_3$), 2.57 (q, J = 7.44 Hz, 2H, $SC\underline{H}_2CH_3$), 4.07 (m, 2H, $OC\underline{H}_2CH_3$), 6.81 (s, 1H, EtOC=C$\underline{H}$).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 14.05 (q, J = 127.7 Hz, $OCH_2\underline{C}H_3$), 18.57 (q, J = 128.3 Hz, $SCH_2\underline{C}H_3$), 21.58 (q, J = 130.7 Hz, $C(O)\underline{C}H_3$), 39.07 (t, J = 141.6 Hz, $S\underline{C}H_2CH_3$), 71.46

(t, J = 146.8 Hz, $O\underline{C}H_2CH_3$), 136.28 (d, J = 156.6 Hz, $EtOC{=}\underline{C}H$), 165.23 (s, $\underline{C}(O)Me$), 207.92, 208.08, 208.87, 208.97, and 214.15 (all s, Fe-CO), 266.07 (s, $MeC(O)O\underline{C}{-}CH$), 283.76 (s, $EtO\underline{C}{=}CH$).

Mass Spectrum (FD); m/z: 482 (M^+)

Isolation of $[Li(12\text{-}Crown\text{-}4)][(\mu\text{-}EtOC{=}C(H)C(O){=})(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ JBH-12-VIII

To the standard $[Li][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ reagent solution (3.03 mmol) was added 0.26 ml (3.03 mmol) of ethoxyacetylene by syringe at room temperature. After the reaction mixture had been stirred for 16 h at room temperature, the solvent was removed in vacuo. The resulting red, foamy solid was dissolved in Et_2O/CH_2Cl_2 (4/1 v/v) and filtered under nitrogen into a 250 ml Schlenk flask equipped with a spin bar. To the resulting red solution was added 0.49 ml (3.03 mmol) of 12-crown-4 by syringe. Within minutes, a red precipitate had formed. After the reaction mixture had been stirred for 3 h at room temperature, the solvent was removed in vacuo to yield a red, foamy solid. This was dissolved in CH_2Cl_2/hexane (5ml/ 4ml) and filtered under nitrogen into a 50 ml Schlenk tube. Subsequent crystallization at -20°C yielded 0.69 g (1.06 mmol, 35%) of $[Li(12\text{-}crown\text{-}4)][(\mu\text{-}EtOC{=}C(H)C(O){=})(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$, $\underline{16}$.

Anal. Calcd. for $C_{23}H_{31}Fe_2O_{12}SLi$: C, 42.49; H, 4.80 %. Found: C, 42.38; H, 4.87 %.

IR(CH_2Cl_2): 2990sh, 2960sh, 2930s, 2880s, 1465sh, 1450vs, 1420s, 1390w, 1362m, 1160sh, 1135sh, 1125vs, 1100vs, 1055m, 1025s, 925m, 860m, 640m, 610s cm^{-1}.

^{1}H NMR(acetone-d_6; 300 MHz): δ 1.20 (t, J = 6.68 Hz, 3H, $OCH_2C\underline{H}_3$), 1.33 (s, 9H, $SC(CH_3)_3$), 3.50 (m, 2H, $OC\underline{H}_2CH_3$), 3.68 (s, 16H, $-OC\underline{H}_2C\underline{H}_2O-$), 5.27 (s, 1H, $EtOC{=}C\underline{H}$).

^{13}C NMR(acetone-d_6; 67.9 MHz): δ 14.92 (q, J = 126.3 Hz, $OCH_2\underline{C}H_3$), 34.57 (q, J = 126.0 Hz, $SC(\underline{C}H_3)_3$), 38.42 (s, $S\underline{C}(CH_3)_3$), 66.36 (t, J = 144.7 Hz, $O\underline{C}H_2CH_3$), 68.89 (t, J = 143.5 Hz, $-O\underline{C}H_2\underline{C}H_2O-$), 125.52 (d, J = 147.6 Hz, $EtOC{=}\underline{C}H$), 212.39, 213.05, 214.00(broad), 219.76, 220.78 (all s, Fe-CO), 231.63 (s, $EtOC{=}C(H)\underline{C}O^-$), 259.78 (s, $EtO\underline{C}{=}CH$).

Mass Spectrum (FAB); m/z: 467 (M^- anion)

Mass Spectrum (FD); m/z: 183 (M^+ cation)

Synthesis of (μ-EtOC(=CH_2)C=O)(μ-^{t}BuS)$Fe_2(CO)_6$ JBH-16-VI

To the standard [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (2.97 mmol) was added 0.26 ml (2.97 mmol) of ethoxyacetylene by syringe at room temperature. After the reaction mixture had been stirred for 30 min at room temperature, 0.23 ml (2.97 mmol) of trifluoroacetic acid was added by syringe. Within a few minutes, a color change to brighter red had occurred. After the mixture had been stirred for an additional 30 min, the solvent was removed in vacuo to yield a red solid which was purified by filtration chromatography. Pentane eluted a yellow-brown band which was not collected. Pentane/CH_2Cl_2 (9/1 v/v) eluted a dark orange band which gave 1.05 g (2.24 mmol, 76%) of (μ-EtOC(=CH_2)C=O)(μ-^{t}BuS)$Fe_2(CO)_6$, 17a (a mixture of two inseparable isomers), as an air-stable, red solid, mp 76.5-78.0°C after recrystallization from pentane.

Anal. Calcd. for $C_{15}H_{16}Fe_2O_8S$: C, 38.49; H, 3.44 %. Found: C, 38.75; H, 3.56 %.

IR($CHCl_3$): 2990s, 2965s, 2942s, 2922s, 2900m, 1600s(C=C), 1482vs(acyl C=O), 1470sh, 1455vs, 1441s, 1390m, 1378m, 1361vs, 1272vs, 1151vs, 1115m, 1091m, 1059vs, 970vs, 950s, 850s, 680w, 620vs, 608vs cm^{-1}.

Terminal carbonyl region (pentane): 2072s, 2034vs, 2008vs, 2000vs, 1989s, 1980s cm^{-1}.

^{1}H NMR($CDCl_3$; 250 MHz): δ 1.24 (s, 9H, $SC(CH_3)_3$ major isomer), 1.42 (t, J = 7.28 Hz, 3H, $OCH_2C\underline{H}_3$ minor isomer), 1.45 (t, J = 7.10 Hz, 3H, $OCH_2C\underline{H}_3$ major isomer), 1.54 (s, 9H, $SC(CH_3)_3$ minor isomer), 3.76 (m, 2H, $OC\underline{H}_2CH_3$ both isomers), 3.84 (d, J = 2.26 Hz, 1H, $C{=}CH_2$ both isomers-diastereotopic CH_2), 4.32 (d, J = 2.25 Hz, 1H, $C{=}CH_2$ both isomers-diastereotopic CH_2). Ratio major/minor = 2.7/1.0.

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 13.86 (q, J = 127.0 Hz, $OCH_2\underline{C}H_3$ both isomers), 34.23 (q, J = 125.7 Hz, $SC(\underline{C}H_3)_3$ minor isomer), 34.82 (q, J = 127.4 Hz, $SC(\underline{C}H_3)_3$ major isomer), 48.02 (s, $S\underline{C}(CH_3)_3$ major isomer), 49.47 (s, $S\underline{C}(CH_3)_3$ minor isomer), 64.04 (t, J = 142.2 Hz, $O\underline{C}H_2CH_3$ both isomers), 84.66 (t, J = 161.6 Hz, $C{=}\underline{C}H_2$ major isomer), 85.68 (t, J = 163.1 Hz, $C{=}\underline{C}H_2$ minor isomer), 159.70 (s, $EtO\underline{C}{=}CH_2$ both isomers), 207.26, 209.51, 210.37, 210.55, 210.72, and 211.21 (all s, Fe-CO), 287.24 (s, acyl C=O both isomers).

Mass Spectrum (EI); m/z (relative intensity): 468 (M^+, 8), 440 (M^+ - CO, 29), 412 (M^+ - 2CO, 28), 384 (M^+ - 3CO, 30), 356 (M^+ - 4CO, 38), 328 (M^+ - 5CO, 62), 300 (M^+ - 6CO, 100), 272 (M^+ - 7CO, 51), 244 ($^tBuSFe_2HOC{=}CH_2$, 63), 216 ($HSFe_2EtOC{=}CH_2$, 82), 188 ($HSFe_2HOC{=}CH_2$, 60), 170 ($SFe_2C{=}CH_2$, 14), 159 ($SFeEtOC{=}CH_2$, 8), 145 (Fe_2SH, 55), 144 (Fe_2S, 56), 112 (Fe_2, 4), 57 (^tBu, 27), 56 (Fe, 6).

Synthesis of $(\mu\text{-}EtOC(=CH_2)C=O)(\mu\text{-}EtS)Fe_2(CO)_6$ and $(\mu\text{-}\sigma,\pi\text{-}EtOC=CH_2)(\mu\text{-}EtS)Fe_2(CO)_6$ JBH-55-VII

To the standard $[Li][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ reagent solution (3.02 mmol) was added 0.26 ml (3.02 mmol) of ethoxyacetylene by syringe at room temperature. After the reaction mixture had been stirred for 30 min at room temperature, 0.23 ml (3.02 mmol) of trifluoroacetic acid was added by syringe. After the mixture had been stirred for an additional 1 h, the solvent was removed in vacuo to yield a red-brown, oily solid which was purified by filtration chromatography. Hexane eluted a pale orange band which was not collected. Hexane then eluted an orange band which gave 0.42 g (1.01 mmol, 34%) of (μ-σ,π-EtOC=CH_2)(μ-EtS)$Fe_2(CO)_6$, 18b, as a slightly air sensitive red oil.

Anal. Calcd. for $C_{12}H_{12}Fe_2O_7S$: C, 34.98; H, 2.94 %. Found: C, 35.27; H, 3.00 %.

IR(CCl_4): 3060vw, 2980sh, 2960m, 2930s, 2870m, 2860sh, 1460sh, 1458s, 1390sh, 1380m, 1280s, 1255m, 1150vs, 1108w, 1028s, 955m, 900m, 840w, 670m, 620vs, 600s, 570s cm^{-1}.
Terminal carbonyl region (pentane): 2070s, 2050vw, 2040vs, 2000vs, 1990vs cm^{-1}.

^1H NMR($CDCl_3$; 300 MHz): δ 1.26 (t, J = 6.73 Hz, 3H, $OCH_2C\underline{H}_3$), 1.30 (t, J = 7.24 Hz, 3H, $SCH_2C\underline{H}_3$), 1.65 (d, J = 4.61 Hz, 1H, C=CH_2 endo), 2.38 (m, 1H, $SC\underline{H}_2CH_3$ diastereotopic CH_2), 2.41 (m, 1H, $SC\underline{H}_2CH_3$ diastereotopic CH_2), 3.21 (d, J = 4.61 Hz, 1H, C=CH_2 exo), 3.64 (m, 1H, $OC\underline{H}_2CH_3$ diastereotopic CH_2), 3.85 (m, 1H, $OC\underline{H}_2CH_3$ diastereotopic CH_2).

^{13}C NMR($CDCl_3$): δ 14.39 (q, J = 127.3 Hz, $OCH_2\underline{C}H_3$), 18.16 (q, J = 126.1 Hz, $SCH_2\underline{C}H_3$), 33.59 (t, J = 144.6 Hz, $S\underline{C}H_2CH_3$), 49.01 (dd, J = 152.0 Hz, J = 161.9 Hz, C=$\underline{C}H_2$), 66.79 (t, J = 146.8 Hz, $O\underline{C}H_2CH_3$), 209.42 and 209.97 (both s, Fe-CO), 218.02 (s, EtO$\underline{C}$=CH_2).

Mass Spectrum (EI); m/z (relative intensity): 412 (M^+, 13), 384 (M^+ - CO, 24), 356 (M^+ - 2CO, 33), 328 (M^+ - 3CO, 41), 300 (M^+ - 4CO, 28), 272 (M^+ - 5CO, 63), 244 (M^+ -

6CO, 100), 216 ($HSFe_2EtOC{=}CH_2$, 67), 188 ($HSFe_2HOC{=}CH_2$, 63), 145 ($HSFe_2$, 48), 144 (SFe_2, 54), 112 (Fe_2, 7), 69 (EtOC=C, 5), 56 (Fe, 7).

Further elution with hexane then yielded a dark green band which was not collected and a dark orange band which gave 0.70 g (1.60 mmol, 53%) of (μ-EtOC(=CH_2)C=O)(μ-EtS)$Fe_2(CO)_6$, 17b (a mixture of inseparable isomers) as a slightly air sensitive red oil. An analytically pure sample for carbon/hydrogen combustion analysis could not be obtained.

IR(CCl_4): 2980sh, 2960vs, 2945vs, 2870s, 2850s, 1600s(C=C), 1480vs(acyl C=O), 1455s, 1378s, 1358m, 1280vs, 1258s, 1151s, 1117m, 1091m, 1061vs, 1028m, 975vs, 950sh, 900w, 872w, 848m, 710m, 695m, 682m, 630vs, 610vs, 590vs cm^{-1}.
Terminal carbonyl region (pentane): 2075s, 2040vs, 2000vs, 1992sh, 1981m, 1975sh cm^{-1}.

^{1}H NMR(CD_2Cl_2; 300 MHz): δ 1.31 (t, J = 7.30 Hz, 3H, $SCH_2C\underline{H}_3$ minor isomer), 1.42 (t, J = 7.14 Hz, 3H, $OCH_2C\underline{H}_3$ major isomer), 1.44 (t, J = 7.11 Hz, 3H, $OCH_2C\underline{H}_3$ minor isomer), 1.49 (t, J = 6.81 Hz, 3H, $SCH_2C\underline{H}_3$ major isomer), 2.11, 2.22, and 2.64 (all m, 2H, $SC\underline{H}_2CH_3$ both isomers), 3.77 (m, 2H, $OC\underline{H}_2CH_3$ both isomers), 3.86 (d, J = 1.73 Hz, 1H, C=CH_2 minor isomer-diastereotopic CH_2), 3.88 (d, J = 2.50 Hz, 1H, C=CH_2 major isomer-diastereotopic CH_2), 4.31 (d, J = 2.50 Hz, 1H, C=CH_2 major isomer-diastereotopic CH_2), 4.35 (d, J = 1.58 Hz, 1H, C=CH_2 minor isomer-diastereotopic CH_2). Ratio major/minor = 1.8/1.0.

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 13.87 (q, J = 127.5 Hz, $OCH_2\underline{C}H_3$ both isomers), 17.78 (q, J = 128.4 Hz, $SCH_2\underline{C}H_3$ minor isomer), 18.28 (q, J = 128.6 Hz, $SCH_2\underline{C}H_3$ major isomer), 25.56 (t, J = 141.5 Hz, S$\underline{C}H_2CH_3$ minor isomer), 32.69 (t, J = 140.8 Hz, S$\underline{C}H_2CH_3$ major isomer), 64.06 (t, J = 144.0 Hz, O$\underline{C}H_2CH_3$ both isomers), 84.03 (t, J = 162.6 Hz, C=$\underline{C}H_2$ minor isomer), 85.22 (t, J = 162.7 Hz, C=$\underline{C}H_2$ major isomer), 160.14 (s, EtO$\underline{C}$=CH_2 major isomer), 160.58 (s, EtO$\underline{C}$=CH_2 minor isomer), 207.88, 209.31, 209.77, 210.19, 210.40, and 211.03 (all s, Fe-CO), 287.64 (s, acyl C=O major isomer), 290.03 (s, acyl C=O minor isomer).

Mass Spectrum (EI); m/z (relative intensity): 440 (M^+, 1), 412 (M^+ - CO, 16), 384 (M^+ - 2CO, 19), 356 (M^+ - 3CO, 28), 328 (M^+ - 4CO, 36), 300 (M^+ - 5CO, 33), 272 (M^+ - 6CO, 68), 244 (M^+ - 7CO, 100), 216 ($HSFe_2EtOC=CH_2$, 65), 188 ($HSFe_2HOC=CH_2$, 66), 169 ($HSFe_2C=C$, 9), 145 (Fe_2SH, 66), 144 (Fe_2S, 65), 112 (Fe_2, 9), 56 (Fe, 8).

Decarbonylation of (μ-EtOC(=CH_2)C=O)(μ-^tBuS)$Fe_2(CO)_6$ JBH-17-VI

A 100 ml round bottomed flask equipped with a stir-bar and rubber septum was charged with 0.34 g (0.72 mmol) of (μ-EtOC(=CH_2)C=O)(μ-^tBuS)$Fe_2(CO)_6$, 17a, and degassed via three evacuation/nitrogen-backfill cycles. The flask then was charged with 30 ml of THF by syringe. After the resulting red reaction mixture had been stirred for 6 days at room temperature, the solvent was removed in vacuo to yield a red oil which was purified by filtration chromatography. Pentane eluted a red band which gave 0.29 g (0.67 mmol, 92%) of (μ-σ,π-EtOC=CH_2)(μ-^tBuS)$Fe_2(CO)_6$, 18a,[1] identified by its ^1H NMR spectrum.

Decarbonylation of (μ-EtOC(=CH_2)C=O)(μ-EtS)$Fe_2(CO)_6$ JBH-72-VII

A 100 ml round bottomed flask equipped with a stir-bar and rubber septum was charged with 0.41 g (0.93 mmol) of

(μ-EtOC(=CH_2)C=O)(μ-EtS)$Fe_2(CO)_6$, 17b, and degassed via three evacuation/nitrogen-backfill cycles. The flask then was charged with 30 ml of THF by syringe. After the resulting red reaction mixture was stirred for 4 days at room temperature, the solvent was removed in vacuo to yield a red oil which was purified by filtration chromatography. Pentane eluted an orange band which gave 0.36 g (0.88 mmol, 95%) of (μ-σ,π-EtOC=CH_2)(μ-EtS)$Fe_2(CO)_6$, 18b, identified by its ^1H NMR spectrum.

Reaction of [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] with EtOC≡CH and CF_3COOH at -78°C JBH-1-VI

To the standard [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (1.58 mmol) cooled to -78°C was added 0.14 ml (1.58 mmol) of ethoxyacetylene by syringe. After the reaction mixture had been stirred for 1 h at -78°C, 0.12 ml (1.80 mmol) of trifluoroacetic acid was added by syringe. After the mixture had been stirred for an additional 15 min at -78°C, warmed to room temperature, and stirred for 15 min at room temperature, the solvent was removed in vacuo to yield a red tar which was purified by filtration chromatography. Pentane eluted a dark orange band which gave 0.40 g (0.92 mmol, 58%) of (μ-σ,π-EtOC=CH_2)(μ-^{t}BuS)$Fe_2(CO)_6$, 18a,[1] identified by its ^1H NMR spectrum. Further elution with pentane yielded a pale green band which was not collected and a pale orange band which gave 0.13 g (0.27 mmol, 17%) of (μ-EtOC(=CH_2)C=O)(μ-^{t}BuS)$Fe_2(CO)_6$, 17a, also identified by its ^1H NMR spectrum.

Reaction of [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] with EtOC≡CH and CF_3COOH under CO at -78°C JBH-56-VII

The standard [Li][(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent solution (1.82 mmol) was prepared and then purged with carbon monoxide for 45 min at room temperature.

Subsequently, the solution was cooled to -78°C and 0.16 ml (1.82 mmol) of ethoxyacetylene was added by syringe. After the reaction mixture had been stirred for 1.5 h at -78°C (with continuous CO purge for the first hour), 0.12 ml (1.82 mmol) of trifluoroacetic acid was added by syringe. After the mixture had been stirred for an additional 15 min at -78°C, warmed to room temperature, and stirred for 15 min at room temperature, the solvent was removed in vacuo to yield a red oil which was purified by filtration chromatography. Pentane eluted an orange band which gave 0.57 g (1.30 mmol, 71%) of (μ-σ,π-EtOC=CH$_2$)(μ-^{t}BuS)Fe$_2$(CO)$_6$, 18a,[1] identified by its ^{1}H NMR spectrum. Pentane/CH$_2$Cl$_2$ (9/1 v/v) eluted a pale orange band which gave 0.09 g (0.19 mmol, 11%) of (μ-EtOC(=CH$_2$)C=O)(μ-^{t}BuS)Fe$_2$(CO)$_6$, 17a, also identified by its ^{1}H NMR spectrum.

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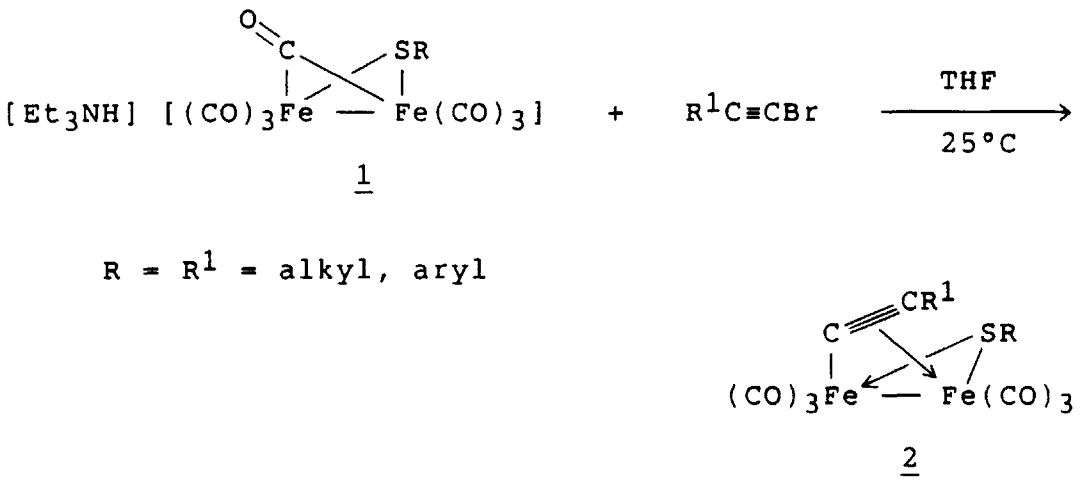
Chapter 5

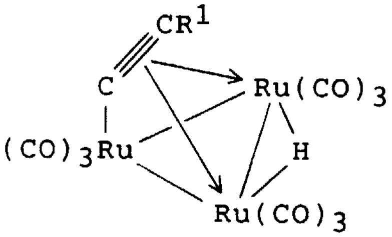
"Synthesis of $(\mu_3,\eta^2\text{-}C{=}CHR^1)(\mu\text{-}CO)Fe_3(CO)_9$"

INTRODUCTION

As described in Chapter 2, the reaction of 1-bromo-1-alkynes ($R^1C{\equiv}CBr$) with $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anions, 1, was shown to be a viable route to the synthesis of new, dinuclear iron acetylide complexes of the type $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR^1)(\mu\text{-}RS)Fe_2(CO)_6$, 2 (Eq. 1). In the past, transition metal acetylide complexes have been prepared by a variety of methods including the reactions of acetylenes,[1] acetylenic Grignard reagents,[2] and sodium or lithium acetylides[3] with metal carbonyls or metal halides. In addition, mono- and binuclear acetylide complexes themselves have been shown to be useful precursors for the synthesis of higher nuclearity and mixed metal acetylide clusters as well.[4] However, the utilization of α-bromoacetylenes as preparative reagents for the introduction of acetylide ligands into metal complexes has remained unexploited. As a result, it was of interest to explore the chemistry of these acetylenes with other iron carbonyl anions as well. In the first experiments, reaction of phenylbromoacetylene with $Na_2[Fe_2(CO)_8]$ and $[PPN]_2[Fe_3(CO)_{11}]$, only intractable oils were obtained. However, in the subsequent reaction of phenylbromoacetylene



(1)



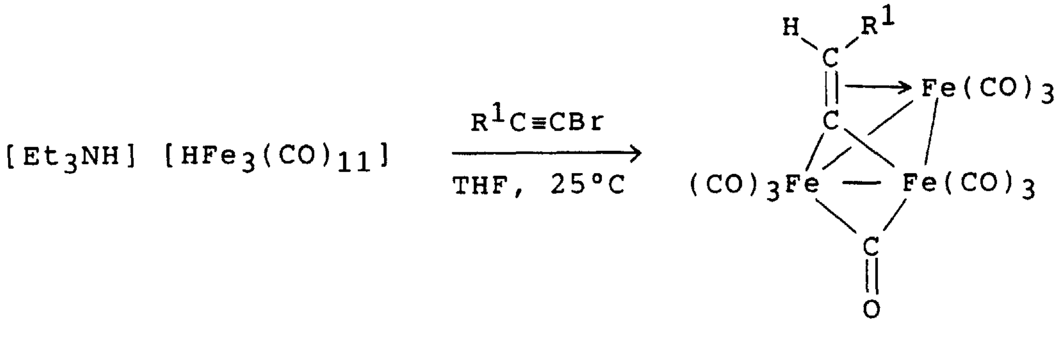
3

Figure 1

with $[Et_3NH][HFe_3(CO)_{11}]$, a stable product was isolated. Triply bridging acetylide clusters of the type $(\mu_3,\eta^2\text{-}C{\equiv}CR^1)(\mu\text{-}H)Ru_3(CO)_9$, 3 (Fig. 1), have been reported,[1e,1f,5] and thus it was thought that reaction of $R^1C{\equiv}CBr$ with $[HFe_3(CO)_{11}]^-$ would generate analogous trinuclear iron species. Unexpectedly, however, these new iron-acetylide clusters were not formed, but instead, products derived from hydride migration to the acetylenic framework were isolated.

RESULTS AND DISCUSSION

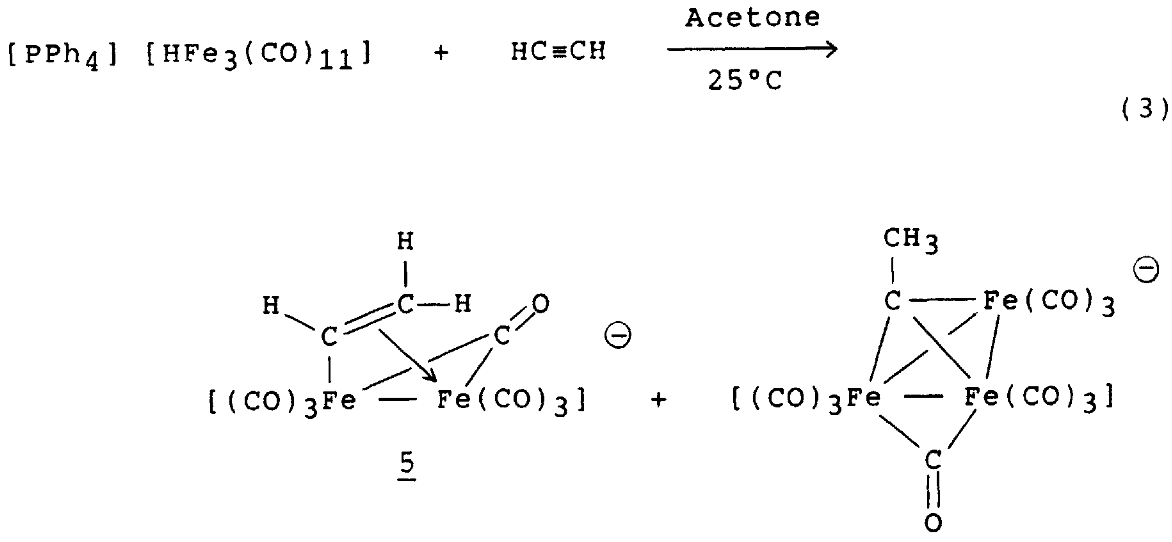
Reaction of $[Et_3NH][HFe_3(CO)_{11}]$ with α-bromoacetylenes, $R^1C{\equiv}CBr$ (R^1 = alkyl, aryl) yielded new trinuclear vinylidene complexes of the type $(\mu_3,\eta^2\text{-}C{=}CHR^1)(\mu\text{-}CO)Fe_3(CO)_9$, 4 (Eq. 2). Although initially formed acetylide species may be implicated as transient reaction intermediates, likely intramolecular rearrangement involving the hydride and acetylide ligands must occur, ultimately producing the new vinylidene clusters in moderate yields. Mathieu has observed hydride migration/insertion in the related reaction of acetylene with $[PPh_4][HFe_3(CO)_{11}]$ which yielded anionic μ-vinyl and μ-methylidyne complexes (Eq.



(2)

4

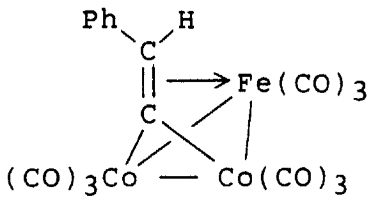
a	R^1 = Ph	51%
b	R^1 = CH_3OCH_2	39%
c	R^1 = Me_3Si	17%
d	R^1 = Et	47%
e	R^1 = ${}^nPr$	48%
f	R^1 = ${}^nBu$	44%



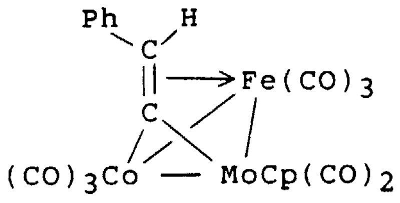
(3)

5

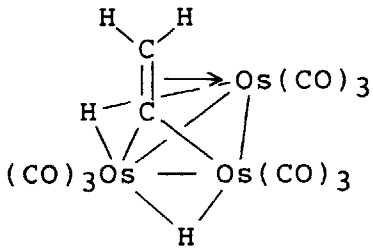
6



7[7b]



8[7b]

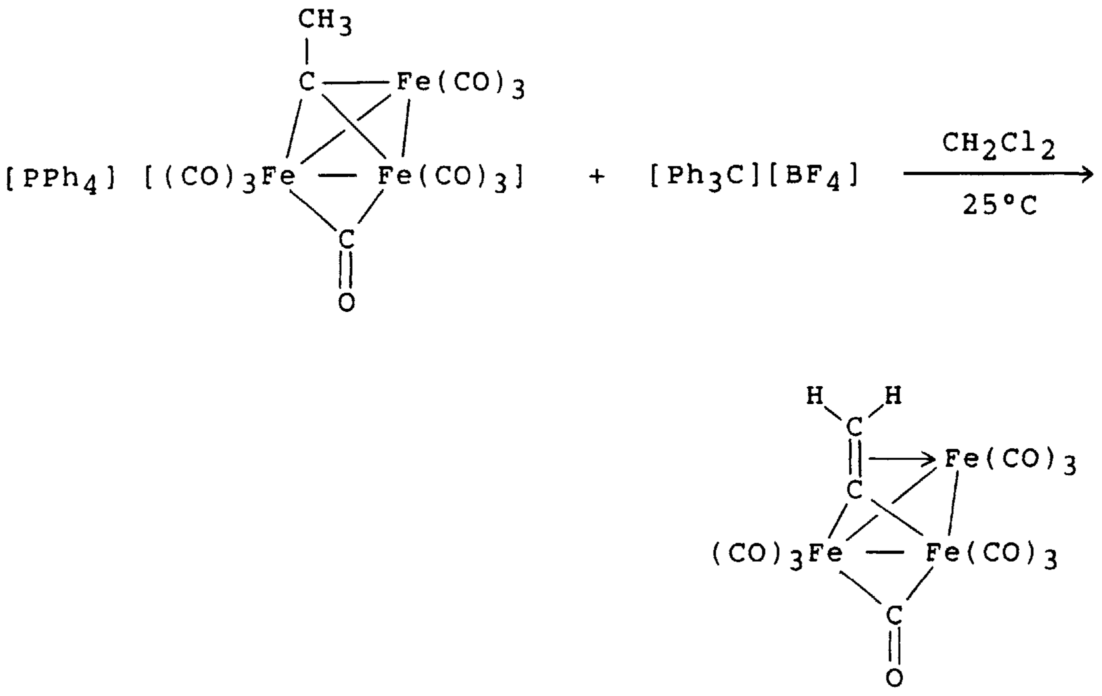


9[7c]

Figure 2

3).[6] Furthermore, vinylidene clusters of the general type 4 are known (Fig. 2);[7] in fact, concurrent with this research, Mathieu reported the synthesis of the parent complex of this class, 10 (R^1 = H), by the reaction of $[PPh_4][(\mu_3,\eta^3\text{-}CCH_3)(\mu\text{-}CO)Fe_3(CO)_9]$ with $[Ph_3C][BF_4]$ (Eq. 4).[8]

Despite their unexpected formation, characterization of these new μ-vinylidene complexes by the standard spectroscopic and analytical techniques was straightforward. While the carbon/hydrogen combustion analyses and electron impact mass spectra were useful in ascertaining the chemical composition of these molecules, the coordination of the bridging ligands was determined primarily from the infrared and ^{13}C NMR data (Table 1). Although shifted somewhat to higher frequency than typically expected for μ-CO ligands,[12] very strong bands assigned to the bridging carbonyl ligands



(4)

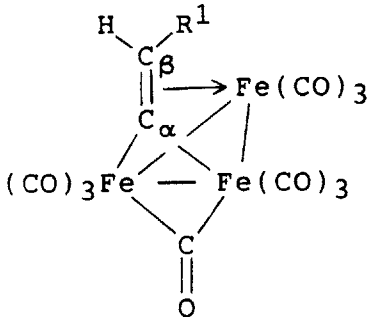
10, 50%

were observed in the infrared spectra in the region of 1880 cm^{-1}. For most of the complexes, a second bridging carbonyl band also was observed as a shoulder or weak absorbtion around 1850 cm^{-1}. The appearance of this lower frequency band is puzzling although it may be a solution phenomenon indicative of a relatively slow (at least on the IR time scale) fluxional process equilibrating two or more bridging carbonyl ligands at room temperature. This conclusion is supported by the ^{13}C NMR spectra of 4a-f. In all cases, rapid exchange of the carbonyl ligands at room temperature is inferred since only one signal is observed in the CO region ($\delta_C \sim 211$).

As expected, the α-carbon resonances of the bridging carbene ligand are observed as singlets far downfield ($\delta_C \sim 288$) in the ^{13}C NMR spectra. In comparison, the β-carbon atoms of the vinylidene ligand appear as higher field

Table 1: IR, ^{1}H NMR, and ^{13}C NMR

Data for 10



	R^1	$\nu_{\mu\text{-CO}}$	$\delta_H(C_\beta)$	$\delta_{C\alpha}$	$\delta_{C\beta}$
a	Ph	1878vs		274.14 (s)	102.73 (d)
b	$MeOCH_2$	1885vs 1850sh	6.06 (t)	288.16 (s)	95.24 (d)
c	Me_3Si	1880s 1842w	5.36 (s)	291.95 (s)	96.72 (d)
d	Et	1880vs 1850sh	5.69 (t)	287.78 (s)	105.05 (d)
e	^{n}Pr	1882vs 1850sh	5.74 (t)	285.78 (s)	101.93 (d)
f	^{n}Bu	1885vs 1860sh	6.04 (t)	285.55 (s)	102.28 (d)

doublets, δ_C ~ 100. Furthermore, although the β-vinylidene protons are observed in the corresponding ^{1}H NMR spectra in the region typical for olefinic protons,[9] an absorption for a carbon-carbon double bond is not observed in the infrared spectra.[9] Likely, this band is shifted well into the range of carbon-carbon single bonds due to coordination of the vinylidene double bond to the third iron center.

The structure of derivative <u>4a</u> has been confirmed by X-ray crystallography. An ORTEP plot showing the atom labeling scheme is displayed in Figure 3 while pertinent bond distances and angles are summarized in Tables 2 and 3, respectively. Fe1, Fe2, and Fe3 define a trinuclear core which is a near equilateral triangle (Fe1-Fe2 = 2.5969(6), Fe1-Fe3 = 2.5616(6), and Fe2-Fe3 = 2.5840(5)Å). Fe1 and Fe3 are linked by the symmetrical carbonyl bridge with Fe1-C1 and Fe3-C1 distances of 1.992(3) and 2.014(4) Å, respectively. In addition, the α-carbon atom of the vinylidene ligand (C11) bridges Fe1 and Fe3 symmetrically with very short "carbene-like" distances of 1.917(3) and 1.909(3)Å, respectively.[13] C11 is bonded further to the third iron atom, Fe2, although this distance, 2.009(2)Å, is nearly 0.1Å longer. Surprisingly, the corresponding C12-Fe2 bond is quite long (2.288(3)Å); however, this is consistent with the structures of other μ_3-vinylidene complexes.[7b,d] As expected due to π-coordination of the vinylidene ligand, the C11-C12 bond of 1.378(4)Å shows some lengthening from that of an uncoordinated double bond[5] although this effect is certainly not dramatic. Conversely, the C12-C13 distance of 1.485(5)Å shows some shortening from that of a carbon-carbon single bond[5] and therefore indicates some delocalization of electron density out of the phenyl ring and into the iron-vinylidene framework. Finally, due to the symmetrical nature of both the carbonyl and vinyldene bridges with respect to the Fe1-Fe3 bond, C1, O1, Fe2, C11, and C12 all define a plane in which the largest deviation from that plane is only 0.009Å for C1.

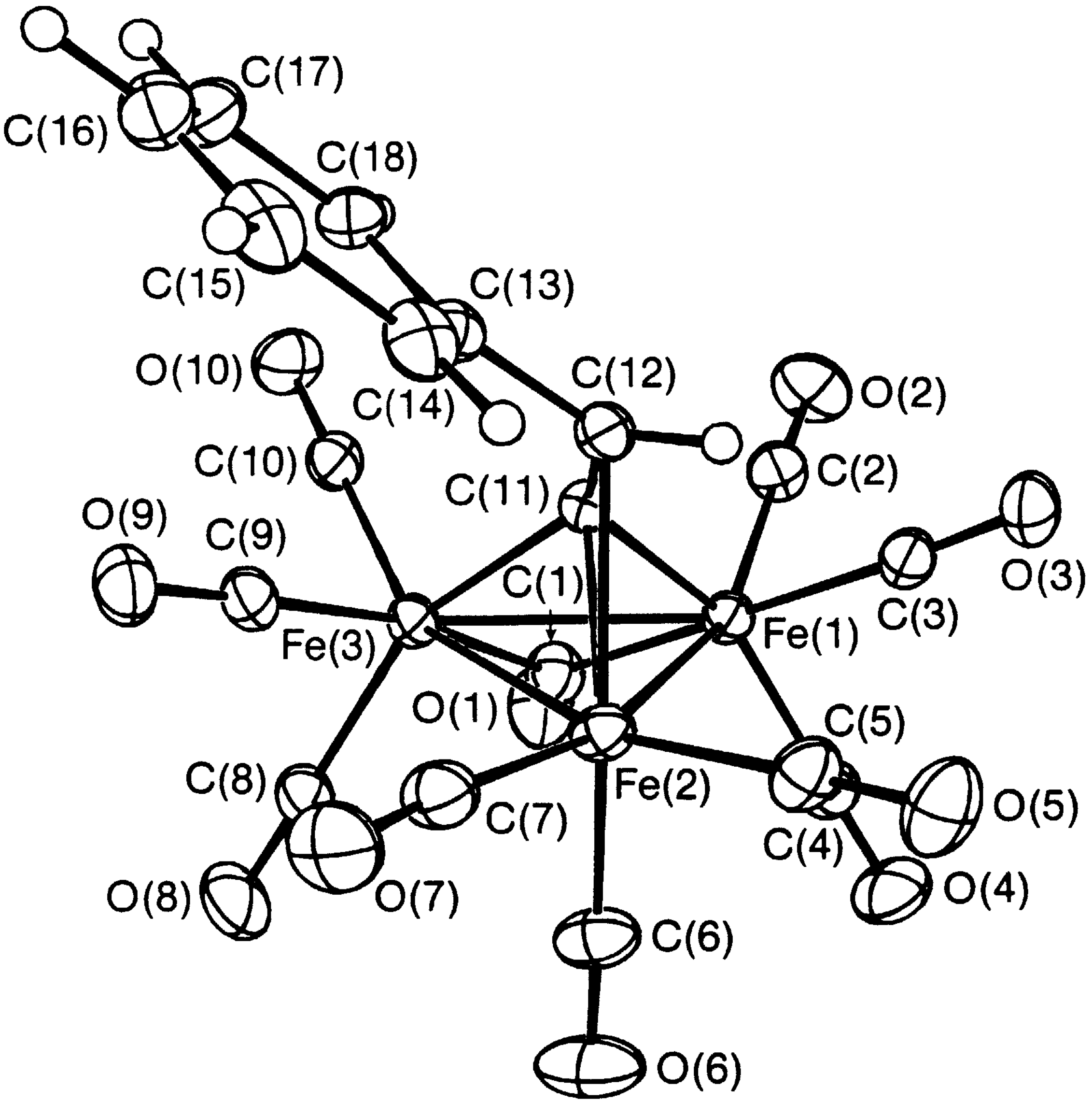


Figure 3: ORTEP plot of 4a

Table 2: Relevant Bond Distances (Å) for 4a

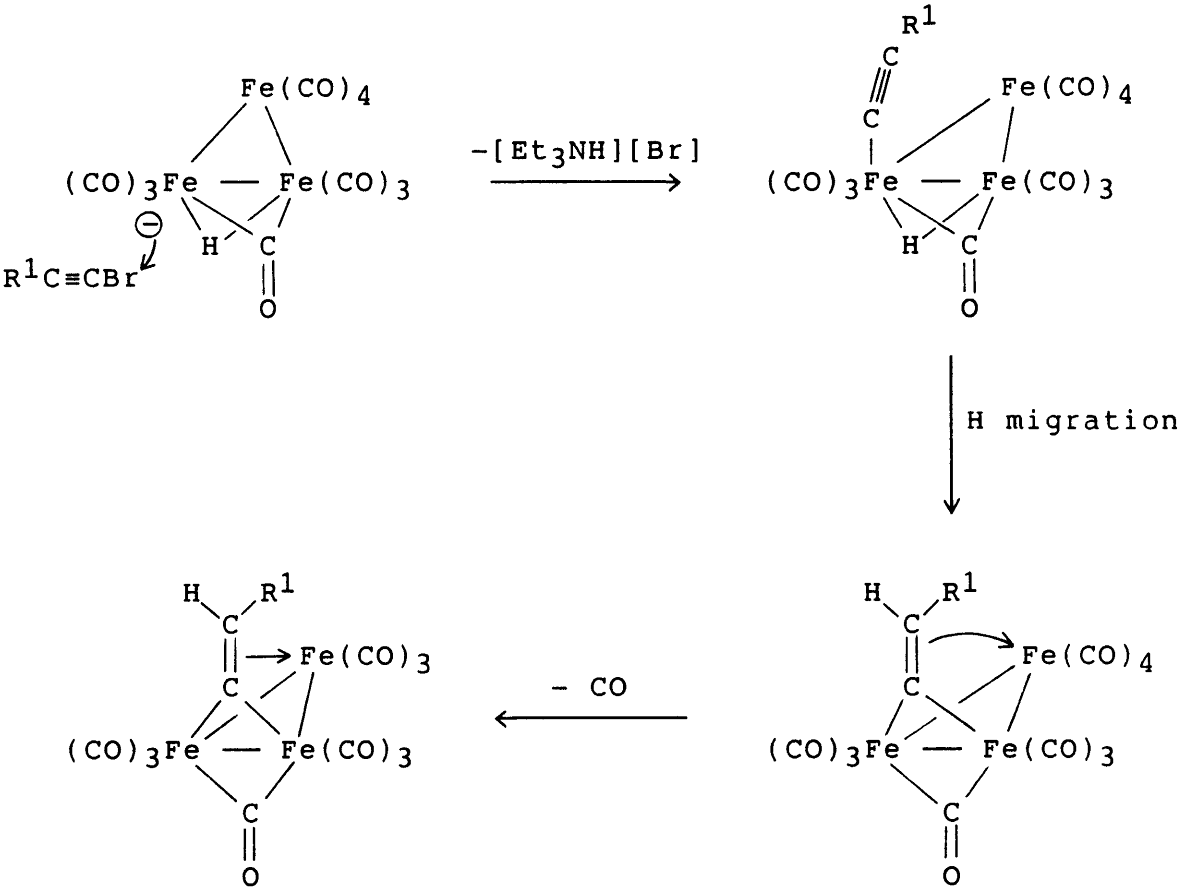
Fe1-Fe2	2.5969(6)	Fe2-C12	2.288(3)
Fe2-Fe3	2.5840(5)	Fe1-C1	1.992(3)
Fe1-Fe3	2.5616(6)	Fe3-C1	2.014(4)
Fe1-C11	1.917(3)	C1-O1	1.154(5)
Fe2-C11	2.009(2)	C12-C13	1.485(5)
Fe3-C11	1.909(3)	C11-C12	1.378(4)

Table 3: Relevant Bond Angles (°) for 4a

Fe1-Fe2-Fe3	59.26(2)	Fe1-C1-Fe3	79.5(1)
Fe2-Fe3-Fe1	60.62(2)	Fe2-Fe1-C11	50.14(7)
Fe3-Fe1-Fe2	60.12(2)	Fe2-Fe3-C11	50.44(7)
Fe1-C11-Fe2	82.8(1)	Fe2-C11-C12	82.7(2)
Fe3-C11-Fe2	82.48(9)	Fe2-C12-C11	60.6(1)
Fe1-C11-Fe3	84.1(1)	Fe2-C12-C13	122.0(2)
Fe1-C11-C12	135.1(2)	Fe2-Fe1-C1	101.2(1)
Fe3-C11-C12	135.2(2)	Fe2-Fe3-C1	101.02(9)
Fe1-Fe3-C11	48.11(9)	Fe3-Fe1-C1	50.6(1)
Fe3-Fe1-C11	47.83(8)	C1-Fe1-C11	96.2(1)
Fe1-Fe2-C11	47.09(9)	C1-Fe3-C11	95.7(1)
Fe3-Fe2-C11	47.08(7)	C12-Fe2-C11	36.7(1)
Fe1-Fe2-C12	77.05(9)	C11-C12-C13	124.6(2)
Fe3-Fe2-C12	77.11(7)	Fe2-C12-H12	87.2(2)
Fe1-C1-O1	141.1(3)	C11-C12-H12	117.9(3)
Fe3-C1-O1	139.3(3)	C13-C12-H12	117.6(3)

In addition, the dihedral angle between this plane and that defined by Fe1, Fe2, and Fe3 is 89.98(4)°.

A possible mechanism that accounts for the formation of these unexpected vinylidene complexes is outlined in Scheme 1. In analogy to proposed mechanisms for nucleophilic substitution of α-bromoacetylenes,[14] the initial step likely results from attack of an iron-centered anion on the bromine atom of the acetylene with eventual elimination of bromide ion and formation of $[Et_3NH][Br]$ (which precipitates out of solution). Subsequent migration of the hydride ligand to the β-carbon atom of the resulting transient terminal acetylide ligand can lead to formation of a μ_2,η^1-vinylidene complex. Bridging of the vinylidene ligand through the π-electron cloud to the third iron atom then gives 4 with concurrent expulsion of carbon monoxide. In general, vinylidene complexes were isolated from both alkyl and aryl bromoacetylenes. Likely due to steric affects, however, reaction of the bulkier bromoacetylenes led to a diminished product yield in the case of $Me_3SiC{\equiv}CBr$ and no reaction for $^tBuC{\equiv}CBr$. In the reaction of $Me_2NCH_2C{\equiv}CBr$, the desired product was initially observed by TLC. However this product appeared to be thermally unstable since after a reaction time of 24 h, none of the desired complex was observed.


Fe(CO)4
(CO)3Fe — Fe(CO)3
H
C
O
R1C≡CBr
-[Et3NH][Br]
R1
C
C
H migration
H R1
- CO

4

Scheme 1

EXPERIMENTAL

General Comments

All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl and purged with nitrogen prior to use. Phenylbromoacetylene ($PhC\equiv CBr$), methoxymethylbromoacetylene ($MeOCH_2C\equiv CBr$), trimethylsilylbromoacetylene ($Me_3SiC\equiv CBr$), ethylbromoacetylene ($EtC\equiv CBr$), n-propylbromoacetylene ($^nPrC\equiv CBr$), and n-butylbromoacetylene ($^nBuC\equiv CBr$) all were prepared by a literature procedure[10] and purged with nitrogen prior to use. Likewise, $[Et_3NH][HFe_3(CO)_{11}]$ was prepared by a literature method.[11]

The progress of all reactions was monitored by thin layer chromatography (Baker Flex - Silica Gel 1B-F). Purification by filtration chromatography in which the reaction products were dissolved in a suitable solvent and chromatographed on a bed of EM Science or Sigma 100-300 mesh silicic acid (ca. 200 ml) in a 350 ml glass fritted filter funnel was used in most cases. Further purification by medium pressure column chromatography was accomplished with a 300x25 mm column using Sigma 230-400 mesh silica gel. All chromatography was completed without exclusion of atmospheric moisture or oxygen. Solid products were recrystallized from deoxygenated solvents at -20°C.

Solution infrared spectra (NaCl windows) were obtained using a Perkin-Elmer Model 1430 double beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a Bruker WM-250 or a Varian XL-300 NMR spectrometer operating at 250 or 300 MHz, respectively. Carbon-13 NMR spectra were recorded on a Bruker WH-270 or Varian XL-300 spectrometer operating at 67.9 or 75.4 MHz, respectively. Electron impact mass spectra were obtained using a Finnigan-3200 spectrometer operating at 70 eV. Masses were correlated using the following isotopes: ^1H, ^{12}C, ^{16}O,

^{28}Si, and ^{56}Fe. Melting points were determined in air on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were perfomed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

X-ray Crystallography

The structure of $(\mu_3,\eta^2\text{-C=CHPh})(\mu\text{-CO})Fe_3(CO)_9$, 4a, was solved by Dr. Allen Hunter in collaboration with Dr. Martin Cowie at the University of Edmonton, Alberta, Canada.

A suitable quality, irregularly shaped black crystal of 4a (which had been grown in pentane) was mounted on a glass fiber using epoxy resin. Unit cell parameters were obtained from a least-squares analysis of the setting angles of 25 reflections in the range $22.3° \leq 2\theta \leq 25.9°$, which were accurately centered at 22°C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. The $\bar{1}$ diffraction symmetry and the lack of systematic absences were consistent with the space groups P1 and $P\bar{1}$, the latter of which was ultimately established as the probable one. A cell reduction[15] failed to show the presence of a higher symmetry cell.

Intensity data in the range $1.0° \leq 2\theta \leq 53°$ were collected at 22°C on the CAD4 diffractometer in the bisecting mode employing the ω-2θ scan technique and using graphite monochromated Mo Kα radiation. Backgrounds were scanned for 25% of the peak width on either end of the peak scan. The intensities of three standard reflections were measured every 1 h of exposure to assess possible crystal decomposition or movement. No significant variations in the standards were detected so no correction was applied. A total of 3877 unique reflections (h, ±k, ±l) were measured and processed in the usual manner using a value of 0.04 for p.[16] Of these, 3147 ($F_o^2 \geq 3\sigma(F_o^2)$) were considered to be observed and were used in subsequent calculations (280 variables). Table 4 summarizes pertinent crystal data.

Table 4: Crystal Data for $(\mu_3,\eta^2\text{-C=CHPh})(\mu\text{-CO})Fe_3(CO)_9$, 4a

$a = 9.254(2)$ Å
$b = 12.717(3)$ Å
$c = 9.114(1)$ Å
$V = 1004.4$ Å^3
$Z = 2$

$\alpha = 102.15(2)°$
$\beta = 100.84(1)°$
$\gamma = 75.45(2)°$
$\rho(\text{calcd}) = 1.818$ g cm^{-1}
$\mu = 21.904$ cm^{-1}

The structure was solved in the space group P1. The iron positions were obtained from the Patterson map and all other atoms were obtained by subsequent least-squares and difference-Fourier calculations. Atomic scattering factors for hydrogen[17] and the other atoms[18] were taken from the usual tabulations; anomalous dispersion terms[19] were included in the calculation of Fe. All hydrogen atoms were located and were input to the least-squares cycle as fixed contributions in their idealized positions using C-H distances of 0.95Å. The hydrogen atoms were assigned isotropic thermal parameters of 1Å^2 greater than the equivalent isotropic B of their attached carbon atom. All other atoms were refined anisotropically. Absorption corrections were applied to the data using Gaussian integration.

Refinement by full-matrix techniques converged at $R = 0.031$ and $R_w = 0.043$. On the final difference-Fourier map, the largest peak was 0.34eÅ^{-3}; this can be compared to carbon atom peaks on earlier Fourier maps that had intensities of 4.2 - 7.7 eÅ^{-3}. The alternate space group P1 was rejected owing to the satisfactory refinement in $P\bar{1}$.

Synthesis of (μ_3,η^2-C=CHPh)(μ-CO)$Fe_3(CO)_9$ JBH-23-V

A 200 ml Schlenk flask equipped with a magnetic stirbar and a rubber septum was charged with 1.73 g (2.99 mmol) of $[Et_3NH][HFe_3(CO)_{11}]$ and subsequently degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 30 ml of THF and 0.37 ml (3.00 mmol) of phenyl bromoacetylene by syringe at room temperature. Over a period of several hours a gradual color change from purple-red to brown-green was observed along with slow gas evolution (CO) and formation of a white precipitate ($[Et_3NH][Br]$). After the reaction mixture had been stirred for 20 h at room temperature, the solvent was removed in vacuo and the resulting red-green tar was purified by filtration chromatography. Pentane/CH_2Cl_2 (9/1 v/v) eluted a green band which gave 0.83 g (1.52 mmol; 51%) of (μ_3,η^2-C=CHPh)(μ-CO)$Fe_3(CO)_9$, 4a, as an air stable, green solid, mp 103.0-104.0°C after recrystallization from pentane/CH_2Cl_2.

Anal. Calcd. for $C_{18}H_6Fe_3O_{10}$: C, 39.32; H, 1.10 %. Found: C, 39.44; H, 1.18 %.

IR(CCl_4): 3100vw, 3080vw, 2965vs, 2935vs, 2880s, 2870sh, 1878vs(μ-CO), 1604vw(Ph), 1582vw(Ph), 1548vw(Ph), 1498m, 1465m, 1434w, 1382w, 1318vw, 1264w, 1197vw, 1180vw, 1076w, 1030w, 1002vw, 923w, 910vw, 870w, 709s, 700s, 631s, 600vs, 580vs cm^{-1}.
Terminal carbonyl region (pentane): 2095m, 2050vs, 2025vs, 1985m, and 1892s(μ-CO) cm^{-1}.

^{1}H NMR(CD_2Cl_2; 250 MHz): δ 7.27-7.56 (m, C_6H_5 and C=C$\underline{H}$Ph).

^{13}C NMR($CDCl_3$; 67.9 MHz): δ 102.73 (d, J = 158.5 Hz, C=$\underline{C}$HPh), 128.42 (d, J = 165.0 Hz, C_6H_5), 129.51 (d, J = 158.6 Hz, C_6H_5), 142.37 (s, ipso C_6H_5), 210.40 (broad s, Fe-CO), 274.14 (s, $\underline{C}$=CHPh).

Mass Spectrum (EI); m/z (relative intensity): 550 (M^+, 12), 522(M^+ - CO, 25), 494 (M^+ - 2CO, 7), 466 (M^+ - 3CO, 31), 438 (M^+ - 4CO, 42), 410 (M^+ - 5CO, 45), 382 (M^+ - 6CO, 85), 354 (M^+ - 7CO, 73), 326 (M^+ - 8CO, 57), 298 (M^+ - 9CO, 89), 270 (M^+ - 10CO, 100), 214 (M^+ - 10CO-Fe, 84), 168 (Fe_3, 9), 158 (FeC=CHPh, 24), 157 (FeC=CPh, 33), 112 (Fe_2, 58), 102 (C=CHPh, 21), 77 (Ph, 3), 56 (Fe, 29).

Synthesis of (μ_3,η^2-C=CHCH$_2$OCH$_3$)(μ-CO)Fe$_3$(CO)$_9$ JBH-6-VI

In an experiment similar to the synthesis of 4a, a THF solution containing 1.46 g (2.53 mmol) of [Et_3NH][$HFe_3(CO)_{11}$] and 0.38 g (2.53 mmol) of methoxymethylbromoacetylene was stirred for 20 h at room temperature. The solvent then was removed in vacuo, and the resulting black oil was purified by filtration chromatography. Pentane eluted pale green and pale orange bands which were not collected and also a dark green band which gave 0.51 g (0.98 mmol; 39%) of (μ_3,η^2-C=CHCH$_2$OCH$_3$)(μ-CO)Fe$_3$(CO)$_9$, 4b, as a slightly air-sensitive, green oil.

Anal. Calcd. for $C_{14}H_6Fe_3O_{11}$: C, 32.48; H, 1.17 %. Found: C, 32.68; H, 1.23 %.

IR(CCl_4): 2990w, 2960w, 2925w, 2890w, 2820w, 1885vs(μ-CO), 1850sh(μ-CO), 1473w, 1450w, 1410w, 1363vw, 1285vw, 1260w, 1225vw, 1192w, 1115s, 1102s, 1063w, 1020w, 960w, 913w, 680m, 632s, 607vs, 580vs cm^{-1}.
Terminal carbonyl region (pentane): 2090w, 2050s, 2020s, 1983w, and 1887w(μ-CO), 1860sh(μ-CO) cm^{-1}.

^{1}H NMR($CDCl_3$; 300 MHz): δ 3.52 (s, 3H, OCH_3), 4.04 (m, 2H, $C\underline{H}_2OCH_3$), 6.06 (t, J = 6.30 Hz, 1H, $C=C\underline{H}CH_2OCH_3$).

^{13}C NMR($CDCl_3$; 75.4 MHz): δ 58.16 (q, J = 141.5 Hz, OCH_3), 78.80 (t, J = 137.7 Hz, $\underline{C}H_2OCH_3$), 95.24 (d, J = 159.0

Hz, C=$\underline{C}HCH_2OCH_3$), 210.44 (s, Fe-CO), 288.16 (s, $\underline{C}=CHCH_2OCH_3$).

Synthesis of (μ_3,η^2-C=CHSiMe$_3$)(μ-CO)Fe$_3$(CO)$_9$ **JBH-55-V**

In an experiment similar to the synthesis of 4a, a THF solution containing 1.73 g (2.99 mmol) of [Et$_3$NH][HFe$_3$(CO)$_{11}$] and 0.45 ml (2.99 mmol) of trimethylsilylbromoacetylene was stirred for 20 h at room temperature. The solvent then was removed in vacuo, and the resulting dark red oil was purified by filtration chromatography. Pentane eluted orange and olive green bands which were collected together. The resulting red-brown oil was repurified by column chromatography. Pentane eluted a pale red band which appeared to decompose slowly on the column and was not collected. Pentane then eluted a brown-green band which gave 0.28 g (0.52 mmol; 17%) of (μ_3,η^2-C=CHSiMe$_3$)(μ-CO)Fe$_3$(CO)$_9$, 4c, as a slightly air-sensitive, brown-green oil.

Anal. Calcd. for $C_{15}H_{10}Fe_3O_{10}Si$: C, 33.00; H, 1.85 %. Found: C, 33.11; H, 2.04 %.

IR(CCl_4): 2958m, 2925m, 2895m, 1880s(μ-CO), 1842w(μ-CO), 1632w, 1405m, 1370s, 1265m, 1250m, 1215vw, 842vs, 653s, 608vs, 568vs cm^{-1}.
Terminal carbonyl region (pentane): 2090m, 2050vs, 2030vs, 2018vs, 1980w, 1973w, and 1880m(μ-CO), 1842vw(μ-CO) cm^{-1}.

^{1}H NMR($CDCl_3$; 300 MHz): δ 0.34 (s, 9H, Si(CH$_3$)$_3$), 5.36 (s, 1H, C=C$\underline{H}$SiMe$_3$).

^{13}C NMR($CDCl_3$; 75.4 MHz): δ 0.91 (q, J = 120.6 Hz, Si(CH$_3$)$_3$), 96.72 (d, J = 133.8 Hz, C=$\underline{C}$HSiMe$_3$), 211.34 (s, Fe-CO), 291.95 (s, $\underline{C}$=CHSiMe$_3$).

Synthesis of (μ_3,η^2-C=CHEt)(μ-CO)$Fe_3(CO)_9$ JBH-65-V

In an experiment similar to the synthesis of 4a, a THF solution containing 1.85 g (3.20 mmol) of $[Et_3NH][HFe_3(CO)_{11}]$ and 0.64 g (4.80 mmol) of ethylbromoacetylene was stirred for 40 h at room temperature. The solvent then was removed in vacuo, and the resulting dark solid was purified by filtration chromatography. Pentane eluted a pale yellow band which was not collected and also an olive green band which gave 0.75 g (1.49 mmol; 47%) of (μ_3,η^2-C=CHEt)(μ-CO)$Fe_3(CO)_9$, 4d, as a slightly air-sensitive, oily, green solid.

Anal. Calcd. for $C_{14}H_6Fe_3O_{10}$: C, 33.51; H, 1.20 %. Found: C, 33.31; H, 1.29 %.

IR(CCl_4): 2965w, 2925w, 2870w, 1880vs(μ-CO), 1850sh(μ-CO), 1453w, 1439w, 1408w, 1381vw, 1315vw, 1285vw, 1260w, 1098w, 1021w, 903w, 863w, 678m, 625vs, 607vs, 580vs cm^{-1}.
Terminal carbonyl region (pentane): 2086w, 2042vs, 2028vs, 1979m, and 1885m(μ-CO), 1859sh(μ-CO) cm^{-1}.

^{1}**H NMR**(C_6D_6; 300 MHz): δ 0.96 (t, J = 7.30 Hz, 3H, $CH_2C\underline{H}_3$), 1.88 (very broad s, 1H, $C\underline{H}_2CH_3$ diastereotopic CH_2), 2.10 (very broad s, 1H, $C\underline{H}_2CH_3$ diastereotopic CH_2), 5.69 (t, J = 6.95 Hz, 1H, $C{=}C\underline{H}CH_2CH_3$).

^{13}**C NMR**(acetone-d_6; 75.4 MHz): δ 16.47(q, J = 126.6 Hz, $CH_2\underline{C}H_3$), 35.92 (t, J = 129.4 Hz, $\underline{C}H_2CH_3$), 105.05 (d, J = 154.9 Hz, $C{=}\underline{C}HEt$), 212.39 (s, Fe-CO), 287.78 (s, $\underline{C}{=}CHEt$).

Synthesis of (μ_3,η^2-C=CH^{n}Pr)(μ-CO)$Fe_3(CO)_9$ JBH-64-V

In an experiment similar to the synthesis of 4a, a THF solution containing 1.83 g (3.16 mmol) of $[Et_3NH][HFe_3(CO)_{11}]$ and 0.59 g (4.75 mmol) of n-propylbromoacetylene was stirred for 40 h at room temperature. The solvent then was removed in vacuo, and the resulting dark green tar was purified via filtration chromatography. Pentane eluted a pale yellow band which was not collected and also an olive green band which gave 0.78 g (1.51 mmol; 48%) of (μ_3,η^2-C=CH^{n}Pr)(μ-CO)Fe$_3$(CO)$_9$, 4e, as a slightly air-sensitive, green oil.

Anal. Calcd. for $C_{15}H_8Fe_3O_{10}$: C, 34.93; H, 1.56 %. Found: C, 35.02; H, 1.56 %.

IR(CCl_4): 2980m, 2925vw, 2865w, 1882vs(μ-CO), 1850sh(μ-CO), 1465w, 1453w, 1440w, 1408w, 1380vw, 1340vw, 1295vw, 1260w, 1103w, 1090w, 993w, 963vw, 672s, 625vs, 608vs, 580vs cm^{-1}.
Terminal carbonyl region (pentane): 2085w, 2042vs, 2025vs, 1979m, and 1885m(μ-CO), 1858sh(μ-CO) cm^{-1}.

^{1}**H NMR**(C_6D_6; 300 MHz): δ 0.81 (t, J = 7.32 Hz, 3H, $CH_2CH_2C\underline{H}_3$), 1.40 (m, 2H, $CH_2C\underline{H}_2CH_3$), 1.99 (overlapping dt, J = 7.43 Hz, J = 6.62 Hz, 2H, $C\underline{H}_2CH_2CH_3$), 5.74 (t, J = 6.59 Hz, $C{=}C\underline{H}CH_2CH_2CH_3$).

^{13}**C NMR**($CDCl_3$; 67.9 MHz): δ 13.54 (q, J = 125.7 Hz, CH_3), 25.20 (t, J = 126.6 Hz, $CH_2\underline{C}H_2CH_3$), 43.92 (t, J = 128.1 Hz, $\underline{C}H_2CH_2CH_3$), 101.93 (d, J = 153.7 Hz, C=$\underline{C}$H^{n}Pr), 211.09 (s, Fe-CO), 285.78 (s, $\underline{C}$=CH^{n}Pr).

Synthesis of (μ_3,η^2-C=CH^{n}Bu)(μ-CO)Fe$_3$(CO)$_9$ JBH-50-V

In an experiment similar to the synthesis of 4a, a THF solution containing 1.74 g (3.01 mmol) of [Et$_3$NH][HFe$_3$(CO)$_{11}$] and 0.39 ml (3.01 mmol) of n-butylbromoacetylene was stirred for 40 h at room temperature. The solvent then was removed in vacuo, and the resulting red-brown oil was purified by filtration chromatography. Pentane eluted a green band which gave 0.70 g (1.32 mmol; 44%) of (μ_3,η^2-C=CH^{n}Bu)(μ-CO)Fe$_3$(CO)$_9$, 4f, as a slightly air-sensitive, green oil.

Anal. Calcd. for $C_{16}H_{10}Fe_3O_{10}$: C, 36.27; H, 1.90 %. Found: C, 36.54; H, 2.05 %.

IR(CCl_4): 2955s, 2920s, 2870m, 2855m, 1885vs(μ-CO), 1860sh(μ-CO), 1455w, 1440w, 1408vw, 1380vw, 1290vw, 1260s, 1215vw, 1108w, 1008vw, 925vw, 890vw, 860vw, 695m, 670s, 625vs, 600vs cm^{-1}.
Terminal carbonyl region (pentane): 2089m, 2055vs, 2032vs, 2010vs, 2002m, 1975m, and 1885m(μ-CO), 1858sh(μ-CO) cm^{-1}.

^{1}**H NMR**($CDCl_3$; 300 MHz): δ 0.99 (t, J = 7.32 Hz, 3H, $CH_2C\underline{H}_3$), 1.54 (m, 2H, CH_2), 1.82 (m, 2H, CH_2), 2.39 (m, 2H, CH_2), 6.04 (t, J = 6.38 Hz, 1H, $C{=}C\underline{H}CH_2CH_2CH_2CH_3$).

^{13}**C NMR**($CDCl_3$; 75.4 MHz): δ 13.77 (q, J = 128.6 Hz, CH_3), 20.68 (t, J = 123.3 Hz, $CH_2CH_2\underline{C}H_2CH_3$), 34.12 (t, J = 127.0 Hz, $CH_2\underline{C}H_2CH_2CH_3$), 41.69 (t, J = 129.4 Hz, $\underline{C}H_2CH_2CH_2CH_3$), 102.28 (d, J = 156.2 Hz, C=$\underline{C}$H^{n}Bu), 211.07 (s, Fe-CO), 285.55 (s, $\underline{C}$=CH^{n}Bu).

Attempted Reaction between $[Et_3NH][HFe_3(CO)_{11}]$ and $^tBuC{\equiv}CBr$

JBH-39-V

In an experiment similar to the synthesis of 4a, a THF solution containing 2.00 g (3.46 mmol) of $[Et_3NH][HFe_3(CO)_{11}]$ and 0.48 ml (3.80 mmol) of t-butylbromoacetylene was stirred for 20 h at room temperature. No reaction was observed by TLC.

Attempted Reaction between $[Et_3NH][HFe_3(CO)_{11}]$ and $Me_2NCH_2C{\equiv}CBr$ JBH-69-V

In an experiment similar to the synthesis of 4a, a THF solution containing 1.97 g (3.40 mmol) of $[Et_3NH][HFe_3(CO)_{11}]$ and 0.55 g (3.40 mmol) of dimethylaminomethylbromoacetylene was stirred for 24 h at room temperature. An initial olive green product was observed by TLC after the reaction mixture had been stirred for 15 min, but apparently this complex was thermally unstable. After the reaction mixture had been stirred for 24 h at room temperature, no product was observed by TLC.

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BIOGRAPHICAL SKETCH

The author was born and raised in State College, Pennsylvania, the son of Mr. and Mrs. John Hoke. The last of five children to attend the State College Area High School (1976-1979), he then enrolled at The Pennsylvania State University. After two unsettling years in the chemical engineering curriculum learning more engineering than chemistry, he finally "saw the light" (thanks Roy!) and "converted" with a glad heart to chemistry. Part-time employment as an assistant computer programmer and membership in the marching and concert Blue Bands provided welcome diversions. After completing several semesters of undergraduate research for Prof. Gregory Geoffroy in organometallic synthesis as well as spending one summer at Brookhaven National Laboratory pursuing research in laser spectroscopy, the author received his Bachelor of Science degree with Honors and Highest Distinction in May 1983. Coincidentally, that was the same year the Penn State Nittany Lions won their first gridiron national championship (WE ARE .....! PENN STATE ......!). Playing clarinet in the marching band had its benefits!

Since the fall of 1983, the author has been engaged in organometallic research for Prof. Dietmar Seyferth at the Massachusetts Institute of Technology, the results of which are embodied in this thesis.

After receiving his Ph. D. degree, the author plans to join Engelhard Corporation - New Business Research, Menlo Park, New Jersey.

ACKNOWLEDGEMENTS

The author would like to recognize the following people who have helped to make this thesis a reality:

Dietmar Seyferth, for his support and encouragement, and his willingness to let me try my own ideas even though they didn't always work;

Dr. John Dewan, Prof. Arnold Rheingold, Prof. Martin Cowie, and Dr. Allen Hunter who solved the crystal structures presented in this thesis. Seyferth crystals may look like "____", but they WORK!;

The spec lab staff, especially Debbie and Ed for providing the EI mass specs, and Jeanne and Adam for their ready advice and assistance;

The staff of the Regional Mass Spec Facility for providing the FD and FAB mass specs;

Tim Wood for being a great teacher and coworker;

Will Rees and David Ruschke for graciously taking their time to proofread this thesis;

David Wheeler for providing technical assistance (as well as Montanan humor);

Gary Womack for discovering the magic reagent, $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$;

The "Big Lab" (Henry, Jutta, Chris and Wilbur) who made the past year and a half the best year and a half of graduate school. It wasn't lonely "over there" anymore;

Other members of the Seyferth group past and present, especially David, Joanne, Karen, and Colin who were there for guidance, companionship, and commiseration;

Bill, Elsa, Uncle Aaron, and Aunt Maude who always welcomed us when we needed to see a familiar face and take a break from student life;

and especially my wife, Elaine, whose constant support and encouragement kept me going these past four years. Her calm always brightened an otherwise sour day when nothing ever seemed to work right. Thanks for all the help in proofreading those dreaded "data" cards and putting up with late nights at the computer (or was it the Averof?). Just remember, "one in the upper left hand corner H" means proton, and "thirteen in the upper left hand corner C" means carbon-13.