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Reactions of $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ Anions with Heterocumulenes and with Elemental Sulfur

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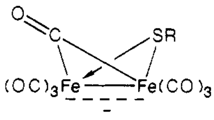
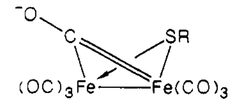
Salts of the type $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ react with CS_2 to give $[Et_3NH][(\mu\text{-SC}{=}S)(\mu\text{-RS})Fe_2(CO)_6]$ complexes which readily react at the exo sulfur atom with diverse organic and inorganic halides. A similar reaction with R′NCS and CH_3NCO gives neutral products via deprotonation of the Et_3NH^+ cation by the $[(\mu\text{-R'NC}{=}X)(\mu\text{-RS})Fe_2(CO)_6]^-$ anion originally formed. $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ also react with S_8 to form $[(\mu\text{-S})(\mu\text{-RS})Fe_2(CO)_6]^-$ anions. The reaction with SO_2 gives $[Et_3NH][(\mu\text{-SO}_2)(\mu\text{-RS})Fe_2(CO)_6]$ complexes. An X-ray diffraction study of the compound where R = *t*-Bu showed that the SO_2 ligand is S-bonded to the iron atoms. Crystal data for $Fe_2C_{16}H_{25}NO_8S_2$: $P2_1$ (No. 4), a = 9.2071 (14) Å, b = 9.3672 (18) Å, c = 14.1126 (26) Å, β = 93.31 (1)°, V = 1215.13 (34) Å^3, Z = 2, R = 0.0428 for 1635 reflections.

Introduction

In previous communications[1] we have described the synthesis of salts of the anions $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ by the reaction of thiolates (RSLi or RSH/Et_3N) in THF with $Fe_3(CO)_{12}$. These anions have ambident reactivity, as might be expected from their description in terms of canonical forms **1a** and **1b**. With the exception of the O-alkylation by $[Et_3O][BF_4]$, all reactions of the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anions can be rationalized in terms of their action as metal-centered nucleophiles. Reactions with acid chlorides, with allyl chloride, and with propargyl bromide, for instance, gave neutral products in which the organic group has replaced the μ-CO ligand of the anion as a bridging group. In this paper we describe reactions of $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anions with some heterocumulenes, as well as with a few other substrates, all of which result in formation of anionic initial products.



1a

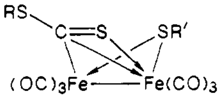


1b

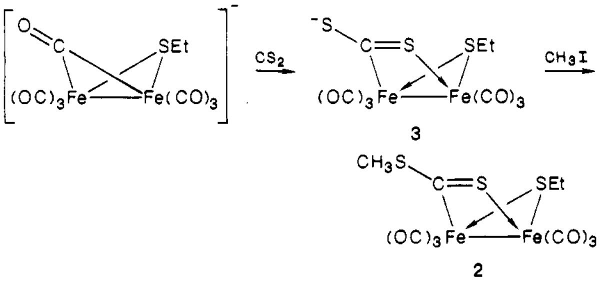
Results and Discussion

The reactivity of carbon disulfide toward charged nucleophiles is well-known,[2] and diverse carbon disulfide complexes of transition metals have been prepared and studied.[3] Accordingly, we examined the reaction of CS_2 with anions prepared by the $RSH/Et_3N/Fe_3(CO)_{12}$ reaction. When a molar equivalent of CS_2 was added to a red-brown THF solution of $[Et_3NH][(\mu\text{-CO})(\mu\text{-C}_2H_5S)Fe_2(CO)_6]$, a color change to red occurred. Examination of this red solution by infrared spectroscopy showed that the $[(\mu\text{-CO})(\mu\text{-EtS})Fe_2(CO)_6]^-$ anion had been consumed since the bridging CO frequency at 1743 cm^{-1} had disappeared; only terminal CO bands in the region 2060–1980 cm^{-1} were observed. Addition of iodomethane resulted in precipitation of a white solid. Workup of the reaction mixture gave a red, air-stable solid in 96% yield. On the basis of its analysis and its IR and ^{1}H and ^{13}C NMR spectra it was identified as the $CH_3S\text{-C}{=}S$-bridged complex **2** (a single isomer by NMR). This product must have been formed as shown in eq 1. Intermediate **3** then is an anionic CS_2 complex. Products of type **2** were already known, having been prepared by the reaction of $Fe_2(CO)_9$ with trithiocarbonate esters (eq 2).[4] An X-ray diffraction study of one such product confirmed this structure.[4]

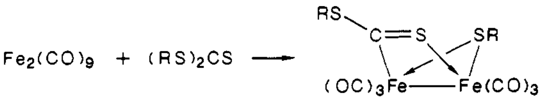
Table I



R	R′	δ_C(C=S)	yield, %
Me	Et	306.0	96
$PhCH_2$	Et	304.6	94
Me	*t*-Bu	307.8	80
Et	*t*-Bu	307.1	79
$PhCH_2$	*t*-Bu	305.8	59
$CH_2{=}CHCH_2$	*t*-Bu	306.4	32
PhC(O)	*t*-Bu	321.2	80



(1)



(2)

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[1] (a) Seyferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398. (b) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Organometallics*, in press.

[2] For instance, reactions with organolithium reagents: (a) Schönberg, A.; Stephenson, A.; Kaltschmitt, H.; Petersen, E.; Schulten, H. *Ber. Deutsch. Chem. Ges.* **1933**, *66*, 237. (b) Micetich, R. G. *Can. J. Chem.* **1970**, *48*, 2006. (c) Meijer, J.; Ruitenberg, K.; Westmijze, H.; Vermeer, P. *Synthesis* **1981**, 551.

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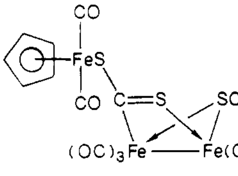
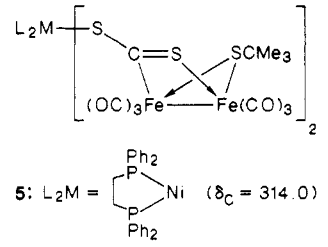
The S-benzyl derivative also was prepared by the eq 1 route. It is noteworthy that it was obtained in high yield even though the CS_2 was added 4 h after the benzyl chloride. Apparently, anion **3** is not reactive toward benzyl chloride, so this halide remains unreacted in solution together with the $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ until the CS_2 has reacted with the latter. Other products of type **2** were prepared, including one derived from an acid chloride. They are listed in Table I. Inorganic electrophiles also reacted readily with anions of type **3**. Prepared by reaction of $[(\mu\text{-}SC{=}S)(\mu\text{-}Me_3CS)Fe_2(CO)_6]^-$ with the appropriate mono- or dihalide were complexes **4**–**7**. As Table I shows, a characteristic of all of the CS_2-derived complexes is a ^{13}C resonance at low field, below 300 ppm, due to the bridging carbon atom of the RSC=S moiety.



4 (δ_C = 320.7)

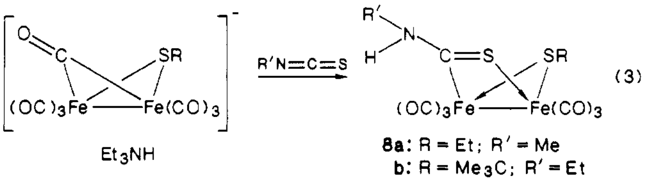


5: L_2M = (δ_C = 314.0)

6: $L_2M = (Ph_3P)_2Pd$ (δ_C = 309.3)

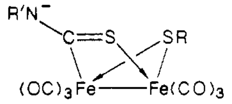
7: $L_2M = (Ph_3P)_2Pt$ (δ_C = 305.6)

As expected,[5] anions of type $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ also reacted with organic isothiocyanates (eq 3). Products of type **8** were isolated even in reactions in which iodomethane was added to the reaction mixture at a time when it was assumed that the anionic product **9** would be present. It would appear that anions of type **9** react rapidly to deprotonate the Et_3NH^+ counterion, so that only the neutral product **8** is present when the CH_3I is added. Methyl isocyanate did not react with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ in THF at room temperature, but a reaction which gave the expected product **10** in 33% yield did take place when the reaction solution was heated at reflux for 30 min.



(3)

8a: R = Et; R′ = Me
b: R = Me_3C; R′ = Et
c: R = Me_3C; R′ = Ph



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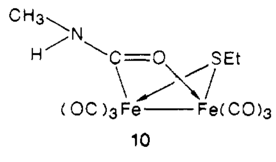


10

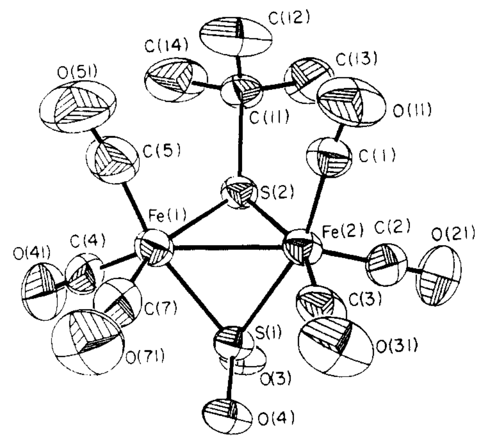
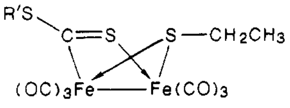


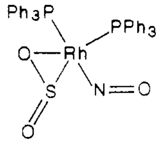
Figure 1. ORTEP representation of the molecular structure of the anion $[(\mu\text{-}SO_2)(\mu\text{-}(CH_3)_3CS)Fe_2(CO)_6]^-$. Probability ellipsoids are drawn at the 50% level.

In all of these reactions only one of the two possible (axial R, equatorial R on S) isomers appeared to have been formed. The ^{13}C NMR spectra of the SEt complexes indicated that the ethyl group is oriented equatorially as in **11**, since the SCH_2 carbon resonances, observed at δ_C = 35.8, 35.1, 32.6, and 35.3, are very similar to those for the equatorial SCH_2 carbons of the μ-acyl complexes $(\mu\text{-}RC{=}O)(\mu\text{-}EtS)Fe_2(CO)_6$.[1] Compounds of type **11** have a chiral framework, which renders the SCH_2 protons diastereotopic. For this reason the SCH_2 proton signals appear as complex multiplets in the ^1H NMR spectra and the SCH_2Ph methylene proton signals as an AB quartet. The C=S ^{13}C resonances of the thiocarbamoyl complexes of type **8** occurred at higher field (244–255 ppm), compared with the C=S ^{13}C resonances of the CS_2-derived complexes.



11

Although sulfur dioxide, when it is a ligand in transition-metal complexes, usually is bonded to the metal via sulfur, there is one example of a rhodium complex in which SO_2 is bonded through sulfur and one oxygen, **12**.[6] In three dinuclear iron complexes, **13**, **14**, and **15**, the SO_2 ligand was sulfur-bonded. We found the reaction of sulfur dioxide with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ (R = t-Bu and Et) to proceed readily at −78 °C as evidenced by a brown-red to red color change when gaseous SO_2 was condensed into solutions of these salts. The SO_2 adducts were isolated in good yield as red-orange crystals, **16**. An



12

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(5) For instance, RNCO and RNCS react with organolithium reagents: (a) LeBel, N. A.; Cherluck, R. M.; Curtis, E. A. *Synthesis* **1973**, 678 (RNCO). (b) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon: Oxford, 1974; Chapter 9 (RNCO). (c) Gilman, H.; Brewer, F. *J. Am. Chem. Soc.* **1933**, *55*, 1262. (d) Gosselin, P.; Masson, S.; Thullier, A. *Tetrahedron Lett.* **1978**, 2715. (e) Zakharkin, L. I.; Kazantseva, A. A. *Zh. Obshch. Khim.* **1967**, *37*, 554.

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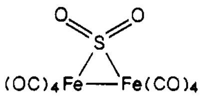
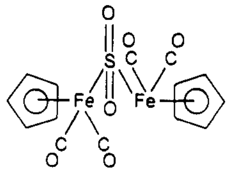
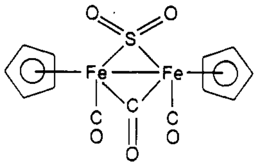


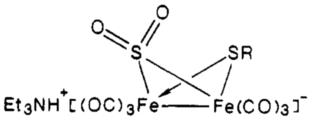
13 (ref 7)



14 (ref 8)



15 (ref 9)



16a: R = Me$_3$C
b: R = Et

X-ray diffraction study of the product with R = *t*-Bu showed the SO_2 ligand to be sulfur-bonded symmetrically between the two Fe atoms of the $Fe_2(CO)_6$ unit, as shown in Figure 1. The Fe–S bond lengths of 2.214 (7) and 2.208 (7) Å involving the SO_2 ligand are comparable to those found in other SO_2-bridged diiron complexes (e.g., 2.220 (5) Å in **13** and 2.184 (3) Å in **15**. The S═O bonds of the μ-SO_2 ligand are 1.462 (9) and 1.482 (9) Å, slightly longer than those in SO_2 in the gas phase, 1.432 (3) Å.[10] This elongation of the S═O bonds of the SO_2 ligand is expected since the orbital used for back bonding in SO_2 is S—O antibonding in nature.[11] The thiolate bridge of **16a** also is bonded symmetrically to the two Fe atoms with Fe-S distances of 2.274 (8) and 2.267 (7) Å; these do not differ markedly from the Fe–S bond lengths of other Fe–SR–Fe bridged species. A complete list of bond lengths and angles is given in Table II.

In the $[(\mu\text{-}SO_2)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]^-$ anion each metal atom may be regarded as Fe(0) and therefore possesses a d^8 electronic configuration. The stable 18-electron configuration for each iron atom is achieved by the donation of six electrons to each metal from the terminal CO ligands, two to each iron atom from the bridging *t*-BuS$^-$ anion and the donation of one electron to each metal by the μ-SO_2 ligand. The Fe–Fe single bond provides the remaining electron required for the noble-gas configuration. The Fe–Fe separation of 2.593 (8) Å and the Fe–S–Fe bond angles of 69.7 (2)° and 71.8 (2)° are indicative of the metal–metal single-bond interaction. From the comparison of bond distances and angles in the $[(\mu\text{-}SO_2)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]^-$ anion to those of related nonionic dimers (e.g., **13** and **15**), it is apparent that the negative charge associated with our anion has not manifested itself in the structure. In the absence of structural changes, the charge may be considered to be delocalized in the four-membered iron–sulfur ring.

In all of the reactions discussed above the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anion reacted with a neutral electrophile to give a new anion. Another reaction of the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anions which results in an anionic product is that with elemental sulfur, which reacts readily with many charged nucleophiles[12] (eq 4). Alkylation of the anionic product **17** with iodomethane gave $(\mu\text{-MeS})(\mu\text{-}$

Table II. Bond Lengths and Bond Angles in $[HNEt_3][(\mu\text{-}SO_2)(\mu\text{-}(CH_3)_3CS)Fe_2(CO)_6]$ with Estimated Standard Deviations in the Last Digit in Parentheses

	Bond Lengths (Å)		
Fe(1)-Fe(2)	2.593 (8)		
	Bridging SO_2 Ligand		
Fe(1)-S(1)	2.214 (7)	Fe(2)-S(1)	2.208 (7)
S(1)-O(4)	1.462 (9)	S(1)-O(3)	1.482 (9)
	Bridging $[CH_3]_3CS$ Ligand		
Fe(1)-S(2)	2.274 (8)	Fe(2)-S(2)	2.267 (7)
S(2)-C(11)	1.878 (12)	C(11)-C(12)	1.529 (20)
C(11)-C(13)	1.493 (20)	C(11)-C(14)	1.522 (19)
	Terminal CO Ligands		
Fe(1)-C(4)	1.820 (13)	Fe(1)-C(5)	1.794 (14)
Fe(1)-C(7)	1.756 (15)	Fe(2)-C(1)	1.804 (11)
Fe(2)-C(2)	1.769 (12)	Fe(2)-C(3)	1.789 (13)
C(1)-O(11)	1.141 (12)	C(2)-O(21)	1.156 (14)
C(3)-O(31)	1.125 (15)	C(4)-O(41)	1.134 (15)
C(5)-O(51)	1.152 (18)	C(7)-O(71)	1.172 (18)
	Triethylammonium Cation		
N(1)-C(21)	1.535 (14)	N(1)-C(31)	1.524 (15)
N(1)-C(41)	1.546 (14)	C(21)-C(22)	1.530 (18)
C(31)-C(32)	1.523 (18)	C(41)-C(42)	1.515 (18)
	Bond Angles (deg)		
	About the Metal Atoms		
	Involving the SO_2 and Thiolate Ligands Only		
Fe(1)-Fe(2)-S(1)	54.2 (2)	Fe(1)-Fe(2)-S(2)	55.3 (2)
Fe(2)-Fe(1)-S(1)	54.0 (2)	Fe(2)-Fe(1)-S(2)	55.0 (2)
S(1)-Fe(1)-S(2)	77.9 (2)	S(1)-Fe(2)-S(2)	78.2 (2)
Fe(1)-S(1)-Fe(2)	71.8 (2)	Fe(1)-S(2)-Fe(2)	69.7 (2)
Fe(1)-S(1)-O(3)	118.0 (4)	Fe(1)-S(1)-O(4)	116.6 (4)
Fe(2)-S(1)-O(3)	118.6 (4)	Fe(2)-S(1)-O(4)	117.0 (3)
Fe(1)-S(2)-C(11)	121.5 (4)	Fe(2)-S(2)-C(11)	120.9 (4)
	Involving the Carbonyl Ligands Only		
C(1)-Fe(2)-C(2)	101.7 (5)	C(1)-Fe(2)-C(3)	88.4 (6)
C(2)-Fe(2)-C(3)	101.0 (5)	C(4)-Fe(1)-C(5)	102.2 (6)
C(4)-Fe(1)-C(7)	98.4 (6)	C(5)-Fe(1)-C(7)	87.2 (7)
Fe(1)-Fe(2)-C(1)	106.9 (3)	Fe(1)-Fe(2)-C(2)	142.5 (4)
Fe(1)-Fe(2)-C(3)	103.5 (4)	Fe(2)-Fe(1)-C(4)	144.0 (4)
Fe(2)-Fe(1)-C(5)	108.2 (4)	Fe(2)-Fe(1)-C(7)	101.9 (4)
Fe(1)-C(4)-O(41)	177.4 (10)	Fe(1)-C(5)-O(51)	172.3 (13)
Fe(1)-C(7)-O(71)	177.8 (10)	Fe(2)-C(1)-O(11)	173.5 (11)
Fe(2)-C(2)-O(21)	180.0 (14)	Fe(2)-C(3)-C(31)	176.9 (9)
	Involving the SO_2 and the Carbonyl Ligands		
S(1)-Fe(1)-C(4)	97.4 (4)	S(1)-Fe(1)-C(5)	160.4 (5)
S(1)-Fe(1)-C(7)	89.0 (4)	S(1)-Fe(2)-C(1)	159.0 (4)
S(1)-Fe(2)-C(2)	99.3 (4)	S(1)-Fe(2)-C(3)	88.0 (4)
	Involving the Thiolate and the Carbonyl Ligands		
S(2)-Fe(1)-C(4)	102.1 (4)	S(2)-Fe(1)-C(5)	98.8 (5)
S(2)-Fe(1)-C(7)	156.9 (4)	S(2)-Fe(2)-C(1)	98.8 (4)
S(2)-Fe(2)-C(2)	97.1 (4)	S(2)-Fe(2)-C(3)	158.8 (4)
	Internal Ligand Angle		
	Thiolate Angles		
S(2)-C(11)-C(12)	116.6 (9)	S(2)-C(11)-C(13)	105.1 (9)
S(2)-C(11)-C(14)	104.3 (8)	C(12)-C(11)-C(13)	110.2 (11)
C(12)-C(11)-C(14)	106.4 (11)	C(13)-C(11)-C(14)	114.4 (12)
	SO_2 Angle		
O(3)-S(1)-O(4)	110.4 (5)		
	Triethylammonium Cation Angles		
C(21)-N(1)-C(31)	111.0 (8)	C(21)-N(1)-C(41)	111.4 (8)
C(31)-N(1)-C(41)	111.4 (8)	N(1)-C(21)-C(22)	115.8 (9)
N(1)-C(31)-C(32)	111.5 (11)	N(1)-C(41)-C(42)	111.8 (9)

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[11] Mingos, D. M. P. *Transition Met. Chem. (Weinheim, Ger.)* **1978**, *3*, 1.

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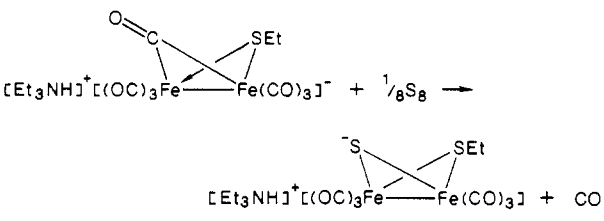

(4)

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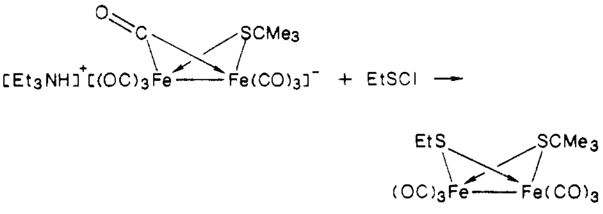
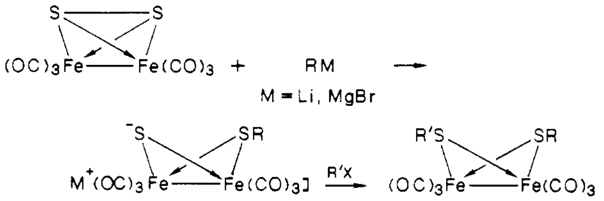
EtS)Fe$_2$(CO)$_6$ in 37% yield, and a 19% yield of (μ-EtS)$_2$Fe$_2$(CO)$_6$ also was obtained. This does not seem to be a useful preparative reaction. However, the [(μ-CO)(μ-RS)Fe$_2$(CO)$_6$]$^-$ anions did provide a useful route to Fe$_2$(CO)$_6$ complexes containing two different bridging thiolate ligands in their reactions with sulfenyl chlorides (eq 5). In earlier work we had developed still another route to such complexes (eq 6).[13]



(5)



(6)

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl. Carbon disulfide was distilled from phosphorus pentoxide. Reagent grade pentane, dichloromethane, ethanol, and methanol were deoxygenated by bubbling nitrogen through them for 15 min prior to use. Ethanethiol and 2-methylpropanethiol were deoxygenated by bubbling nitrogen through them for 15 min and used as obtained.

Filtration chromatography, in which the reaction products were dissolved in a suitable solvent and poured on top of a bed of Mallinckrodt 100-mesh silicic acid (ca. 200 mL) in a 350-mL glass-frit filter funnel, was used in most cases. Column chromatography was performed with a 350 × 25 mm column using silicic acid. All chromatography was done without exclusion of atmospheric oxygen or moisture. Solid products were recrystallized from deoxygenated solvents at −20 °C.

Infrared spectra were obtained by 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 250 NMR spectrometer operating at 90 and 250 MHz, respectively. ^{13}C NMR spectra were obtained by using a JEOL/FX-90Q or Bruker 270 NMR instrument operating at 22.5 and 67.9 MHz, respectively. ^{31}P{^{1}H} NMR spectra were obtained by using a JEOL/FX-90Q instrument operating at 36.2 MHz referencing to external 85% aqueous H$_3$PO$_4$. Mass spectra were obtained with a Finnigan-3200 spectrometer operating at 70 eV. Melting points were determined on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

The mass spectra were diagnostic of the doubly bridged Fe$_2$(CO)$_6$ complexes, showing (usually, but not always) the molecular ion and then six fragment ions, M$^+$ − nCO (n = 1–6).

Standard in Situ Preparation of [Et$_3$NH][(μ-CO)(μ-RS)Fe$_2$(CO)$_6$] Reagents. A 300-mL, three-necked, round-bottomed flask equipped with a stir bar and serum caps was charged with 1.5 g (2.98 mmol) of Fe$_3$(CO)$_{12}$ and flushed with nitrogen. Tetrahydrofuran (50 mL) was added by syringe followed by the addition of 0.25 mL (3.38 mmol) of ethanethiol and 0.48 mL (3.50 mmol) of triethylamine. The solution was stirred for 15 min prior to the addition of any reactants, during which time a color change of green to red-brown occurred.

Reactions of the Carbon Disulfide/[Et$_3$NH][(μ-CO)(μ-RS)Fe$_2$(CO)$_6$] Reaction Product 3 with Electrophiles. (1) Benzyl Chloride (R = Et). The standard Fe$_3$(CO)$_{12}$/EtSH/Et$_3$N reagent solution was prepared; to this solution was added 1.0 mL (8.7 mmol) of benzyl chloride. The solution was stirred at room temperature for 4 h, but TLC analysis of the mixture showed no product formation. At this point, 0.5 mL (8.0 mmol) of carbon disulfide was added. The solution was stirred for 20 h during which time it became red and a white precipitate formed. The solution was filtered and the solvent removed leaving a red oil. This oil was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Pentane/CH$_2$Cl$_2$ (9/1, v/v) eluted a red band which gave 1.42 g (2.79 mmol, 94% yield) of (μ-PhCH$_2$SCS)(μ-EtS)Fe$_2$(CO)$_6$ as a red, air-stable solid, mp 83–85 °C after crystallization from pentane/CH$_2$Cl$_2$.

Anal. Calcd for C$_{16}$H$_{12}$O$_6$S$_3$Fe$_2$: C, 37.82; H, 2.38. Found: C, 37.99; H, 2.57. IR, terminal carbonyl region (pentane): 2068 (s), 2027 (vs), 2000 (vs), 1997 (s), 1981 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): δ 1.47 (t, J = 7.5 Hz, 3 H, CH$_3$), 2.62 (m, 2 H, SCH$_2$), 4.32 (AB quartet, 2 H, J_{AB} = 13.1 Hz, SCH_2Ph), 7.30 (m, 5 H, Ph). ^{13}C NMR (CD$_2$Cl$_2$, 67.9 MHz): δ_C 18.7 (q, J = 129 Hz, CH$_3$), 35.8 (t, J = 142 Hz, SCH$_2$), 46.1 (t, J = 144 Hz, SCH$_2$Ph), 128.4 (d, J = 154 Hz, Ph), 129.3 (d, J = 160 Hz, Ph), 129.6 (d, J = 161 Hz, Ph), 134.3 (s, ipso Ph), 207.7, 210.8, 211.6 (all s, CO), 304.6 (s, C=S). Mass spectrum: m/z (relative intensity) 508 (M$^+$, 7), 480 (M$^+$ − CO, 10), 452 (M$^+$ − 2CO, 5), 424 (M$^+$ − 3CO, 82), 396 (M$^+$ − 4CO, 59), 368 (M$^+$ − 5CO, 39), 340 (M$^+$ − 6CO, 100), 312 (Fe$_2$S$_3$C$_8$H$_8$, 96), 249 (Fe$_2$S$_3$C$_3$H$_5$, 11), 264 (M$^+$ − 6CO − CS$_2$, 31), 236 (Fe$_2$SC$_7$H$_8$, 98), 221 (Fe$_2$S$_3$CH, 73), 176 (Fe$_2$S$_2$, 60), 144 (Fe$_2$S, 70), 91 (PhCH$_2$, 76).

(2) Iodomethane (R = Et). The standard Fe$_3$(CO)$_{12}$/EtSH/Et$_3$N reagent solution was prepared; to this solution was added 0.5 mL (8.0 mmol) of carbon disulfide. The mixture was stirred for 1 h prior to the addition of 0.5 mL (8.0 mmol) of iodomethane. Stirring then was continued for 2.5 h during which time the solution became red and a white precipitate formed. The solution was filtered and the solvent removed, leaving a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Pentane/CH$_2$Cl$_2$ (9/1, v/v) eluted a red band which gave 1.23 g (2.84 mmol, 96% yield) of (μ-MeSCS)(μ-EtS)Fe$_2$(CO)$_6$ as a red, air-stable solid, mp 77–78 °C after crystallization from pentane/CH$_2$Cl$_2$.

Anal. Calcd for C$_{10}$H$_8$O$_6$S$_3$Fe$_2$: C, 27.80; H, 1.87. Found: C, 28.01; H, 2.24. IR, terminal carbonyl region (pentane): 2068 (s), 2028 (vs), 2000 (vs), 1997 (s), 1982 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 1.46 (t, J = 7.3 Hz, 3 H, CH$_3$), 2.54 (s, 3 H, SCH$_3$), 2.59 (m, 2 H, SCH$_2$). ^{13}C NMR (CDCl$_3$, 67.9 MHz): δ_C 18.3 (q, J = 128 Hz, CH$_3$), 24.1 (q, J = 140 Hz, SCH$_3$), 35.1 (t, J = 141 Hz, SCH$_2$), 207.1, 210.2, 210.8 (all s, CO), 209.6 (br, CO), 306.0 (s, C=S).

(3) Iodomethane (R = t-Bu). The anion was generated in 50 mL of THF by using 3.07 g of Fe$_3$(CO)$_{12}$ (6.09 mmol), 0.61 g of Et$_3$N (6.02 mmol), and 0.54 g of [CH$_3$]$_3$CSH (6.04 mmol). After the green to red-brown color change occurred (indicating formation of the anion), 0.91 g of CS$_2$ (11.98 mmol) was added by syringe to the stirred reaction mixture. Gas evolution was observed, and the solution changed from red-brown to cherry red in color. This mixture was stirred for 15 min, and then 1.69 g of MeI (11.88 mmol) was added to the reaction mixture. No further color changes occurred. The reaction mixture was stirred at room temperature for an additional hour. The solvents were removed in vacuo to give a reddish residue which was extracted with 80:20

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[13] Seyferth, D.; Henderson, R. S.; Song, L-C.; Womack, G. B. *J. Organomet. Chem.* **1985**, *292*, 9.

pentane/$\mathrm{CH_2Cl_2}$ (v/v) and subjected to filtration chromatography on a pad of silicic acid (7 cm) packed in a 350-mL ground-glass fritted funnel. Elution with pentane gave one major band which yielded a red, crystalline, air-stable solid which was recrystallized from pentane to give 2.22 g (80%) of (μ-MeSCS)(μ-$\mathrm{Me_3CS}$)$\mathrm{Fe_2(CO)_6}$, mp 113.0–113.7 °C.

Anal. Calcd for $\mathrm{C_{12}H_{12}O_6S_3Fe_2}$: C, 31.33; H, 2.63. Found: C, 31.47; H, 2.65. IR, terminal CO region (pentane): 2064 (vs), 2028 (vs), 1992 (vs), 1959 (s), 1908 (w) $\mathrm{cm^{-1}}$. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): δ 1.47 (s, 9 H, $-\mathrm{SC(CH_3)_3}$), 2.78 (s, 3 H, $-\mathrm{SCSC}\mathit{H}_3$). ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): δ_C 24.2 (q, J_CH = 142.0 Hz, $-\mathrm{S}\mathit{C}\mathrm{H_3}$), 34.2 (q, J_CH = 127.1 Hz, $-\mathrm{SC}(\mathit{C}\mathrm{H_3})_3$), 50.7 (s, $-\mathrm{S}\mathit{C}\mathrm{(CH_3)_3}$), 207.3, 209.9 (br), 210.9 (all s's, carbonyl C's), 307.8 (s, S*C*SMe).

(4) Iodoethane (R = *t*-Bu). The same procedure as in (3), but with addition of iodoethane, gave (μ-EtSCS)(μ-$\mathrm{Me_3CS}$)$\mathrm{Fe_2(CO)_6}$, mp 108.4–109.0 °C, a red solid, in 79% yield.

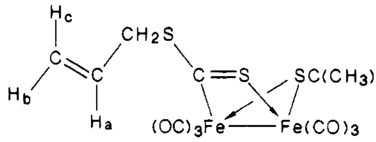
Anal. Calcd for $\mathrm{C_{13}H_{14}O_6S_3Fe_2}$: C, 32.94; H, 2.98. Found: C, 33.29; H, 3.04. IR, terminal CO region (pentane): 2064 (s), 2039 (vs), 1996 (vs), 1979 (s), 1953 (w) $\mathrm{cm^{-1}}$. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): δ 1.25 (t, J = 7.6 Hz, 3 H, $-\mathrm{SCH_2C}\mathit{H}_3$), 1.47 (s, 9 H, $-$ $\mathrm{SC[C}\mathit{H}_3]_3$), 3.09 (q, 2 H, J = 7.6 Hz, $-\mathrm{SC}\mathit{H}_2\mathrm{CH_3}$). ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): δ_C 11.7 (q, J_CH = 129.1 Hz, $-\mathrm{SCH_2}\mathit{C}\mathrm{H_3}$), 34.2 (q, $-$ $\mathrm{SC(}\mathit{C}\mathrm{H_3)_3}$), 35.0 (t, $-\mathrm{S}\mathit{C}\mathrm{H_2CH_3}$), 50.6 (s, $-$ $\mathrm{S}\mathit{C}\mathrm{(CH_3)_3}$), 207.3, 209.8 (br), 211.0 (all s's, carbonyl C's), 307.1 (s, S*C*SEt).

(5) Benzyl Chloride (R = *t*-Bu). The same procedure was used, but $\mathrm{PhCH_2Cl}$ was the added electrophile. The product (μ-$\mathrm{PhCH_2SCS}$)(μ-$\mathrm{Me_3CS}$)$\mathrm{Fe_2(CO)_6}$, a red solid, mp 80–81 °C, was obtained in 59% yield.

Anal. Calcd for $\mathrm{C_{18}H_{16}O_6S_3Fe_2}$: C, 40.32; H, 3.01. Found C, 40.33; H, 3.08. IR, terminal CO region (pentane): 2064 (s), 2038 (vs), 1966 (vs), 1979 (s), 1940 (w) $\mathrm{cm^{-1}}$. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): δ 1.41 (s, 9 H, $-\mathrm{SC(C}\mathit{H}_3)_3$), 4.22 (s, 2 H, $-\mathrm{SCSC}\mathit{H}_2-$), 7.18 (s, br, 5 H, phenyl H's). ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): δ_C 34.2 (q, J_CH = 126.9 Hz, $-\mathrm{SC[}\mathit{C}\mathrm{H_3]_3}$), 45.8 (t, J_CH = 143.4 Hz, $-\mathrm{S}\mathit{C}\mathrm{H_2C_6H_5}$), 50.8 (s, $-\mathrm{S}\mathit{C}\mathrm{(CH_3)_3}$), 128.0, 128.9, 129.1 (m, phenyl C's), 133.4 (s, ipso phenyl C), 207.1, 209.9 (br), 210.8 (all s's, carbonyl C's), 305.8 (s, $\mathrm{S}\mathit{C}\mathrm{SCH_2C_6H_5}$).

(6) Allyl Chloride (R = *t*-Bu). The same procedure was used with $\mathrm{CH_2{=}CHCH_2Cl}$ as the added electrophile. The red solid product (μ-$\mathrm{CH_2{=}CHCH_2SCS}$)($\mu$-$\mathrm{Me_3CS}$)$\mathrm{Fe_2(CO)_6}$, mp 54.5–55.5 °C (from pentane at −78 °C), was obtained in 32% yield.

Anal. Calcd for $\mathrm{C_{14}H_{14}O_6S_3Fe_2}$: C, 34.59; H, 2.90. Found: C, 34.60; H, 3.01.



^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ 1.47 (s, 9 H, $-\mathrm{SC(C}\mathit{H}_3)_3$), 3.74 (t, J = 6.3 Hz, $-$ $\mathrm{SCSC}\mathit{H}_2\mathrm{CH{=}CH_2}$), 5.19 (d, J = 5.3 Hz, 1 H, $\mathrm{H_b}$), 5.24 (d, J = 12.3 Hz, $\mathrm{H_C}$), 5.76 (m, 1 H, $\mathrm{H_a}$). ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): δ_C 34.2 (q, J_CH = 127.9 Hz, $-\mathrm{SC(}\mathit{C}\mathrm{H_3)_3}$), 43.7 (t, J_CH = 137.5 Hz, $-\mathrm{S}\mathit{C}\mathrm{H_2CH{=}CH_2}$), 50.8 (s, $-\mathrm{S}\mathit{C}\mathrm{[CH_3]_3}$), 120.7 (t, J_CH = 155.5 Hz, $-$ $\mathrm{SCH_2CH{=}}\mathit{C}\mathrm{H_2}$), 129.3 (d, J_CH = 150.1 Hz, $-\mathrm{SCH_2}\mathit{C}\mathrm{H{=}CH_2}$), 207.2, 209.9 (br), 210.8 (all s's, carbonyl C's), 306.4 (s, $\mathrm{S}\mathit{C}\mathrm{SCH_2CH{=}CH_2}$).

(7) Benzoyl Chloride (R = $\mathbf{Me_3C}$). The same procedure was used in the preparation of (μ-PhC(O)SCS)(μ-$\mathrm{Me_3CS}$)$\mathrm{Fe_2(CO)_6}$, a dark red solid, mp 91 °C, in 80% yield when benzoyl chloride was the electrophile. Solutions of this compound are air-sensitive.

Anal. Calcd for $\mathrm{C_{18}H_{14}O_7S_3Fe_2}$: C, 39.30; H, 2.56. Found: C, 39.29; H, 2.71. IR ($\mathrm{CCl_4}$): ν(C=O) 1670 $\mathrm{cm^{-1}}$. IR, terminal CO region ($\mathrm{CCl_4}$): 2080 (w), 2058 (vs), 2027 (s), 2014 (vs), 2000 (vs), 1995 (s), 1977 (m) $\mathrm{cm^{-1}}$. ^{1}H NMR (90 MHz, $\mathrm{CD_2Cl_2}$): δ 1.58 (s, 9 H, $-\mathrm{SC(C}\mathit{H}_3)_3$), 7.50–8.40 (m, 5 H, phenyl protons). ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): δ_C 30.7 (q, J_CH = 124.0 Hz, $-\mathrm{SC(}\mathit{C}\mathrm{H_3)_3}$), 42.1 (s, $-$ $\mathrm{S}\mathit{C}\mathrm{(CH_3)_3}$), 127.4–133.5 (m, phenyl C's), 137.6 (s, ipso phenyl carbon), 207.2, 209.1, 209.4 (all s's, carbonyl C's), 321.2 (s, $\mathrm{S}\mathit{C}\mathrm{SC[O]C_6H_5}$). Mass spectrum: *m/z* (relative intensity) 522 ($\mathrm{M^+}$ − CO, 1), 494 ($\mathrm{M^+}$ − 2CO, 2), 466 ($\mathrm{M^+}$ − 3CO, 7), 438 ($\mathrm{M^+}$ − 4CO, 4), 410 ($\mathrm{M^+}$ − 5CO, 4), 382 ($\mathrm{M^+}$ − 6CO, 18), 326 ($\mathrm{Fe_2CS_2Cl[O]C_6H_5][SH]}$, 13), 298 ($\mathrm{Fe_2[CS_2C_6H_5][SH]}$, 15), 254 ($\mathrm{Fe_2SC_6H_5][SH]}$, 4), 222 ($\mathrm{C_6H_6SFe_2}$, 4), 221 ($\mathrm{Fe_2SC_6H_5}$, 5), 176 ($\mathrm{Fe_2S_2}$, 11), 144 ($\mathrm{Fe_2S}$, 5), 105 ($\mathrm{C_7H_5O}$, 100), 77 ($\mathrm{C_6H_5}$, 49), 56 (Fe, 27).

(8) (η^5-$\mathbf{C_5H_5}$)Fe(CO)$_2$I (R = $\mathbf{Me_3C}$). The anion was generated in 50 mL of THF by using 1.54 g of $\mathrm{Fe_3(CO)_{12}}$ (3.06 mmol), 0.31 g of $\mathrm{Et_3N}$ (3.01 mmol), and 0.27 g of $\mathrm{(CH_3)_3CSH}$ (3.02 mmol). After the green to red-brown color change had occurred, 0.46 g of $\mathrm{CS_2}$ (5.99 mmol) was added to the stirred solution. After 30 min, 1.87 g of (η^5-$\mathrm{C_5H_5}$)$\mathrm{Fe(CO)_2I}$ (6.16 mmol) was added to the reaction mixture. The resulting mixture was stirred at room temperature for an additional 2 h. The solvents were removed in vacuo to give a dark residue which was extracted with 50:50 pentane/$\mathrm{CH_2Cl_2}$ (v/v) and subjected to filtration chromatography (silicic acid). The column was washed with 300 mL of pentane, and then a red-orange band was eluted with 9:1 pentane/$\mathrm{CH_2Cl_2}$ (v/v). This yielded a red-orange, crystalline, air-stable solid which was recrystallized from pentane/$\mathrm{CH_2Cl_2}$ to give 1.47 g (83%) of (μ-η^5-$\mathrm{C_5H_5Fe(CO)_2SCS}$)($\mu$-$\mathrm{Me_3CS}$)$\mathrm{Fe_2(CO)_6}$ which decomposed over the range 95–130 °C.

Anal. Calcd for $\mathrm{C_{18}H_{18}O_8S_3Fe_3}$: C, 34.76; H, 2.27. Found: C, 34.79; H, 2.30. IR, terminal carbonyls ($\mathrm{CCl_4}$): 2030 (s), 2020 (s), 2010 (vs), 2001 (s), 1984 (vs, br), 1973 (m, sh) $\mathrm{cm^{-1}}$. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): δ 1.44 (s, 9 H, $-\mathrm{SC(C}\mathit{H}_3)_3$), 4.97 (s, 5 H, η^5-$\mathrm{C_5}\mathit{H}_5$. ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): δ_C 34.2 (q, J_CH = 128.1 Hz, $-\mathrm{SC(}\mathit{C}\mathrm{H_3)_3}$), 49.9 (s, $-$ $\mathrm{S}\mathit{C}\mathrm{(CH_3)_3}$), 85.9 (d, J_CH = 180.5 Hz, η^5-$\mathrm{C_5H_5}$), 208.2, 210.7, 211.2, 212.0 (all s's, carbonyl C's), 320.7 (s, $-\mathrm{S}\mathit{C}\mathrm{SFe}-$). Mass spectrum: *m/z* (relative intensity) 624 ($\mathrm{M^+}$, 1), 594 ($\mathrm{M^+}$ − CO, 0.5), 566 ($\mathrm{M^+}$ − 2CO, 7), 538 ($\mathrm{M^+}$ − 3CO, 3), 510 ($\mathrm{M^+}$ − 4CO, 3), 482 ($\mathrm{M^+}$ − 5CO, 4), 454 ($\mathrm{M^+}$ − 6CO, 7), 426 ($\mathrm{M^+}$ − 7CO, 7), 398 ($\mathrm{M^+}$ − 8CO, 14), 342 ($\mathrm{Fe_3[CS_2C_5H_5][SH]}$, 16), 276 ($\mathrm{Fe_2[CS_2]SC[CH_3]_3}$, 5), 264 ($\mathrm{Fe_3S_3}$, 12), 186 ($\mathrm{FeCpCS_2H}$, 100), 121 (FeCp, 50), 76 ($\mathrm{SC_2}$, 48), 65 ($\mathrm{C_5H_5}$, 31), 56 (Fe, 39).

(9) ($\mathbf{Ph_2PCH_2CH_2PPh_2}$)$\mathbf{NiCl_2}$ (R = $\mathbf{Me_3C}$). The anion was generated in 50 mL of THF by using 1.50 g of $\mathrm{Fe_3(CO)_{12}}$ (2.98 mmol), 0.31 g of $\mathrm{Et_3N}$ (3.01 mmol), and 0.27 g of $\mathrm{(CH_3)_3CSH}$ (3.02 mmol). After the green to red-brown color change had occurred, 0.46 g of $\mathrm{CS_2}$ (5.99 mmol) was added to the stirred solution. After the solution was stirred for an additional 30 min, 0.85 g of (diphos)$\mathrm{NiCl_2}$ (1.62 mmol) was added to the reaction mixture by cannula as a suspension in 20 mL of THF. This reaction mixture was stirred for 3 h at room temperature. The solvents were removed in vacuo leaving a solid residue which was taken up in 50:50 pentane/$\mathrm{CH_2Cl_2}$ (v/v) and subjected to filtration chromatography. Elution with 80:20 pentane/$\mathrm{CH_2Cl_2}$ (v/v) yielded a red-orange, air-stable crystalline solid which was recrystallized from $\mathrm{CH_2Cl_2}$ to give 1.32 g (64%) of compound **5**. The latter decomposed over the range 95–135 °C, giving a black solid which did not melt below 400 °C.

Anal. Calcd for $\mathrm{C_{48}H_{42}O_{12}S_6P_2Fe_4Ni}$: C, 42.80; H, 3.14. Found: C, 42.35; H, 3.27. IR, terminal CO region ($\mathrm{CCl_4}$): 2057 (s), 2050 (s), 2019 (vs), 1978 (vs, br) $\mathrm{cm^{-1}}$. ^{1}H NMR (90 MHz, $\mathrm{CD_2Cl_2}$): δ 1.43 (s, 18 H, $-\mathrm{SC(CH_3)_3}$), 2.09 and 2.29 (t, br, 4 H, $-\mathrm{PCH_2CH_2P}-$), 7.30–7.70 (m, 20 H, phenyl H's). ^{13}C NMR (67.9 MHz, $\mathrm{CD_2Cl_2}$): δ_C 27.5 (t, J_CH = 116.1 Hz, $-\mathrm{P}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2P}-$), 33.5 (q, J_CH = 126.4 Hz, $-\mathrm{SC(}\mathit{C}\mathrm{H_3)_3}$), 50.8 (s, $-\mathrm{S}\mathit{C}\mathrm{(CH_3)_3}$), 128.0–134.2 (m, phenyl C's), 208.6, 212.2 (s's, carbonyl C's), 314.0 (s, $-\mathrm{S}\mathit{C}\mathrm{S}-$ carbons). ^{31}P NMR (36.2 MHz, $\mathrm{CD_2Cl_2}$): δ_P 52.0.

(10) *cis*-($\mathbf{Ph_3P}$)$_2$$\mathbf{PdCl_2}$ (R = $\mathbf{Me_3C}$). The anion solution was prepared as described in (9), and then 1.05 g of $\mathrm{[(C_6H_5)_3P]_2PdCl_2}$ (1.50 mmol) was added against a positive flow of nitrogen. This reaction mixture was stirred for 2 h at room temperature. The solvents were removed in vacuo leaving a dark red residue which was taken up in 50:50 pentane/$\mathrm{CH_2Cl_2}$ (v/v) and chromatographed on a pad of silicic acid. Elution with 90:10 pentane/$\mathrm{CH_2Cl_2}$ (v/v) yielded one major product, a red, air-stable crystalline solid, which was recrystallized from $\mathrm{CH_2Cl_2}$ to give bright red microcrystals. This compound exhibits a decomposition range of 95–135 °C, leaving a black solid. The recrystallized product loses color slowly until 117 °C when its color matches that of the unrecrystallized compound. Both leave a black solid which does not melt below 400 °C. The recrystallized material exhibited a positive Beilstein test while the unrecrystallized material did not. Analysis was performed on the recrystallized material which passes as the 1:1 $\mathrm{CH_2Cl_2}$ adduct (analysis, mass spectrum, ^{1}H NMR) **6**·$\mathrm{CH_2Cl_2}$ (1.92 g, 84%).

Anal. Calcd for $\mathrm{C_{58}H_{48}O_{12}S_6P_2Fe_4Pd{\cdot}CH_2Cl_2}$: C, 44.12; H, 3.14. Found: C, 43.92, H, 3.20. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): δ 1.30, 1.43 (s's 18 H, $-\mathrm{SC(C}\mathit{H}_3)_3$), 5.28 (s, br, 2 H, $\mathrm{CH_2Cl_2}$), 7.36–7.50 (s, br, 30 H, phenyl H's). ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): δ_C 34.2

(q, J_{CH} = 127.0 Hz, $-SC(\mathit{C}H_3)_3$), 49.6 and 49.7 (s's, $-SC(\mathit{C}H_3)_3$), 128.4–134.4 (m, phenyl C's), 208.0, 211.4, 211.6 (s's, carbonyl C's), 309.3 (s, $-S\mathit{C}S-$ carbons). ^{31}P NMR (36.2 MHz, $CDCl_3$): δ_P 20.7. Mass spectrum (fast atom bombardment volatilization operating in the positive ion mode): *m/z* 1174, which corresponds to the parent ion for the CH_2Cl_2 adduct.

(11) *cis*-$(Ph_3P)_2PtCl_2$ (R = Me_3C). The procedure described in (9) was used. To the anion solution was added 0.41 g of *cis*-$[(C_6H_5)_3P]_2PtCl_2$ (0.52 mmol) in 20 mL of THF. This solution was stirred for an additional 3 h at room temperature. The solvents were removed in vacuo leaving an orange-red residue which was taken up in 50:50 pentane/CH_2Cl_2 (v/v) and chromatographed on a pad of silicic acid. Elution with 50:50 pentane/CH_2Cl_2 (v/v) gave one compound, a red-orange, air-stable, crystalline solid which was recrystallized from $CHCl_3$. The melting point behavior of this compound was similar to that of the nickel and palladium analogues. The compound decomposed, as evidenced by a gradual loss of color over the range of 59–130 °C, to give a black residual solid which did not change when heated up to 400 °C. The yield of compound 7 was 0.74 g (93%).

Anal. Calcd for $C_{58}H_{48}O_{12}S_6P_2Fe_2Pt$: C, 43.28; H, 3.00. Found: C, 43.18; H, 3.16. IR, terminal CO region (CCl_4): 2054 (s), 2019 (vs), 1983 (vs, br), 1965 (m, sh) cm^{-1}. ^1H NMR (250 MHz, CD_2Cl_2): δ 1.26, 1.44, 146 (s's, 18 H, $-SC(C\mathit{H}_3)_3$), 7.22–7.72 (m, 30 H, phenyl H's). ^{13}C NMR (67.9 MHz, CD_2Cl_2): δ_C 34.6 (q, J_{CH} = 126.2 Hz, $-SC(\mathit{C}H_3)_3$), 49.9 (s, $-$ $SC(\mathit{C}H_3)_3$), 128.6–135.0 (m, phenyl C's), 207.3, 211.9, 212.4 (s's, carbonyl C's), 305.6 (s, $-S\mathit{C}S-$ carbons). ^{31}P NMR (367.2 MHz, $CDCl_3$): δ_P 4.71 (td, $^2J_{PP}$ = 39 Hz, J_{PP} = 2869 Hz).

Reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}SR)Fe_2(CO)_6]$ with Isothiocyanates. (1) Methyl Isothiocyanate (R = Et). The standard $Fe_3(CO)_{12}/EtSH/Et_3N$ reagent solution was prepared; to this solution was added 0.25 mL (3.50 mmol) of methyl isothiocyanate. The mixture was stirred for 30 min prior to the addition of 0.50 mL (8.0 mmol) of iodomethane. Stirring then was continued for 20 h during which time the solution became red. The solvent was removed leaving a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Pentane/CH_2Cl_2 (4/1, v/v) eluted a red band which gave 1.10 g (2.65 mmol, 89% yield) of $(\mu\text{-}Me(H)NCS)(\mu\text{-}EtS)Fe_2(CO)_6$ as a red-brown, air-stable solid, mp 127–129 °C dec after crystallization from pentane/CH_2Cl_2.

Anal. Calcd for $C_{10}H_9O_6S_2NFe_2$: C, 28.94; H, 2.19. Found: C, 28.96; H, 2.23. IR ($CHCl_3$): 3420 (s), ν(N—H), 3005 (m), 2990 (s), 2973 (m), 2941 (w), 2928 (w), 1511 (s), ν (C—N), 1457 (m), 1437 (w), 1380 (w), 1357 (s), 1256 (m), 1160 (m), 1000 (s), 874 (s), 617 (s), 580 (s), 490 (m) cm^{-1}. IR, terminal carbonyl region (pentane): 2068 (s), 2017 (vs), 2000 (vs), 1989 (s), 1967 (1) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.48 (t, J = 7.4 Hz, 3 H, CH_3), 2.61 (m, 2 H, SCH_2), 3.0 (d, J = 4.9 Hz, 3 H, NCH_3), 7.29 (br, 1 H, NH). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 18.4 (q, J = 129 Hz, CH_3), 35.3 (t, J = 140 Hz, SCH_2), 35.5 (q, J = 139 Hz, NCH_3), 209.0, 209.4, 213.1 (all s, CO), 210.2 (br, CO), 249.7 (s, C=S).

(2) Ethyl Isothiocyanate (R = Me_3C). The same procedure was used in this reaction. The product $(\mu\text{-}Et(H)NCS)(\mu\text{-}Me_3CS)Fe_2(CO)_6$, a red-orange solid of mp 92 °C (dec), was obtained in 80% yield.

Anal. Calcd for $C_{13}H_{15}O_6S_2NFe_2$: C, 34.16; H, 3.31. Found: C, 34.28; H, 3.39. ^1H NMR (90 MHz, $CDCl_3$): δ 1.21 (t, J = 7.3 Hz, $-NHCH_2C\mathit{H}_3$), 1.49 (s, 9 H, $-SC(C\mathit{H}_3)_3$), 3.42 (m, 2 H, $-NC\mathit{H}_2CH_3$), 7.23 (s, br, 1 H, $-N\mathit{H}-$). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ_C 13.2 (q, J_{CH} = 127.9 Hz, $-NCH_2\mathit{C}H_3$), 38.2 (q, J_{CH} = 126.3 Hz, $-SC(\mathit{C}H_3)_3$), 43.9 (t, J_{CH} = 144.6 Hz, $-N\mathit{C}H_2CH_3$), 50.2 (s, $-S\mathit{C}(CH_3)_3$), 210.3, 210.5 (br), 213.3 (all s's, carbonyl C's), 249.5 (s, $S\mathit{C}NH-$). Mass spectrum: *m/z* (relative intensity) 457 (M^+, 8), 429 (M^+ – CO, 19), 401 (M^+ – 2CO, 21), 373 (M^+ – 3CO, 34), 345 (M^+ – 4CO, 15), 317 (M^+ – 5CO, 45), 289 (M^+ – 6CO), 72), 233 ($Fe_2[SH][SCNHEt]$, 100), 204 ($Fe_2[SH][SCNH]$, 29), 203 ($Fe_2[SH][SCN]$, 12), 177 ($Fe_2[SH][S]$, 47), 176 (Fe_2S_2, 20), 144 (Fe_2S, 8), 56 (Fe, 44).

(3) Phenyl Isothiocyanate (R = Me_3C). The same procedure gave $(\mu\text{-}Ph(H)NCS)(\mu\text{-}Me_3CS)Fe_2(CO)_6$, a red-orange solid, mp 90–91 °C, in quantitative yield.

Anal. Calcd for $C_{17}H_{15}O_6S_2NFe_2$: C, 40.43; H, 2.99. Found: c, 40.63; H, 3.16. IR, terminal CO region (CCl_4): 2061 (s), 2022 (vs), 1997 (vs), 1994 (vs), 1985 (s), 1962 (s) cm^{-1}. ^1H NMR (90 MHz, CD_2Cl_2): δ 1.56 (s, 9 H, $-SC((C\mathit{H}_3)_3)$, 7.35 (s, 5 H, phenyl H's), 9.07 (s, br, 1 H, $-N\mathit{H}-$). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ_C 34.2 (q, J_{CH} = 127.7 Hz, $-SC(\mathit{C}H_3)_3$), 50.5 (s, $-S\mathit{C}(CH_3)_3$), 123.2, 127.5, 129.1 (m, phenyl C's), 139.2 (s, ipso phenyl C), 208.9, 210.2, 211.1, 213.1 (all s's, carbonyl C's), 255.0 (s, $S\mathit{C}NH-$). Mass spectrum: *m/z* (relative intensity: 505 (M^+, 2), 477 (M^+ – CO, 7), 449 (M^+ – 2CO, 6), 421 (M^+ – 3CO, 7), 393 (M^+ – 4CO, 10), 365 (M^+ – 5CO, 12), 337 (M^+ – 6CO, 23), 281 ($Fe_2[SH]$-$[SCNHC_6H_5]$, 34), 247 ($Fe_2[SCNHC_6H_5]$, 10), 177 ($Fe_2[SH][S]$, 13), 176 (Fe_2S_2, 7), 144 (Fe_2S, 10), 103 ([C_6H_5NCH, 100), (C_6H_5N, 20), 76 (C_6H_4, 56), 56 (Fe, 30).

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ with Methyl Isocyanate. The standard $Fe_3(CO)_{12}/EtSH/Et_3N$ reagent solution was prepared; to this solution was added 0.25 mL (4.5 mmol) of methyl isocyanate. The mixture then was refluxed for 30 min and stirred for an additional 30 min without heating prior to removal of the solvent. A red tar was left which was taken up in pentane/CH_2Cl_2 (4/1, v/v) and filtered through a pad of silicic acid. The solvent was removed from the red filtrate leaving a red tar which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Pentane/CH_2Cl_2 (4/1, v/v) eluted a red band which gave 0.39 g (0.98 mmol, 33% yield) of $(\mu\text{-}Me(H)NCO)(\mu\text{-}EtS)$-$Fe_2(CO)_6$ as a red, air-stable solid, mp 96–97 °C dec after crystallization from pentane/CH_2Cl_2.

Anal. Calcd for $C_{10}H_9O_7SNFe_2$: C, 30.11; H, 2.27. Found: C, 30.06; H, 2.34. IR ($CHCl_3$): 3470 (s), ν(N—H), 2990 (w), 2972 (m), 2936 (m), 2870 (w), 1506 (s), ν(C—N), 1480 (s), ν(C=O), 1457 (m), 1397 (s), 1380 (m), 1258 (m), 1154 (m), 983 (m), 612 (s), 582 (s) cm^{-1}. IR, terminal carbonyl region (pentane): 2078 (s), 2033 (vs), 2003 (vs), 1994 (vs), 1970 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz): δ 1.50 (t, J = 7.1 Hz, 3 H, $CH_2C\mathit{H}_3$), 2.55 (d, J = 4.4 Hz, 3 H, NCH_3), 2.53 (m, 2 H, SCH_2), 5.59 (br, 1 H, NH). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 18.4 (q, J = 130 Hz, $CH_2C\mathit{H}_3$), 28.0 q, J = 139 Hz, NCH_3), 32.6 (t, J = 144 Hz, SCH_2), 209.5, 213.8, 214.3 (all s, carbonyl groups). Mass spectrum: *m/z* (relative intensity) 399 (M^+, 15), 371 (M^+ – CO, 25), 343 (M^+ – 2CO, 34), 315 (M^+ – 3CO, 65), 287 (M^+ – 4CO, 31), 259 (M^+ – 5CO, 49), 231 (M^+ – 6CO, 100), 203 ($Fe_2(SEt)NMeH$, 97), 188 (Fe_2NSEt, 4), 174 (Fe_2SNMeH, 35), 173 (Fe_2SNMe, 58), 145 (Fe_2SH, 78), 144 (Fe_2S, 74), 112 (Fe_2, 8), 56 (Fe, 29).

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ with Elemental Sulfur. The anion was generated from 1.50 g of $Fe_3(CO)_{12}$ (2.98 mmol), 0.18 g of EtSH (2.97 mmol), and 0.31 g of Et_3N (3.01 mmol) in 50 mL of THF. The reaction mixture was stirred at room temperature for 30 min after which time the reaction mixture had changed color from green to red-brown. Subsequently, 0.15 g of elemental sulfur (4.68 g·atom) was added as a solid against a flow of nitrogen. The reaction mixture was stirred for 30 min, and then 0.80 g of MeI (5.62 mmol) was added. The mixture was stirred overnight. The solvents then were removed in vacuo, and the residue was taken up in pentane and subjected to filtration chromatography (silicic acid). Elution with 80:20 pentane/CH_2Cl_2 (v/v) gave one major band which was concentrated, taken up in pentane, and subjected to filtration chromatography (silicic acid). Elution with 80:20 pentane/CH_2Cl_2 (v/v) gave one major band which was concentrated, taken up in a minimum amount of pentane, and chromatographed on a silica gel column (25 × 300 mm). Elution with pentane gave two red-orange bands. The first to elute yielded a slightly air-sensitive, red oil which was identified as the known compound $(\mu\text{-}MeS)(\mu\text{-}EtS)Fe_2(CO)_6$(0.43 g, 1.11 mmol, 37%) by mass spectral data and by comparison of its IR and ^1H NMR spectra with those of an authentic sample.[13] The second band gave a red-orange solid identified as the known compound $(\mu\text{-}EtS)_2Fe_2(CO)_6$ (0.22 g, 0.56 mmol, 19%) by comparison of its ^1H NMR spectrum with that of a sample of authentic material.[13]

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ with Ethanesulfenyl Chloride. The anion was generated from 1.50 g of $Fe_3(CO)_{12}$ (2.98 mmol), 0.27 g of $(CH_3)_3CSH$ (3.02 mmol), and 0.31 g of Et_3N (3.01 mmol) in 50 mL of THF. The reaction mixture was stirred at room temperature for 30 min. At the same time ethanesulfenyl chloride was prepared by the reaction of 0.40 g of EtSSEt (3.25 mmol) and 0.45 g (3.31 mmol) of sulfuryl chloride in 10 mL of CH_2Cl_2 at –78 °C according to ref 14. The

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for the Anion in [$HNEt_3$][(μ-SO_2)(μ-$(CH_3)_3CS$)$Fe_2(CO)_6$]^a

atom	*x*	*y*	*z*	*U*^{b}
Fe(1)	1678 (1)	−115 (3)	2262 (1)	49 (1)
Fe(2)	3831 (1)	0	3528 (1)	44 (1)
S(1)	4018 (2)	−216 (3)	1983 (1)	44 (1)
S (2)	2553 (3)	1919 (3)	2965 (2)	45 (1)
O (3)	4648 (9)	985 (8)	1459 (5)	54 (3)
O (4)	4556 (8)	−1579 (8)	1640 (5)	57 (3)
C(1)	3063 (10)	−148 (15)	4672 (6)	59 (3)
C(2)	5482 (11)	906 (12)	3823 (7)	57 (4)
O(11)	2674 (9)	−340 (12)	5414 (5)	96 (4)
O(21)	6560 (9)	1497 (10)	4016 (7)	89 (4)
N(1)	5372 (9)	−6173 (9)	1406 (6)	55 (3)
C(21)	6261 (12)	−5613 (12)	2282 (7)	61 (4)
C(22)	7046 (15)	−4193 (14)	2153 (10)	80 (5)
C(31)	4052 (11)	−5229 (16)	1170 (8)	77 (4)
C(32)	2986 (13)	−5940 (16)	542 (9)	87 (5)
C(41)	6325 (12)	−6330 (14)	544 (7)	69 (4)
C(42)	7631 (14)	−7282 (15)	768 (9)	85 (5)
C(7)	1550 (13)	−1956 (15)	2038 (9)	74 (5)
O(71)	1427 (12)	−3176 (11)	1868 (8)	120 (5)
C(11)	1426 (11)	3008 (11)	3765 (7)	59 (4)
C(12)	581 (17)	2184 (19)	4488 (10)	115 (7)
C(14)	296 (17)	3724 (20)	3092 (10)	125 (8)
C(3)	4404 (13)	−1819 (12)	3646 (7)	65 (4)
O(31)	4747 (12)	−2961 (9)	3762 (6)	104 (4)
C(4)	1024 (11)	525 (12)	1096 (8)	63 (4)
O(41)	650 (10)	889 (12)	355 (6)	97 (4)
C(5)	25 (14)	−278 (18)	2866 (8)	87 (5)
O(51)	−1080 (12)	−502 (15)	3182 (8)	148 (6)
C(13)	2473 (15)	4015 (22)	4260 (13)	151 (9)

^{a}Estimated standard deviations in the last digit are given in parentheses. ^{b}Equivalent isotropic thermal parameter *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

EtSCl solution was added by cannula to the anion solution which had been cooled to −78 °C. Vigorous gas evolution was observed. The resulting reaction mixture then was stirred at −78 °C for 30 min and then at room temperature for 1 h. The solvents were removed in vacuo, and the residue was taken up in pentane and subjected to filtration chromatography (silicic acid). Elution with pentane gave one major band which yielded an air-sensitive, red-orange oil. This was identified as (μ-EtS)(μ-$(CH_3)_3CS$)$Fe_2(CO)_6$ (0.89 g, 2.08 mmol, 70%).

Anal. Calcd for $C_{12}H_{14}O_6S_2Fe_2$: C, 33.52; H, 3.28. Found: C, 33.91; H, 3.36. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.96–1.57 (m, 12 H, $-SC(CH_3)_3$ and $-SCH_2CH_3$), 2.13–2.45 (complex m, 2 H, isomers, $-SCH_2CH_3$).

Reactions of [Et_3NH][(μ-CO)(μ-RS)$Fe_2(CO)_6$] with Sulfur Dioxide. (1) R = *t*-Bu. The anion was generated by using 2.98 mmol of $Fe_3(CO)_{12}$ (1.50 g), 30.2 mmol of $(CH_3)_3CSH$ (0.27 g), and 3.01 mmol of Et_3N (0.31 g) in 50 mL of THF at room temperature. After 30 min the reaction mixture was cooled to −78 °C by using an acetone/dry ice bath. An excess of sulfur dioxide then was condensed into the reaction mixture, causing a color change from red-brown to red. This solution was stirred for 2 h at −78 °C, after which time the cold bath was removed. After the reaction mixture had warmed to room temperature and the excess sulfur dioxide had evaporated, the solvents were removed in vacuo. The residue was redissolved in 100 mL of Et_2O and filtered through a pad of Celite under nitrogen. The clear red solution was concentrated under a stream of nitrogen and then placed in the freezer at −20 °C. Red-orange crystals were collected from this solution (mp 107.0–107.5 °C). This product was identified as [Et_3NH][(μ-SO_2)(μ-$(CH_3)_3CS$)$Fe_2(CO)_6$]. The yields for three such reactions were 60%, 78%, and 47% of isolated crystalline product.

Anal. Calcd for $C_{16}H_{25}O_8S_2NFe_2$: C, 35.91; H, 4.71. Found: C, 35.95; H, 4.85. ^{1}H NMR (90 MHz, C_6D_6): δ 0.54 (t, *J* = 7.2 Hz, 9 H, $-N[CH_2CH_3]_3$), 1.38 (s, 9 H, $-SC(CH_3)_3$), 1.98 (q, *J* = 7.1 Hz, 6 H, $-N[CH_2CH_3]_3$), 9.26 (s, br, 1 H, $-NH$). ^{13}C NMR (67.9 MHz, C_6D_6): δ_C 8.1 (q, J_{CH} = 128.6 Hz, $-N[CH_2CH_3]_3$), 34.1 (s, J_{CH} = 126.4 Hz, $-SC(CH_3)_3$), 45.5 (t, J_{CH} = 142.4 Hz, $-N[CH_2CH_3]_3$), 48.1 (s, $-SC(CH_3)_3$), 211.5, 212.6 (s's, carbonyl C's). IR (C_6H_6, NaCl): 2050 (s), 2008 (vs), 1975 (vs), 1970 (vs, br), 1965 (vs), 1950 (s), 1370 (m), 1209 (m), 1152 (m), 1013 (m), 984 (s, br), 600 (s), 557 (m) cm^{-1}. Mass spectrum (obtained by using fast atom bombardment volatilization from a 2-nitrophenyl octyl ether matrix): anion detection mode, *m/z* 433 [(μ-SO_2)(μ-$(CH_3)_3CS$)$Fe_2(CO)_6$]$^-$, 369 [(μ-$CH_3)_3CS$)$Fe_2(CO)_6$]$^-$; cation detection mode, *m/z* 637 [μ-SO_2)(μ-$(CH)_3)_3CS$)$Fe_2CO)_6$]$^-$[Et_3NH^+]$_2$.

(2) R = Et. Essentially the same procedure was used. The product was obtained in 50% yield as red-orange crystals, mp 91.5–92.5 °C, and was identified as [Et_3NH][(μ-SO_2)(μ-EtS)$Fe_2(CO)_6$].

Anal. Calcd for $C_{14}H_{21}O_8S_2Fe_2$: C, 33.16; H, 4.18, N, 2.76. Found: C, 32.88; H, 4.23, N, 2.67. ^{1}H NMR (90 MHz, C_6D_6): δ 0.63 (t, *J* = 7.0 Hz, 9 H, $-N[CH_2CH_3]_3$), 1.13 (t, 3 H, $-SCH_2CH_3$), 2.10 (q, *J* = 7.0 Hz, 6 H, $-N[CH_2CH_3]_3$), 2.33 (q, *J* = 7.0 Hz, 2 H, $-SCH_2CH_3$), 7.82 (s, br, 1 H, $-NH$). ^{13}C NMR (67.9 MHz, C_6D_6): δ_C 7.1 (q, J_{CH} = 129.0 Hz, $-N[CH_2CH_3]_3$), 17.3 (q, J_{CH} = 127.4 Hz, $-SCH_2CH_3$), 32.1 (t, J_{CH} = 141.0 Hz, $-SCH_2CH_3$), 44.5 (t, J_{CH} = 141.0 Hz, $-N[CH_2CH_3]_3$), 211.2 (s, carbonyl C's).

Crystal and Molecular Structure of [Et_3NH][(μ-SO_2)(μ-*t*-BuS)$Fe_2(CO)_6$]. An orange-red crystal of approximate size 0.3 × 0.3 × 0.5 mm was mounted on the tip of a glass fiber. All geometric and intensity data were collected at ambient temperature by using an automated four-circle diffractometer (Nicolet P3F), equipped with graphite-monochromated Mo Kα radiation and controlled by a Data General Eclipse S/140 minicomputer.

The lattice vectors were identified by an application of the automated indexing routine of the diffractometer to the positions of 12 reflections taken from a rotation photograph and located and centered by the diffractometer. The crystal orientation matrix and unit-cell dimensions were refined by a least-squares fit to the goniometer positions of 20 accurately located reflections in the range 20° ≤ 2θ ≤ 35°. The W–2θ technique was used to measure 2438 reflections in the range 4° ≤ 2θ ≤ 45°. The scan speed was variable in the range 2–30°/min. Three standard reflections, remeasured every 100 data scans, showed no loss in intensity over the X-ray exposure time. The data were corrected for Lorentz and polarization effects before structure factors were derived. An empirical absorption correction (μ(Mo Kα) = 13.95 cm^{-1}) was based on azimuthal scans of eight reflections near χ = 90°. In all, there were 1635 data with $F_o^2 \geq 3\sigma(F_o^2)$ for use in structure solution and refinement. Systematically absent data identified the space group as $P2_1$ or $P2_1/m$. The noncentrosymmetric space group was chosen because a disorder model was required in order to meet the symmetry requirements of $P2_1/m$. The positions of the iron atoms were derived from a three-dimensional Patterson map. Iterative application of least-squares refinement and difference Fourier maps led to the development of the entire, well-ordered structure. The last cycle gave residuals of *R* = 0.0428, R_w = 0.0462, and a quality of fit = 1.261 for a fit of 261 variables to 1633 observations. Refinement in negative phasing produced no measurable improvement in the statistics. Table III lists atomic coordinates and isotropic thermal parameters.

Crystallographic computations were performed by using the SHELXTL (Revision 4.1) crystallographic computational package installed on a Data General Eclipse S/140 minicomputer.

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Registry No. **1a**·Et_3NH (R = Et), 93530-38-2; **1a**·Et_3NH (R = Me_3C), 105040-77-5; **2**, 118378-31-7; **4**, 118378-37-3; **5**, 118378-44-2; **6**, 118378-38-4; **7**, 118378-39-5; **8a**, 118378-40-8; **8b**, 118378-41-9; **8c**, 118378-42-0; **10**, 118398-28-0; **11** (R′ = $PhCH_2$), 118378-30-6; **16a**, 118398-30-4; $Fe(CO)_{12}$, 17685-52-8; (μ-MeSCS)(μ-Me_3CS)$Fe_2(CO)_6$, 118378-32-8; (μ-EtSCS)(μ-Me_3CS)$Fe_2(CO)_6$, 118378-33-9; (μ-$PhCH_2SCS$)(μ-Me_3CS)$Fe_2(CO)_6$, 118378-34-0; (μ-CH_2-$CHCH_2SCS$)(μ-Me_3CS)$Fe_2(CO)_6$, 118378-35-1;

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(14) Anzai, K. *J. Heterocycl. Chem.* **1979**, *16*, 567.

(μ-PhC(O)SCS)(μ-Me$_3$CS)Fe$_2$(CO)$_6$, 118378-36-2; [CH$_3$]$_3$CSH, 75-66-1; CH$_2$-CHCH$_2$Cl, 107-05-1; (η^5-C$_5$H$_5$)Fe(CO)$_2$I, 12078-28-3; (diphos)NiCl$_2$, 14647-23-5; *cis*-(Ph$_3$P)$_2$PdCl$_2$, 15604-37-2; *cis*-(Ph$_3$P)$_2$PtCl$_2$, 15604-36-1; (μ-MeS)(μ-EtS)Fe$_2$(CO)$_6$, 69480-75-7; (μ-EtS)$_2$Fe$_2$(CO)$_6$, 15634-62-5; (μ-EtS)(μ-(CH$_3$)$_3$CS)Fe$_2$(CO)$_6$, 118378-43-1; benzyl chloride, 100-44-7; ethanethiol, 75-08-1; iodoethane, 75-03-6; benzoyl chloride, 98-88-4; methyl isothiocyanate, 556-61-6; ethyl isothiocyanate, 542-85-8; phenyl isothiocyanate, 103-72-0; methyl isocyanate, 624-83-9; ethanesulfenyl chloride, 1496-75-9.

Supplementary Material Available: Tables of crystal data and anisotropic thermal parameters (2 pages); a listing of observed and calculated structure factors for [Et$_3$NH][(μ-SO$_2$)(μ-*t*-BuS)-Fe$_2$(CO)$_6$ (10 pages). Ordering information is given on any current masthead page.

Nine-Membered Metallacyclic Metaloxycarbene Complexes by Means of Sequential Coupling of Butadiene with a Ketone and a Metal Carbonyl at Bis(cyclopentadienyl)zirconium

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The metallacyclic zirconoxycarbene complexes Cp$_2$Zr(η^3-C$_3$H$_4$)CH$_2$C[=M(CO)$_5$]O (**3**) (M = Cr, Mo, W) were prepared by reacting M(CO)$_6$ with (butadiene)ZrCp$_2$. The (π-allyl)Zr functional group of complexes **3** was added to acetone, benzophenone, or acetophenone to regioselectively yield the nine-membered metallacyclic metaloxycarbene complexes Cp$_2$ZrOC(R^{1}R^2)CH$_2$CH=CHCH$_2$C[=M(CO)$_5$]O (**4a–e**), exhibiting a trans carbon–carbon double bond. The (MeCp)$_2$Zr analogue **4c′** (R^1 = R^2 = CH$_3$; M = W) was characterized by X-ray diffraction (space group $P2_1/n$, a = 15.623 (2) Å, b = 8.008 (1) Å, c = 21.672 (5) Å, β = 99.65 (1)°, Z = 4, R = 0.036, R_w = 0.034). Gibbs activation energies of topomerization, $\Delta G^{\ddagger}_{\text{ent}}$ between 16.6 and 17.0 kcal/mol, were estimated from the dynamic NMR spectra of the nine-membered metallacycles **4**.

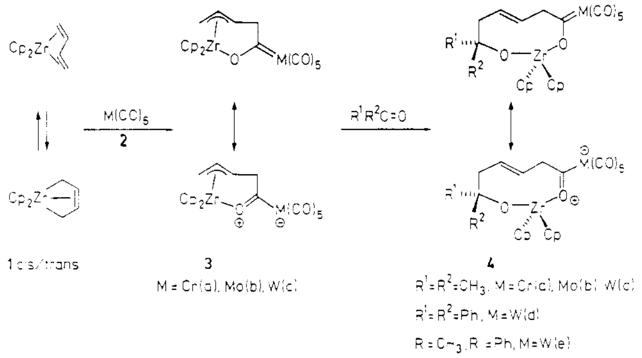
Introduction

The medium-ring-sized *trans*-cycloalkenes are extraordinary olefins with regard to their reactivity and stereochemical features. In the sequence of *trans*-cyclodecene, *trans*-cyclononene, and *trans*-cyclooctene increasing ring strain and decreasing ring perimeter make the conformational equilibration more difficult. These *trans*-cycloalkenes exhibit chiral ground-state geometries. Racemization requires at least one olefinic hydrogen substituent to be moved through the inside of the circular framework. Rapidly increasing activation energies of enantiomerization are therefore observed on going from *trans*-C$_{10}$H$_{18}$ ($\Delta G^{\ddagger}_{\text{ent}}$(276 K) ≈ 12 kcal/mol) through *trans*-C$_9$H$_{16}$ ($\Delta G^{\ddagger}_{\text{ent}}$(263 K) ≈ 19 kcal/mol) to the *trans*-C$_8$H$_{14}$ system ($\Delta G^{\ddagger}_{\text{ent}}$(428 K) ≈ 35 kcal/mol).[1] We have prepared a group of organometallic compounds exhibiting very similar stereochemical features (with regard to their structural characteristics as well as their dynamic properties) although their composition is quite different from that of the *trans*-cycloalkenes.

Results and Discussion

Preparation of the Metallacyclic Carbene Complexes. Nine-membered metallacyclic organometallic systems were constructed by coupling 1,3-butadiene, a (CO)$_5$M-bound carbonyl ligand (M = Cr, Mo, W), and the C=O functionality of a ketone at the bis(cyclopentadienyl)zirconium bent metallocene unit. Reaction of the (butadiene)zirconocene system with the group 6 metal carbonyls yielded the metallacyclic (π-allyl)-zirconoxycarbene complexes **3a–c**, as described previously.[2] Complexes **3** contain a zirconium-bound allyl ligand which

Scheme I



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(1) *trans*-Cycloalkenes. (a) Ten-membered ring: Binsch, G.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 5157. Noe, E. A.; Wheland, R. C.; Glazer, E. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 3488. (b) Nine-membered ring: Cope, A. C.; Banholzer, K.; Keller, H.; Pawson, B. A.; Whang, J. J.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1965**, *87*, 3644. (c) Eight-membered ring: Cope, A. C.; Pawson, B. A. *J. Am. Chem. Soc.* **1965**, *87*, 3649. (d) See also: Marshall, J. A. *Acc. Chem. Res.* **1980**, *13*, 213.

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