Unusual Reactions of Cationic Bridging Carbyne Complexes of Dimethylsilane-Bridged Bis(η^5-cyclopentadienyl)diiron Tricarbonyl with Nucleophiles. A Route to Iron−Sulfur Cluster Bridging Carbene Complexes

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The reactions of diiron cationic carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ (**4**, Ar = C_6H_5; **5**, Ar = p-$CH_3C_6H_4$; **6**, Ar = p-$CF_3C_6H_4$) with NaSR (R = CH_3, C_6H_5, p-$CH_3C_6H_4$) in THF at low temperature afford diiron bridging mercaptocarbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SR)Ar\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**9**, Ar = C_6H_5, R = CH_3; **10**, Ar = C_6H_5, R = C_6H_5; **11**, Ar = C_6H_5, R = p-$CH_3C_6H_4$; **12**, Ar = p-$CH_3C_6H_4$, R = CH_3; **13**, Ar = p-$CH_3C_6H_4$, R = C_6H_5; **14**, Ar = p-$CH_3C_6H_4$, R = p-$CH_3C_6H_4$; **15**, Ar = p-$CF_3C_6H_4$, R = CH_3; **16**, Ar= p-$CF_3C_6H_4$, R = C_6H_5; **17**, Ar = p-$CF_3C_6H_4$, R = p-$CH_3C_6H_4$). Compound **6** reacts with $[(\mu\text{-}SLi)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$ to give the novel iron−sulfur cluster bridging carbene complex $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CF_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$ (**18**). Analogous iron−sulfur cluster bridging carbene complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2\text{-}(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$ (**19**, Ar = C_6H_5; **20**, Ar = p-$CH_3C_6H_4$) can also be obtained by the reactions of diiron cationic carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**7**, Ar = C_6H_5; **8**, Ar = p-$CH_3C_6H_4$) with $[(\mu\text{-}SLi)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$. The structures of complexes **9**, **13**, **16**, and **18** have been established by X-ray crystallography.

Introduction

In recent years, our interest in developing the methodologies of the synthesis of transition metal bridging carbene and carbyne complexes stems from the fact that many such complexes are themselves metal clusters or are the precursors of metal cluster complexes, which have played important roles in many catalytic reactions.[1,2] A considerable number of di- or trimetal bridging carbene and bridging carbyne complexes have been synthesized by Stone and co-workers[3−6] and by us.[7,8] Most recently, we found a new method for the preparation of dimetal bridging carbene and carbyne complexes: the reactions of highly electrophilic diiron cationic carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (Ar = C_6H_5, p-$CH_3C_6H_4$) with nucleophiles to give a series of diiron bridging carbene complexes.[9,10] This offers a new and useful method for the preparation and structural modification of dimetal bridging carbene complexes.

In the meantime, we have noted our previously reported reactions of cationic carbyne complexes [η^5-

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(1) Suess-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41.

(2) (a) Gladfelter, W. L.; Roesselet, K. J. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: Weinheim, Germany, 1990; p 392. (b) Maire, G. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knoezinger, H., Eds.; Elsevier: Amsterdam, The Netherlands, 1986; p 509. (c) Dickson, R. S.; Greaves, B. C. *Organometallics* **1993**, *12*, 3249.

(3) Stone, F. G. A. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; p 11.

(4) (a) Ashworth, T. V.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1593. (b) Carriedo, G. A.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1555. (c) Garcia, M. E.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 1209. (d) Busetto, L.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 101.

(5) (a) Howard, J. A. K.; Mead, K. A.; Moss, J. R.; Navarro, R.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 743. (b) Hodgson, D.; Howard, J. A. K.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1331.

(6) Pilotti, M. U.; Stone, F. G. A.; Topaloglu, L. *J. Chem. Soc., Dalton Trans.* **1991**, 1621.

(7) (a) Chen, J.-B.; Yu, Y.; Liu, K.; Wu, G.; Zheng, P.-J. *Organometallics* **1993**, *12*, 1213. (b) Yu, Y.; Chen, J.-B.; Chen, J.; Zheng, P.-J. *J. Chem. Soc., Dalton Trans.* **1996**, 1443.

(8) (a) Tang, Y.-J.; Sun, J.; Chen, J.-B. *Organometallics* **1999**, *18*, 4337. (b) Tang, Y.-J.; Sun, J.; Chen, J.-B. *J. Chem. Soc., Dalton Trans.* **1998**, 931. (c) Tang, Y.-J.; Sun, J.; Chen, J.-B. *J. Chem. Soc., Dalton Trans.* **1998**, 4003. (d) Tang, Y.-J.; Sun, J.; Chen, J.-B. *Organometallics* **1998**, *17*, 2945. (e) Tang, Y.-J.; Sun, J.; Chen, J.-B. *Organometallics* **2000**, *19*, 72. (f) Tang, Y.-J.; Sun, J.; Chen, J.-B. *Organometallics* **1999**, *18*, 2459.

(9) Liu, Y.-J.; Wang, R.-T.; Sun, J.; Chen, J.-B. *Organometallics* **2000**, *19*, 3498.

(10) Liu, Y.-J.; Wang, R.-T.; Sun, J.; Chen, J.-B. *Organometallics* **2000**, *19*, 3784.

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$C_5H_5(CO)_2M{\equiv}CC_6H_5]BBr_4$ (M = Mn, Re) with the (μ-phenylthio)(μ-thiolato)hexacarbonyldiiron anion, $[(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]^-$, which afforded novel iron−sulfur cluster carbene complexes $[\eta^5\text{-}C_5H_5(CO)_2M{=}C(C_6H_5)(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$ (M = Mn, Re).[11,12] In view of the catalytic activity and use in organic synthesis of the iron−sulfur cluster complexes,[13,14] we take a great interest in this type of complex.

To explore the reactivity of the cationic carbyne complexes of diiron containing different cyclopentadienyl ligands and the effect of different substituents at the μ-carbyne carbon on the reactivity of the diiron cationic carbyne complexes and to further examine the scope of this preparation of dimetal bridging carbene and bridging carbyne complexes, we chose (dicyclopentadienyldimethylsilane)diiron bridging alkoxycarbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**1**, Ar = C_6H_5; **2**, Ar = p-$CH_3C_6H_4$; **3**, Ar = p-$CF_3C_6H_4$),[15] obtained by the reactions of di-μ-carbonyl-*cis*-μ-(1−5-η:1′-5′-η-dicyclopentadienyldimethylsilane)bis(carbonyliron), $[Fe_2(\mu\text{-}CO)_2(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$, with aryllithium reagents followed by alkylation with Et_3OBF_4, as starting materials for the reaction with a Lewis acid such as BBr_3 to form the diiron cationic bridging carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ (**4**, Ar = C_6H_5; **5**, Ar = p-$CH_3C_6H_4$; **6**, Ar = p-$CF_3C_6H_4$). The cationic carbyne complexes **4**−**6** reacted with the nucleophiles involving $[(\mu\text{-}SLi)(\mu\text{-}SC_6H_5)\ Fe_2(CO)_6]$. For comparison, the reactions of diiron cationic carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**7**, Ar = C_6H_5; **8**, p-$CH_3C_6H_4$), where the cyclopentadienyl ligands are the two nonbridged cyclopentadienyl groups, with $[(\mu\text{-}SLi)(\mu\text{-}SC_6H_5)\ Fe_2(CO)_6]$ were also made. These reactions produced a series of novel dimetal bridging carbene complexes. Herein we report these unusual reactions and the structural characterizations of the resulting products.

Experimental Section

All procedures were performed under a dry, oxygen-free N_2 atmosphere using standard Schlenk techniques. All solvents employed were reagent grade and dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under a N_2 atmosphere. The tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl, while petroleum ether (30−60 °C) and CH_2Cl_2 were distilled from CaH_2. The neutral alumina (Al_2O_3) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% w/w N_2-saturated water, and stored under N_2. Compounds $NaSCH_3$ and $NaSC_6H_5$ were purchased from Fluka Chemical Co. and Aldrich Chemical Co., respectively. $NaSC_6H_4CH_3$-p,[16] $[(\mu\text{-}S)_2Fe_2(CO)_6]$,[17] and $[(\mu\text{-}SLi)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$[18] were prepared by literature methods. Compounds **1**−**3**[15] and $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_5)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**7**)[9] and $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CH_3\text{-}p)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**8**)[9] were prepared as previously described.

IR spectra were measured on a Perkin-Elmer 983G spectrophotometer. All ^1H NMR spectra were recorded at ambient temperature in acetone-d_6 solution with TMS as the internal reference using a Bruker AM-300 spectrometer. Electron ionization mass spectra (EIMS) were run on a Hewlett-Packard 5989A spectrometer. Melting points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

Preparation of $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_5)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ (4). Following the known preparations of the analogous cationic carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (Ar = C_6H_5, p-$CH_3C_6H_4$), to a solution of $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OC_2H_5)C_6H_5\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**1**)[15] (0.30 g, 0.581 mmol) in 150 mL of ether was added 0.30 mL (3.20 mmol) of BBr_3 at −65 °C with vigorous stirring. Immediately a brown-red solid precipitated from the reaction solution. After stirring for 10 min at −65 °C, the resulting mixture was filtered, and the solids were washed with ether (2 × 30 mL) at −65 °C and then dried under high vacuum at −50 °C to give 0.40 g (85%, based on **1**) of **4** as a brown-red solid: IR (CH_2Cl_2) ν(CO) 2041 (s), 2012 (s, br), 1848 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 8.09−7.92 (m, 5H, C_6H_5), 6.81 (s, 4H, C_5H_4), 6.08 (d, 2H, C_5H_4), 5.45 (d, 2H, C_5H_4) 3.41 (q, 1H, $(CH_3\mathit{CH_2})_2O$), 1.12 (t, 1.5H, $(\mathit{CH_3}CH_2)_2O$), 0.64 (s, 3H, $SiCH_3$), 0.30 (s, 3H, $SiCH_3$).

The following complexes were prepared by similar reactions.

$[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CH_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ (5): brown-red solid (84% yields); IR (CH_2Cl_2) ν(CO) 2039 (s), 2018 (br), 1848 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 8.41 (d, 2H, $\mathit{C_6H_4}CH_3$), 7.76 (d, 2H, $\mathit{C_6H_4}CH_3$), 6.78 (d, 2H, C_5H_4), 6.76 (d, 2H, C_5H_4), 6.03 (d, 2H, C_5H_4), 5.42 (d, 2H, C_5H_4), 3.42 (q, 1.5H, $(CH_3\mathit{CH_2})_2O$), 2.59 (s, 3H, $C_6H_4\mathit{CH_3}$), 1.13 (t, 2H, $(\mathit{CH_3}CH_2)_2O$), 0.62(s, 3H, $SiCH_3$), 0.29(s, 3H, $SiCH_3$).

$[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CF_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ (6): brown-red solid (87%, yield); IR (CH_2Cl_2) ν(CO) 2046 (s), 2019 (br, m), 1857 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 8.76 (d, 2H, $C_6H_4CF_3$), 8.22 (d, 2H, $C_6H_4CF_3$), 6.88 (s, 4H, C_5H_4), 6.13(s, 2H, C_5H_4), 5.53(s, 2H, C_5H_4), 3.46 (q, 1.5H, $(CH_3\mathit{CH_2})_2O$), 1.12 (t, 2H, $(\mathit{CH_3}CH_2)_2O$), 0.68(s, 3H, $SiCH_3$), 0.33(s, 3H, $SiCH_3$).

Reaction of 4 with $NaSCH_3$ to Give $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SCH_3)C_6H_5\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (9). To 0.400 g (0.494 mmol) of freshly prepared (in situ) **4** dissolved in 60 mL of THF at −80 °C was added 0.041 g (0.581 mmol) of $NaSCH_3$. The reaction mixture was stirred at −80 to −60 °C for 1 h, during which time the turbid solution turned clear deep-red gradually. After stirring at −60 to −20 °C for an additional 3 h, the resulting solution was evaporated under high vacuum at −30 °C to dryness and the dark red residue was chromatographed on an alumina column (1.6 × 15−20 cm) at −25 °C with petroleum ether/CH_2Cl_2 (10:1) as the eluant. The red band was eluted and collected. After vacuum removal of the solvent, the residue was recrystallized from petroleum ether/CH_2Cl_2 (15:1) solution at −80 °C to give 0.18 g (70%, based on **4**) of purple-red crystals of **9**: mp 132−134 °C dec; IR (CH_2Cl_2) ν(CO) 1982 (s), 1950 (m), 1772 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.47−6.88 (m, 5H, C_6H_5), 6.15 (s, 2H, C_5H_4), 5.78 (s, 2H, C_5H_4), 5.24 (s, 2H, C_5H_4), 5.07 (s, 2H, C_5H_4), 2.03 (s, 3H, SCH_3), 0.61 (s, 3H, $SiCH_3$), 0.47 (s, 3H, $SiCH_3$); MS *m/e* 490 (M^+ − CO), 462 (M^+ − 2CO), 434 (M^+ − 3CO), 415 (M^+ − 2CO − SCH_3). Anal. Calcd for $C_{23}H_{22}O_3SFe_2Si$: C, 53.30; H, 4.28. Found: C, 52.79; H, 4.38.

The following complexes were prepared by similar reactions.

$[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SC_6H_5)C_6H_5\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (10): red crystals (72% yield); mp 114−116 °C dec; IR (CH_2Cl_2) ν(CO) 1983 (vs), 1951 (s), 1772 (s) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.47−6.26 (m, 10H, $2C_6H_5$), 5.69 (s, 2H, C_5H_4), 5.63 (s, 2H, C_5H_4), 5.29 (s, 2H, C_5H_4), 5.22 (s, 2H, C_5H_4), 5.25 (m, 3H, CH_2Cl_2), 0.64 (s, 3H, $SiCH_3$), 0.51 (s, 3H, $SiCH_3$); MS

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(11) Chen, J.-B.; Lei, G.-X.; Zhang, Z.-Y.; Tang, Y.-Q. *Acta Chim. Sin., Engl. Ed.* **1986**, *4*, 311.

(12) Chen, J.-B.; Lei, G.-X.; Zhang, Z.-Y.; Tang, Y.-Q. *Acta Chim. Sin., Engl. Ed.* **1989**, *47*, 31.

(13) De Beer, J. A.; Haines, R. J.; Greatrex, G.; Greenwood, N. N. *J. Organomet. Chem.* **1971**, *27*, C33.

(14) Nametkim, N. S.; Tyurin, V. D.; Kulina, M. A. *J. Organomet. Chem.* **1978**, *149*, 355.

(15) Wang, R.-T.; Sun, J.; Chen, J.-B. *J. Organomet. Chem.* **2001**, *617*−*618*, 292.

(16) Reid, E. E. *Organic Chemistry of Bivalent Sulfur*; Chemical Publishing Co. Inc.: New York, 1958; Vol. 1, p 127.

(17) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

(18) Seyferth, D.; Kiwan, A. M. *J. Organomet. Chem.* **1985**, *286*, 219.

Table 1. Crystal Data and Experimental Details for Complexes 9, 13, 16, and 18

	9·CH_2Cl_2	**13**	**16**	**18**·CH_2Cl_2
formula	$C_{25}H_{26}O_3Cl_2SFe_2Si$	$C_{29}H_{26}O_3SFe_2Si$	$C_{29}H_{23}O_3F_3SFe_2S_i$	$C_{36}H_{25}O_9Cl_2F_3S_2Fe_4Si$
fw	617.22	594.36	648.33	1045.07
space group	R-3 (No. 148)	$P2_{1/a}$ (No. 14)	$P2_{1/a}$ (No. 14)	$Pna2_1$ (No. 33)
a (Å)	32.849(8)	14.496(4)	14.776(3)	25.324(5)
b (Å)		10.066(4)	10.203(5)	16.970(3)
c (Å)	11.603(3)	19.059(6)	19.003(7)	9.4415(19)
α (deg)				90
β (deg)		106.52(2)	104.97(2)	90
γ (deg)				90
V (Å^3)	10843(4)	2666(1)	2767(1)	4057.5(14)
Z	18	4	4	4
D_{calcd} (g /cm^3)	1.701	1.481	1.556	1.711
F(000)	5688.00	1224.00	1320.00	2096
μ(Mo Kα) (cm$^{-1)}$	15.89	12.40	12.16	17.32
orientation reflns: no.; range (2θ) (deg)	15; 14.1−19.5	20; 13.6−19.4	21; 13.7−16.4	4.79−29.58
no. of unique data, total	3924	3494	4085	9195
with $I > 2.00\sigma(I)$	1409 ($I > 2.80\sigma(I)$)	1707	1778 ($I > 3.00\sigma(I)$)	9195
no. of params refined	284	325	355	540
correct. factors, max. min.	0.8857−1.0000	0.7931−1.0000	0.8791−1.0557	0.8290−1.0000
R^a	0.058	0.058	0.071	0.0590
$R_w{}^b$	0.056	0.050	0.079	0.0707
quality of fit indicator^c	1.42	1.43	2.21	0.656
max shift/esd. final cycle	0.00	0.00	0.00	0.00
largest peak, e$^-$/Å^3	0.46	0.47	0.54	0.347
minimum peak, e$^-$/Å^3	−0.54	−0.44	−0.63	−0.312

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2]^{1/2}$; $w = I/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum_w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$.

m/e 580 (M^+), 524 ($M^+ - 2CO$), 496 ($M^+ - 2CO$), 84 ($CH_2Cl_2^+$). Anal. Calcd for $C_{28}H_{24}O_3SFe_2Si{\cdot}1.5CH_2Cl_2$: C, 50.07; H, 3.85. Found: C, 49.48; H, 3.77.

[Fe$_2$(μ-CO){μ-C(SC$_6$H$_4$CH$_3$-p)C$_6$H$_5$}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] (11): purple-red crystals(75% yield); mp 126−128 °C dec; IR (CH_2Cl_2) ν(CO) 1983 (vs), 1952 (s), 1772 (s) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.42−6.61 (m, 9H, C_6H_5 + $C_6H_4CH_3$-p), 6.22 (s, 2H, C_5H_4), 5.67 (s, 2H, C_5H_4), 5.25 (s, 4H, C_5H_4), 2.23 (s, 3H, $C_6H_4CH_3$), 0.63 (s, 3H, $SiCH_3$), 0.51 (s, 3H, $SiCH_3$); MS *m/e* 594 (M^+), 538 ($M^+ - 2CO$), 510 ($M^+ - 3CO$), 471 ($M^+ - SC_6H_4CH_3$). Anal. Calcd for $C_{29}H_{26}O_3SFe_2Si$: C, 58.60; H, 4.41. Found: C, 58.91; H, 4.45.

[Fe$_2$(μ-CO){μ-C(SCH$_3$)C$_6$H$_4$CH$_3$-p}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] (12): purple-red crystals (73% yield); mp 126−127 °C dec; IR (CH_2Cl_2) ν(CO) 1981 (s), 1949 (m), 1773 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.35−6.83 (dd, 4H, $C_6H_4CH_3$), 6.13 (s, 2H, C_5H_4), 5.56 (s, 2H, C_5H_4), 5.22 (s, 2H, C_5H_4), 5.05 (s, 2H, C_5H_4), 2.19 (s, 3H, SCH_3), 2.03 (s, 3H, $C_6H_4CH_3$), 0.61 (s, 3H, $SiCH_3$), 0.47 (s, 3H, $SiCH_3$); MS *m/e* 532 (M^+), 504 ($M^+ - CO$), 476 ($M^+ - 2CO$), 448 ($M^+ - 3CO$), 485 ($M^+ - SCH_3$). Anal. Calcd for $C_{24}H_{24}O_3SFe_2Si$: C, 53.23; H, 4.54. Found: C, 53.79; H, 5.09.

[Fe$_2$(μ-CO){μ-C(SC$_6$H$_5$)C$_6$H$_4$CH$_3$-p}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] (13): red crystals (70% yield); mp 135−136 °C dec; IR (CH_2Cl_2) ν(CO) 1982 (vs), 1951 (s), 1772 (s) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.36−6.54 (m, 9H, C_6H_5 + $C_6H_4CH_3$), 6.23 (s, 2H, C_5H_4), 5.66 (s, 2H, C_5H_4), 5.26 (s, 2H, C_5H_4), 5.20 (s, 2H, C_5H_4), 2.02 (s, 3H, $C_6H_4CH_3$), 0.64 (s, 3H, $SiCH_3$), 0.51 (s, 3H, $SiCH_3$); MS *m/e* 594 (M^+), 538 ($M^+ - 2CO$), 485 ($M^+ - SC_6H_5$). Anal. Calcd for $C_{29}H_{26}O_3SFe_2Si$: C, 58.60; H, 4.41. Found: C, 58.24; H, 4.55.

[Fe$_2$(μ-CO){μ-C(SC$_6$H$_4$Me-p)C$_6$H$_4$Me-p}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] (14): purple-red crystals (64% yield); mp 108−110 °C dec; IR (CH_2Cl_2) ν(CO) 1982 (s), 1950 (m), 1771 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.33−6.55 (m, 8H, $2C_6H_4$-CH_3), 6.20 (s, 2H, C_5H_4), 5.65 (s, 2H, C_5H_4), 5.25 (s, 2H, C_5H_4), 5.22 (s, 2H, C_5H_4), 2.24(s, 3H, $SC_6H_4CH_3$), 2.03 (s, 3H, $C_6H_4CH_3$), 0.62 (s, 3H, $SiCH_3$), 0.49 (s, 3H, $SiCH_3$); MS *m/e* 608 (M^+), 580 ($M^+ - CO$), 524 ($M^+ - 3CO$), 485 ($M^+ - SC_6H_4CH_3$). Anal. Calcd for $C_{30}H_{28}O_3SFe_2Si$: C, 59.22; H, 4.64. Found: C, 59.24; H, 4.77.

[Fe$_2$(μ-CO){μ-C(SCH$_3$)C$_6$H$_4$CF$_3$-p}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] (15): purple-red crystals (77% yield); mp 104−110 °C dec; IR (CH_2Cl_2) ν(CO) 1983 (s), 1952 (m), 1777 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.66−7.35 (dd, 4H, $C_6H_4CF_3$), 6.21 (s, 2H, C_5H_4), 5.64 (s, 2H, C_5H_4), 5.28 (s, 2H, C_5H_4), 5.08 (s, 2H, C_5H_4), 2.09 (s, 3H, SCH_3), 0.62 (s, 3H, $SiCH_3$), 0.49 (s, 3H, $SiCH_3$); MS *m/e* 586 (M^+), 558 ($M^+ - CO$), 530 ($M^+ - 2CO$), 502 ($M^+ - 3CO$), 455 ($M^+ - 3CO - SCH_3$). Anal. Calcd for $C_{24}H_{21}O_3F_3SFe_2Si$: C, 49.17; H, 3.61. Found: C, 49.21; H, 3.76.

[Fe$_2$(μ-CO){μ-C(SC$_6$H$_5$)C$_6$H$_4$CF$_3$-p}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] (16): red crystals (73% yield); mp 136−138 °C dec; IR (CH_2Cl_2) ν(CO) 1984 (s), 1954 (m), 1779 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.61−7.03 (m, 9H, C_6H_5 + $C_6H_4CF_3$), 6.30 (s, 2H, C_5H_4), 5.76 (s, 2H, C_5H_4), 5.32 (s, 2H, C_5H_4), 5.24 (s, 2H, C_5H_4), 0.65 (s, 3H, $SiCH_3$), 0.53 (s, 3H, $SiCH_3$); MS *m/e* 648 (M^+), 564 ($M^+ - 3CO$), 539 ($M^+ - SC_6H_5$). Anal. Calcd for $C_{29}H_{23}O_3F_3SFe_2Si$: C, 53.72; H, 3.55. Found: C, 53.73; H, 3.48.

[Fe$_2$(μ-CO){μ-C(SC$_6$H$_4$CH$_3$-p)C$_6$H$_4$CF$_3$-p}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] (17): purple-red crystals (78% yield); mp 119−121 °C dec; IR (CH_2Cl_2) ν(CO) 1983 (s), 1952 (m), 1777 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.56−7.00 (m, 8H, $C_6H_4CF_3$ + $C_6H_4CH_3$), 6.27 (s, 2H, C_5H_4), 5.75 (s, 2H, C_5H_4), 5.30 (s, 2H, C_5H_4), 5.26 (s, 2H, C_5H_4), 2.24 (s, 3H, $C_6H_4CH_3$), 0.65 (s, 3H, $SiCH_3$), 0.53 (s, 3H, $SiCH_3$); MS *m/e* 662 (M^+), 578 ($M^+ - 3CO$), 539 ($M^+ - SC_6H_4CH_3$). Anal. Calcd for $C_{30}H_{25}O_3F_3SFe_2Si$: C, 54.40; H, 3.8. Found: C, 54.77; H, 4.02.

Preparation of [Fe$_2$(μ-CO)(μ-CC$_6$H$_4$CF$_3$-p)(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}(μ-S)(μ-SC$_6$H$_5$)Fe$_2$(CO)$_6$] (18). To a solution of 0.179 g (0.52 mmol) of [(μ-S)$_2$Fe$_2$(CO)$_6$][17] in 30 mL of THF at −78 °C was added dropwise 0.52 mmol of C_6H_5Li with vigorous stirring within 10 min. The color of the solution turned from red to emerald green. After 10 min stirring at −78 °C, the resulting solution of [(μ-SLi)(μ-SC$_6$H$_5$)Fe$_2$(CO)$_6$][18] was cooled to −100 °C and then poured rapidly onto 0.370 g (0.437 mmol) of freshly (in situ) prepared **6** in 50 mL of THF previously cooled to −100 °C. The reaction proceeded rapidly to form a dark solution. The mixture was stirred at −100 to −50 °C for 5−6 h, during which time the dark solution turned dark red. The resulting mixture was evaporated under high vacuum at −50 to −40 °C to dryness. The dark residue was chromatographed on an alumina column at −25 °C with petroleum ether as the eluant. After removal of a small yellow band from the column, the purple-red band was eluted with petroleum ether/CH_2Cl_2 (10:1) and collected. The solvent was removed in vacuo, and the residue was recrystallized from

Table 2. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 9, 13, and 16

	9	**13**	**16**		**9**	**13**	**16**
Fe(1)−Fe(2)	2.515(3)	2.510(2)	2.516(3)	C(1)−C(2)	1.55(2)	1.52(1)	1.47(2)
Fe(1)−C(1)	2.04(1)	2.032(10)	2.08(2)	C(1)−S	1.81(1)	1.81(1)	1.80(1)
Fe(2)−C(1)	2.00(1)	2.01(1)	2.01(1)	S−C(26)	1.81(2)	1.78(1)	1.79(2)
Fe(1)−C(10)	1.88(2)	1.90(1)	1.87(2)	Si−C(17)	1.88(1)	1.87(1)	1.87(1)
Fe(2)−C(10)	1.96(2)	1.91(1)	1.88(2)	Si−C(18)	1.88(1)	1.90(1)	1.90(2)
C(10)−O(2)	1.18(2)	1.18(1)	1.21(2)	Si−C(23)	1.83(2)	1.85(1)	1.85(2)
Fe(1)−C(8)	1.75(2)	1.76(1)	1.73(2)	Si−C(24)	1.83(2)	1.85(1)	1.88(2)
C(8)−O(1)	1.14(2)	1.15(1)	1.18(2)	Fe(1)−C(Cp) (av)	2.134	2.134	2.122
Fe(2)−C(9)	1.75(2)	1.74(1)	1.73(2)	Fe(2)−C(Cp) (av)	2.130	2.134	2.126
C(9)−O(3)	1.14(2)	1.14(1)	1.18(2)				
Fe(1)−Fe(2)−C(1)	52.2(4)	52.0(3)	53.2(4)	Fe(2)−C(1)−S	123.2(7)	118.2(5)	119.5(7)
Fe(1)−C(1)−Fe(2)	77.0(4)	76.9(4)	76.0(5)	Fe(1)−C(1)−C(2)	118.0(9)	119.2(7)	116.2(9)
Fe(2)−Fe(1)−C(1)	50.8(4)	51.1(3)	50.8(3)	Fe(2)−C(1)−C(2)	121.5(9)	125.2(8)	124.7(9)
Fe(1)−Fe(2)−C(10)	47.8(4)	48.7(4)	47.7(5)	Fe(1)−C(8)−O(1)	173(1)	172(1)	172(1)
Fe(1)−C(10)−Fe(2)	81.9(7)	82.3(6)	84.1(8)	Fe(2)−C(9)−O(3)	175(1)	172(1)	173(1)
Fe(2)−Fe(1)−C(10)	50.4(5)	49.0(4)	48.1(5)	Fe(1)−C(17)−Si	119.5(6)	120.3(5)	121.0(7)
C(1)−Fe(1)−C(10)	96.7(6)	95.6(5)	94.7(6)	Fe(2)−C(18)−Si	120.2(6)	120.5(6)	121.2(7)
C(1)−Fe(2)−C(10)	95.6(6)	96.1(5)	96.5(7)	C(17)−Si−C(18)	106.8(6)	104.9(4)	104.1(7)
Fe(1)−C(10)−O(2)	143(1)	137.9(10)	137(1)	C(10)−Fe(2)−C(1)	95.6(6)	96.1(5)	96.5(7)
Fe(2)−C(10)−O(2)	134(1)	139(1)	138(1)	C(1)−S−C(26)	104.2(7)	110.1(5)	107.3(8)
Fe(1)−C(1)−S	111.9(6)	109.9(5)	109.5(7)				

[a] Estimated standard deviations in the least significant figure are given in parentheses.

Table 3. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complex 18

Fe(1)−Fe(2)	2.505(3)	Fe(2)−C(9)	1.761(14)	Si−C(24)	1.863(11)
Fe(1)−C(1)	2.053(11)	C(9)−O(3)	1.148(14)	S(1)−Fe(3)	2.297(4)
Fe(2)−C(1)	2.041(11)	C(1)−C(2)	1.510(15)	S(1)−Fe(4)	2.296(3)
Fe(1)−C(10)	1.895(15)	S(1)−C(1)	1.847(12)	S(2)−Fe(3)	2.236(4)
Fe(2)−C(10)	1.936(14)	S(2)−C(26)	1.780(11)	S(2)−Fe(4)	2.246(4)
C(10)−O(2)	1.183(14)	Si−C(17)	1.870(15)	Fe(3)−Fe(4)	2.531(3)
Fe(1)−C(8)	1.762(16)	Si−C(18)	1.859(14)	Fe(1)−C(Cp) (av)	2.106
C(8)−O(1)	1.150(15)	Si−C(23)	1.826(13)	Fe(2)−C(Cp) (av)	2.092
Fe(1)−Fe(2)−C(1)	52.5(3)	Fe(2)−C(10)−O(2)	137.7(13)	S(1)−C(1)−C(2)	109.6(7)
Fe(1)−C(1)−Fe(2)	75.4(4)	Fe(1)−C(1)−S(1)	112.9(5)	C(1)−S(1)−Fe(3)	123.9(4)
Fe(2)−Fe(1)−C(1)	52.1(3)	Fe(2)−C(1)−S(1)	112.6(6)	C(1)−S(1)−Fe(4)	124.5(4)
Fe(1)−Fe(2)−C(10)	48.5(4)	Fe(1)−C(1)−C(2)	120.0(9)	S(1)−Fe(3)−Fe(4)	56.55(10)
Fe(1)−C(10)−Fe(2)	81.7(6)	Fe(2)−C(1)−C(2)	122.8(8)	S(1)−Fe(4)−Fe(3)	56.56(10)
Fe(2)−Fe(1)−C(10)	49.9(4)	Fe(1)−C(17)−Si	121.4(7)	Fe(3)−S(1)−Fe(4)	66.88(11)
C(1)−Fe(1)−C(10)	97.6(5)	Fe(2)−C(18)−Si	122.7(7)	S(2)−Fe(3)−Fe(4)	55.82(11)
C(1)−Fe(2)−C(10)	96.7(5)	Fe(1)−C(1)−S(1)	112.9(5)	S(2)−Fe(4)−Fe(3)	55.42(11)
Fe(1)−C(10)−O(2)	140.6(13)	Fe(2)−C(1)−S(1)	112.6(6)	Fe(3)−S(2)−Fe(4)	68.77(12)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

petroleum ether/CH_2Cl_2 solution at −80 °C to give 0.28 g (68%, based on **7**) of blackish red crystals of **18**: mp 96−98 °C dec; IR (CH_2Cl_2) ν(CO) 2059 (m), 2024 (s), 1991 (s), 1787 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.75−7.15 (m, 9H, $C_6H_5 + C_6H_4CF_3$), 5.62−5.31 (m, 8H, C_5H_4), 0.83 (s, 3H, $SiCH_3$), 0.69 (s, 3H, $SiCH_3$); MS *m/e* 539 [$M^+ - (\mu\text{-S})(\mu\text{-SC}_6H_5)Fe_2(CO)_6$], 421 [$(\mu\text{-S})(\mu\text{-SC}_6H_5)Fe_2(CO)_6{}^+$], 337 $(\mu\text{-S})(\mu\text{-SC}_6H_5)Fe_2(CO)_3{}^+$], 84 ($CH_2Cl_2{}^+$). Anal. Calcd for $C_{35}H_{23}O_9F_3S_2Fe_4Si{\cdot}CH_2Cl_2$: C, 41.37; H, 2.41. Found: C, 40.95; H, 2.51.

Preparation of [$Fe_2(\mu\text{-CO})(\mu\text{-CC}_6H_5)(CO)_2(\eta^5\text{-C}_5H_5)_2(\mu\text{-S})(\mu\text{-SC}_6H_5)Fe_2(CO)_6$] (19). As used in the reaction of **6** with [$(\mu\text{-SLi})(\mu\text{-SC}_6H_5)Fe_2(CO)_6$], compound **7** (0.51 g, 0.68 mmol) was treated with [$(\mu\text{-SLi})(\mu\text{-SC}_6H_5)Fe_2(CO)_6$], prepared (in situ) by the reaction of [$(\mu\text{-S})_2Fe_2(CO)_6$] (0.275 g, 0.80 mmol) with 0.80 mmol of C_6H_5Li, at −100 to −40 °C for 5 h, during which time the green solution turned dark red. Further treatment as that for the preparation of **18** gave 0.39 g (68%, based on **7**) of blackish red crystals of **19**: mp 54−56 °C dec; IR (CH_2Cl_2) ν(CO) 2062 (s), 2053 (s), 2025 (vs), 1977 (vs, br), 1811 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.82−7.11 (m, 10H, $2C_6H_5$), 5.26 (s, 5H, C_5H_5), 4.97 (s, 5H, C_5H_5); MS *m/e* 338 [$M^+ - C_6H_5 - (\mu\text{-S})(\mu\text{-SC}_6H_5)\ Fe_2(CO)_6$], 282 [$M^+ - 2CO - C_6H_5 - (\mu\text{-S})(\mu\text{-SC}_6H_5)Fe_2(CO)_6$], 344 [$(\mu\text{-S})_2Fe_2(CO)_6{}^+$], 288 [$(\mu\text{-S})_2Fe_2(CO)_4{}^+$], 260 [$(\mu\text{-S})_2Fe_2(CO)_3{}^+$], 232 [$(\mu\text{-S})_2Fe_2(CO)_2{}^+$], 204 [$(\mu\text{-S})_2Fe_2(CO)^+$], 176 [$(\mu\text{-S})_2Fe_2{}^+$]. Anal. Calcd for $C_{32}H_{20}O_9S_2Fe_4$: C, 45.97; H, 2.41. Found: C, 46.13; H, 2.66.

Preparation of [$Fe_2(\mu\text{-CO})(\mu\text{-CC}_6H_4CH_3\text{-p})(CO)_2(\eta^5\text{-C}_5H_5)_2(\mu\text{-S})(\mu\text{-SC}_6H_5)Fe_2(CO)_6$] (20). Similar to the procedures for the reaction of **6** with [$(\mu\text{-SLi})(\mu\text{-SC}_6H_5)Fe_2(CO)_6$], compound **8** (0.52 g, 0.69 mmol) was treated with [$(\mu\text{-SLi})(\mu\text{-SC}_6H_5)Fe_2(CO)_6$], prepared (in situ) by the reaction of [$(\mu\text{-S})_2Fe_2(CO)_6$] (0.275 g, 0.80 mmol) with 0.80 mmol of C_6H_5Li, at −100 to −40 °C for 5 h, during which time the green solution turned dark red. Further treatment as that for the preparation of **18** yielded 0.42 g (72%, based on **8**) of **20** as blackish red crystals: mp 58−59 °C dec; IR (CH_2Cl_2) ν(CO) 2062 (m), 2052 (s), 2015 (vs, br), 1974 (vs, br), 1810 (s) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.60−7.25 (m, 10H, $2C_6H_5$), 5.28 (m, 2H, CH_2Cl_2), 5.14 (s, 5H, C_5H_5), 4.94 (s, 5H, C_5H_5), 2.51 (s, 3H, $C_6H_4CH_3$); MS *m/e* 254 [$M^+ - 3CO - C_6H_5 - (\mu\text{-S})(\mu\text{-SC}_6H_5)\text{-}Fe_2(CO)_6$], 344 [$(\mu\text{-S})_2Fe_2(CO)_6{}^+$], 232 [$(\mu\text{-S})_2Fe_2(CO)_2{}^+$], 204 [$(\mu\text{-S})_2Fe_2(CO)^+$], 176 [$(\mu\text{-S})_2Fe_2{}^+$], 84 ($CH_2Cl_2{}^+$). Anal. Calcd for $C_{33}H_{22}O_9S_2Fe_4{\cdot}CH_2Cl_2$: C, 43.68; H, 2.59. Found: C, 43.87; H, 2.81.

X-ray Crystal Structure Determinations of Complexes 9, 13, 16, and 18. The single crystals of **9**, **13**, **16**, and **18** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH_2Cl_2 solution at −80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data were collected with Rigaku AFC7R and Brock Smart diffractometer at 20 °C using Mo Kα radiation ($\lambda = 0.71069$ Å) with a $\omega - 2\theta$ scan mode.

The structures of **9**, **13**, and **18** were solved by direct methods and expanded using Fourier techniques. For **9**, some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. For **13** and **18**, the non-

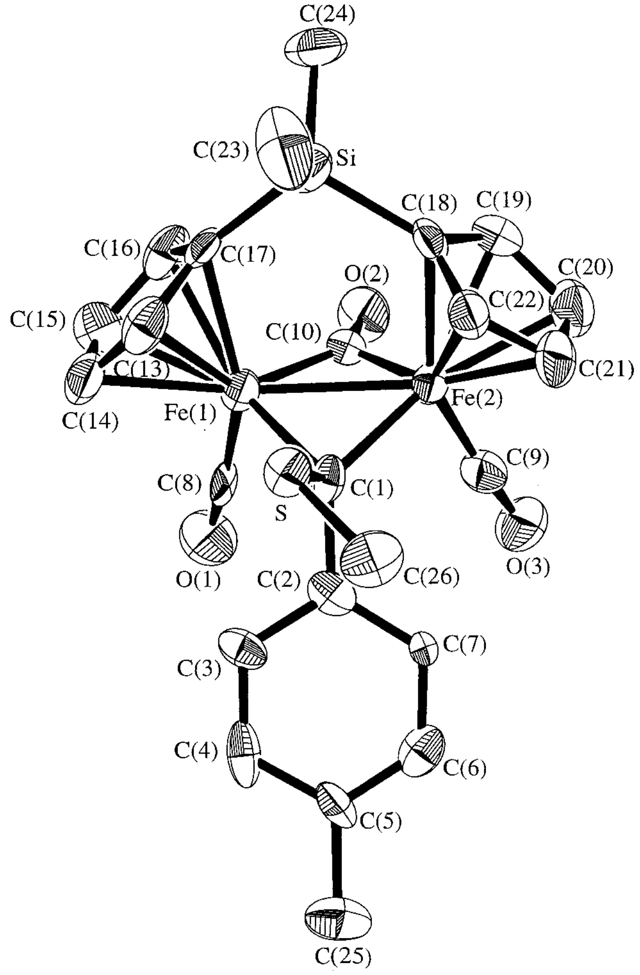


Figure 1. Molecular structure of **9**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 45% probability. CH_2Cl_2 has been omitted for clarity.

hydrogen atoms were refined anisotropically. For the three complexes the hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement gave agreement factors of $R = 0.058$ and $R_w = 0.056$ for **9**, $R = 0.058$ and $R_w = 0.050$ for **13**, and $R = 0.0590$ and $R_w = 0.0707$ for **18**. The structure of **16** was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement gave agreement factors of $R = 0.071$ and $R_w = 0.079$.

The details of the crystallographic data and the procedures used for data collection and reduction information for **9**, **13**, **16**, and **18** are given in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3. The atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, complete bond lengths and angles, least-squares planes for **9**, **13**, **16**, and **18**, and the molecular structure of **16**) are given in the Supporting Information. The molecular structures of **9**, **13**, and **18** are given in Figures 1, 2, and 3, respectively.

Results and Discussion

The dimethylsilane-bridged bis(η^5-cyclopentadienyl)-diiron bridging alkoxy carbene complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ (**1**, Ar = C_6H_5; **2**, Ar = p-$CH_3C_6H_4$; **3**, Ar = p-$CF_3C_6H_4$)[15] in ether were treated, similar to the procedures for the preparation of the cationic carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**7**, Ar = C_6H_5; **8**, Ar = p-$CH_3C_6H_4$),[9] with an excess of BBr_3 at −65 °C to produce diiron cationic bridging carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ (**4**, Ar = C_6H_5; **5**, Ar = p-$CH_3C_6H_4$; **6**, Ar = p-$CF_3C_6H_4$) as brown-red solids in 84−87% yields (eq 1).

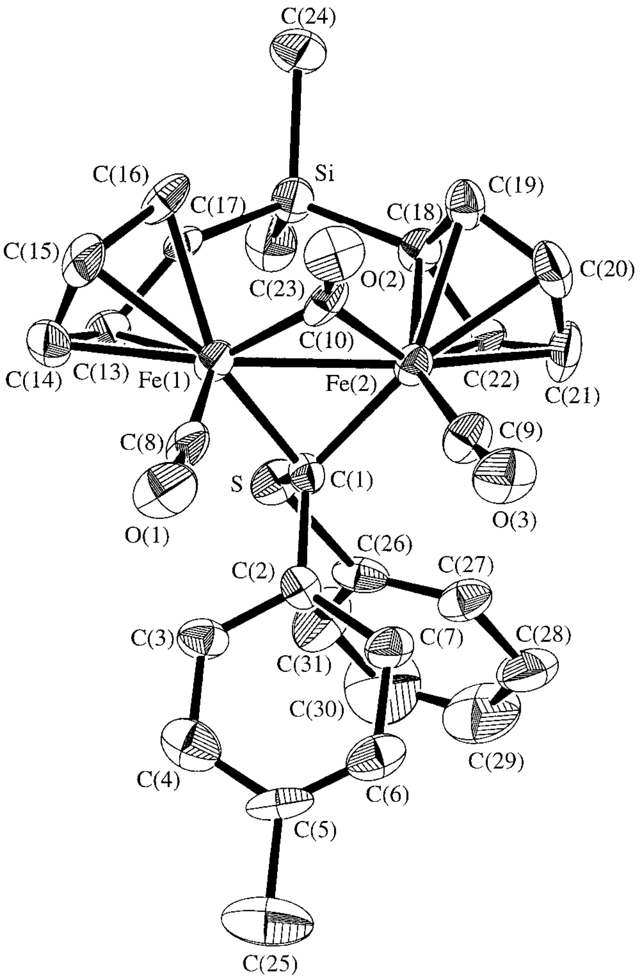
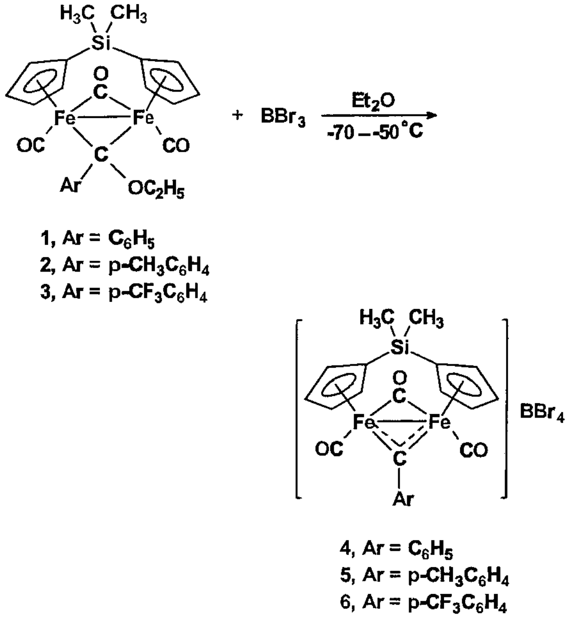


Figure 2. Molecular structure of **13**, showing the atom-numbering scheme with 40% thermal ellipsoids.

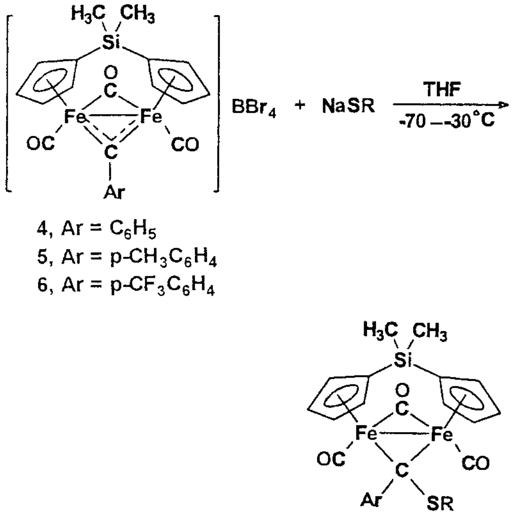


(1)

Cationic bridging carbyne complexes **4**−**6** are only sparingly soluble in polar organic solvents, such as THF and CH_2Cl_2. They are very sensitive to air, moisture, and temperature and can be stored at low temperature (below −65 °C) only for a short period. The compositions and structures of complexes **4**−**6** were established on the basis of their IR and ^1H NMR spectra. Since complexes **4**−**6** contain diethyl ether and are extremely labile, we cannot get satisfactory results of the elemental analyses.

The freshly prepared (in situ) cationic carbyne complex $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_5)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**4**) reacts with about 15−20% molar excess of NaSR (R = CH_3, C_6H_5, p-$CH_3C_6H_4$), in THF at low temperature (−80 to −20 °C) for 4−5 h. After workup as described in the Experimental Section, the brown-red diiron bridging mercaptocarbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SR)C_6H_5\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**9**, R = CH_3; **10**, R = C_6H_5; **11**, R = p-$CH_3C_6H_4$) were isolated in 70−75% yields (eq 2).

The analogous reactions of $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**5**, Ar = p-$CH_3C_6H_4$; **6**, Ar = p-$CF_3C_6H_4$) with NaSR under the same conditions yielded the corresponding bridging mercaptocarbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SR)Ar\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**12**, Ar = p-$CH_3C_6H_4$, R = CH_3; **13**, Ar = p-$CH_3C_6H_4$, R = C_6H_5; **14**, Ar = p-$CH_3C_6H_4$, R = p-$CH_3C_6H_4$; **15**, Ar = p-$CF_3C_6H_4$, R = CH_3; **16**, Ar = p-$CF_3C_6H_4$, R = C_6H_5; **17**, Ar = p-$CF_3C_6H_4$, R = p-$CH_3C_6H_4$) (eq 2) in 64−78% yields.



4, Ar = C_6H_5
5, Ar = p-$CH_3C_6H_4$
6, Ar = p-$CF_3C_6H_4$

(2)

	CH_3	C_6H_5	p-$CH_3C_6H_4$
C_6H_5	9	10	11
p-$CH_3C_6H_4$	12	13	14
p-$CF_3C_6H_4$	15	16	17

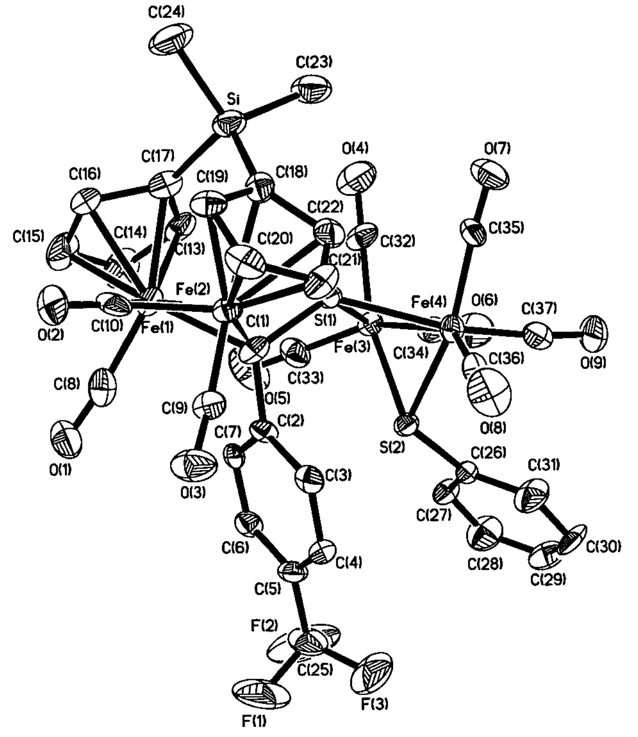


Figure 3. Molecular structure of **18**, showing the atom-numbering scheme with 40% thermal ellipsoids. CH_2Cl_2 has been omitted for clarity.

Complexes **9**−**17** are readily soluble in polar organic solvents but slightly soluble in nonpolar solvents. They are sensitive to air and temperature in solution but relatively stable in the solid state. The formulas shown in eq 2 for complexes **9**−**17** were established by elemental analysis and IR, ^1H NMR, and mass spectroscopy (Experimental Section). The IR spectra of **9**−**17** showed two CO absorption bands at 1984−1949 cm^{-1} and one at 1779−1771 cm^{-1} in the bridging ν(CO) region, evidence for an $Fe_2(\mu\text{-}CO)(CO)_2$ moiety in these complexes. In the ^1H NMR spectra of **9**−**17**, the proton signals attributed to the dicyclopentadienyl protons showed four resonances at about 6.30−5.05 ppm, similar to those of precursor complexes **1**−**3**.[15]

The structures of complexes **9**, **13**, and **16**, which have been established by X-ray diffraction studies, resemble that of **1**, except that the substituent on the μ-carbene carbon is a SR group in **9**, **13**, and **16** and an OEt group in **1**. The mercapto and aryl groups are attached to the μ-carbene carbon, and the two cyclopentadienyl rings are in totally eclipsed configuration, as anticipated from the IR and ^1H NMR spectra.

The distances of the Fe−Fe bond bridged by the μ-carbene ligand in **9**, **13**, and **16** are 2.515(3), 2.510(2), and 2.516(3) Å, respectively, which are the same as that found in **1** (2.513(1) Å).[15] The μ-carbene carbon almost symmetrically bridges the Fe−Fe bond with a C(1)−Fe(1) of 2.03−2.08 Å and a C(1)−Fe(2) of 2.00−2.01 Å for **9**, **13**, and **16**. The μ-C−Fe distances are much longer than the μ-Fe−CO bond (C(10)−Fe(1) 1.87−1.90 Å, C(10)−Fe(2) 1.88−1.96 Å) but approximately equal to that in $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(CN)NHPh\}CC(CO)_2(\eta^5\text{-}C_5H_5)]$ (C(4)−Fe(1) 2.004(2) Å, C(4)−Fe(2) 2.028(2) Å).[19] The C(1)−S distances (1.81(1) Å for **9** and **13**, 1.80(1) Å for **16**) indicate that they are essentially single bonds by comparison with standard C(sp^2)−S (1.76 Å)[20] single bond and C(sp^3)−S(1.81 Å)[20] single bond distances.

Like NaSR, (μ-phenylthio)(μ-thiolato)hexacarbonyldiiron, $[(\mu\text{-}SLi)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$, can also react with cationic carbyne complex **6** under similar conditions to produce the iron−sulfur cluster bridging carbene

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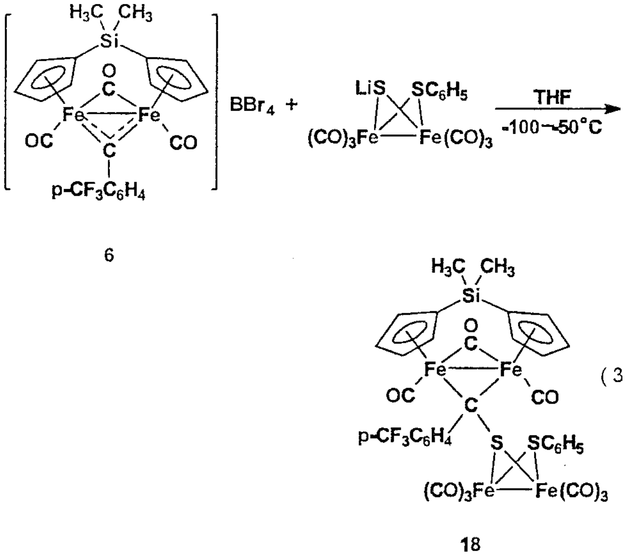
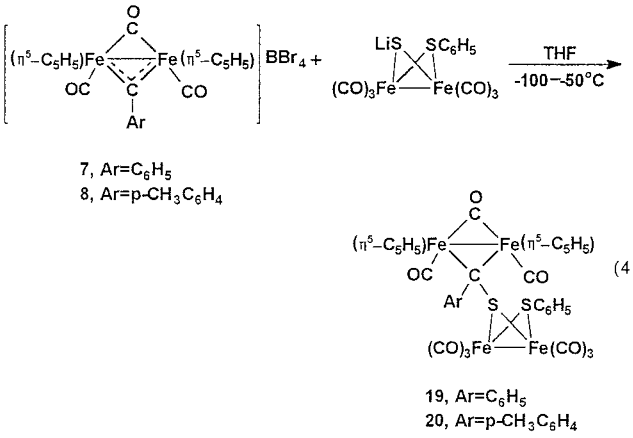
[19] Albano, V. G.; Bordoni, S.; Braga, D.; Busetto, L.; Palazzi, A.; Zanotti, V. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 847.

[20] (a) Rozsondai, B.; Schultz, G.; Hargittai, I. *J. Mol. Struct.* **1981**, *70*, 309. (b) Samdal, S.; Seip, H. M.; Torgrimsen, T. *J. Mol. Struct.* **1979**, *57*, 105.

complex $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CF_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$ (**18**) in 68% yield (eq 3).



Analogous iron−sulfur cluster bridging carbene complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_5)(CO)_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$ (**19**) and $[Fe_2(\mu\text{-}CO)(\mu\text{-}CCH_3C_6H_4\text{-}p)(CO)_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$ (**20**) in 68% and 72%, respectively, were also obtained by the reactions of diiron cationic bridging carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**7**, Ar = C_6H_5; **8**, p-$CH_3C_6H_4$) with $[(\mu\text{-}SLi)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$ (eq 4).



However, not all such diiron cationic bridging carbyne complexes can react with $[(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]^-$ anion to produce the iron−sulfur cluster bridging carbene complexes since the cationic bridging carbyne complexes, **4** and **5**, where the aryl substituents at the μ-carbyne carbon are a phenyl and a *p*-tolyl group, respectively, react with $[(\mu\text{-}SLi)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$ under the same conditions to give not analogous iron−sulfur cluster bridging carbene complex but rather a decomposition mixture which cannot be isolated by column chromatography or by recrystallization. This suggests that the different cyclopentadienyl ligands and aryl substituents at the bridging carbyne carbon exert a great influence on the reactivity of the diiron cationic bridging carbyne complexes. In the case of complex **6**, the electron-withdrawing *p*-$CF_3C_6H_4$ group increased electrophilic reactivity of the bridging carbyne carbon owing to its strong electron-withdrawing action, which promotes the nucleophilic attack of the $[(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]^-$ anion on the μ-carbyne carbon of **6**, resulting in the formation of iron−sulfur cluster bridging carbene complex **18**.

The formulas shown in eqs 3 and 4 for complexes **18**−**20** were based on the elemental analysis and IR, ^1H NMR, and mass spectroscopy (Experimental Section) as well as X-ray crystallography. The IR spectra of **18**−**20** in the ν(CO) region showed an absorption band at ca. 1810 cm^{-1} attributed to the bridging CO ligand, in addition to four terminal CO absorption bands at 2062−1974 cm^{-1}, which signified $Fe_2(\mu\text{-}CO)(CO)_2$ and $Fe_2(CO)_6$ moieties in these complexes.

The molecular structure (Figure 3) of **18** was established by X-ray diffraction studies, which show that it is a derivative of $(\mu\text{-}S)_2Fe_2(CO)_6$ in which the bridging carbene carbon is bonded by a $(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6$ moiety. The average Fe−μ-C distance of 2.047 Å is slightly longer than that found (2.020−2.022 Å) in mercaptocarbene complexes **9** and **13**. The μ-C−S(1) bond length of 1.847(12) Å in **25** is significantly longer than that in the analogous iron−sulfur cluster carbene complex $[\{\eta^5\text{-}C_5H_5(CO)_2Re{=}CC_6H_5\}(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$ (1.70(2) Å)[12] and slightly longer than that in complexes **9** and **13** (1.80(1)−1.81(1) Å). Except for the $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CF_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ unit, the structure of the $(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6$ portion of **18** is nearly the same as that in analogous complexes $[\{\eta^5\text{-}C_5H_5(CO)_2Re{=}CC_6H_5\}(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$,[12] $[(C_6H_5S)Fe_2(CO)_6S{-}S(CO)_6Fe_2(SC_6H_5)]$,[21] and $[(\mu\text{-}CH_3S)Fe_2(CO)_6]_2[\mu\text{-}S\text{-}(m\text{-}CH_2C_6H_4CH_2)\text{-}S\text{-}\mu]$,[22] as illustrated by the following parameters (the value for **18** is followed by the same parameters for Re carbene complexes, $[(C_6H_5S)Fe_2(CO)_6S{-}S(CO)_6Fe_2(SC_6H_5)]$, and $[(\mu\text{-}CH_3S)Fe_2(CO)_6]_2[\mu\text{-}S\text{-}(m\text{-}CH_2C_6H_4CH_2)\text{-}S\text{-}\mu]$: Fe−Fe (2.531(3), 2.523(4), 2.523 (av), 2.510 (av) Å), average Fe−S (2.269, 2.260, 2.261, 2.260 Å), average Fe−S−Fe (67.825, 67.45, 68.25, 67.46°). The distance of the S atom to the phenyl (S(2)−C(26) 1.780(11) Å) in **18** is somewhat shorter than that in $[\{\eta^5\text{-}C_5H_5(CO)_2Re{=}CC_6H_5\}(\mu\text{-}S)(\mu\text{-}SC_6H_5)Fe_2(CO)_6]$ (S(2)−C(13) 1.82(2) Å)[12] but is the same within experimental error as that in $[(C_6H_5S)Fe_2(CO)_6S{-}S(CO)_6Fe_2(SC_6H_5)]$ (average 1.786 Å).[21]

The structural features of the $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4\text{-}CF_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ unit of **18** are very similar to those of the same unit in complex **1**, as illustrated by the following parameters (the value for **18** is followed by the same parameters for **1**): Fe(1)−Fe(2) (2.505, 2.513(1) Å), average Fe−C(Cp) (2.099, 2.123 Å), average μ-C−Fe (2.047, 2.045 Å), average Fe−C(10) (1.916, 1.906 Å), Fe(1)−C(1)−Fe(1) (75.4(4)°, 76.9(2)°), Fe(1)−C(10)−Fe(2) (81.7(6)°, 82.5(2)°).

The title reaction shows a variety of reactions of the dimethylsilane-bridged bis(η^5-cyclopentadienyl)diiron cationic bridging carbyne complexes with nucleophiles to give a series of diiron bridging carbene complexes. This offers a new, convenient, and useful method for the preparation and structural modification of dimetal

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(21) Seyferth, D.; Kinwan, A. M. *J. Organomet. Chem.* **1985**, *281*, 111.

(22) Song, Li.-C.; Kadiata, M.; Wang, J.-T. *J. Organomet. Chem.* **1990**, *391*, 387.

bridging carbene complexes. In particular, it offers a new route to the iron−sulfur cluster bridging carbene complexes.

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Supporting Information Available: Tables of positional parameters and B_{iso}/B_{eq}, H atom coordinates, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **9**, **13**, **16**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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