

Reactions of Cationic Bridging Carbyne Complexes of Bis(η -cyclopentadienyl)diiron Tricarbonyl with Nucleophiles. A Route to Diiron Bridging Carbene Complexes

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The reactions of the cationic carbyne complex of diiron, $[\text{Fe}_2(\mu\text{-CO})(\mu\text{-CPh})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]\text{-BBr}_4$ (**3**), with NaSMe, NaSEt, NaSPh, $\text{NaSC}_6\text{H}_4\text{Me-p}$, and $\text{NaSC}_6\text{H}_4\text{NO}_2\text{-p}$ in THF at low temperature afforded diiron bridging thiocarbene complexes $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SR})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**5**, R = Me; **6**, R = Et; **7**, R = Ph; **8**, R = p-MeC₆H₄; **9**, R = p-NO₂C₆H₄). Complex $[\text{Fe}_2(\mu\text{-CO})(\mu\text{-CC}_6\text{H}_4\text{Me-p})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]\text{BBr}_4$ (**4**) reacted similarly with NaSPh and $\text{NaSC}_6\text{H}_4\text{-Me-p}$ to give corresponding bridging carbene complexes $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SR})\text{C}_6\text{H}_4\text{Me-p}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**10**, R = Ph; **11**, R = p-MeC₆H₄). Complex **3** also reacted with NaOPh and $\text{NaN}(\text{SiMe}_3)_2$ to yield bridging carbene complexes $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{OPh})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**12**) and $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{N}(\text{SiMe}_3)_2)\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**13**), respectively. Complexes **3** and **4** reacted with reactive salt $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SBu}^n)(\text{CO})_6]$ to yield the bridging mercapto-carbene complex $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SH})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**14**) and the bridging butylthio-carbene complex $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SBu}^n)\text{C}_6\text{H}_4\text{Me-p}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**15**), respectively. The analogous reactions of $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SPh})(\text{CO})_6]$ with **3** and **4** afforded the thiolato-bridged iron carbonyl compound $[\text{Fe}_2(\mu\text{-SPh})_2(\text{CO})_6]$ (**16**) and the bridging arylcarbene complexes $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})\text{Ar}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**17**, Ar = Ph; **18**, Ar = p-MeC₆H₄), while $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SC}_6\text{H}_4\text{Me-p})(\text{CO})_6]$ reacted with **3** to yield **17** and $[\text{Fe}_2(\mu\text{-SC}_6\text{H}_4\text{Me-p})_2(\text{CO})_6]$ (**19**). The reaction of metal carbonyl anion compounds $\text{Na}_2\text{W}(\text{CO})_5$ and $\text{Na}_2\text{Fe}(\text{CO})_4$ with **3** gave the same product, **17**. The structures of **6**, **7**, **15**, and **17** have been established by X-ray diffraction studies.

Introduction

The considerable interest in the synthesis and structure of a variety of metal–metal bonded cluster complexes is largely due to their important role in many catalytic reactions.^{1–3} Since many dinuclear and polynuclear metal bridging carbene and carbyne complexes are themselves metal clusters or are the precursors of metal cluster complexes, the chemistry of transition metal complexes that contain bridging carbene and carbyne ligands is an area of current interest. In this regard, we are interested in developing the methodologies for the synthesis of such complexes. Metal complexes that contain bridging carbene and carbyne ligands have been examined extensively by Stone and co-workers. Many dimetal bridging carbene and carbyne complexes have been synthesized by reactions^{4–6} of carbene and carbyne complexes with low-valent metal

species, by reactions⁷ of neutral and anionic carbyne complexes with metal hydrides and cationic metal compounds, or by reactions^{8,9} of cationic carbyne complexes with monoanionic carbonylmetal compounds such as $\text{Na}[\text{Re}(\text{CO})_5]$, $[(\text{Ph}_3\text{P})_2\text{N}][\text{Mn}(\text{CO})_5]$, and $[(\text{Ph}_3\text{P})_2\text{N}][\text{Fe}(\text{CO})_3\text{NO}]$. In our laboratory, one of the methods for the preparation of bridging carbene and carbyne complexes has used the reactions of the highly electro-

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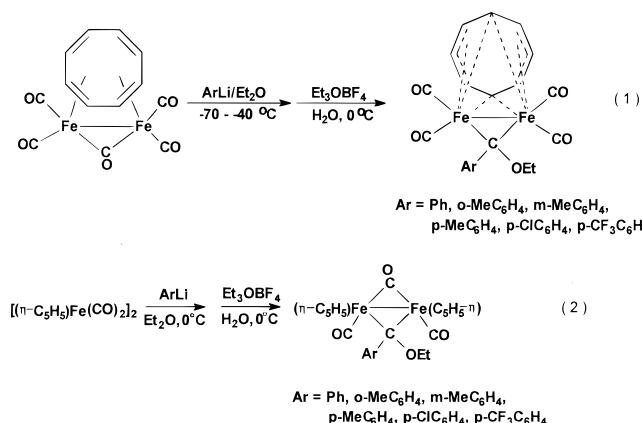
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philic cationic carbyne complexes of manganese and rhenium, $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{M}\equiv\text{CPh}]\text{BBr}_4$ ($\text{M} = \text{Mn}$ or Re), with anionic carbonylmethyl compounds. Both of these cationic carbyne complexes reacted not only with monoanionic carbonylmethyl compounds such as $(\text{Me}_4\text{N})\text{-}[\text{FeH}(\text{CO})_4]$, $\text{Li}[\text{Co}(\text{CO})_4]$, $\text{Na}[\eta\text{-C}_5\text{H}_5\text{M}(\text{CO})_3]$ ($\text{M} = \text{Mo}$ or W), $\text{Na}[\text{Co}(\text{CO})_3\text{PPh}_3]$, and $\text{Na}[\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]$ but also with dianionic carbonylmethyl compounds such as $\text{Na}_2[\text{Fe}(\text{CO})_4]$, $(\text{Et}_4\text{N})_2[\text{Fe}_2(\text{CO})_8]$, $\text{Na}_2[\text{Fe}_3(\text{CO})_{11}]$, and $\text{Na}_2[\text{W}(\text{CO})_5]$, and mixed-dimetal carbonyl anion compounds such as $(\text{Ph}_3\text{P})_2\text{N}[\text{FeCo}(\text{CO})_8]$ and $(\text{Ph}_3\text{P})_2\text{N}[\text{WCo}(\text{CO})_9]$ to form heteronuclear dimetal bridging carbene and/or bridging carbyne complexes.¹⁰ The synthesis of these new dimetal bridging carbene and/or bridging carbyne complexes is based on preparative methods developed earlier.^{8,9} Recently, we found another method for the preparation of bridging carbene and carbyne complexes: the reactions of olefin-ligated dimetal carbonyl compounds with nucleophiles, followed by alkylation with $[\text{Et}_3\text{O}]\text{BF}_4$. For instance, the reactions of pentacarbonyl(cyclooctatetraene)diiron and bis(η -cyclopentadienyl)diiron tetracarbonyl with aryl-lithium reagents followed by alkylation with $[\text{Et}_3\text{O}]\text{BF}_4$ gave olefin-coordinated dimetal bridging alkoxy-carbene complexes, $[\text{Fe}_2\{\mu\text{-C}(\text{OEt})\text{Ar}\}(\text{CO})_4(\text{C}_8\text{H}_8)]$ ¹¹ (eq 1) and $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{OEt})\text{Ar}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ ¹² (eq 2), respectively.



To examine the scope of this new synthetic method for dimetal complexes containing bridging carbene and carbyne ligands, we chose bis(η -cyclopentadienyl)diiron complexes containing bridging alkoxy-carbene ligands $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{OEt})\text{Ar}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**1**, Ar = Ph; **2**, Ar = p-MeC₆H₄) as starting material for use in reactions with Lewis acids such as BBr_3 to form the respective diiron cationic bridging carbyne complexes $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{Ar})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]\text{BBr}_4$ (**3**, Ar = Ph; **4**, Ar = p-MeC₆H₄). The analogous conversion of dimetal $\mu\text{-CR}(\text{OR}')$ complexes to cationic $\mu\text{-CR}$ species using

$[\text{Me}_3\text{O}]\text{BF}_4$ or $\text{HBF}_4\cdot\text{OEt}_2$ is known.¹³ Cationic carbyne complexes **3** and **4** react with nucleophilic carbonylmethyl anions to produce a series of new dimetal bridging carbene complexes. Herein we describe these reactions and the structural characterizations of the resulting products.

Experimental Section

All procedures were performed under an 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. 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 . 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 $\text{NaN}(\text{SiMe}_3)_2$ (~2 M in THF), NaSMe , and NaSPh were purchased from Fluka Chemical Co. and Aldrich Chemical Co., respectively. Compounds **1**¹² and **2**,¹² and NaSeT ,¹⁴ $\text{NaSC}_6\text{H}_4\text{Me-p}$,¹⁴ $\text{NaSC}_6\text{H}_4\text{NO}_2\text{-p}$,¹⁵ NaOPh ,¹⁶ $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-RS})(\text{CO})_6]$ ¹⁷ ($\text{R} = \text{Bu}^n$, Ph, p-MeC₆H₄), $\text{Na}_2\text{W}(\text{CO})_5$,¹⁸ and $\text{Na}_2\text{Fe}(\text{CO})_4$ ¹⁹ were prepared by literature methods.

The 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 of samples in sealed nitrogen-filled capillaries are uncorrected.

Preparation of $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{Ph})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]\text{BBr}_4$ (3**).** Following the known preparations of the analogous cationic carbyne complexes $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{M}\equiv\text{CPh}]\text{BBr}_4$ ($\text{M} = \text{Mn}$, Re),^{20,21} to a solution of $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{OEt})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**1**) (0.30 g, 0.652 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 –40 °C to give 0.37 g (76%) of **3** as a brown-red solid: mp 84–85 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 2095 (m), 2030 (s), 1851 (m) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 8.51 (m, 2H, C₆H₅), 8.06–7.92 (m, 3H, C₆H₅), 5.86 (s, 10H, C₅H₅), 3.42 (q, 6H, $(\text{CH}_3\text{CH}_2)_2\text{O}$), 1.12 (t, 9H, $(\text{CH}_3\text{CH}_2)_2\text{O}$). Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{O}_3\text{BBr}_4\text{Fe}_2\cdot 1.5(\text{C}_2\text{H}_5)_2\text{O}$: C, 36.45; H, 3.53. Found: C, 36.82; H, 3.27.

Preparation of $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-CC}_6\text{H}_4\text{Me-p}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]\text{BBr}_4$ (4**).** This complex was prepared in manner similar to **3** using $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{OEt})\text{C}_6\text{H}_4\text{Me-p}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**2**) (0.30

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g, 0.632 mmol) and BBr_3 (0.30 mL, 3.20 mmol). A brown-red solid product, **4**, was obtained, yield 0.36 g (75%), mp 76–78 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 2035 (vs), 2005 (m), 1844(s) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 8.40 (m, 2H, C_6H_5), 7.73 (m, 1H, C_6H_5), 7.36 (m, 1H, C_6H_5), 5.82 (s, 10H, C_5H_5), 3.48 (q, 2H, $(\text{CH}_3\text{CH}_2)_2\text{O}$), 2.85 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 1.14 (t, 3H, $(\text{CH}_3\text{CH}_2)_2\text{O}$). Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_3\text{BBr}_4\text{Fe}_2 \cdot 0.5(\text{C}_2\text{H}_5)_2\text{O}$: C, 34.68; H, 2.78. Found: C, 35.01; H, 2.96.

Reaction of 3 with NaSMe To Give $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SMe})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (5**).** To 0.250 g (0.335 mmol) of freshly prepared (in situ) **3** dissolved in 50 mL of THF at –80 °C was added 0.024 g (0.342 mmol) of NaSMe. 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 –35 °C to dryness and the dark red residue was chromatographed on an alumina column (1.6 \times 15–20 cm) at –25 °C with petroleum ether/ CH_2Cl_2 (5:1) as the eluant. The purple-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 0.087 g (56%, based on **3**) of purple-red crystals of **5**: mp 147–148 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 1983 (vs), 1939 (vs), 1756(s) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 7.62–6.95 (m, 5H, C_6H_5), 5.13 (s, 10H, C_5H_5), 2.28 (s, 3H, CH_3); MS m/e 254 ($\text{M}^+ - 3\text{CO} - \text{Ph} - \text{SMe}$), 168 [$\text{C}_5\text{H}_5\text{FeSMe}$] $^+$. Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_3\text{SFe}_2$: C, 54.59; H, 3.93. Found: C, 54.44; H, 3.77.

Reaction of 3 with NaSEt To Give $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SEt})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (6**).** Similar to the procedures for the reaction of **3** with NaSMe, compound **3** (0.250 g, 0.335 mmol) was treated with NaSEt (0.029 g, 0.344 mmol) at –80 to –20 °C for 4 h, during which time the turbid solution turned clear deep red gradually. Further treatment of the resulting mixture as described above gave 0.099 g (62%, based on **3**) of dark reddish red crystals of **6**: mp 138–140 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 1983 (vs), 1943 (m), 1774(s) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 7.65–6.94 (m, 5H, C_6H_5), 5.28 (m, 1H, CH_2Cl_2), 5.12 (s, 10H, C_5H_5), 2.47 (q, 2H, CH_2CH_3), 0.94 (t, 3H, CH_2CH_3); MS m/e 254 ($\text{M}^+ - 3\text{CO} - \text{Ph} - \text{SEt}$), 182 [$\text{C}_5\text{H}_5\text{FeSEt}$] $^+$, 84 (CH_2Cl_2). Anal. Calcd for $\text{C}_{22}\text{H}_{20}\text{O}_3\text{SFe}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 52.07; H, 4.08. Found: C, 52.26; H, 3.99.

Reaction of 3 with NaSPh To Give $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SPh})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (7**).** Compound **3** (0.250 g, 0.335 mmol) was treated, in a manner similar to that in the reaction of **3** with NaSMe, with 0.045 g (0.339 mmol) of NaSPh at –80 to –20 °C for 4–5 h. Further treatment of the resulting dark red solution as described for the reaction of **3** with NaSMe afforded 0.123 g (70%, based on **3**) of **7** as red crystals: mp 107–108 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 1985 (vs), 1946 (s), 1780(s) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 8.06–6.76 (m, 10H, C_6H_5), 5.26 (s, 10H, C_5H_5); MS m/e 254 ($\text{M}^+ - 3\text{CO} - \text{Ph} - \text{SPh}$), 230 [$\text{C}_5\text{H}_5\text{FeSPh}$] $^+$. Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{O}_3\text{SFe}_2$: C, 59.57; H, 3.85. Found: C, 59.46; H, 3.74.

Reaction of 3 with $\text{NaSC}_6\text{H}_4\text{Me-p}$ To Give $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SC}_6\text{H}_4\text{Me-p})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (8**).** Similar to that for the reaction of **3** with NaSMe, **3** (0.250 g, 0.335 mmol) was treated with 0.050 g (0.340 mmol) of $\text{NaSC}_6\text{H}_4\text{Me-p}$ at –80 to –20 °C for 4–5 h. Further treatment of the resulting mixture as described for the preparation of **5** yielded 0.134 g (74%, based on **3**) of purple-red crystalline **8**: mp 100–101 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 1984 (vs), 1945 (s), 1772 (vs) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 7.48–6.75 (m, 9H, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4\text{CH}_3$), 5.22 (s, 10H, C_5H_5), 2.21 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$); MS m/e 254 ($\text{M}^+ - 3\text{CO} - \text{Ph} - \text{SC}_6\text{H}_4\text{Me}$), 244 [$\text{C}_5\text{H}_5\text{FeSC}_6\text{H}_4\text{Me}$] $^+$. Anal. Calcd for $\text{C}_{27}\text{H}_{22}\text{O}_3\text{SFe}_2$: C, 60.22; H, 4.12. Found: C, 59.86; H, 4.02.

Reaction of 3 with $\text{NaSC}_6\text{H}_4\text{NO}_2\text{-p}$ To Give $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SC}_6\text{H}_4\text{NO}_2\text{-p})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (9**).** The reaction of **3** (0.250 g, 0.335 mmol) with $\text{NaSC}_6\text{H}_4\text{NO}_2\text{-p}$ (0.060 g, 0.338 mmol) was as described in the reaction of **3** with NaSMe at –80 to –20 °C for 5 h. Further treatment as described for the

preparation of **5** gave 0.097 g (51%, based on **3**) of blackish red crystals of **9**: mp 70–72 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 1994 (vs), 1898 (m), 1781 (m) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 8.30–6.94 (m, 9H, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4\text{NO}_2$), 5.43 (s, 10H, C_5H_5); MS m/e 254 ($\text{M}^+ - 3\text{CO} - \text{Ph} - \text{SC}_6\text{H}_4\text{NO}_2$), 275 [$\text{C}_5\text{H}_5\text{FeSC}_6\text{H}_4\text{NO}_2$] $^+$. Anal. Calcd for $\text{C}_{26}\text{H}_{19}\text{O}_5\text{NSFe}_2$: C, 54.86; H, 3.36; N, 2.46. Found: C, 55.01; H, 3.51; N, 2.11.

Reaction of 4 with NaSPh To Give $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SPh})\text{C}_6\text{H}_4\text{Me-p}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (10**).** To 0.240 g (0.316 mmol) of freshly prepared **4** dissolved in 50 mL of THF at –80 °C was added 0.043 g (0.324 mmol) of NaSPh. The reaction mixture was stirred at –80 to –40 °C for 4–5 h, during which time the turbid solution turned clear purple-red gradually. Further treatment as described in the reaction of **3** with NaSMe afforded 0.122 g (72%, based on **4**) of purple-red crystals of **10**: mp 92–93 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 1983 (vs), 1945 (m), 1780 (s) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 7.42–6.34 (m, 9H, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4\text{CH}_3$), 5.22 (s, 10H, C_5H_5), 2.11 (m, 3H, $\text{CH}_3\text{C}_6\text{H}_4$); MS m/e 254 ($\text{M}^+ - 3\text{CO} - \text{MeC}_6\text{H}_4 - \text{SPh}$), 230 [$\text{C}_5\text{H}_5\text{FeSPh}$] $^+$. Anal. Calcd for $\text{C}_{27}\text{H}_{22}\text{O}_3\text{SFe}_2$: C, 60.26; H, 4.12. Found: C, 60.10; H, 4.03.

Reaction of 4 with $\text{NaSC}_6\text{H}_4\text{Me-p}$ To Give $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SC}_6\text{H}_4\text{Me-p})\text{C}_6\text{H}_4\text{Me-p}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (11**).** Similar to the reaction of **4** with NaSPh, 0.240 g (0.316 mmol) of **4** reacted with 0.048 g (0.327 mmol) of $\text{NaSC}_6\text{H}_4\text{Me-p}$ at –80 to –40 °C for 4–5 h. Further treatment as described for the preparation of **10** yielded 0.131 g (75%, based on **4**) of **11** as purple-red crystals: mp 116–118 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 1984 (s), 1942 (m), 1786 (s) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 7.38–6.34 (m, 2H, $2\text{C}_6\text{H}_4\text{CH}_3$), 7.02 (m, 4H, $2\text{C}_6\text{H}_4\text{CH}_3$), 6.71 (m, 2H, $2\text{C}_6\text{H}_4\text{CH}_3$), 5.17 (s, 10H, C_5H_5), 2.24 (s, 3H, $\text{CH}_3\text{C}_6\text{H}_4\text{S}$), 2.14 (s, 3H, $\text{CH}_3\text{C}_6\text{H}_4$); MS m/e 254 ($\text{M}^+ - 3\text{CO} - \text{MeC}_6\text{H}_4 - \text{SC}_6\text{H}_4\text{Me}$), 244 [$\text{C}_5\text{H}_5\text{FeSC}_6\text{H}_4\text{Me}$] $^+$. Anal. Calcd for $\text{C}_{28}\text{H}_{24}\text{O}_3\text{SFe}_2$: C, 60.90; H, 4.38. Found: C, 60.83; H, 4.40.

Reaction of 3 with NaOPh To Give $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{OPh})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (12**).** Compound **3** (0.250 g, 0.335 mmol) was treated, in a manner similar to that for the reaction of **3** with NaSMe, with NaOPh (0.040 g, 0.343 mmol) at –80 to –20 °C for 4 h, during which time the turbid solution turned dark brown-red gradually. Further treatment of the resulting mixture as described in the reaction of **3** with NaSMe afforded 0.065 g (38%, based on **3**) of brown-red crystalline **12**: mp 62–64 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 2010 (vs), 1977 (s), 1813 (m) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 8.43 (m, 3H, C_6H_5), 7.74 (m, 4H, C_6H_5), 7.40 (m, 3H, C_6H_5), 5.26 (s, 10H, C_5H_5); MS m/e 254 ($\text{M}^+ - 3\text{CO} - \text{Ph} - \text{OPh}$), 186 [$(\text{C}_5\text{H}_5)_2\text{Fe}$] $^+$. Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{O}_4\text{Fe}_2$: C, 57.80; H, 3.84. Found: C, 57.66; H, 3.53.

Reaction of 3 with $\text{NaN}(\text{SiMe}_3)_2$ To Give $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{N}(\text{SiMe}_3)_2)\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (13**).** As described for the reaction of **3** with NaSMe, compound **3** (0.250 g, 0.335 mmol) was treated with $\text{NaN}(\text{SiMe}_3)_2$ (0.062 g, 0.338 mmol) at –80 to –20 °C for 5 h, during which time the turbid solution turned blackish red gradually. Further treatment of the resulting mixture as described for the preparation of **5** gave 0.063 g (31%, based on **3**) of blackish red crystals of **13**: mp 50 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 1996(s), 1969 (s), 1786 (w) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 7.80–6.97 (m, 5H, C_6H_5), 5.11 (s, 10H, C_5H_5), 0.89 (s, 18H, CH_3); MS m/e 254 [$\text{M}^+ - 3\text{CO} - \text{Ph} - \text{N}(\text{SiMe}_3)_2$], 186 [$(\text{C}_5\text{H}_5)_2\text{Fe}$] $^+$. Anal. Calcd for $\text{C}_{26}\text{H}_{33}\text{O}_3\text{NSi}_2\text{Fe}_2$: C, 54.27; H, 5.78; N, 2.44. Found: C, 54.13; H, 5.92; N, 2.59.

Reaction of 3 with $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SBu}^n)(\text{CO})_6]$ To Give $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SH})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (14**).** To a solution of 0.338 g (0.671 mmol) of $\text{Fe}_3(\text{CO})_{12}$ in 50 mL of THF was added 0.072 mL (0.676 mmol) of *n*-BuSH and 0.094 mL (0.672 mmol) of Et_3N with stirring. The mixture was stirred at room temperature for 40 min. The resulting brown-red solution of $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SBu}^n)(\text{CO})_6]$ 17 was cooled to –80 °C and then was poured rapidly into 0.50 g (0.671 mmol) of freshly prepared **3** previously cooled to a –80 °C. The mixture was stirred at –80 to –40 °C for 6 h, during which

time the brown-red solution gradually turned deep red and finally dark red. The resulting mixture was evaporated to dryness under high vacuum at -50 to -40 °C. The dark red residue was chromatographed on Al_2O_3 at -25 °C with petroleum ether/ CH_2Cl_2 (20:1) as the eluant. After elution of a small red band which contains unidentified compound from the column, the brown band was eluted with petroleum ether/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (10:1:1) and collected. After vacuum removal of the solvent, the residue was recrystallized from petroleum ether/ CH_2Cl_2 (10:1) at -80 °C to give 0.18 g (56%, based on **3**) of reddish crystals of **14**: mp 180 – 182 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 1972 (vs), 1932 (m), 1772 (s) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 8.01–7.60 (m, 5H, C_6H_5), 5.68 (s, 1H, SH), 5.39 (s, 10H, C_5H_5); MS m/e 448 (M^+), 420 ($\text{M}^+ - \text{CO}$), 254 ($\text{M}^+ - 3\text{CO} - \text{Ph} - \text{SH}$), 154 [$\text{C}_5\text{H}_5\text{FeSH}$] $^+$. Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_3\text{SFe}_2$: C, 53.61; H, 3.60. Found: C, 53.89; H, 3.46.

Reaction of 4 with $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SBU})(\text{CO})_6]$ To Give $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SBU})\text{C}_6\text{H}_4\text{Me-p}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (15**).** Similar to that in the reaction of **3** with $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SBU})(\text{CO})_6]$, compound **4** (0.51 g, 0.672 mmol) was treated with $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SBU})(\text{CO})_6]$, prepared (in situ) by the reaction of $\text{Fe}_3(\text{CO})_{12}$ (0.338 g, 0.671 mmol) with 0.094 mL (0.672 mmol) of $n\text{-BuSH}$ and 0.072 mL (0.676 mmol) of Et_3N , at -80 to -40 °C for 5 h, during which time the brown-red solution gradually turned dark red. Further treatment as that for the preparation of **14** yielded 0.23 g (66%, based on **4**) of **15** as purple-red crystals: mp 109 – 110 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 1981 (s), 1940 (w), 1771 (s) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 7.53–6.9 (dd, 4H, $\text{C}_6\text{H}_4\text{CH}_3$), 5.10 (s, 10H, C_5H_5), 2.53 (t, 2H, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.27 (s, 3H, $\text{CH}_3\text{C}_6\text{H}_4$), 1.30 (m, 4H, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.80 (t, 3H, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); MS m/e 254 ($\text{M}^+ - 3\text{CO} - \text{MeC}_6\text{H}_4 - \text{BuS}$), 210 [$\text{C}_5\text{H}_5\text{FeBuS}$] $^+$. Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{O}_3\text{SFe}_2$: C, 57.94; H, 5.06. Found: C, 58.08; H, 5.01.

Reaction of 3 with $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SPh})(\text{CO})_6]$ To Give $[\text{Fe}_2(\mu\text{-SPh})_2(\text{CO})_6]$ (16**) and $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{HPh})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**17**).** To a solution of 0.338 g (0.671 mmol) of $\text{Fe}_3(\text{CO})_{12}$ in 50 mL of THF was added 0.047 mL (0.680 mmol) of PhSH and 0.094 mL (0.672 mmol) of Et_3N with stirring. The mixture was stirred at room temperature for 40 min. The resulting brown-red solution of $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SPh})(\text{CO})_6]$ ¹⁷ was cooled to -80 °C and then treated, as that in the reaction of **3** with $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SBU})(\text{CO})_6]$, with 0.50 g (0.671 mmol) of **3** at -80 to -40 °C for 5 h, during which time the brown-red solution gradually turned dark red. The solvent was removed at -40 °C in vacuo, and the dark red residue was chromatographed on Al_2O_3 at -25 °C with petroleum ether followed by petroleum ether/ CH_2Cl_2 (20:1) as the eluant. The red band which eluted first was collected, and then the brown-red band was eluted with petroleum ether/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (10:1:1). The solvents were removed from the above two eluates under vacuum, and the residues were recrystallized from petroleum ether/ CH_2Cl_2 (10:1) solution at -80 °C. From the first fraction, 0.038 g (11%, based on **3**) of orange-red crystals of **16**²² were obtained: mp 150 °C dec (lit.²² 153 °C); IR (CH_2Cl_2) $\nu(\text{CO})$ 2074 (s), 2038 (vs), 2001 (vs) cm^{-1} (lit.²² (CCl_4) 2073 (s), 2038 (vs), 2003 (vs), 1957 (w) cm^{-1}); ^1H NMR (CD_3COCD_3) δ 7.86 (m, 2H, C_6H_5), 7.68 (m, 3H, C_6H_5); MS m/e 498 (M^+), 470 ($\text{M}^+ - 2\text{CO}$), 442 ($\text{M}^+ - 3\text{CO}$), 414 ($\text{M}^+ - 4\text{CO}$), 386 ($\text{M}^+ - 5\text{CO}$), 358 ($\text{M}^+ - 6\text{CO}$). Anal. Calcd for $\text{C}_{18}\text{H}_{10}\text{O}_6\text{S}_2\text{Fe}_2$: C, 43.40; H, 2.02. Found: C, 43.31; H, 2.10. From the second fraction, 0.19 g (68%, based on **3**) of purple-red crystalline **17** was obtained: mp 79 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 1973 (vs), 1934 (m), 1772 (s) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 12.38 (s, 1H, $\mu\text{-CH}$), 7.56 (m, 2H, C_6H_5), 7.19 (m, 2H, C_6H_5), 7.07 (m, 1H, C_6H_5), 4.96 (s, 10H, C_5H_5); MS m/e 388 ($\text{M}^+ - \text{CO}$), 360 ($\text{M}^+ - 2\text{CO}$), 332 ($\text{M}^+ - 3\text{CO}$), 254 ($\text{M}^+ - 3\text{CO} - \text{C}_6\text{H}_5 - \text{H}$), 211 ($\text{M}^+ - 3\text{CO} - \text{C}_5\text{H}_5$), 186 [$(\text{C}_5\text{H}_5)_2\text{Fe}$] $^+$. Anal.

Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_3\text{Fe}_2$: C, 57.74; H, 3.88. Found: C, 57.27; H, 3.86.

Reaction of 4 with $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SPh})(\text{CO})_6]$ To Give **16 and $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})\text{C}_6\text{H}_4\text{Me-p}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**18**).** As in the reaction of **3** with $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SPh})(\text{CO})_6]$, compound **4** (0.51 g, 0.672 mmol) was treated with $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SPh})(\text{CO})_6]$, prepared (in situ) by the reaction of 0.338 g (0.671 mmol) of $\text{Fe}_3(\text{CO})_{12}$ with 0.047 mL (0.680 mmol) of PhSH and 0.094 mL (0.672 mmol) of Et_3N , at -80 to -40 °C for 5 h. Further treatment as that in the reaction of **3** yielded 0.027 g (8%, based on **4**) of orange-red crystals of **16** and 0.162 g (56%, based on **4**) of purple-red crystals of **18**. **16** was identified by its mp and IR and ^1H NMR spectra. **18**: mp 140 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 1969 (vs), 1933 (m), 1775 (vs) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 12.40 (s, 1H, $\mu\text{-CH}$), 7.47–7.36 (m, 2H, C_6H_5), 7.00 (d, 2H, C_6H_5), 4.94 (s, 10H, C_5H_5); MS m/e 430 (M^+), 402 ($\text{M}^+ - \text{CO}$), 374 ($\text{M}^+ - 2\text{CO}$), 346 ($\text{M}^+ - 3\text{CO}$), 254 ($\text{M}^+ - 3\text{CO} - \text{MeC}_6\text{H}_4 - \text{H}$), 225 ($\text{M}^+ - 3\text{CO} - \text{C}_5\text{H}_5\text{Fe}$). Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_3\text{Fe}_2$: C, 58.65; H, 4.22. Found: C, 58.37; H, 4.49.

Reaction of 3 with $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SC}_6\text{H}_4\text{Me-p})(\text{CO})_6]$ To Give **17 and $[\text{Fe}_2(\mu\text{-SC}_6\text{H}_4\text{Me-p})_2(\text{CO})_6]$ (**19**).** Compound **3** (0.50 g, 0.671 mmol) was treated, similar to that in the reaction of **3** with $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SPh})(\text{CO})_6]$, with $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SC}_6\text{H}_4\text{Me-p})(\text{CO})_6]$ ¹⁷ prepared (in situ) by reaction of 0.338 g (0.671 mmol) of $\text{Fe}_3(\text{CO})_{12}$ in 50 mL of THF with 0.084 g (0.676 mmol) of $p\text{-MeC}_6\text{H}_4\text{SH}$ and 0.094 mL (0.672 mmol) of Et_3N at -80 to -40 °C for 4–5 h. Further treatment as described above gave 0.034 g (10%, based on **3**) of orange-red crystals of **19**²³ and 0.143 g (51%, based on **3**) of purple-red crystalline **17**. Compound **17** was identified by its melting point and IR and ^1H NMR spectra. **19**: mp 103 – 104 °C dec (lit.²³ 105 °C); IR (CH_2Cl_2) $\nu(\text{CO})$ 2072 (s), 2037 (vs), 1997 (vs) cm^{-1} (lit.²³ (CH_2Cl_2) 2065 (s), 2030 (s), 1995 (s) cm^{-1}); ^1H NMR (CD_3COCD_3) δ 7.30 (m, 4H, $\text{C}_6\text{H}_4\text{CH}_3$), 7.13 (m, 4H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.27 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.23 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$) (lit.²⁷ (CDCl_3) δ 7.16 (d, 2H), 7.14 (d, 2H), 6.96 (d, 4H), 2.21 (s, 6H)); MS m/e 526 (M^+), 470 ($\text{M}^+ - 2\text{CO}$), 442 ($\text{M}^+ - 3\text{CO}$), 414 ($\text{M}^+ - 4\text{CO}$), 386 ($\text{M}^+ - 5\text{CO}$), 358 ($\text{M}^+ - 6\text{CO}$). Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{O}_6\text{S}_2\text{Fe}_2$: C, 45.66; H, 2.68. Found: C, 45.31; H, 2.90.

Reaction of 3 with $\text{Na}_2\text{W}(\text{CO})_6$ To Give **17.** $\text{W}(\text{CO})_6$ (0.175 g, 0.497 mmol) and sodium amalgam (1.13 mL of 0.8% Na in Hg) were stirred at room temperature in 20 mL of DME. After 2 h, the solution was a deep red, and the IR spectrum in the $\nu(\text{CO})$ region indicated almost complete reduction to $\text{Na}_2\text{W}(\text{CO})_5$.¹⁸ The red solution was evaporated in vacuo to about 5 mL, 50 mL of THF were added, and the reaction mixture was then cooled to -80 °C. This solution was poured rapidly onto a solution of freshly prepared **3** (0.370 g, 0.496 mmol) in THF previously cooled to -90 °C. The solution rapidly turned dark purple-red. The mixture was stirred at -90 to -40 °C for 3–4 h then evaporated to dryness in vacuo at -40 °C and the residue chromatographed on Al_2O_3 at -25 °C with petroleum ether/ CH_2Cl_2 (10:1) as the eluant. The brown-red band was collected. The solvent was removed and the crude product was recrystallized from petroleum ether/ CH_2Cl_2 (10:1) at -80 °C to give 0.162 g (85%, based on **3**) of **17** as purple-red crystals, which were identified by their mp and IR and ^1H NMR spectra.

Reaction of 3 with $\text{Na}_2\text{Fe}(\text{CO})_4$ To Give **17.** To 0.212 g (0.280 mmol) of **3** dissolved in 50 mL of THF at -90 °C was

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Table 1. Crystal Data and Experimental Details for Complexes **6**, **7**, **15**, and **17**

	6 ·1/2CH ₂ Cl ₂	7	15	17
formula	C _{22.5} H ₂₁ O ₃ ClSFe ₂	C ₂₆ H ₂₀ O ₃ SFe ₂	C ₂₅ H ₂₆ O ₃ SFe ₂	C ₂₀ H ₁₆ O ₃ Fe ₂
fw	518.62	524.20	518.23	416.04
space group	<i>I</i> -4 (No. 82)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> (Å)	17.640(5)	11.840(3)	8.797(7)	7.068(1)
<i>b</i> (Å)	17.640(5)	12.170(3)	14.906(7)	15.988(3)
<i>c</i> (Å)	13.979(3)	8.117(3)	17.428(3)	15.671(2)
α (deg)	90	103.60(2)		
β (deg)	90	102.34(3)	92.59(3)	90.47(1)
γ (deg)	90	79.02(2)		
<i>V</i> (Å ³)	4348(1)	1098.4(6)	2282(2)	1770.7(5)
<i>Z</i>	8	2	4	4
d_{calc} (g/cm ³)	1.584	1.585	1.508	1.561
<i>F</i> (000)	2120.00	536.00	1072.00	848.00
μ (Mo K α) (cm ⁻¹)	15.73	14.41	13.85	16.51
radiation (monochromated in incident beam)	Mo K α (λ = 0.71069 Å)	Mo K α (λ = 0.71069 Å)	Mo K α (λ = 0.71069 Å)	Mo K α (λ = 0.71069 Å)
diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R
temperature (°C)	20	20	20	20
orientation reflns: no.; range (2 θ) (deg)	23; 18.7–23.8	20; 13.7–24.4	23; 14.3–21.6	20; 14.1–24.3
scan method	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ
data coll range, 2 θ (deg)	5–50	5–50	5–50	5–49.5
no. of unique data, total	4198	3406	4204	2458
with <i>I</i> > 2.00 σ (<i>I</i>)	1319	2038	1427 (<i>I</i> > 2.80 σ (<i>I</i>))	1369
no. of params refined	267	290	280	226
corr factors, max. min.	0.9530–1.0000	0.8497–1.0000	0.9240–1.2168	0.8707–1.0000
<i>R</i> ^a	0.049	0.057	0.066	0.043
<i>R</i> _w ^b	0.047	0.064	0.070	0.045
quality-of-fit indicator ^c	1.24	1.83	1.70	1.22
largest shift/esd final cycle	0.00	0.00	0.02	0.03
max. peak, e ⁻ /Å ³	0.63	1.68	0.50	0.31
min. peak, e ⁻ /Å ³	-0.42	-0.65	-0.58	-0.34

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

added 0.062 g (0.290 mmol) of Na₂Fe(CO)₄. The reaction mixture was stirred at -90 to -45 °C for 4 h. Further treatment of the resulting mixture as described above for the reaction of **3** with Na₂W(CO)₅ gave 0.096 g (82%, based on **3**) of purple-red crystalline **17**, which was identified by its mp and IR and ¹H NMR spectra.

X-ray Crystal Structure Determinations of Complexes 6, 7, 15, and 17. Single crystals of **6**, **7**, **15**, and **17** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH₂Cl₂ solution at -80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for 4285, 3406, 4204, and 2458 independent reflections, of which 1319, 2038, and 1369 with *I* > 2.00 σ (*I*) for **6**, **7**, and **17**, and 1427 with *I* > 2.80 σ (*I*) for **15** were observable, were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo K α radiation with an ω -2 θ scan mode within the ranges 5° ≤ 2 θ ≤ 50° for **6**, **7**, and **15** and 5° ≤ 2 θ ≤ 49.5° for **17**, respectively.

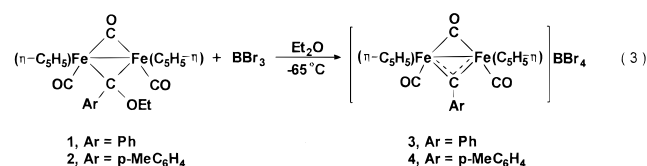
The structures of **6** was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1319 observed reflections and 267 variable parameters and converged with unweighted and weighted agreement factors of *R* = 0.049 and *R*_w = 0.047. The structures of **7**, **15**, and **17** were solved by direct 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 was respectively based on 2038, 1427, and 1369 observed reflections and 290, 280, and 226 variable parameters and converged with unweighted and weighted agreement factors of *R* = 0.057 and *R*_w = 0.064 for **7**, *R* = 0.066 and *R*_w = 0.070 for **15**, and *R* = 0.043 and *R*_w = 0.045 for **17**, respectively. All the calculations were

performed using the teXsan crystallographic software package of Molecular Structure Corporation.

The details of the crystallographic data and the procedures used for data collection and reduction information for **6**, **7**, **15**, and **17** are given in Table 1. Selected bond lengths and angles are listed in Table 2. Atomic coordinates and *B*_{iso}/*B*_{eq}, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **6**, **7**, **15**, and **17** are given in the Supporting Information. The molecular structures of **6**, **7**, **15**, and **17** are given in Figures 1–4, respectively.

Results and Discussion

The complexes [Fe₂(μ -CO){ μ -C(OEt)Ar}(CO)₂(η -C₅H₅)₂] (**1**, Ar = Ph; **2**, Ar = p-MeC₆H₄) in ether were treated, similar to the procedure for the preparation of the cationic carbyne complexes [η -C₅H₅(CO)₂M≡CPh]BBr₄ (M = Mn, Re),^{20,21} with an excess of BBr₃ at -65 °C to give cationic bridging carbyne complexes [Fe₂(μ -CO){ μ -C(Ar)(CO)₂(η -C₅H₅)₂]BBr₄ (**3**, Ar = Ph; **4**, Ar = p-MeC₆H₄) as brown-red solids in 75–76% yields (eq 3).



Complexes **3** and **4** are only sparingly soluble in polar organic solvents, such as THF and CH₂Cl₂. They are very sensitive to air, moisture, and temperature and can

Table 2. Selected Bond Lengths (Å)^a and Angles (deg)^a for Complexes **6**, **7**, **15**, and **17**

	6 ·1/2CH ₂ Cl ₂	7	15	17
Fe(1)–Fe(2)	2.527(2)	2.523(2)	2.530(3)	2.523(2)
Fe(1)–C(1)	2.03(1)	2.026(8)	2.00(2)	1.997(7)
Fe(2)–C(1)	2.00(1)	2.032(8)	2.02(1)	1.991(7)
Fe(1)–C(10)	1.91(1)	1.89(1)	1.89(1)	1.923(8)
Fe(2)–C(10)	1.91(1)	1.902(9)	1.90(2)	1.913(8)
C(1)–S	1.83(1)	1.829(8)	1.82(1)	
C(1)–C(2)	1.54(1)	1.50(1)	1.52(2)	1.463(9)
S–C(23)	1.81(1)	1.785(9)	1.82(1)	
Fe(1)–C(11)	1.75(1)	1.73(1)	1.74(2)	1.707(9)
Fe(2)–C(12)	1.75(2)	1.72(1)	1.73(2)	1.742(9)
C(10)–O(2)	1.18(1)	1.19(1)	1.18(1)	1.175(8)
C(11)–O(3)	1.13(1)	1.16(1)	1.16(2)	1.165(9)
C(12)–O(4)	1.15(1)	1.17(1)	1.18(2)	1.143(9)
Fe(1)–C(Cp) (av)	2.11	2.124	2.13	2.114
Fe(2)–C(Cp) (av)	2.12	2.125	2.13	2.088
Fe(1)–C(1)–Fe(2)	77.7(4)	76.9(3)	77.9(5)	78.5(3)
C(1)–Fe(1)–Fe(2)	50.6(4)	52.7(2)	51.5(4)	50.7(2)
C(1)–Fe(2)–Fe(1)	51.7(3)	51.5(2)	50.6(4)	50.8(2)
C(1)–Fe(1)–C(10)	97.8(5)	98.2(4)	97.8(6)	98.5(3)
C(1)–Fe(2)–C(10)	99.0(6)	97.7(4)	96.7(6)	99.0(3)
Fe(1)–C(10)–Fe(2)	82.9(5)	83.3(4)	83.6(5)	82.3(3)
C(10)–Fe(1)–Fe(2)	48.5(4)	48.5(3)	48.3(5)	48.7(2)
C(10)–Fe(2)–Fe(1)	48.6(5)	48.2(3)	48.0(4)	49.0(2)
Fe(1)–C(10)–O(2)	138(1)	138.2(8)	138(1)	137.5(7)
Fe(2)–C(10)–O(2)	138(1)	138.5(8)	137(1)	140.3(7)
Fe(1)–C(11)–O(3)	173(1)	174.1(8)	173(1)	173.7(8)
Fe(2)–C(12)–O(4)	172(1)	175.3(9)	175(1)	174.4(7)
Fe(1)–C(1)–S	111.9(6)	118.6(4)	118.8(7)	
Fe(2)–C(1)–S	119.1(6)	110.7(4)	110.5(7)	
C(10)–Fe(1)–C(11)	88.1(6)	85.7(4)	85.8(6)	90.5(4)
C(10)–Fe(2)–C(12)	86.2(6)	88.2(4)	86.9(7)	90.0(3)
C(1)–Fe(1)–C(11)	93.0(5)	93.6(4)	95.4(7)	95.7(3)
C(1)–Fe(2)–C(12)	95.1(5)	90.7(4)	93.3(6)	97.5(3)
Fe(1)–C(1)–C(2)	118.9(8)	121.9(5)	121.3(10)	126.9(5)
Fe(2)–C(1)–C(2)	122.9(8)	120.5(5)	120.7(9)	128.1(5)
C(2)–C(1)–S	104.7(7)	106.1(6)	105.8(9)	
C(1)–S–C(23)	107.4(5)	110.2(4)	107.6(6)	

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

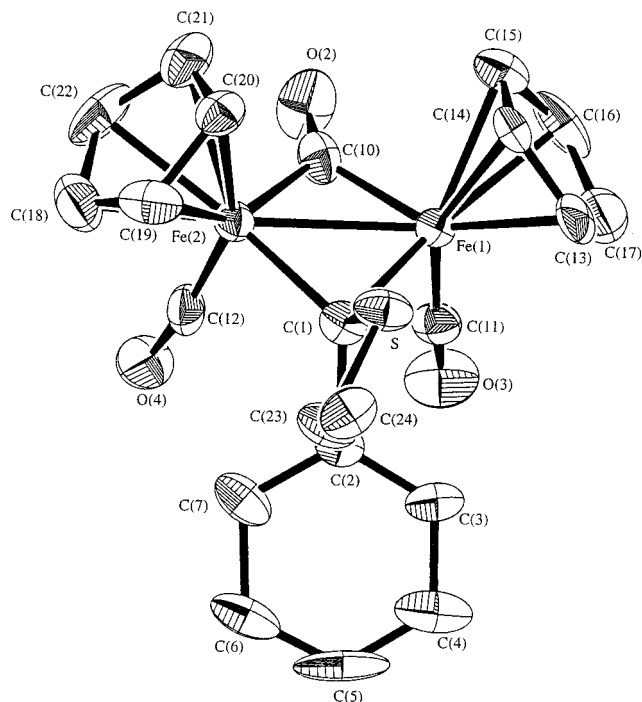


Figure 1. Molecular structure of **6**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 40% probability. CH₂Cl₂ has been omitted for clarity.

be stored at low temperature (below –60 °C) for a short period. The composition and structure for complexes **3**

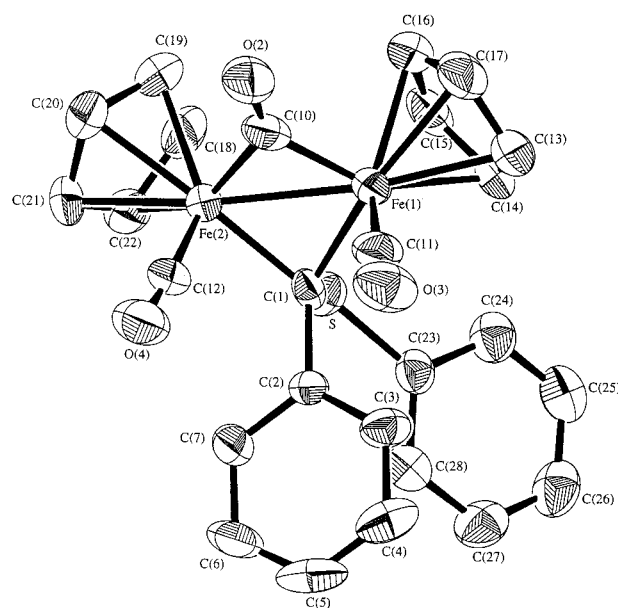


Figure 2. Molecular structure of **7**, showing the atom-numbering scheme with 40% thermal ellipsoids.

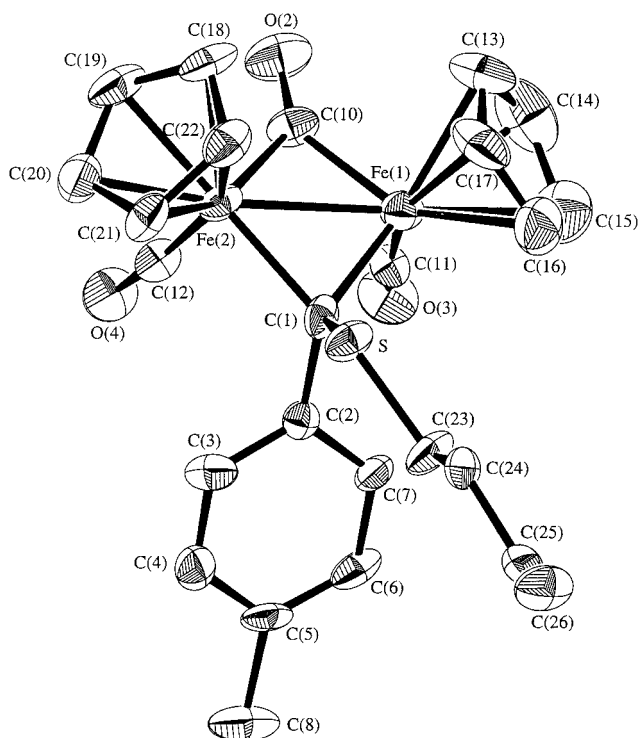


Figure 3. Molecular structure of **15**, showing the atom-numbering scheme with 40% thermal ellipsoids.

and **4** were established on the basis of their elemental analyses and IR and ¹H NMR spectra.

The freshly prepared (in situ) cationic carbyne complex [Fe₂(μ-CO){μ-CPh}(CO)₂(η-C₅H₅)₂] (**3**) was treated with an equimolar quantity of nucleophiles, NaSR (R = Me, Et, Ph, p-MeC₆H₄, p-NO₂C₆H₄), in THF at low temperature (–80 to –20 °C) for 4–5 h to yield the diiron bridging mercaptocarbene complexes [Fe₂(μ-CO){μ-C(SR)Ph}(CO)₂(η-C₅H₅)₂] (**5**, R = Me; **6**, R = Et; **7**, R = Ph; **8**, R = p-MeC₆H₄; **9**, R = p-NO₂C₆H₄) in 51–74% yields (eq 4). The analogous reaction of [Fe₂–

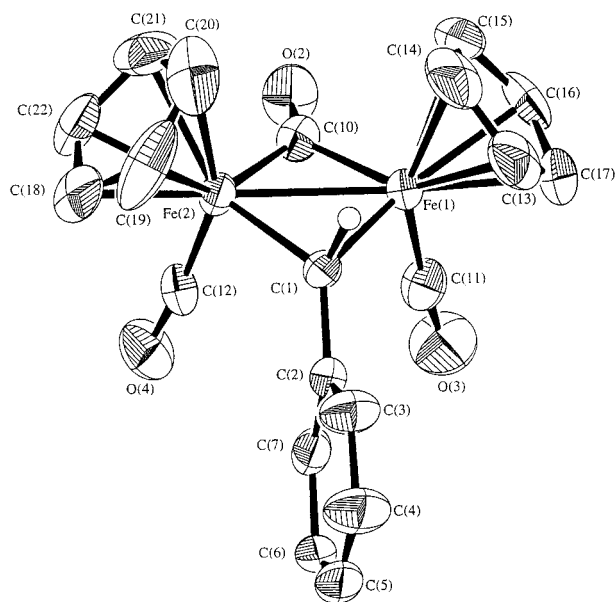
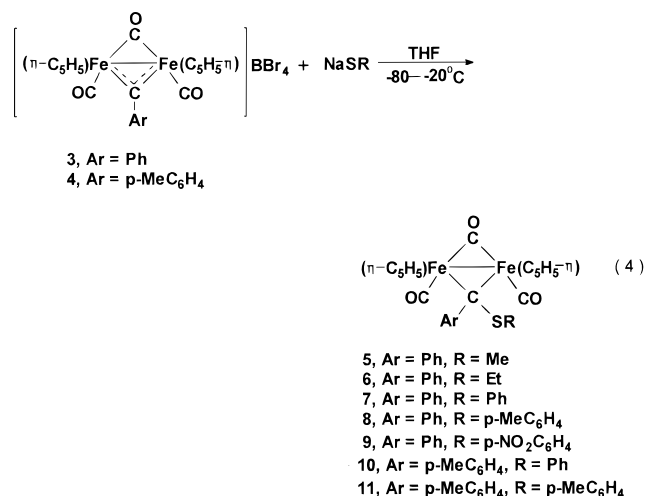


Figure 4. Molecular structure of **17**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 45% probability.

$(\mu\text{-CO})\{\mu\text{-CC}_6\text{H}_4\text{Me-p}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2$ (**4**) with NaSR (R = Ph, p-MeC₆H₄) under the same conditions gave the corresponding bridging mercaptocarbene complexes $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SR})\text{C}_6\text{H}_4\text{Me-p}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**10**, R = Ph; **11**, R = p-MeC₆H₄) (eq 4) in 72–75% yields.



Complexes **5–11** are soluble in polar organic solvents but sparingly 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 4 for complexes **5–11** were established by elemental analysis and IR, ¹H NMR, and mass spectroscopy (Experimental Section). The IR spectra of complexes **5–11** showed two CO absorption bands at 1898–1994 cm⁻¹ and one at 1756–1786 cm⁻¹ in the bridging $\nu(\text{CO})$ region, evidence for an $\text{Fe}_2(\mu\text{-CO})(\text{CO})_2$ moiety in these complexes. In the ¹H NMR spectra of **5–11**, the signal due to the cyclopentadienyl protons at about 5.1–5.4 ppm was only a single resonance. However, in a complex with a μ -carbene with different substituents, the cis form displays one C₅H₅ resonance and the trans form

two, as shown in complexes $[\text{Ru}_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})\text{COOEt}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ ²⁴ and $[\text{Ru}_2(\mu\text{-CO})\{\mu\text{-C}(\text{R})\text{CH}_2\text{R}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$.²⁵ Hence, complexes **5–11** are the cis products as shown in eq 4.

The structures of complexes **6** and **7** have been confirmed by X-ray diffraction studies. The results of the X-ray diffraction work for both complexes are summarized in Table 1, and the structures are shown in Figures 1 and 2, respectively.

The structures of both complexes resemble that of complexes **1** and **2**, except that the substituent on the μ -carbene carbon is an SR group in **6** and **7** and an OEt group in **1** and **2**. The mercapto and aryl groups are attached to the $\mu\text{-C}(1)$, and the two cyclopentadienyl rings are in a cis, almost totally eclipsed configuration, as anticipated from the IR and ¹H NMR spectra. The distance between the Fe atom and the Cp ring plane is nearly 1.76 Å. The least-squares plane calculations show that the carbon atoms in the Cp ring are coplanar and the two CO groups coordinated on the same Fe atom are not coplanar arising from bridging.

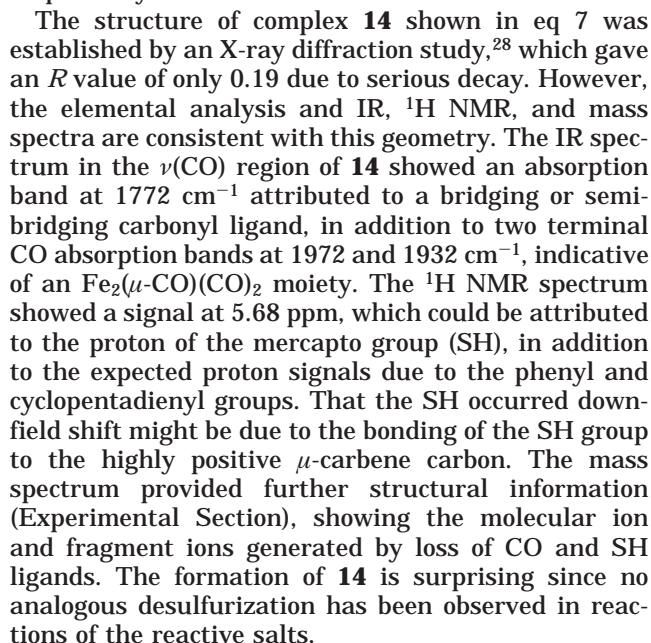
The distances of the Fe–Fe bond bridged by the μ -carbene ligand in **6** and **7** are 2.527(2) and 2.523(2) Å, respectively, which are slightly longer than those found in **1** (2.512(1) Å)¹² and **2** (2.519(2) Å)¹² but obviously shorter than that found (2.686(1) Å) in the diiron bridging carbene complex $[\text{Fe}_2\{\mu\text{-C}(\text{OEt})\text{C}_6\text{H}_4\text{CF}_3\text{-p}\}(\text{CO})_4(\text{C}_8\text{H}_8)]$.¹¹ The μ -carbene carbon almost symmetrically bridges the Fe–Fe bond with C(1)–Fe(1) 2.03(1) Å and C(1)–Fe(2) 2.00(1) Å for **6** and C(1)–Fe(1) 2.026(8) Å and C(1)–Fe(2) 2.032(8) Å for **7**. The $\mu\text{-C-Fe}$ distances in **6** and **7** are much longer than the $\mu\text{-Fe-CO}$ bond (C(10)–Fe(1) 1.91(1) Å, C(10)–Fe(2) 1.91(1) Å for **6**; C(10)–Fe(1) 1.89(1) Å, C(10)–Fe(2) 1.902(9) Å for **7**) but approximately equal to those in complexes $[\text{Fe}_2\{\mu\text{-C}(\text{OEt})\text{C}_6\text{H}_4\text{CF}_3\text{-p}\}(\text{CO})_4(\text{C}_8\text{H}_8)]$ (C–Fe(1) 2.063(3) Å, C–Fe(2) 2.010(3) Å)¹¹ and $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})\text{NHPh}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (C(4)–Fe(1) 2.004(2) Å, C(4)–Fe(2) 2.028(2) Å).²⁶ The C(1)–S bond lengths (1.83(1) Å for **6** and 1.829(8) Å for **7**) indicate that they are essentially single bonds by comparison with standard C(sp²)–S (1.76 Å)²⁷ single bond and C(sp³)–S (1.81 Å)²⁷ single bond distances.

In **6** and **7**, the benzene ring lies in the trans position of the cyclopentadienyl rings. The angles between the benzene ring C(2) through C(7) and the Cp ring C(13) through C(17) planes and the benzene ring C(2) through C(7) and Cp ring C(18) through C(22) planes are respectively 75.53° and 62.87° for **6** and 65.20° and 102.25° for **7**. The benzene ring composed by C(2) through C(7) plane is at angles of 75.53° and 62.87° in **6** and 65.20° and 102.25° in **7** to the planes of the two Cp rings. Thus, complexes **6** and **7** exist in a cis structure to avoid steric repulsion between the six-membered aryl ring and the cyclopentadienyl rings.

Like NaSR, compounds NaOPh and NaN(SiMe₃)₂ also reacted with complex **3** under the same conditions to produce diiron bridging carbene complex $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{OPh})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**12**) (eq 5) and $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{N}(\text{SiMe}_3)_2)\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**13**) (eq 6) in 38 and 32% yield, respectively.

Complexes **12** and **13** are soluble in polar organic solvents and sensitive to air and temperature in solution. The IR spectra, the solution ¹H NMR spectra, and

thiocarbene complex $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{SBu}^n)\text{C}_6\text{H}_4\text{Me-p}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**15**) (eq 7) in 56 and 66% isolated yield, respectively.



The structure of **15** was established by X-ray crystallography. The molecular structure (Figure 3) of **15** is nearly identical with that of **6** and **7**, as illustrated by the following parameters. The Fe–Fe distance is 2.530(3) Å, which is the same within experimental error as those found in **6** and **7**. The Fe– μ -C_{carbene} bond distances, Fe(1)–C(1) and Fe(2)–C(1), are 1.997(7) and 1.991(7) Å, respectively, which are essentially the same as those found in **6** and **7**. The C(1)–S bond length of 1.82(1) Å in **15** is very close to those in **6** and **7**.

It is not clear how the SH group is formed and how it becomes bonded to the μ -carbene carbon atom during the reaction. Presumably, the formation of complex **14** occurred via an $[\text{Fe}(\text{CO})_4(\text{SH})]^-$ anion derived from cleavage of the reactive salt, a process involving the breaking of Fe–S and R–S bonds. The anion might then attack the μ -carbyne carbon of **3** to produce an unstable bridging carbene intermediate $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{Fe}(\text{CO})_4(\text{SH}))\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$, in which the $\text{Fe}(\text{CO})_4(\text{SH})$ moiety is directly bonded to the μ -carbene carbon through the Fe atom. The carbene intermediate would then undergo a SH group migration from Fe to the μ -carbene carbon accompanied by loss of an $\text{Fe}(\text{CO})_4$ moiety to afford complex **14**. A possible alternative formation pathway might involve loss of the $\text{Fe}(\text{CO})_4$ moiety from the $[\text{Fe}(\text{CO})_4(\text{SH})]^-$ anion to generate an HS^- species, which then attacks the μ -carbyne carbon of **3** to yield **14**. The origin of the hydrogen atom in the SH group could be solvent THF (see below). To our knowledge, no such breaking of Fe–S and R–S bonds in the reactions of the reactive $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-RS})(\text{CO})_6]$ salts has been reported.

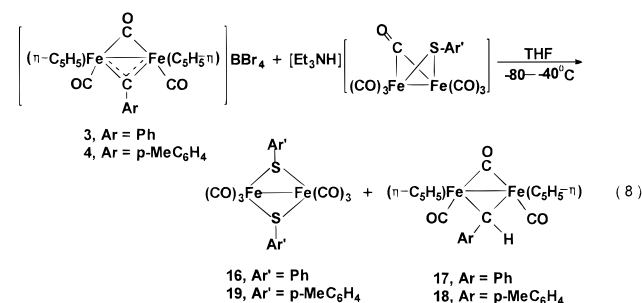
The formation of complex **15** could have proceeded via dissociation of the reactive salt to generate a Bu^nS^- species, which then becomes bonded to the μ -carbene carbon to afford complex **15**. Such a process appears to have occurred in the reaction of the cationic carbyne



(29) Qiu, Z.-L.; Sun, J.; Chen, J.-B. *Organometallics* **1998**, *17*, 600.

complexes $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{M}\equiv\text{CPh}]\text{BBr}_4$ ($\text{M} = \text{Mn}$ or Re) with $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SPh})(\text{CO})_6]$ to produce phenylcarbene complexes $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{M}=\text{C}(\text{SPh})\text{Ph}]$ ($\text{M} = \text{Mn}$ or Re).²⁹

To examine the effect of different RS substituents on the reactivity of the reactive salts and reaction products, $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SPh})(\text{CO})_6]$ was used in a reaction with **3** under the same conditions. Unlike $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-S}^i\text{Bu}^n)(\text{CO})_6]$, the reactive salt $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SPh})(\text{CO})_6]$ did not undergo cleavage to generate a HS^- or PhS^- species, and formation of bridging mercaptocarbene complex **14** or bridging phenylthiocarbene complex **7** was not observed. Instead, a known thiolato-bridged iron carbonyl compound $[\text{Fe}_2(\mu\text{-SPh})_2(\text{CO})_6]$ (**16**)²² and a bridging phenylcarbene complex $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**17**) (eq 8) were obtained in 11 and 68% yield, respectively. The analogous reaction of $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SPh})(\text{CO})_6]$ with **4** gave **16** and the bridging *p*-tolylcarbene complex $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{H})\text{C}_6\text{H}_4\text{Me-p}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (**18**) (eq 8) in 8 and 56% isolated yield, respectively.



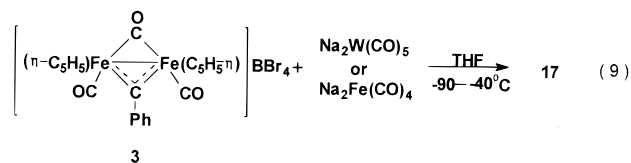
Analogous thiolato-bridged iron carbonyl compound $[\text{Fe}_2(\mu\text{-SC}_6\text{H}_4\text{Me-p})_2(\text{CO})_6]$ (**19**)²³ and bridging carbene complex **17** in 10 and 51% yield, respectively, also were obtained in the reaction of $[\text{Et}_3\text{NH}][\text{Fe}_2(\mu\text{-CO})(\mu\text{-SC}_6\text{H}_4\text{Me-p})(\text{CO})_6]$ with **3** (eq 8).

The formulation of complexes **17** and **18** is supported by microanalytical and spectroscopic data and X-ray crystallography. Their ¹H NMR spectra had a resonance at δ 12.38 and 12.40, respectively, characteristic for a $\mu\text{-CHR}$ group. Unexpectedly, this resonance has undergone a significant downfield shift, compared with that of analogous bridging arylcarbene complexes $[\text{ReFe}\{\mu\text{-C}(\text{H})\text{Ph}\}(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$ (δ 9.03)^{10a} and $[(\text{Ph}_3\text{P})_2\text{N}][\text{WRe}\{\mu\text{-C}(\text{H})\text{C}_6\text{H}_4\text{Me-p}\}(\text{CO})_9]$ (δ 8.09).³⁰

The structure of **17** (Figure 4) is very similar to that of **6**, **7**, and **15** except that the SR group in **6**, **7**, and **15** is replaced by a H atom in **17**. Many structural features of **17** are essentially the same as those in **6** (or **7** and **15**): the angles between the ligand planes C(2) through C(7) and C(13) through C(17) and C(2) through C(7) and C(18) through C(22), the Fe–Fe distance, the two $\mu\text{-C}(1)\text{--Fe}$ and $\mu\text{-C}(10)\text{--Fe}$ distances. An apparent difference in the structures of **6** (or **7** and **15**) and **17** is the shorter C(1)–C(2) bond in **17** (1.463(9) Å), which is intermediate between C–C single and C=C double bond distances, as compared to **6** (1.54(1) Å) (or **7** (1.50(1) Å) and **15** (1.52(2) Å)).

It is not clear by what pathway complexes **17** and **18** form in reaction 8. However, it seems that no initial

PhS^- or $p\text{-MeC}_6\text{H}_4\text{S}^-$ species was formed since no bridging mercaptocarbene complex was obtained in the reaction. The reaction of $\text{Na}_2[\text{W}(\text{CO})_5]$ or $\text{Na}_2[\text{Fe}(\text{CO})_4]$ with **3** (eq 9) under the same conditions afforded **17** in high yield (82–85%).



These reactions possibly could involve the formation of $[\text{MH}(\text{CO})_n]^-$ ($\text{M} = \text{W}$, $n = 5$, or $\text{M} = \text{Fe}$, $n = 4$) via protonation of $[\text{M}(\text{CO})_n]^{2-}$. Hydride transfer from the $[\text{MH}(\text{CO})_n]^-$ anion to the $\mu\text{-carbyne}$ carbon of **3** could give the bridging arylcarbene complex **17**. Indeed, the attack of $[\text{CrH}(\text{CO})_5]^-$ or $[\text{WH}(\text{CO})_5]^-$ species on unsaturated $\text{M}\equiv\text{C}_{\text{carbyne}}$ species has been documented.³¹ Since $\text{Na}_2[\text{W}(\text{CO})_5]$ and $\text{Na}_2[\text{Fe}(\text{CO})_4]$ cannot provide a hydride for the formation of **17**, the only other source of the H^- in this reaction is the THF solvent. It is not excluded that the source of the H^- could be water, which is a trace contaminant in solvent THF or from glassware. Analogous H-abstrating reactions from THF solvent to form the bridging arylcarbene complexes have been observed in the reactions of $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}\equiv\text{CPh}]\text{BBr}_4$ with $\text{Na}_2[\text{Fe}(\text{CO})_4]$ and $\text{Na}_2[\text{W}(\text{CO})_5]$, which yielded $[\text{ReFe}\{\mu\text{-C}(\text{H})\text{Ph}\}(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]^{10a}$ and $[\text{WRe}\{\mu\text{-C}(\text{H})\text{Ph}\}(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]^{10e}$ respectively. It is certain that complexes **17** and **18** were not formed directly by reaction of cationic **3** or **4** with THF solvent in reaction 8 because no product **17** or **18** was isolated in the absence of the reactive salt. This suggests that the carbonylmethyl anions $[\text{Fe}_2(\mu\text{-CO})(\mu\text{-SAr}')(\text{CO})_6]^-$ ($\text{Ar}' = \text{Ph}$ or $p\text{-MeC}_6\text{H}_4$) and $[\text{W}(\text{CO})_5]^{2-}$ or $[\text{Fe}(\text{CO})_4]^{2-}$ are important; they probably promote the reactions by forming a metal hydride species.

The title reaction shows a variety of reactions of the cationic diiron carbene complexes with nucleophilic carbonylmethyl anions to afford a series of dimetal bridging carbene complexes. This offers a new, convenient and useful method for preparation and structural modification of dimetal bridging carbene complexes.

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Supporting Information Available: Tables of the positional parameters and $B_{\text{iso}}/B_{\text{eq}}$, H atom coordinates, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **6**, **7**, **15**, and **17**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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