1816 *Organometallics* **2003,** *22,* 1816−1826

Novel Reactions of Cyclooctatetraene (COT)-Coordinated Diiron Cationic Bridging Carbyne Complexes with Nucleophiles

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Received December 16, 2002

The COT-coordinated diiron cationic bridging carbyne complexes $[Fe_2(\mu\text{-CAr})(CO)_4(\eta^8\text{-}C_8H_8)][BF_4]$ (**1**, Ar = C_6H_5; **2**, Ar = p-$CH_3C_6H_4$; **3**, Ar = p-$CF_3C_6H_4$) were prepared by the reactions of the diiron bridging alkoxycarbene complexes $[Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$ with $HBF_4\cdot Et_2O$ at low temperature. Cationic **3** reacts with NaSR (R = C_2H_5, p-$CH_3C_6H_4$) in THF at low temperature to afford diiron bridging sulfonylcarbene complexes $[Fe_2\{\mu\text{-}C(SO_2R)\text{-}C_6H_4CF_3\text{-p}\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**7**, R = C_2H_5; **8**, R = p-$CH_3C_6H_4$), while the reactions of **1**−**3** with $NaBH_4$ under similar conditions gave diiron bridging arylcarbene complexes $[Fe_2\{\mu\text{-}C(H)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**9**, Ar = C_6H_5; **10**, Ar = p-$CH_3C_6H_4$; **11**, Ar = p-$CF_3C_6H_4$). Complexes **1**−**3** can also react with anionic carbonylmetal compounds Na[M(CO)$_5$(CN)] (**4**, M = Cr; **5**, M = Mo; **6**, M = W) to produce diiron bridging aryl(pentacarbonylcyanometal)carbene complexes $[Fe_2\{\mu\text{-}C(Ar)NCM(CO)_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**12**, Ar = C_6H_5, M = Cr; **13**, Ar = p-$CH_3C_6H_4$, M = Cr; **14**, Ar = p-$CF_3C_6H_4$, M = Cr; **15**, Ar = C_6H_5, M = Mo; **16**, Ar = p-$CH_3C_6H_4$, M = Mo; **17**, Ar = p-$CF_3C_6H_4$, M = Mo; **18**, Ar = C_6H_5, M = W; **19**, Ar = p-$CH_3C_6H_4$, M = W; **20**, Ar = p-$CF_3C_6H_4$, M = W). Unexpectedly, aniline and 2-naphthylamine react with cationic **1** and **3** to give novel COT-coordinated iron carbene complexes $[Fe_2\{{=}C(Ar)NHAr'\}(\mu\text{-}CO)(CO)_3(\eta^8\text{-}C_8H_8)]$ (**21**, Ar = C_6H_5, Ar′ = C_6H_5; **22**, Ar = p-$CF_3C_6H_4$, Ar′ = C_6H_5; **23**, Ar = p-$CF_3C_6H_4$, Ar′ = 2-naphthyl). In solution, products **21**−**23** were transformed into chelated iron carbene complexes $[Fe_2\{{=}C(Ar)NAr'\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2\text{-}C_8H_9)]$ (**24**, Ar = C_6H_5, Ar′ = C_6H_5; **25**, Ar = p-$CF_3C_6H_4$, Ar′ = C_6H_5; **26**, Ar = p-$CF_3C_6H_4$, Ar′ = 2-naphthyl) in high yields. The structures of complexes **7**, **8**, **11**, **14**, **15**, **20**, **22**, and **24** have been established by X-ray diffraction studies.

Introduction

A considerable number of di- or trimetal bridging carbene and bridging carbyne complexes have been synthesized by Stone and co-workers.[1−3] 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.[4,5] Recently, we have shown a convenient and useful method for the preparation of the bridging carbene and bridging carbyne complexes: the reactions[6,7] of highly electrophilic cationic carbyne complexes of manganese and rhenium, $[\eta^5\text{-}C_5H_5(CO)_2M{\equiv}CC_6H_5][BBr_4]$ (M = Mn, Re), with mono- or dimetal carbonyl anions or mixed-dimetal carbonyl anions such as $[HFe(CO)_4]^-$, $[\eta^5\text{-}C_5H_5M(CO)_x]^-$ (M = Mo, W, x = 3; M = Fe, x = 2), $[Fe(CO)_4]^{2-}$, $[Fe_2(CO)_8]^{2-}$, $[W(CO)_5]^{2-}$, and $[MCo(CO)_n]^-$ (M = Fe or W; n = 8 or 9). Most recently, we found a new method for the preparation of dimetal bridging carbene and carbyne complexes: the reactions[8,9] of 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-$CH_3C_6H_4$) and $[Fe_2(\mu\text{-}CO)(\mu\text{-CAr})(CO)_2\text{-}\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}][BBr_4]$ (Ar = C_6H_5, p-$CH_3C_6H_4$,

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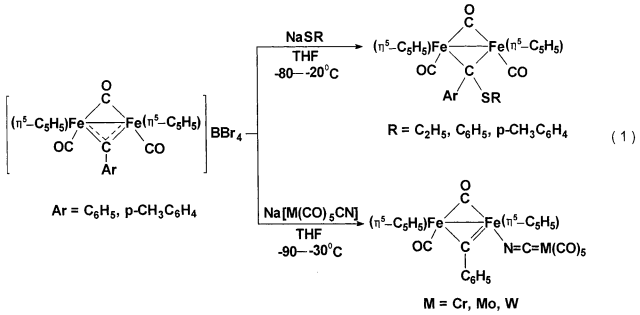
10.1021/om0210098 CCC: $25.00
Publication on Web 04/01/2003

p-$CF_3C_6H_4$) with nucleophiles involving anionic carbonylmetal compounds. For instance, the cationic carbyne complexes [$Fe_2(\mu$-CO)(μ-CAr)$(CO)_2(\eta^5$-$C_5H_5)_2$][BBr_4] reacted with nucleophiles such as NaSR (R = C_2H_5, C_6H_5, p-$CH_3C_6H_4$) and Na[$M(CO)_5$(CN)] (M = Cr, Mo, W) to give a series of diiron bridging carbene complexes [$Fe_2(\mu$-CO){μ-C(SR)Ar}$(CO)_2(\eta^5$-$C_5H_5)_2$][8a] and diiron bridging carbyne complexes [$Fe_2(\mu$-CO)(μ-CC_6H_5)(CO)-$(\eta^5$-$C_5H_5)_2NCM(CO)_5$][8b] (eq 1), respectively. This offers a new and useful method for the preparation and structural modification of dimetal bridging carbene and bridging carbyne complexes.



(1)

To explore the reactivity of the diiron cationic carbyne complexes containing cycloolefin ligands and to further examine the scope of this preparation of dimetal bridging carbene and bridging carbyne complexes,we studied the reactivity of the cyclooctatetraene (COT)-coordinated diiron derivatives in this paper. In our early works,[8,9] it turned out that the substituents with different electron effects at the μ-carbyne carbon induced different reactions of the diiron cationic bridging carbyne complexes. So we chose the cyclooctatetraene (COT)-coordinated diiron bridging alkoxycarbene complexes [Fe_2{μ-C(OC_2H_5)Ar}$(CO)_4(\eta^8$-C_8H_8)] (Ar = C_6H_5, p-$CH_3C_6H_4$, p-$CF_3C_6H_4$), obtained by the reactions of [$Fe_2(CO)_5(\eta^8$-C_8H_8)] with aryllithium reagents followed by alkylation with Et_3OBF_4,[10] as starting materials for the reaction with Lewis acids such as $HBF_4{\cdot}Et_2O$ to form the COT-coordinated diiron cationic bridging carbyne complexes [$Fe_2(\mu$-CAr)$(CO)_4(\eta^8$-C_8H_8)][BF_4] (**1**, Ar = C_6H_5; **2**, Ar = p-$CH_3C_6H_4$; **3**, Ar = p-$CF_3C_6H_4$). The bridging COT ligand in these diiron bridging carbene complexes participates in a novel two-electron three-center (Fe−C−Fe) interaction, similar to that in compound [$Fe_2(CO)_5(\eta^8$-C_8H_8)].[11] In a recent communication,[12] we showed that COT-coordinated diiron cationic bridging carbyne complexes **1**−**3** react with N-nucleophiles $NaN(SiMe_3)_2$ or $LiN(SiMe_3)_2$ and $LiNEt_2$ to lead to nucleophilic addition to and ring-breaking of the coordinated cyclooctatetraene, giving COT ring addition products or ring-opening products. To examine the effect of different nucleophiles on the reactivity of the diiron cationic carbyne complexes and resulting products, we studied the reactions of cationic carbyne complexes **1**−**3** with a variety of nucleophiles. In the present paper we give full details of the syntheses of diiron cationic bridging carbyne complexes **1**−**3** and their reactions with nucleophiles including NaSR, $NaBH_4$, Na[$M(CO)_5$-(CN)] (M = Cr, Mo, W), and arylamines. These reactions lead to nucleophilic addition to bridging carbyne carbon of the cationic bridging carbyne complexes to give a range of novel dimetal bridging carbene complexes.

Experimental Section

All procedures were performed under a dry, oxygen-free N_2 atmosphere by 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 N_2 atmosphere. Tetrahydrofuran and diethyl ether 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, 100−200 mesh) 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 atmosphere. Compounds $HBF_4{\cdot}Et_2O$ and $NaBH_4$ were purchased from Aldrich Chemical Co. Compounds $NaSC_2H_5$,[13] $NaC_6H_4CH_3$-p,[13] Na[$Cr(CO)_5$(CN)] (**4**),[14] Na[Mo-$(CO)_5$(CN)] (**5**),[14] and Na[$W(CO)_5$(CN)] (**6**)[14] were prepared by literature methods.

The IR spectra were measured on a Perkin-Elmer 983G spectrophotometer. All ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature in acetone-d_6 with TMS as the internal reference using a Bruker AM-300 spectrometer. The ^{13}C NMR data for some compounds were not obtained due to their sensitivity to temperature (complexes **1**−**3**, **7**, **8**, and **12**−**23**) and poor solubility (complex **10**). 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 [$Fe_2(\mu$-CC_6H_5)$(CO)_4(\eta^8$-C_8H_8)][BF_4] (1). To a stirred, red solution of [Fe_2{μ-C(OC_2H_5)C_6H_5}$(\eta^8$-C_8H_8)] (0.150 g, 0.32 mmol) in 40 mL of ether at approximately −60 °C was added 45 μL (0.32 mmol) of $HBF_4{\cdot}Et_2O$. The reaction mixture was stirred at −60 to −30 °C for 30 min, during which time a brick red precipitate formed gradually. The resulting mixture was filtered, and the solids were washed with ether (2 × 20 mL) at −65 °C and then dried under high vacuum at −30 °C to give 0.155 g (95%, based on [Fe_2{μ-C(OC_2H_5)C_6H_5}-$(\eta^8$-C_8H_8)]) of **1** as a brick red solid: IR (CH_2Cl_2) ν(CO) 2049 (s), 2036 (w), 1983 (vs, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.44−7.02 (m, 5H, C_6H_5), 6.15 (br, 2H, C_8H_8), 5.21−5.06 (m, 2H, C_8H_8), 4.41 (br, 2H, C_8H_8), 3.42−3.17 (m, 2H, C_8H_8). Anal. Calcd for $C_{19}H_{13}BF_4Fe_2O_4$: C, 45.30; H, 2.60. Found: C, 44.95; H, 2.84.

Preparation of [$Fe_2(\mu$-$CC_6H_4CH_3$-p)$(CO)_4(\eta^8$-C_8H_8)][BF_4] (2). This complex was prepared in a manner similar to that for **1** using [Fe_2{μ-C(OC_2H_5)$C_6H_4CH_3$-p}$(\eta^8$-C_8H_8)] (0.160 g, 0.34 mmol) and $HBF_4{\cdot}Et_2O$ (46 μL, 0.34 mmol). A brick red solid product of **2** was obtained in a yield of 0.167 g (96%, based on [Fe_2{μ-C(OC_2H_5)$C_6H_4CH_3$-p}$(\eta^8$-C_8H_8)]): IR (CH_2Cl_2) ν(CO) 2055 (w), 2032 (vs, br), 2007 (s, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.22 (d, 2H, J = 8.6 Hz, $C_6H_4CH_3$), 7.02 (d, 2H, J = 8.6 Hz, $C_6H_4CH_3$), 6.08 (br, 2H, C_8H_8), 5.06 (m, 2H, C_8H_8), 4.36 (m, 2H, C_8H_8), 3.42−3.24 (m, 2H, C_8H_8), 2.21 (s, 3H, $CH_3C_6H_4$). Anal. Calcd for $C_{20}H_{15}BF_4Fe_2O_4$: C, 46.39; H, 2.87. Found: C, 46.21; H, 2.94.

Preparation of [$Fe_2(\mu$-$CC_6H_4CF_3$-p)$(CO)_4(\eta^8$-C_8H_8)][BF_4] (3). This complex was prepared in a manner similar to that for **1** from [Fe_2{μ-C(OC_2H_5)$C_6H_4CF_3$-p}$(\eta^8$-C_8H_8)] (0.150 g, 0.28 mmol) and $HBF_4{\cdot}Et_2O$ (40 μL, 0.29 mmol). A brown-yellow solid product of **3** was obtained, yield 0.150 g (93%, based on [Fe_2{μ-C(OC_2H_5)$C_6H_4CF_3$-p}$(\eta^8$-C_8H_8)]): IR (CH_2Cl_2) ν(CO) 2052 (s), 2019 (m), 1987 (vs, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.59−7.38 (m, 4H, $C_6H_4CF_3$), 6.03 (m, 2H, C_8H_8), 5.29−5.05 (m, 2H, C_8H_8), 4.54 (m, 2H, C_8H_8), 3.29−3.08 (m, 2H, C_8H_8).

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Anal. Calcd for $C_{20}H_{12}BF_7Fe_2O_4$: C, 42.01; H, 2.12. Found: C, 41.89; H, 2.35.

Reaction of $[Fe_2(\mu\text{-}CC_6H_4CF_3\text{-}p)(CO)_4(\eta^8\text{-}C_8H_8)][BF_4]$ (3) with $NaSC_2H_5$ to Give $[Fe_2\{\mu\text{-}C(SO_2C_2H_5)C_6H_4CF_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (7). To a stirred, brick red solution of 0.110 g (0.19 mmol) of freshly prepared (in situ) **3** in 50 mL of THF at −100 °C was added 0.018 g (0.21 mmol) of $NaSC_2H_5$. The solution turned immediately from brick red to brown-red in color. After stirring at −90 to −50 °C for 3−4 h, the resulting solution was evaporated under high vacuum at −50 °C to dryness, and the brick red residue was chromatographed on an alumina column (1.6 × 15−20 cm) at −25 °C with petroleum ether/CH_2Cl_2/Et_2O (5:2:1) as the eluant. The brown-red band was eluted and collected. After vacuum removal of the solvent, the residue was recrystallized from petroleum ether/CH_2Cl_2 (5:1) solution at −80 °C to give 0.064 g (50%, based on **3**) of deep red crystals of **7**: mp 160−162 °C dec; IR (CH_2Cl_2) ν(CO) 2030 (m), 2000 (s), 1945 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 8.86 (d, 2H, $J = 8.2$ Hz, $CF_3C_6H_4$), 7.48 (d, 2H, $J = 8.2$ Hz, $CF_3C_6H_4$), 5.62 (s, 2H, CH_2Cl_2), 4.47 (s, 8H, C_8H_8), 2.67 (q, 2H, $J = 6.6$ Hz, CH_2CH_3), 0.73 (t, 3H, $J = 6.6$ Hz, CH_2CH_3); MS *m/e* 578 (M^+), 550 ($M^+ - CO$), 522 ($M^+ - 2CO$), 84 ($CH_2Cl_2^+$). Anal. Calcd for $C_{22}H_{17}F_3Fe_2O_6S{\cdot}CH_2Cl_2$: C, 41.66; H, 2.89. Found: C, 41.60; H, 2.86.

Reaction of 3 with $NaSC_6H_4CH_3$-p to Give $[Fe_2\{\mu\text{-}C(SO_2C_6H_4CH_3\text{-}p)C_6H_4CF_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (8). Using the same procedures for the reaction of **3** with $NaSC_2H_5$, freshly prepared (in situ) **3** (0.175 g, 0.31 mmol) was treated with $NaSC_6H_4CH_3$-p (0.051 g, 0.35 mmol) at −90 to −50 °C for 3−4 h, during which time the brick red solution gradually turned to brown-red. Workup as described above gave 0.110 g (52%, based on **3**) of deep red crystalline **8**: mp 150−152 °C; IR (CH_2Cl_2) ν(CO) 2028 (m), 1998 (s, br), 1954 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 8.66 (d, 2H, $J = 8.1$ Hz, $CF_3C_6H_4$), 7.43 (d, 2H, $J = 8.1$ Hz, $CF_3C_6H_4$), 7.18 (d, 2H, $J = 7.9$ Hz, $CH_3C_6H_4$), 7.12 (d, 2H, $J = 7.9$ Hz, $CH_3C_6H_4$), 5.64 (s, 1H, CH_2Cl_2), 4.58 (s, 8H, C_8H_8), 2.35 (s, 3H, $CH_3C_6H_4$); MS *m/e* 612 ($M^+ - CO$), 584 ($M^+ - 2CO$), 84 ($CH_2Cl_2^+$). Anal. Calcd for $C_{27}H_{19}F_3Fe_2O_6S{\cdot}0.5CH_2Cl_2$: C, 48.38; H, 2.95. Found: C, 48.01; H, 2.75.

Reaction of 1 with $NaBH_4$ to Give $[Fe_2\{\mu\text{-}C(H)C_6H_5\}(\eta^8\text{-}C_8H_8)]$ (9). To a stirred solution of 0.120 g (0.26 mmol) of freshly prepared (in situ) **1** dissolved in 50 mL of THF at −78 °C was added 0.013 g of $NaBH_4$. The solution turned immediately from brick red to purple red. After stirring at −78 to −50 °C for 3 h, the resulting solution was evaporated under high vacuum at −50 °C to dryness, and the brick red residue was extracted with CH_2Cl_2. The red extracted solution was evaporated in vacuo at −30 °C to dryness, and the residue was recrystallized from petroleum ether/CH_2Cl_2 (2:1) at −80 °C to give 0.065 g (61%, based on **2**) of purple-red crystals of **9**: mp >200 °C; IR (CH_2Cl_2) ν(CO) 2007 (m), 1978 (vs), 1944 (s) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 9.39 (s, 1H, μ-CH), 7.27−7.00 (m, 5H, C_6H_5), 4.51 (s, 8H, C_8H_8); ^{13}C NMR (CD_3COCD_3) δ 217.68 (CO), 217.36 (CO), 158.55 (μ-C), 130.31, 127.97, 127.47, 125.64 (C_6H_5), 71.18 (C_8H_8); MS *m/e* 362 [$M^+ - 2CO$], 306 [$M^+ - Fe(CO)_2$], 250 [$M^+ - Fe(CO)_2 - 2CO$], 194 [$M^+ - 2Fe(CO)_2$]. Anal. Calcd for $C_{19}H_{14}Fe_2O_4$: C, 54.59; H, 3.38. Found: C, 54.45; H, 3.30.

Reaction of 2 with $NaBH_4$ to Give $[Fe_2\{\mu\text{-}C(H)C_6H_4CH_3\text{-}p\}(\eta^8\text{-}C_8H_8)]$ (10). Using the same procedures as described for the reaction of **1** with $NaBH_4$, 0.125 g (0.24 mmol) of freshly prepared **2** was treated with 0.032 g of $NaBH_4$ at −78 to −50 °C for 3 h. Further treatment of the resulting solution as done above for the reaction of **1** with $NaBH_4$ yielded 0.070 g (68%, based on **2**) of purple-red crystals of **10**: mp 200−202 °C dec; IR (CH_2Cl_2) ν(CO) 2006 (m), 1976 (s), 1942 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 9.42 (s, 1H, μ-CH), 7.14 (d, 2H, $J = 7.8$ Hz, $CH_3C_6H_4$), 6.91 (d, 2H, $J = 7.8$ Hz, $CH_3C_6H_4$), 4.49 (s, 8H, C_8H_8), 2.19 (s, 3H, $CH_3C_6H_4$); MS *m/e* 320 [$M^+ - Fe(CO)_2$], 264 [$M^+ - Fe(CO)_2 - 2CO$], 208 [$M^+ - 2Fe(CO)_2$], 193 [$M^+ - 2Fe(CO)_2 - CH_3$]. Anal. Calcd for $C_{20}H_{16}Fe_2O_4$: C, 55.60; H, 3.73. Found: C, 55.62; H, 3.75.

Reaction of 3 with $NaBH_4$ to Give $[Fe_2\{\mu\text{-}C(H)C_6H_4CF_3\text{-}p\}(\eta^8\text{-}C_8H_8)]$ (11). Freshly prepared (in situ) **3** (0.070 g, 0.12 mmol) was treated, in a manner similar to that described for the preparation of **9**, with $NaBH_4$ (0.022 g, 0.58 mmol) at −78 to −50 °C for 3 h. The resulting solution was worked up as described for the reaction of **2** with $NaBH_4$ to yield 0.045 g (75%, based on **3**) of **11** as purple-red crystals: mp >220 °C; IR (CH_2Cl_2) ν(CO) 2010 (m), 1981 (s), 1947 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 9.17 (s, 1H, μ-CH), 7.44 (d, 2H, $J = 8.5$ Hz, p-$CF_3C_6H_4$), 7.38 (d, 2H, $J = 8.5$ Hz, $CF_3C_6H_4$), 4.55 (s, 8H, C_8H_8); ^{13}C NMR (CD_3COCD_3) δ 216.60 (CO), 162.51 (μ-C), 124.45, 129.88, 121.39 ($CF_3C_6H_4$), 70.99 (C_8H_8); MS *m/e* 374 [$M^+ - Fe(CO)_2$], 346 [$M^+ - Fe(CO)_2 - CO$], 318 [$M^+ - Fe(CO)_2 - 2CO$], 298 [$M^+ - C_8H_8 - 3CO$], 262 [$M^+ - 2Fe(CO)_2$]. Anal. Calcd for $C_{20}H_{13}F_3Fe_2O_4$: C, 49.42; H, 2.70. Found: C, 49.40; H, 2.50.

Reaction of 1 with $Na[Cr(CO)_5(CN)]$ (4) to Give $[Fe_2\{\mu\text{-}C(C_6H_5)NCCr(CO)_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (12). To 0.104 g (0.21 mmol) of freshly prepared (in situ) **1** dissolved in 60 mL of THF at −100 °C was added 0.052 g (0.22 mmol) of $Na[Cr(CO)_5(CN)]$ (**4**). The reaction mixture was stirred at −90 to −60 °C for 2 h, during which time the turbid solution gradually turned purple-red. After stirring at −60 to −35 °C for an additional 2 h, the resulting solution was evaporated under high vacuum at −45 °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 (2:1) as the eluant. The brown band was eluted and collected. After vacuum removal of the solvent, the residue was recrystallized from petroleum ether/CH_2Cl_2 (4:1) solution at −80 °C to give 0.086 g (66%, based on **1**) of brown-red crystals of **12**: mp >200 °C; IR (CH_2Cl_2) ν(CO) 2052 (s), 2017 (m), 1996 (vs), 1942 (vs, br) cm^{-1}; ν(CN) 2120 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.36−7.21 (m, 5H, C_6H_5), 4.76 (s, 8H, C_8H_8); MS *m/e* 387 [$M^+ - Cr(CO)_5 - 2CO$], 328 [$C_8H_8Fe_2(CO)_4^+$], 272 [$C_8H_8Fe(CO)_4^+$], 244 [$C_8H_8Fe(CO)_3^+$], 218 [$Cr(CO)_5(CN)^+$]. Anal. Calcd for $C_{25}H_{13}CrFe_2NO_9$: C, 47.28; H, 2.06; N, 2.21. Found: C, 47.46; H, 1.85; N, 1.90.

Reaction of 2 with 4 to Give $[Fe_2\{\mu\text{-}C(C_6H_4CH_3\text{-}p)NCCr(CO)_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (13). Using the same procedure above, freshly prepared **2** (0.136 g, 0.26 mmol) was treated with **4** (0.086 g, 0.30 mmol) at −90 to −35 °C for 4 h. Further treatment of the resulting solution as described in the reaction of **1** with **4** gave 0.106 g (59%, based on **2**) of brown crystalline **13**: mp >200 °C; IR (CH_2Cl_2) ν(CO) 2053 (m), 2017 (w), 1996 (s), 1944 (vs) cm^{-1}; ν(CN) 2119 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.21−7.06 (m, 4H, $CH_3C_6H_4$), 4.76 (s, 8H, C_8H_8), 2.23 (s, 3H, $CH_3C_6H_4$); MS *m/e* 593 [$M^+ - 2CO$], 457 [$M^+ - Cr(CO)_5$], 328 [$C_8H_8Fe_2(CO)_4^+$]. Anal. Calcd for $C_{26}H_{15}CrFe_2NO_9$: C, 48.11; H, 2.33; N, 2.16. Found: C, 47.80; H, 2.51; N, 2.23.

Reaction of 3 with 4 to Give $[Fe_2\{\mu\text{-}C(C_6H_4CF_3\text{-}p)NCCr(CO)_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (14). As described for the reaction of **1** with **4**, freshly prepared (in situ) **3** (0.126 g, 0.22 mmol) reacted with **4** (0.057 g, 0.24 mmol) at −90 to − 35 °C for 4 h. The resulting mixture was worked up as described for the reaction of **1** with **4** to give 0.110 g (67%, based on **3**) of deep red crystalline **14**: mp >200 °C; IR (CH_2Cl_2) ν(CO) 2053 (s), 2020 (w), 2000 (vs), 1948 (vs, br) cm^{-1}; ν(CN) 2118 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.58 (d, $J = 8.9$ Hz, 2H, $CF_3C_6H_4$), 7.50 (d, $J = 8.9$ Hz, 2H, $CF_3C_6H_4$), 4.80 (s, 8H, C_8H_8); MS *m/e* 515 [$M^+ - C_8H_8 - 3CO$], 403 [$M^+ - C_8H_8 - Fe(CO)_2 - 3CO$], 375 [$M^+ - C_8H_8 - 2Fe(CO)_2$]. Anal. Calcd for $C_{26}H_{12}CrF_3Fe_2NO_9$: C, 44.42; H, 1.72; N, 1.99. Found: C, 44.07; H, 1.88; N, 2.01.

Reaction of 1 with $Na[Mo(CO)_5(CN)]$ (5) to Give $[Fe_2\{\mu\text{-}C(C_6H_5)NCMo(CO)_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (15). Using the same procedures for the reaction of **1** with **4**, freshly prepared **1** (0.124 g, 0.25 mmol) was treated with $Na[Mo(CO)_5(CN)]$ (**5**) (0.074 g, 0.26 mmol) to yield 0.117 g (65%, based on **3**) of deep red crystalline **15**: mp >200 °C; IR (CH_2Cl_2) ν(CO) 2057 (w), 2022 (m), 1994 (s), 1950 (vs) cm^{-1}; ν(CN) 2117 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.31−7.22 (m, 5H, C_6H_5), 4.79 (s, 8H, C_8H_8), 4.76 (q, J = 6.8 Hz, 2H, CH_2CH_3), 3.30 (br, 1H, C_2H_5OH), 0.87 (t, 3H, J = 6.8 Hz, CH_2CH_3); MS *m/e* 328 [$C_8H_8Fe_2(CO)_4^+$], 300 [$C_8H_8Fe_2(CO)_3^+$], 272 [$C_8H_8Fe_2(CO)_2^+$], 46 ($C_2H_5OH^+$). Anal. Calcd for $C_{25}H_{13}Fe_2MoNO_9\cdot C_2H_5OH$: C, 44.73; H, 2.82; N, 1.93. Found: C, 44.81; H, 2.71; N, 2.20.

Reaction of 2 with 5 to Give $[Fe_2\{\mu\text{-}C(C_6H_4CH_3\text{-}p)NCMo(CO)_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (16). As described for the reaction of **1** with **4**, freshly prepared **2** (0.136 g, 0.26 mmol) reacted with **5** (0.086 g, 0.30 mmol) to produce 0.108 g (60%, based on **2**) of brown crystalline **16**: mp >200 °C; IR (CH_2Cl_2) ν(CO) 2057 (m), 2018 (w), 1996 (s), 1946 (s) cm^{-1}; ν(CN) 2117 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.21−7.06 (m, 4H, $CH_3C_6H_4$), 4.76 (s, 8H, C_8H_8), 2.11 (s, 3H, $CH_3C_6H_4$); MS *m/e* 692 (M^+ − 1), 665 (M^+ − CO), 589 (M^+ − C_8H_8), 553 (M^+ − 5CO). Anal. Calcd for $C_{26}H_{15}Fe_2MoNO_9$: C, 45.06; H, 2.18; N, 2.02. Found: C, 44.85; H, 2.41; N, 2.18.

Reaction of 3 with 5 to Give $[Fe_2\{\mu\text{-}C(C_6H_4CF_3\text{-}p)NCMo(CO)_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (17). Similar to the reaction of **1** with **4**, freshly prepared **3** (0.150 g, 0.26 mmol) was treated with **5** (0.080 g, 0.28 mmol) to afford 0.105 g (58%, based on **3**) of deep red crystalline **17**: mp >200 °C; IR (CH_2Cl_2) ν(CO) 2055 (m), 2020 (w), 2000 (s), 1946 (vs), 1943 (vs) cm^{-1}; ν(CN) 2125 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.60 (d, J = 8.3 Hz, 2H, $CF_3C_6H_4$), 7.53 (d, J = 8.3 Hz, 2H, $CF_3C_6H_4$), 4.79 (s, 8H, C_8H_8); MS *m/e* 747 (M^+), 691 (M^+ − 2CO), 391 (M^+ − C_8H_8 − 8CO). Anal. Calcd for $C_{26}H_{12}F_3Fe_2MoNO_9$: C, 41.80; H, 1.62; N, 1.88. Found: C, 41.58; H, 1.79; N, 2.03.

Reaction of 1 with Na[W(CO)$_5$(CN)] (6) to Give $[Fe_2\{\mu\text{-}C(C_6H_5)NCW(CO)_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (18). Using the same procedures as described for the reaction of **1** with **4**, freshly prepared **1** (0.104 g, 0.21 mmol) was treated with Na[W(CO)$_5$(CN)] (**6**) (0.081 g, 0.22 mmol) to give 0.120 g (76%, based on **3**) of **18** as brown crystals: mp >200 °C; IR (CH_2Cl_2) ν(CO) 2052 (s), 2017 (m), 1996 (vs), 1942 (vs, br) cm^{-1}; ν(CN) 2120 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.36−7.21 (m, 5H, C_6H_5), 4.76 (s, 8H, C_8H_8); MS *m/e* 579 [M^+ − C_8H_8 − $Fe(CO)_2$], 551 [M^+ − C_8H_8 − $Fe(CO)_2$ − CO], 350 [$W(CO)_5(CN)^+$]. Anal. Calcd for $C_{25}H_{13}Fe_2NO_9W$: C, 39.15; H, 1.71; N, 1.83. Found: C, 39.35; H, 1.94; N, 1.86.

Reaction of 2 with 6 to Give $[Fe_2\{\mu\text{-}C(C_6H_4CH_3\text{-}p)NCW(CO)_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (19). In a manner similar to the procedure described for the reaction of **1** with **4**, 0.125 g (0.24 mmol) of freshly prepared **2** was treated with **6** (0.094 g, 0.25 mmol) to afford 0.117 g (62%, based on **2**) of brown-red crystals of **19**: mp >200 °C; IR (CH_2Cl_2) ν(CO) 2054 (m), 2017 (w), 1996 (s), 1940 (vs) cm^{-1}; ν(CN) 2119 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.24−7.05 (m, 4H, $CH_3C_6H_4$), 4.75 (s, 8H, C_8H_8), 2.22 (s, 3H, $CH_3C_6H_4$); MS *m/e* 355 [M^+ − C_8H_8 − $W(CO)_4(CN)$], 327 [M^+ − C_8H_8 − $W(CO)_5(CN)$], 299 [M^+ − C_8H_8 − $W(CO)_5(CN)$ − CO]. Anal. Calcd for $C_{26}H_{15}Fe_2NO_9W$: C, 39.99; H, 1.94; N, 1.79. Found: C, 39.71; H, 2.20; N, 2.04.

Reaction of 3 with 6 to Give $[Fe_2\{\mu\text{-}C(C_6H_4CF_3\text{-}p)NCW(CO)_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (20). Freshly prepared **3** (0.133 g, 0.23 mmol)) was treated, in a manner similar to that described in the reaction of **1** with **4**, with 0.094 g (0.25 mmol) of **6** to yield 0.158 g (81%, based on **3**) of deep red crystalline **20**: mp >200 °C; IR (CH_2Cl_2) ν(CO) 2054 (m), 2021 (w), 2000 (s), 1940 (vs, br) cm^{-1}; ν(CN) 2119 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.58 (d, J = 8.7 Hz, 2H, $CF_3C_6H_4$), 7.50 (d, J = 8.7 Hz, 2H, $CF_3C_6H_4$), 4.80 (s, 8H, C_8H_8); MS *m/e* 563 [M^+ − C_8H_8 − 6CO], 535 [M^+ − C_8H_8 − 7CO], 507 [M^+ − C_8H_8 − 8CO]. Anal. Calcd for $C_{26}H_{12}F_3Fe_2NO_9W$: C, 37.40; H, 1.45; N, 1.68. Found: C, 37.54; H, 1.60; N, 1.68.

Reaction of 1 with $C_6H_5NH_2$ to Give $[Fe_2\{{=}C(C_6H_5)NHC_6H_5\}(\mu\text{-}CO)(CO)_3(\eta^8\text{-}C_8H_8)]$ (21). To 0.176 g (0.35 mmol) of freshly prepared **1** dissolved in 50 mL of THF at −78 °C was added 0.095 mL (1.04 mmol) of $C_6H_5NH_2$. After stirring at −78 to −40 °C for 3 h, the resulting solution was evaporated under high vacuum at −40 °C to dryness, and the dark red residue was extracted with petroleum ether/CH_2Cl_2 (10:3). The red extracted solution was evaporated in vacuo at −40 °C to dryness, and the residue was recrystallized from petroleum ether/CH_2Cl_2 (5:1) at −80 °C to give 0.118 g (66%, based on **1**) of deep red crystals of **21**: mp 168−170 °C dec; IR (CH_2Cl_2) ν(CO) 1987 (s, br), 1931 (s), 1697 (m, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 11.4 (br, 1H, C_6H_5NH), 7.28−6.86 (m, 10H, C_6H_5 + C_6H_5NH), 4.39 (s, 8H, C_8H_8); MS *m/e* 453 (M^+ − 2CO), 425 (M^+ − 3CO), 397 [M^+ − $Fe(CO)_2$], 341 [M^+ − $Fe(CO)_2$ − 2CO], 285 [M^+ − $2Fe(CO)_2$]. Anal. Calcd for $C_{25}H_{19}Fe_2NO_4$: C, 58.98; H, 3.76; N, 2.75. Found: C, 58.76; H, 4.01; N, 3.01.

Reaction of 3 with $C_6H_5NH_2$ to Give $[Fe_2\{{=}C(C_6H_4CF_3\text{-}p)NHC_6H_5\}(\mu\text{-}CO)(CO)_3(\eta^8\text{-}C_8H_8)]$ (22). A 0.107 g (0.19 mmol) sample of freshly prepared **3** in 50 mL of THF was reacted as described for the reaction of **1** with $C_6H_5NH_2$, with 0.048 mL (0.51 mmol) of $C_6H_5NH_2$ at −78 to −40 °C for 3 h. Further treatment of the resulting solution as described above gave 0.100 g (56%, based on **1**) of deep red crystals of **22**: mp 88−90 °C dec; IR (CH_2Cl_2) ν(CO) 1985 (s, br), 1934 (s), 1703 (m, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 11.4 (br, 1H, C_6H_5NH), 7.62−6.53 (m, 9H, $CF_3C_6H_4$ + C_6H_5NH), 5.63 (s, 1H, CH_2Cl_2), 4.41 (s, 8H, C_8H_8); MS *m/e* 465 [M^+ − $Fe(CO)_2$], 353 [M^+ − $2Fe(CO)_2$], 84 ($CH_2Cl_2^+$). Anal. Calcd for $C_{26}H_{18}F_3Fe_2NO_4\cdot 0.5CH_2Cl_2$: C, 51.37; H, 3.09; N, 2.36. Found: C, 51.66; H, 3.10; N, 2.82.

Reaction of 3 with 2-Naphthylamine to Give $[Fe_2\{{=}C(C_6H_4CF_3\text{-}p)NHC_{10}H_7\}(\mu\text{-}CO)(CO)_3(\eta^8\text{-}C_8H_8)]$ (23). To 0.161 g (0.28 mmol) of freshly prepared **3** dissolved in 50 mL of THF at −78 °C was added 0.114 g (0.80 mmol) of β-naphthylamine (β-$C_{10}H_7NH_2$). After stirring at −78 to −50 °C for 2 h, the resulting solution was evaporated under high vacuum at −40 °C to dryness, and the dark red residue was extracted with petroleum ether/CH_2Cl_2 (5:1). The deep red extracted solution was evaporated in vacuo at −40 °C to dryness and the residue recrystallized from petroleum ether/CH_2Cl_2 (5:1) at −80 °C to give 0.133 g (76%, based on **3**) of deep red crystals of **23**: 110−112 °C dec; IR (CH_2Cl_2) ν(CO) 2011 (m), 1985 (s, br), 1936 (s), 1703 (m, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 11.5 (br, 1H, $C_{10}H_7NH$), 7.79−6.77 (m, 11H, $CF_3C_6H_4$ + $C_{10}H_7NH$), 4.44 (s, 8H, C_8H_8); MS *m/e* 515 [M^+ − $Fe(CO)_2$], 487 [M^+ − $Fe(CO)_2$ − CO], 459 [M^+ − $Fe(CO)_2$ − 2CO], 403 [M^+ − $2Fe(CO)_2$]. Anal. Calcd for $C_{30}H_{20}F_3Fe_2NO_4$: C, 57.45; H, 3.21; N, 2.23. Found: C, 57.15; H, 3.32; N, 2.35.

Transformation of 21 into $[Fe_2\{{=}C(C_6H_5)NC_6H_5\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2\text{-}C_8H_9)]$ (24). A solution of **21** (0.050 g, 0.10 mmol) in 10 mL of CH_2Cl_2 was kept at room temperature for 1−2 h, during which time the deep red solution gradually turned red. The solvent was removed in vacuo, and the residue was chromatographed on Al_2O_3 (neutral) with petroleum/CH_2Cl_2 (10:1) as the eluant. The orange-red band was eluted and collected. After removal of the solvent, the residue was recrystallized from petroleum/CH_2Cl_2 (15:1) at −50 °C to give 0.045 g (90%) of red crystals of **24**: mp 178−180 °C dec; IR (CH_2Cl_2) ν(CO) 1999 (m), 1965 (s), 1935 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.21−6.50 (m, 10H, C_6H_5), 4.44 (t, 1H, J = 6.3 Hz, CH), 4.07 (t, 1H, J = 6.8 Hz, CH), 3.62 (dd, 1H, J = 15.4, 8.4 Hz, CH), 3.43 (t, 1H, J = 6.5 Hz, CH), 3.37 (t, 1H, J = 6.9 Hz, CH), 3.02 (dd, 1H, J = 8.7, 6.0 Hz, CH), 2.76 (m, 1H, CH_2), 2.61 (dd, 1H, J = 13.5, 7.5 Hz, CH), 1.62 (m, 1H, CH_2); ^{13}C NMR (CD_3COCD_3) δ 235.6 (C_{carbene}), 217.7, 217.1, 216.5, 215.5 (CO), 158.3, 150.8, 128.9, 128.2, 126.8, 125.1, 124.1, 123.5 (Ar−C), 87.6, 80.1, 68.7, 53.9, 52.8, 42.1, 20.7, 19.1; MS *m/e* 481 (M^+ − CO), 453 (M^+ − 2CO), 425 (M^+ − 3CO), 397 [M^+ − $Fe(CO)_2$], 341 [M^+ − $Fe(CO)_2$ − 2CO], 285 [M^+ − $2Fe(CO)_2$]. Anal. Calcd for $C_{25}H_{19}Fe_2NO_4$: C, 58.98; H, 3.76; N, 2.75. Found: C, 58.78; H, 3.92; N, 2.82.

Transformation of 22 into $[Fe_2\{{=}C(C_6H_4CF_3\text{-}p)NC_6H_5\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2\text{-}C_8H_9)]$ (25). Compound **22** (0.050 g, 0.09 mmol) in 10 mL of CH_2Cl_2 was transformed as described for the transformation of **21** to give 0.040 g (80%) of red crystals of **25**: mp 165−167 °C dec; IR (CH_2Cl_2) ν(CO) 2002 (m), 1968

Table 1. Crystal Data and Experimental Details for Complexes 7, 8, 11, 14, 22, and 24

	7·CH_2Cl_2	**8**·THF	**11**	**14**	**22**	**24**
formula	$C_{23}H_{19}Cl_2F_3Fe_2O_6S$	$C_{31}H_{27}F_3Fe_2O_7S$	$C_{20}H_{13}F_3Fe_2O_4$	$C_{26}H_{12}CrF_3Fe_2NO_9$	$C_{26.5}H_{19}ClF_3Fe_2NO_4$	$C_{25}H_{19}Fe_2NO_4$
fw	663.04	712.29	486.00	703.07	619.59	509.11
space group	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)
a (Å)	8.700(3)	12.300(2)	13.8670(16)	10.0716(16)	8.005(2)	9.5539(6)
b (Å)	12.172(4)	15.408(3)	11.7277(13)	11.4042(18)	9.895(3)	13.8890(9)
c (Å)	24.202(8)	16.336(3)	11.4018(13)	12.538(2)	17.150(5)	16.6249(10)
α (deg)	90		90	82.440(3)	97.069(6)	90
β (deg)	90	91.196(4)	90	75.834(3)	96.442(5)	90
γ (deg)	90		90	73.951(3)	107.101(5)	90
V (Å^3)	2562.9(15)	3095.3(10)	1854.3(4)	1338.7(4)	1272.8(7)	2206.0(2)
Z	4	4	4	2	2	4
D_{calcd} (g /cm^3)	1.718	1.528	1.741	1.744	1.630	1.533
F(000)	1336	1456	976	700	630	1040
μ (Mo Kα) cm^{-1})	14.82	10.68	16.18	15.44	13.02	13.47
radiation (monochromated in incident beam)	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
	($\lambda = 0.71073$ Å)	($\lambda = 0.71073$ Å)	($\lambda = 0.71073$ Å)	($\lambda = 0.71073$ Å)	($\lambda = 0.71073$ Å)	($\lambda = 0.71073$ Å)
diffractometer	Brock Smart	Brock Smart	Brock Smart	Brock Smart	Brock Smart	Brock Smart
temperature (°C)	20	20	20	20	20	20
orientation reflns: no.; range (2θ) (deg)	4.76−24.24	4.88−39.32	4.549−42.702	4.84−48.68	4.632−45.759	4.918−42.739
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
data coll range, 2θ (deg)	3.36−50.00	3.32−51.00	4.54−56.54	3.72−50.00	4.36−50.00	3.82−56.56
no. of unique data, total	4525	5753	3905	4701	4035	5118
with $I > 2.00\sigma(I)$	1265	2806	1978	2952	2491	3165
no. of params refined	341	454	275	411	367	317
correct. factors, max. min.	0.7053−1.0000	0.8631−1.0000	0.7828−1.0000	0.3264−1.0000	0.5631−1.0000	0.81203−1.00000
R^a	0.0601	0.0515	0.0468	0.0603	0.1098	0.0453
$R_w{}^b$	0.1307	0.1064	0.1192	0.1016	0.2259	0.0818
quality of fit in dicator^c	0.698	0.826	0.893	0.935	1.101	0.862
max. shift/esd final cycle	0.003	0.003	0.094	0.020	0.006	0.032
largest peak, e$^-$/Å^3	0.418	0.396	0.402	0.718	1.018	0.374
min. peak, e$^-$/Å^3	−0.438	−0.216	−0.359	−0.716	−0.707	−0.240

[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 $= [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$.

(s), 1939 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.44 (d, 2H, J = 8.3 Hz, $CF_3C_6H_4$), 7.22−6.97 (m, 5H, C_6H_5), 6.78 (d, 2H, J = 8.3 Hz, $CF_3C_6H_4$), 4.47 (t, 1H, J = 6.3 Hz, CH), 4.13 (t, 1H, J = 6.9 Hz, CH), 3.65 (dd, 1H, J = 15.5, 8.6 Hz, CH), 3.47 (t, 1H, J = 6.5 Hz, CH), 3.38 (t, 1H, J = 7.1 Hz, CH), 3.05 (dd, 1H, J = 8.7, 6.3 Hz, CH), 2.77 (m, 1H, CH_2), 2.65 (m, 1H, CH), 1.60 (m, 1H, CH_2); ^{13}C NMR (CD_3COCD_3) δ 234.8 ($C_{carbene}$), 218.2, 217.5, 216.8, 216.0 (CO), 158.4, 154.4, 129.4, 125.8, 125.7, 124.8, 123.7 (Ar−C), 88.2, 80.9, 69.3, 54.6, 53.5, 42.9, 21.3, 19.3; MS m/e 465 [M$^+$ − Fe(CO)$_2$], 353 [M$^+$ − 2Fe(CO)$_2$]. Anal. Calcd for $C_{26}H_{18}F_3Fe_2NO_4$: C, 54.11; H, 3.14; N, 2.43. Found: C, 54.10; H, 3.32; N, 2.51.

Transformation of 23 into [$Fe_2\{{=}C(C_6H_4CF_3\text{-}p)NC_{10}H_7\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2\text{-}C_8H_9)$] (26). Using the same procedures for the transformation of **21**, complex **23** (0.090 g, 0.14 mmol) was transformed into red crystalline **26** (0.077 g, 86%): mp 170−172 °C dec; IR (CH_2Cl_2) ν(CO) 2002 (m), 1969 (s), 1940 (m), 1919 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.84−6.80 (m, 11H, $CF_3C_6H_4$ + $C_{10}H_7$), 4.57 (t, 1H, J = 6.2 Hz, CH), 4.17 (t, 1H, J = 6.8 Hz, CH), 3.52 (t, 1H, J = 6.2 Hz, CH), 3.45 (t, 1H, J = 6.6 Hz, CH), 3.18 (dd, 1H, J = 8.8, 6.0 Hz, CH), 2.81 (m, 1H, CH_2), 2.70 (dd, 1H, J = 13.5, 7.8 Hz, CH), 1.67 (m, 1H, CH_2); ^{13}C NMR (CD_3COCD_3) δ 235.0 ($C_{carbene}$), 217.6, 216.8, 216.2, 215.4 (CO), 155.3, 134.0, 131.7, 129.0, 128.22, 128.21, 128.1, 127.1, 126.1, 125.5, 125.4, 124.5, 120.3 (Ar−C), 87.7, 80.4, 68.8, 54.1, 52.9, 42.4, 20.7, 18.8 (C_8H_9); MS m/e 599 (M$^+$ − CO), 515 [M$^+$ − Fe(CO)$_2$], 487 [M$^+$ − Fe(CO)$_2$ − CO], 459 [M$^+$ − Fe(CO)$_2$ − 2CO], 403 [M$^+$ − 2Fe(CO)$_2$]. Anal. Calcd for $C_{30}H_{20}F_3Fe_2NO_4$: C, 57.45; H, 3.21; N, 2.23. Found: C, 57.27; H, 3.26; N, 2.45.

X-ray Crystal Structure Determinations of Complexes 7, 8, 11, 14, 22, and 24. The single crystals of complexes **7**, **8**, **11**, **14**, **22**, and **24** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH_2Cl_2 or petroleum ether/THF and petroleum ether/C_2H_5OH at −80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for **7**, **8**, **11**, **14**, **22**, and **24** were collected with a Brock Smart diffractometer at 20 °C.

The structures of **7**, **8**, **11**, **14**, **22**, and **24** were solved by direct methods and expanded using Fourier techniques. For six complexes, the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included but not refined. The absorption corrections were applied using SADABS. The final cycle of full-matrix least-squares refinement was based on the observed reflections and the variable parameters and converged with unweighted and weighted agreement to give agreement factors of $R = 0.0601$ and $R_w = 0.1307$ for **7**, $R = 0.0515$ and $R_w = 0.1064$ for **8**, $R = 0.0468$ and $R_w = 0.1192$ for **11**, $R = 0.0603$ and $R_w = 0.1016$ for **14**, $R = 0.1098$ and $R_w = 0.2259$ for **22**, and $R = 0.0453$ and $R_w = 0.0818$ for **24**. For complex **22**, the R factor is relatively high since the single crystals suitable for X-ray diffraction were very difficult to obtain and the intensity data were collected at 20 °C. The reflection intensity was evidently decayed during the collection.

The details of the crystallographic data and the procedures used for data collection and reduction information for **7**, **8**, **11**, **14**, **22**, and **24** are given in Table 1. The selected bond lengths and angles are listed in Tables 2 and 3, respectively. The atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **7**, **8**, **11**, **14**, **15**, **20**, **22**, and **24** are given in the Supporting Information. The molecular structures of **7**, **8**, **11**, **14**, **15**, **20**, **22**, and **24** are given in Figures 1−6, respectively.

Results and Discussion

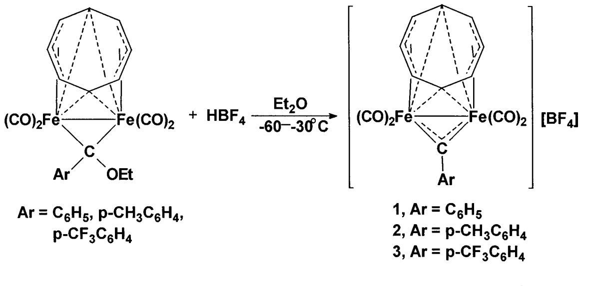
The diiron bridging alkoxycarbene complexes [$Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)$] react with 1 equiv of $HBF_4\cdot Et_2O$ at low temperature (below −30 °C) for 30 min to give COT-coordinated diiron cationic bridging carbyne

Table 2. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 7, 8, 11, and 14

	7	8	11	14
Fe(1)−Fe(2)	2.680(3)	2.6605(10)	2.7069(11)	2.7151(10)
Fe(1)−C(1)	2.023(14)	2.042(4)	2.025(10)	2.043(5)
Fe(2)−C(1)	2.058(12)	2.020(4)	2.036(13)	2.018(5)
Fe(1)−C(12)	2.328(16)	2.415(9)	2.308(15)	
Fe(1)−C(13)	2.057(17)	2.125(6)	1.994(16)	2.237(6)
Fe(1)−C(14)	2.109(16)	2.106(6)	2.032(18)	2.089(7)
Fe(1)−C(15)	2.116(19)	2.138(6)	2.141(15)	2.075(6)
Fe(1)−C(16)	2.615(16)	2.413(8)		2.202(6)
Fe(2)−C(12)	2.361(16)	2.320(9)		2.200(6)
Fe(2)−C(16)			2.330(17)	
Fe(2)−C(17)	2.120(18)	2.142(6)	2.165(14)	2.219(6)
Fe(2)−C(18)	2.136(16)	2.081(6)	2.113(14)	2.085(5)
Fe(2)−C(19)	2.095(15)	2.076(7)	2.179(16)	2.087(6)
C(12)−C(13)	1.46(2)	1.382(10)	1.41(3)	1.410(8)
C(13)−C(14)	1.33(2)	1.353(10)	1.429(16)	1.398(10)
C(14)−C(15)	1.35(2)	1.371(10)	1.433(16)	1.384(11)
C(15)−C(16)	1.40(2)	1.374(10)	1.394(16)	1.388(11)
C(16)−C(17)	1.39(2)	1.429(10)	1.396(15)	1.416(11)
C(17)−C(18)	1.47(2)	1.414(10)	1.326(15)	1.374(9)
C(18)−C(19)	1.46(2)	1.352(11)	1.35(2)	1.365(8)
C(19)−C(12)	1.40(2)	1.418(11)	1.35(3)	1.386(8)
C(1)−C(2)	1.567(17)	1.525(6)	1.478(8)	1.500(6)
C(1)−S	1.767(14)	1.810(4)		
S−O(5)	1.435(10)	1.447(3)		
S−O(6)	1.468(11)	1.444(3)		
C(1)−N				1.434(6)
N−C(21)				1.156(5)
Cr−C(21)				2.005(5)
Fe(1)−C(CO) (av)	1.725	1.755	1.752	1.759
Fe(2)−C(CO) (av)	1.769	1.749	1.735	1.776
Cr−C(CO) (av)				1.888
Fe(1)−Fe(2)−C(1)	48.4(4)	49.46(12)	48.0(3)	48.43(13)
Fe(2)−Fe(1)−C(1)	49.5(4)	48.72(12)	48.4(4)	47.64(13)
Fe(1)−C(1)−Fe(2)	82.1(5)	81.83(17)	83.6(2)	83.93(18)
Fe(1)−C(1)−C(2)	119.5(10)	118.9(3)	123.1(8)	119.2(3)
Fe(1)−C(1)−S	119.4(7)	112.4(2)		
Fe(2)−C(1)−S	111.0(7)	117.8(2)		
Fe(2)−C(1)−C(2)	115.5(8)	121.7(3)	121.8(10)	123.5(3)
C(2)−C(1)−S	107.3(9)	103.8(3)		
C(1)−S−O(5)	110.0(7)	111.2(2)		
C(1)−S−O(6)	112.3(6)	109.74(18)		
Fe(1)−C(1)−N				110.8(3)
Fe(2)−C(1)−N				109.8(3)
C(2)−C(1)−N				107.8(4)
C(1)−N−C(21)				177.2(5)
N−C(21)−Cr				176.1(4)
C(12)−C(13)−C(14)	133.6(19)	128.8(8)	125.1(14)	135.1(7)
C(13)−C(14)−C(15)	121.6(19)	128.1(7)	121.7(14)	128.3(7)
C(14)−C(15)−C(16)	137(2)	131.2(7)	138.6(15)	126.9(7)
C(15)−C(16)−C(17)	138(2)	137.8(7)	132.2(16)	135.7(7)
C(16)−C(17)−C(18)	133(2)	133.1(7)	129.9(16)	136.3(8)
C(17)−C(18)−C(19)	120.9(17)	123.5(7)	130.2(18)	126.5(6)
C(18)−C(19)−C(12)	129.2(16)	128.5(7)	131.6(18)	128.1(6)
C(19)−C(12)−C(13)	132.2(16)	136.7(8)	139.3(13)	135.0(6)

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

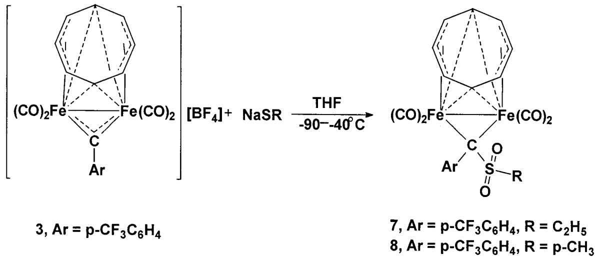
complexes $[Fe_2(\mu\text{-CAr})(CO)_4(\eta^8\text{-}C_8H_8)][BF_4]$ (**1**, Ar = C_6H_5; **2**, Ar = p-$CH_3C_6H_4$; **3**, Ar = p-$CF_3C_6H_4$) as brick red solids in 93−96% yields (eq 2).



(2)

The cationic complexes **1**−**3** are novel olefin-coordinated dimetal complexes with bridging carbyne ligands. They are very sensitive to air and moisture and can be stored for only a short time at low temperatures (below −65 °C). The compositions and structures of complexes **1**−**3** were established on the basis of their elemental analysis and IR and ^1H NMR spectra.

The freshly prepared (in situ) diiron cationic carbyne complex **3** reacts with NaSR (R = C_2H_5, p-$CH_3C_6H_4$) in THF at −100 to −50 °C for 3−4 h. After workup as described in the Experimental Section, the air- and temperature-sensitive purple-red crystalline complexes $[Fe_2\{\mu\text{-C}(SO_2R)C_6H_4CF_3\text{-p}\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**7**, R = C_2H_5; **8**, R = p-$CH_3C_6H_4$) (eq 3) were obtained in 50 and 52% isolated yields, respectively. However, cationic bridging carbyne complexes **1** and **2** do not react with $NaSC_2H_5$ or $NaSC_6H_4CH_3$-p under the same conditions.



(3)

Complexes **7** and **8** were readily soluble in polar organic solvents but slightly soluble in nonpolar solvents. They are very sensitive to air and temperature in solution and in the solid state. The formulas shown in eq 3 for both complexes were established by microanalytical data and IR, ^1H NMR, and mass spectroscopy, as well as X-ray crystallography. The IR spectra of **7** and **8** exhibit three absorption bands (at ca. 2028−2030, 1998−2000, and 1945−1954 cm^{-1}) in the ν(CO) region with a pattern similar to that of $[Fe_2\{\mu\text{-C}(OC_2H_5)\text{-}Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$. The ^1H NMR spectrum of **7** and **8** showed signals attributed to the COT ring at 4.47 and 4.58 ppm, respectively, similar to those of bridging alkoxycarbene complexes, suggesting that, in complexes **7** and **8**, the eight-membered ring of the COT ligand has an approximately planar configuration and is fluxional. This has been confirmed by an X-ray diffraction study of **7** (Figure 1) and **8** (Figure 2). The X-ray structures firmly confirmed that products **7** and **8** are novel diiron bridging sulfonylcarbene complexes with an SO_2R group added on the μ-carbene carbon. This site of nucleophilic attack resembles the reactions[8,9] of the cationic bridging carbyne complexes $[Fe_2(\mu\text{-CO})(\mu\text{-CAr})(CO)_2(\eta^5\text{-}C_5H_5)_2]\text{-}[BBr_4]$ and $[Fe_2(\mu\text{-CO})(\mu\text{-CAr})(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]\text{-}[BBr_4]$ with NaSR, but the product contrasts with the reactions of both complexes, which results in nucleophilic addition to the μ-carbyne carbon to give diiron bridging mercaptocarbene complexes.[8a,9]

The molecular structures of complexes **7** and **8** resemble that of $[Fe_2\{\mu\text{-C}(OC_2H_5)C_6H_4CF_3\text{-p}\}(CO)_4(\eta^8\text{-}C_8H_8)]$, except that the substituent on the μ-carbene carbon is a SO_2R group in **7** and **8** but an OC_2H_5 group in the latter. The distances of the Fe−Fe bond bridged by the μ-carbene ligand in **7** and **8** are 2.680(3) and 2.6605(10) Å, respectively, which are nearly the same as that found in $[Fe_2\{\mu\text{-C}(OC_2H_5)C_6H_4CF_3\text{-p}\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (2.686(1) Å).[10] The μ-carbene carbon almost symmetrically bridges the Fe−Fe bond with a C(1)−Fe(1) of 2.023−2.042 Å and a C(1)−Fe(2) of 2.020−2.058 Å for **7** and **8**. The μ-C−Fe distances in **7** and **8** are also approximately equal to that in $[Fe_2\{\mu\text{-C}(OC_2H_5)C_6H_4\text{-}$

Table 3. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 22 and 24

	22	24		22	24
Fe(1)−Fe(2)	2.753(2)	2.6920(9)	Fe(2)−C(8)	1.966(11)	
Fe(1)−C(1)	1.911(11)	1.962(4)	C(1)−N	1.320(13)	1.296(5)
Fe(2)−N		1.957(3)	N−C(20)	1.434(14)	1.410(5)
Fe(1)−C(13)	2.171(13)	2.237(5)	C(1)−C(2)	1.477(14)	1.447(6)
Fe(1)−C(14)	2.141(12)	2.200(5)	C(12)−C(13)	1.39(2)	1.476(8)
Fe(1)−C(15)	2.137(13)		C(13)−C(14)	1.41(2)	1.406(8)
Fe(1)−C(16)	2.270(12)	2.266(5)	C(14)−C(15)	1.37(2)	1.506(8)
Fe(1)−C(17)		2.299(5)	C(15)−C(16)	1.42(2)	1.504(8)
Fe(2)−C(12)	2.261(14)	2.122(5)	C(16)−C(17)	1.420(19)	1.345(8)
Fe(2)−C(17)	2.171(11)		C(17)−C(18)	1.412(19)	1.400(8)
Fe(2)−C(18)	2.059(11)	2.123(6)	C(18)−C(19)	1.356(18)	1.395(8)
Fe(2)−C(19)	2.068(12)	2.050(5)	C(12)−C(19)	1.411(19)	1.446(8)
Fe(1)−C(8)	1.908(12)	1.759(5)	C(8)−O(1)	1.203(13)	1.152(5)
Fe(1)−C(9)	1.730(16)	1.758(5)	C(9)−O(2)	1.156(15)	1.149(5)
Fe(2)−C(10)	1.705(17)	1.764(6)	C(10)−O(3)	1.163(17)	1.140(6)
Fe(2)−C(11)	1.788(12)	1.778(6)	C(11)−O(4)	1.117(13)	1.133(6)
Fe(1)−C(8)−Fe(2)	90.6(5)		C(1)−N−C(20)	131.0(9)	122.4(3)
Fe(1)−Fe(2)−C(8)	43.9(4)		C(12)−C(13)−C(14)	135.8(16)	128.7(6)
Fe(2)−Fe(1)−C(8)	45.5(3)	89.09(15)	C(13)−C(14)−C(15)	126.4(14)	121.1(6)
Fe(1)−Fe(2)−N		69.52(10)	C(14)−C(15)−C(16)	127.9(13)	104.9(4)
Fe(2)−Fe(1)−C(1)	129.1(3)	68.74(12)	C(15)−C(16)−C(17)	136.0(13)	122.2(6)
Fe(1)−C(1)−N	122.7(8)	111.5(3)	C(16)−C(17)−C(18)	131.4(14)	133.2(6)
Fe(2)−N−C(1)		110.3(3)	C(17)−C(18)−C(19)	129.0(12)	128.8(6)
Fe(1)−C(1)−C(2)	122.1(7)	124.6(3)	C(18)−C(19)−C(12)	127.2(13)	125.3(5)
Fe(2)−N−C(20)		126.9(3)	C(19)−C(12)−C(13)	133.6(14)	128.2(6)
Fe(1)−C(8)−O(1)	136.5(9)	176.8(5)	Fe(1)−C−O (CO) (av)	177.5	176.6
Fe(2)−C(8)−O(1)	132.7(9)		Fe(2)−C−O (CO) (av)	175.9	177.93
N−C(1)−C(2)	115.1(9)	123.3(4)			

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

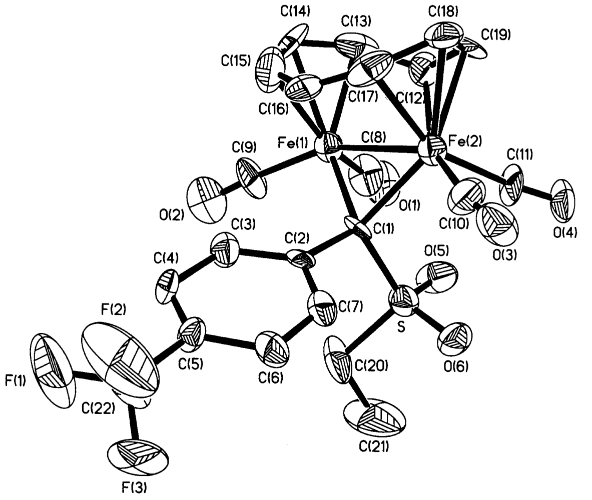


Figure 1. Molecular structure of **7**, showing the atom-numbering scheme with 45% thermal ellipsoids. CH_2Cl_2 has been omitted for clarity.

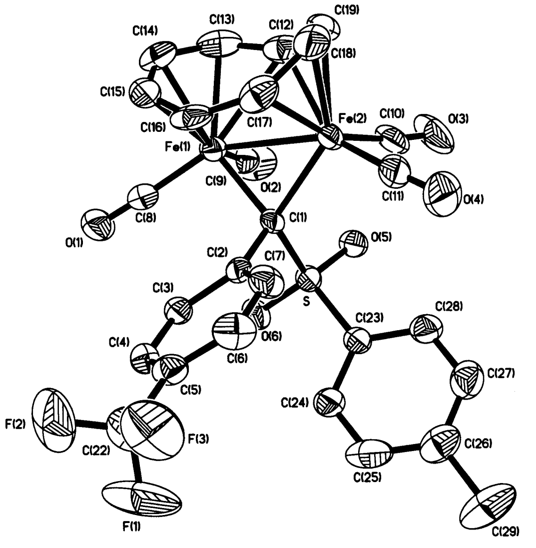


Figure 2. Molecular structure of **8**, showing the atom-numbering scheme with 40% thermal ellipsoids. THF has been omitted for clarity.

CF_3-p}$(CO)_4(\eta^8$-$C_8H_8)$] (average 2.037 Å).[10] The C(1)−S bond lengths, 1.767(14) Å for **7** and 1.810(4) Å for **8**, indicate that they are essentially single bonds by comparison with standard C(sp^2)−S (1.76 Å)[15] single bond and C(sp^3)−S (1.81 Å)[15] single bond distances.

The formation of complexes **7** and **8** is unexpected, and we do not know the chemistry involved. We presumed that their formation could be via a bridging mercaptocarbene intermediate [Fe_2{μ-C(SR)$C_6H_4CF_3$-p}$(CO)_4(\eta^8$-$C_8H_8)$] formed by attack of the $^-$SR anion on the more positive μ-carbyne carbon of **3**, where the aryl substituent on the μ-carbyne carbon is an electron-withdrawing p-$CF_3C_6H_4$ group, while in the case of **1** and **2**, where the aryl substituents on the μ-carbyne carbon are an electron-donating phenyl and a p-tolyl group, respectively, the bridging mercaptocarbene intermediate [Fe_2{μ-C(SR)Ar}$(CO)_4(\eta^8$-$C_8H_8)$] (Ar = C_6H_5, p-$CH_3C_6H_4$) does not form due to the electron-pushing action of the phenyl and p-tolyl groups. The [Fe_2{μ-C(SR)$C_6H_4CF_3$-p}$(CO)_4(\eta^8$-$C_8H_8)$] intermediate was then oxygenated to produce bridging sulfonylcarbene complex **7** or **8**. The source of oxygen in this reaction could be the solvent THF or air, which is a trace contaminant in THF solvent or from glassware. However, the latter can be excluded in the experimental conditions. Indeed, the transfer of oxygen from THF solvent to a complex has been documented. In the reaction[16] of $Mo_3S_7Br_4$ with $(^nBu)_3P$, the solvent THF provides the oxygen for the formation of $Mo_2O_2S_2Br_4^{2-}$, whose countercation is $(^nBu)_3P(CH_2)_4P(^nBu)_3^{2+}$.

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[15] (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.

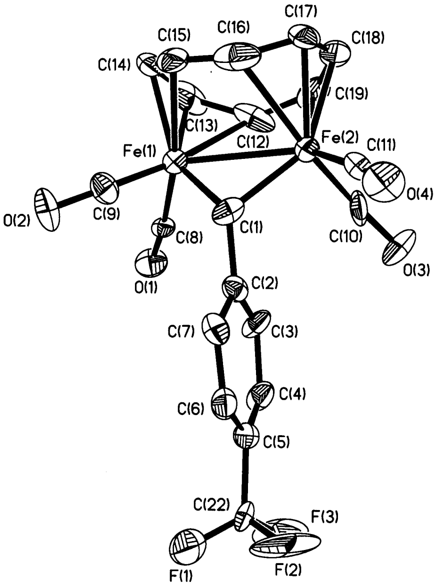
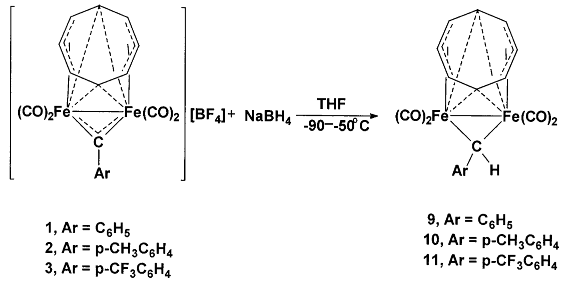


Figure 3. Molecular structure of **11**, showing the atom-numbering scheme with 45% thermal ellipsoids.

Interestingly, $NaBH_4$ reacts not only with cationic carbyne complex **3** but also with cationic complexes **1** and **2**. The reactions of $NaBH_4$ with cationic bridging carbyne complexes **1**−**3** under similar conditions as those for NaSR yield diiron bridging arylcarbene complexes $[Fe_2\{\mu\text{-}C(H)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**9**, Ar = C_6H_5; **10**, Ar = p-$CH_3C_6H_4$; **11**, Ar = p-$CF_3C_6H_4$) (eq 4) in 61−75% yields, among which the structure of **11** has been established by X-ray crystallography.



(4)

The formulation of complexes **9**−**11** is supported by elemental analysis and spectroscopic data and an X-ray diffraction study of **11**. Their ^1H NMR spectra had a resonance at 9.39, 9.42, and 9.17 ppm, respectively, characteristic for a μ-CHR group. Unexpectedly, this resonance has undergone a significant upfield shift, compared with that of analogous diiron bridging arylcarbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(H)C_6H_5\}(CO)_2(\eta\text{-}C_5H_5)_2]$ (δ 12.38)[8a] and $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(H)C_6H_4CH_3\text{-}p\}(CO)_2(\eta\text{-}C_5H_5)_2]$ (δ 12.40).[8a]

The structure of **11** (Figure 3) is very similar to that of **7** and **8** except that the SO_2R group in **7** and **8** is replaced by a H atom in **11**. Many structural features of **11** are essentially the same as those in **7** and **8**: the Fe−Fe distance, the two μ-C(1)−Fe, the Fe−C(COT) distances, the angles of Fe−Fe−μ-C and Fe−μ-C−Fe. An apparent difference in the structures of **7** (or **8**) and **11** is the shorter C(1)−C(2) bond in **11** (1.478(8) Å), which is intermediate between C−C single and C=C double bond lengths, as compared to **7** (1.567(17) Å) or **8** (1.525(6) Å).

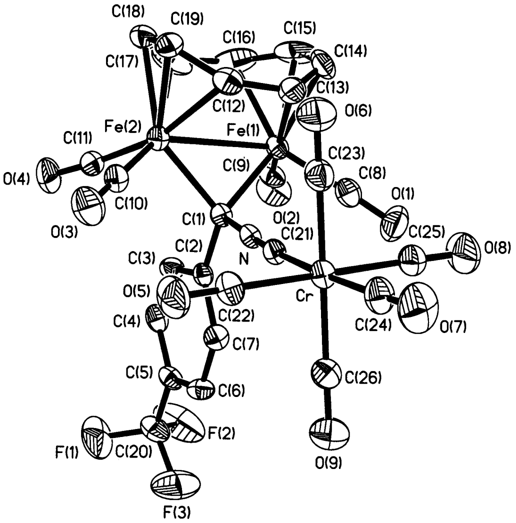
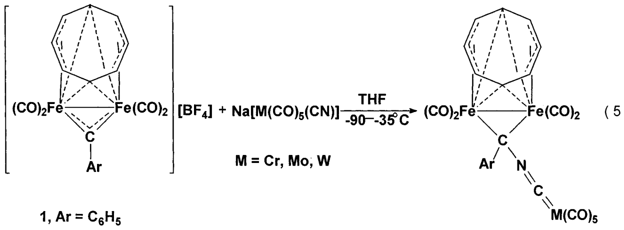


Figure 4. Molecular structure of **14**, showing the atom-numbering scheme with 45% thermal ellipsoids.

The highly electrophilic diiron cationic complexes **1**−**3** also react with an anionic carbonylmetal compound containing a CN negative substituent, $Na[Cr(CO)_5(CN)]$ (**4**), in THF at low temperature (−90 to −35 °C) to afford the diiron bridging aryl(pentacarbonylcyanochromium)carbene complexes $[Fe_2\{\mu\text{-}C(Ar)NCCr(CO)_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**12**−**14**) (eq 5) in 59−67% isolated yields. Complexes **1**−**3** react similarly with $Na[Mo(CO)_5(CN)]$ (**5**) to give corresponding bridging aryl(pentacarbonylcyanometal)carbene complexes $[Fe_2\{\mu\text{-}C(Ar)NCMo(CO)_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**15**−**17**) (eq 5) in similar yields (58−65%). Likely, anionic compound $Na[W(CO)_5(CN)]$ (**6**) reacts with cationic carbyne complexes **1**−**3** under the same conditions to produce bridging aryl(pentacarbonylcyanometal)carbene complexes $[Fe_2\{\mu\text{-}C(Ar)NCW(CO)_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**18**−**20**) (eq 5) in higher (62−81%) yields.



(5)

	C_6H_5	p-$CH_3C_6H_4$	p-$CF_3C_6H_4$
Cr	12	13	14
Mo	15	16	17
W	18	19	20

Complexes **12**−**20** are sensitive to air and temperature in solution but relatively stable in the solid state. On the basis of elemental analyses and spectroscopic evidence, as well as X-ray crystallography, products **12**−**20** are formulated as COT-coordinated diiron bridging carbene complexes with a $M(CO)_5CN$ (M = Cr, Mo, W) moiety bonded to a bridging carbene carbon through the N atom of the CN group.

The IR and ^1H NMR spectra of complexes **12**−**20** are fully consistent with their structures shown in eq 5. The IR spectra of **12**−**20** in the ν(CO) region show that the

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[16] (a) Cotton, F. A.; Luck, R. L.; Miertschin, C. S. *Inorg. Chem.* **1991**, *30*, 1155. (b) Breen, T. L.; Stephan, D. W. *Inorg. Chem*. **1992**, *31*, 4019.

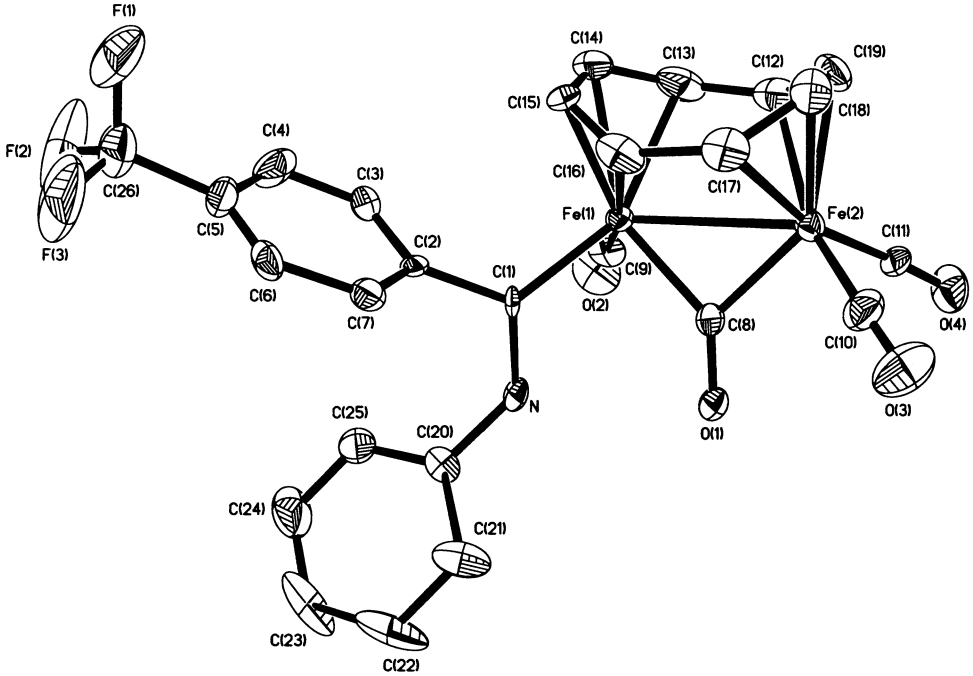

Figure 5. Molecular structure of **22**, showing the atom-numbering scheme with 40% thermal ellipsoids.

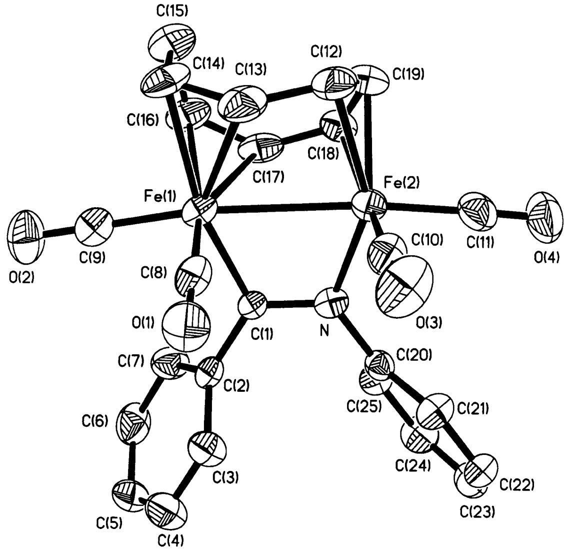

Figure 6. Molecular structure of **24**, showing the atom-numbering scheme with 45% thermal ellipsoids.

absorption band of the CO group appears at ca. 2057−1940 cm^{-1}. The characteristic ν(CN) stretching vibration occurs at ca. 2125−2117 cm^{-1}, similar to those of [$Fe_2(\mu\text{-}CO)\{\mu\text{-}C(C_6H_5)NCM(CO)_5\}(CO)_2(\eta^5\text{-}C_5H_5)_2$] (at ca. 2125 cm^{-1}).[8b] The ^{1}H NMR spectra of **12**−**20** showed the signals attributed to the COT rings at 4.75−4.80 ppm, which are downfield of those in **7** and **8** (at 4.47−4.58 ppm) and in **9**−**11** (at 4.49−4.55 ppm), because of the stronger electron-accepting ability of $(CO)_5MCN$ as compared with SO_2R and H groups. The structures of complexes **12**−**20** are further confirmed by X-ray studies of **14**, **15**, and **20**. The results of the X-ray diffraction work for complexes **14**, **15**, and **20** are summarized in Table 1 and the Supporting Information, respectively, and their structures are shown in Figure 4 and Figures 7 and 8 in the Supporting Information, respectively.

The molecular structure of **14** (Figure 4) resembles that of the diiron bridging alkoxycarbene complex [$Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)$],[10] except that the substituents at the μ-carbene carbon are a p-$CF_3C_6H_4$ and a $Cr(CO)_5CN$ group in **14** but a p-$CF_3C_6H_4$ and an OC_2H_5 group in the latter. The structural features of the principal portion of [$Fe_2(\mu\text{-}CC_6H_4CF_3\text{-}p)(CO)_4(\eta^8\text{-}C_8H_8)$] of **14** are very similar to those of the same unit in the complex [$Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)$], as illustrated by the following parameters (the value for **14** is followed by the same parameters for [$Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)$]: Fe−Fe (2.7151(10), 2.686(2) Å), Fe(1)−μ-C (2.043(5), 2.063(3) Å), Fe(2)−μ-C (2.018(5), 2.010(3) Å), average Fe(1)−C(COT) (2.151, 2.187 Å), average Fe(2)−C(COT) (2.148, 2.165 Å), average C−C(COT) (1.390, 1.406 Å), μ-C−Fe(1)−Fe(2) (47.64(13)°, 47.9(1)°), μ-C−Fe(2)−Fe(1) (48.43(13)°, 49.6(1)°), Fe(1)−μ-C−Fe(2) (83.93(18)°, 82.5(1)°). The structure of the $M(CO)_5CN$ (M = Cr) moiety bonded to the μ-carbene carbon is essentially the same as that in the analogous complex [$Fe_2(\mu\text{-}CO)\{\mu\text{-}C(C_6H_4CH_3\text{-}p)NCW(CO)_5\}(CO)_2(\eta^5\text{-}C_5H_5)_2$].[8b] The two C−N bond lengths in **14** are very different. C(21)−N has a bond length of 1.156(5) Å, which indicates high triple-bond character and is essentially the same as the corresponding distance in [$Fe_2(\mu\text{-}CO)\{\mu\text{-}C(C_6H_4CH_3\text{-}p)(CO)_2(\eta^5\text{-}C_5H_5)_2NCW(CO)_5\}$] (C(23)−N 1.15(2) Å).[8b] The other is C(1)−N, with a bond length of 1.434 (6) Å, which is between the normal C−N and C═N distances and slightly shorter than the corresponding C−N distance in complexes [$Fe_2(\mu\text{-}CO)\{\mu\text{-}C(C_6H_4CH_3\text{-}p)(CO)_2(\eta^5\text{-}C_5H_5)_2\text{-}NCW(CO)_5\}$] (1.47(2) Å)[8b] and [$WN(Bu^tCMe_2(Me)\text{-}(NBu^t)\{N(Bu^t)CMe = CMe_2\}$) (1.438−1.521 Å).[17] The shorter Cr−C(21) distance (2.005(5) Å) in **14** signifies its high double-bond character. The C(1), N, C(21), and Cr atoms are coplanar, with a C(1)−N−C(21) angle of 177.2(5)° and a N−C(21)−Cr angle of 176.1(4)°, indicating that the C(1)−N−C(21)−Cr fragment is almost linear.

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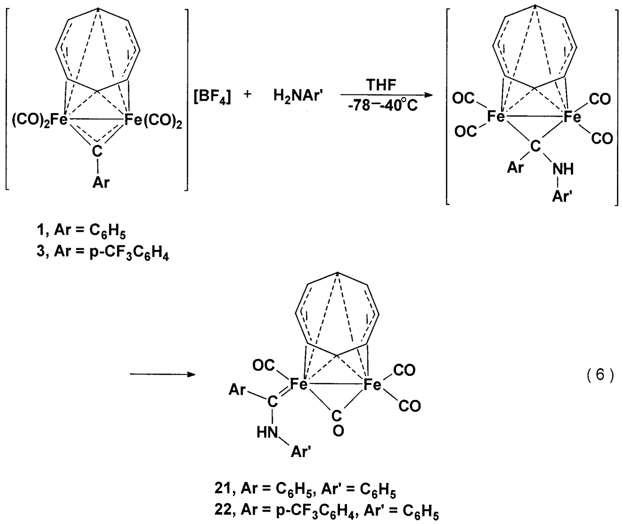
[17] Chiu, K. W.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1981**, 2088.

The structures of **15** (Figure 7) and **20** (Figure 8) (Supporting Information) are fundamentally the same as that of **14**, except that the p-$CF_3C_6H_4$ and $(CO)_5CrCN$ groups on the μ-carbene carbon in **14** are displaced by the C_6H_5 and $(CO)_5MoCN$ groups in **15** and by the $(CO)_5WCN$ group in **20**. The distances of Fe(1)−Fe(2), average Fe−μ-C, C(1)−N, N−C(21), and M−C(21) are 2.7153(14), 2.018, 1.423(7), 1.167(7), and 2.124(7) Å in **15** and 2.722(2), 2.034, 1.412(13), 1.174, and 2.147(14) Å in **20**, respectively, similar to those of **14**.

The reaction pathway to complexes **12**−**20** could proceed via attack of the $(CO)_5M{=}C{=}N^-$ (M = Cr, Mo, W) anion, a representation of the same electronic structure of the $^-M(CO)_5(CN)$ anion, at the μ-carbyne carbon of cationic **1** or **2** or **3**. Not all such carbonylmetal anions containing a CN group can react with cationic carbyne complexes **1**−**3** to afford the bridging carbene complexes since the analogous carbonylmetal compound $Na[Fe(CO)_4(CN)]$ reacted with **1** or **2** and **3** under the same conditions to give no corresponding bridging aryl(pentacarbonylcyanometal)carbene complexes, which indicates that the metal atom in the anionic carbonylmetal compound is important; the Cr, Mo, and W atoms probably promote the reaction by forming a stable $(CO)_5M{=}C{=}N{-}C$ (M = Cr, Mo, W) core.

Of special interest are the reactions of arylamines with the diiron cationic carbyne complexes. The reactions of aniline and 2-naphthylamine with cationic carbyne complexes **1** and **3** in THF at low temperature (−78 to −40 °C) give unexpected COT-coordinated iron carbene complexes $[Fe_2\{{=}C(Ar)NHAr'\}(\mu\text{-}CO)(CO)_3(\eta^8\text{-}C_8H_8)]$ (**21**, Ar = C_6H_5, Ar′ = C_6H_5; **22**, Ar = p-$CF_3C_6H_4$ Ar′ = C_6H_5; **23**, Ar = p-$CF_3C_6H_4$, Ar′ = 2-naphthyl) (eq 6) in 56−76% yields.



1, Ar = C_6H_5
3, Ar = p-$CF_3C_6H_4$

(6)

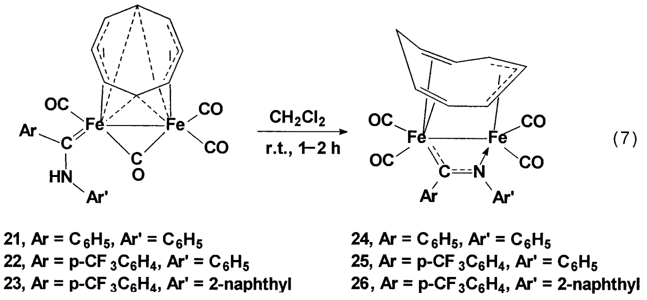
21, Ar = C_6H_5, Ar′ = C_6H_5
22, Ar = p-$CF_3C_6H_4$, Ar′ = C_6H_5
23, Ar = p-$CF_3C_6H_4$, Ar′ = 2-naphthyl

The IR spectra of complexes **21**−**23** showed a CO absorption band at ca. 1697−1703 cm^{-1} in the ν(CO) region in addition to two strong CO absorption bands at ca. 1985−1987 and 1931−1936 cm^{-1}, characteristic for a bridging CO ligand. The ^{1}H NMR spectra of complexes **21**−**23** showed a single-line signal for the COT ligand as that of the original eight-membered ring in starting diiron bridging alkoxycarbene complexes $[Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$, which is fluxional,[10,11] suggesting that the COT ring is retained in these complexes. This has been confirmed by the X-ray diffraction study of complex **22**.

The products **21**−**23** were shown by their spectroscopic data and the X-ray crystallography of **22** to be iron carbene complexes with a carbene ligand C(Ar)NHAr′ bonded to an Fe atom of the $(CO)_3Fe_2(\mu\text{-}CO)$ core. The molecular structure of **22** (Figure 5) shows that the two Fe atoms are bridged by a CO group, as anticipated from its IR spectrum. Of the two Fe atoms, one carries two terminal CO groups and the other carries one terminal CO group and a $C(C_6H_4CF_3\text{-}p)NHC_6H_5$ ligand, in addition to coordination to the COT ring and bridging a CO ligand, thus giving each Fe atom 18 valence electrons. The Fe−Fe distance of 2.753(2) Å is somewhat longer than that in diiron bridging carbene complex $[Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (2.686(1) Å),[4] and in **7** (or **8**) and **11**. The Fe−C(1) bond length of 1.911(11) Å is comparable with the Fe−$C_{carbene}$ bond in analogous carbene complexes $[(\eta^4\text{-}C_{10}H_{16})(CO)_2FeC(OC_2H_5)C_6H_4CH_3\text{-}o]$ (1.915(15) Å)[18] and $[(CO)_3Fe(1{-}4\text{-}\eta{:}5{-}8\text{-}\eta\text{-}C_8H_8)(CO)_2FeC(OC_2H_5)C_6H_5]$ (1.87(2) Å).[19] The C(1)−N bond length is 1.320(13) Å, which is between the normal C−N and C=N distances.

The reaction pathway to complexes **21**−**23** might be via a bridging carbene intermediate $[Fe_2\{\mu\text{-}C(Ar)NHAr'\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (Ar′ = C_6H_5 or 2-naphthyl), which was formed by attack of the neutral $C_6H_5NH_2$ or $C_{10}H_7NH_2$ on the bridging carbyne carbon of **1** or **3** followed by deprotonation by the excess of amine. This intermediate was analogous to those diiron bridging carbene complexes obtained from the reactions[8,9] of diiron bridging carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2][BBr_4]$ and $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}][BBr_4]$ with nucleophiles. Then cleavage of the μ-C(1)−Fe(2) bond and formation of the Fe(1)−$C_{carbene}$ bond with bridging of a terminal CO ligand on Fe(1) to the Fe(2) atom could occur to produce complex **21**, **22**, or **23**.

Interestingly, when the solution of products **21**−**23** in CH_2Cl_2 or acetone was kept at room temperature for 1−2 h, the deep red solution gradually turned orange-red. After workup as described in the Experimental Section, the red chelated iron carbene complexes $[Fe_2\{{=}C(Ar)NAr'\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2\text{-}C_8H_9)]$ (**24**, Ar = C_6H_5, Ar′ = C_6H_5; **25**, Ar = p-$CF_3C_6H_4$, Ar′ = C_6H_5; **26**, Ar = p-$CF_3C_6H_4$, Ar′ = 2-naphthyl) were obtained in high yields (80−90%) (eq 7), of which the structure of **24** has been established by X-ray crystallography.



(7)

21, Ar = C_6H_5, Ar′ = C_6H_5
22, Ar = p-$CF_3C_6H_4$, Ar′ = C_6H_5
23, Ar = p-$CF_3C_6H_4$, Ar′ = 2-naphthyl

24, Ar = C_6H_5, Ar′ = C_6H_5
25, Ar = p-$CF_3C_6H_4$, Ar′ = C_6H_5
26, Ar = p-$CF_3C_6H_4$, Ar′ = 2-naphthyl

The transformations of products **21**−**23** into complexes **24**−**26** were initially revealed by their ^{1}H NMR

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[18] Chen, J.-B.; Lei, G.-X.; Jin, Z.-S.; Hu, L.-H.; Wei, G.-C. *Organometallics* **1988**, *7*, 1652.

[19] Yu, Y.; Sun, J.; Chen, J.-B. *J. Organomet. Chem.* **1997**, *533*, 13.

spectra. The acetone-d_6 solution of **21** or **22** or **23**, whose NMR spectrum had been measured, was kept at room temperature for about 1−2 h, during which time the solution changed from deep red to red. Its ^{1}H NMR spectrum now showed only the proton signals attributable to the C_8H_9 ring and aryl and phenyl protons of **24**, **25**, or **26** but none of the original proton signals assigned to **21**, **22**, or **23**. Further evidence for this transformation came from the isolation of crystals of **24**, **15**, and **26** from the CH_2Cl_2 solution shown in eq 7.

Complexes **24**, **25**, and **26** are the corresponding isomers of the products **21**, **22**, and **23**. The difference between their structures arises only from that the H atom of the HNAr′ group in **21**−**23** migrated to a carbon atom of the COT ring and the N atom is coordinated to the iron (Fe(2)) atom in **24**−**26**.

The molecular structure of **24** (Figure 6) shows that the eight-membered ring of the COT ligand is retained but the planarity of the COT ring has been destroyed to become a boat form configuration. Atoms C(12), C(18), and C(19) form an allyl-type unit η^3-bonded to Fe(2), while C(13), C(14) and C(16), C(17) are η^2-bonded to Fe(1). The N atom now is coordinated to the Fe(2) atom and provided two electrons for Fe(2) to satisfy the 18-electron configuration. The Fe(2)−N bond length is 1.957(3) Å, which is somewhat shorter than the Fe−N bond length found in the diiron complexes with a bridging RC═NR(E) unit, (μ-p-MeC_6H_4Te)(μ-PhC═NPh)-$Fe_2(CO)_6$ (1.993(4) Å),[20] [$Fe_2(CO)_4$(μ_2-RN═CH)(μ-PCy_2)-(μ-dppm)] (R = ally) (2.015(13) Å),[21] and (μ-PhSe)(σ,μ-PhC═NPh)$Fe_2(CO)_6$ (2.000(3) Å),[22] but is nearly the same as that in the diiron bridging carbyne complex [Fe_2(μ-CO)(μ-CC_6H_5)$(CO)_2$(η^5-C_5H_5)$_2$NCW$(CO)_5$] (1.95-(1) Å)[8b] and the diiron complex [$Fe_2(CO)_6(N{=}CHCH_3)_2$] (1.942(7) Å),[23] in which the closing of the Fe_2N_2 core with the shorter Fe−N bond distance results in partial double-bond character in the Fe−N bonds. The shorter Fe(2)−N distance suggests that there exists some double-bond character in the Fe(2)−N bond in complex **24**. The Fe−Fe distance of 2.6920(9) Å is slightly longer than that in (μ-p-MeC_6H_4Te)(μ-PhC═NPh)$Fe_2(CO)_6$ (2.616(1) Å)[20] and [$Fe_2(CO)_4$(μ_2-RN═CH)(μ-PCy_2)-(μ-dppm)] (R = ally) (2.680(3) Å).[21] The Fe(1)−C(1) bond length of 1.962(4) Å is slightly shorter than the corresponding bond lengths found in (μ-p-MeC_6H_4Te)-(μ-PhC═NPh)$Fe_2(CO)_6$ (1.985(4) Å)[20] and (μ-PhSe)(σ,μ-PhC═NPh)$Fe_2(CO)_6$ (1.982(4) Å),[22] while the C(1)−N distance of 1.296(5) Å is somewhat shorter than the corresponding distance in [$Fe_2(CO)_4$(μ_2-RN═CH)(μ-PCy_2)(μ-dppm)] (R = ally) (1.210(23) Å)[21] but is significantly shorter than that in **22** (1.320(13) Å), which indicates high double-bond character.

The very interesting structure feature of complex **24** is the C_8H_9 ligand. In **24**, the eight-membered ring is no longer planar and the bond distances have changed. In contrast to the planar eight-membered ring in **22**, only C(13), C(14), C(16), and C(17) are in a plane (±0.0049 Å) and C(12), C(13), C(17), and C(18) are in another plane (±0.0271 Å) in **24**; the C(15) atom is out of the C(13)C(14)C(16)C(17) plane by 0.8062 Å, while the C(19) atom is out of the C(12)C(13)C(17)C(18) plane by 0.2852 Å. Another measure of the nonplanarity of the ring is the 36.88° dihedral angle between the C(13), C(14), C(16), C(17) and C(12), C(13), C(17), C(18) planes and the 26.11° dihedral angle between the C(12), C(13), C(17), C(18) and C(12), C(18), C(19) planes. The nonplanarity of the COT ring in **24** suggests that the π-system is not delocalized in complex **24** (and **25**, **26**) as it is in **22**. Another indication is the change in bond distances in **24** as compared to **22**. In contrast to the nearly equal bond distances in C(12) to C(19) of the eight-membered ring in **22**, in **24** the C(12)−C(13) (1.476(8) Å), C(14)−C(15) (1.506(8) Å), and C(15)−C(16) (1.504(8) Å) bonds are considerably longer than C(13)−C(14) (1.406(8) Å), C(16)−C(17) (1.345(8) Å), C(17)−C(18) (1.400(8) Å), C(18)−C(19) (1.395(8) Å), and C(12)−C(19) (1.446(8) Å).

In summary, we have discovered novel reactions of COT-coordinated diiron cationic bridging carbyne complexes with a variety of nucleophiles involving arylamines to give a range of diiron bridging carbene complexes. The title reaction shows a quite different reaction pattern of nucleophiles such as NaSR, $NaBH_4$, and Na[$M(CO)_5(CN)$] (M = Cr, Mo, W) as compared with that of arylamine. In the title reaction, the nucleophiles attack the highly electrophilic bridging carbyne carbon atom. This sort of nucleophilic attack contrasts with reactions[12] of amine with cationic bridging carbyne complexes, which result in nucleophilic addition to and ring-breaking of the coordinated COT ring to give COT ring addition products or ring-opening products. The title reaction represents a new, convenient, and useful method for the synthesis and structural modification of dimetal bridging carbene complexes.

Acknowledgment. Financial support from the National Natural Science Foundation of China and the NEDO of Japan is gratefully acknowledged.

Supporting Information Available: Tables of the positional parameters and B_{iso}/B_{eq}, H atom coordinates, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **7**, **8**, **11**, **14**, **22**, and **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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