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Nucleophilic Attack on Carbonyl Ligands in a Cyclooctatetraene (COT)-Coordinated Pentacarbonyl Diiron Complex. Isolation and Transformation of the Diiron Bridging Alkoxycarbyne Complexes $[Fe_2\{\mu\text{-}COC_2H_5\}(COAr)(CO)_3(\eta^8\text{-}C_8H_8)]$

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The reactions of pentacarbonyl(cyclooctatetraene)diiron, $[Fe_2(CO)_5(\eta^8\text{-}C_8H_8)]$ (**1**), with aryllithium reagents, ArLi (Ar = C_6H_5, $p\text{-}CH_3C_6H_4$, $p\text{-}CF_3C_6H_4$), in ether at low temperature followed by alkylation with Et_3OBF_4 in aqueous or CH_2Cl_2 solution at low temperature gave the COT-coordinated diiron bridging alkoxycarbene complexes $[Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**2**, Ar = C_6H_5; **3**, Ar = $p\text{-}CH_3C_6H_4$; **4**, Ar = $p\text{-}CF_3C_6H_4$) and the novel COT-coordinated bridging alkoxycarbyne complexes $[Fe_2\{\mu\text{-}C(OC_2H_5)\}(COAr)(CO)_3(\eta^8\text{-}C_8H_8)]$ (**5**, Ar = C_6H_5; **6**, Ar = $p\text{-}CH_3C_6H_4$; **7**, Ar = $p\text{-}CF_3C_6H_4$) in 60−74% and 2−8% isolated yields, respectively. In solution complexes **5**−**7** were transformed into thermodynamically more stable complexes **2**−**4**. The structure of **6** has been established by the X-ray diffraction studies.

Introduction

The synthesis of μ-hydrocarbon transition-metal complexes is of great interest, due to their unique structure and chemical properties.[1] They are models for intermediates in the Fischer−Tropsch process,[2] in the polymerization of alkenes[3a] and alkynes,[3b] and for unsaturated hydrocarbons chemisorbed on metal surfaces—the first step during heterogeneous catalyses.[4] In light of the very common method to synthesize mononuclear metal Fischer-type carbene complexes, we have previously developed a facile way to prepare diiron bridging alkoxycarbene complexes: that is, carbonyl-bridged diiron complexes, such as $[Fe_2(\mu\text{-}CO)(CO)_4(\eta^8\text{-}C_8H_8)]$, $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta^5\text{-}C_5H_5)_2]$, and $[Fe_2(\mu\text{-}CO)_2(CO)_2\{SiMe_2(\eta^5\text{-}C_5H_5)_2\}]$, reacted with aryllithium reagents followed by alkylation with alkylating agent Et_3OBF_4 in aqueous solution at 0 °C to give the cyclooctatetraene (COT)-,[5a] dicyclopentadienyl-,[5b] and $SiMe_2$-bridged dicyclopentadienyl[5c]-coordinated diiron bridging alkoxycarbene complexes, respectively. Our current interest in exploring the reactivity of COT-coordinated diiron cationic bridging carbyne complexes $[Fe_2(\mu\text{-}CAr)(CO)_4(\eta^8\text{-}C_8H_8)]BF_4$ (Ar = C_6H_5, $p\text{-}CH_3C_6H_4$, $p\text{-}CF_3C_6H_4$), synthesized by the reactions[6] of diiron bridging alkoxycarbene complexes with Lewis acids such as $HBF_4{\cdot}Et_2O$, prompts us to improve the synthesis of the parent COT-coordinated diiron bridging alkoxycarbene complexes $[Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**2**, Ar = C_6H_5; **3**, Ar = $p\text{-}CH_3C_6H_4$; **4**, Ar = $p\text{-}CF_3C_6H_4$) in order to magnify the scale of the reactions and raise the yields of complexes **2**−**4**. Thus, $[Fe_2(\mu\text{-}CO)(CO)_4(\eta^8\text{-}C_8H_8)]$ (**1**), which bears both bridging and terminal carbonyl ligands, was used for the reactions with aryllithium reagents, followed by alkylation with Et_3OBF_4 in CH_2Cl_2 at low temperature (−60 to −30 °C) or in water at 0 °C to give the major product of the desired bridging alkoxycarbene complexes **2**−**4** and the minor product of an unexpected new type of COT-coordinated diiron bridging alkoxycarbyne complex, $[Fe_2\{\mu\text{-}C(OC_2H_5)\}(COAr)(CO)_3(\eta^8\text{-}C_8H_8)]$ (Ar = C_6H_5, $p\text{-}CH_3C_6H_4$, $p\text{-}CF_3C_6H_4$). In this paper, we wish to report the isolation and structural characterization of novel diiron bridging alkoxycarbyne complexes and their transformation into the thermodynamically more stable isomers **2**−**4**.

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 an 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 an N_2 atmosphere. The compound $[Fe_2(\mu\text{-}CO)(CO)_4(\eta^8\text{-}C_8H_8)]$ (**1**),[7] aryllithium reagents,[8−10] $n\text{-}C_4H_9Li$,[11] and Et_3OBF_4[12] were prepared by literature methods.

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The IR spectra were measured on a Nicolet AV-360 spectrophotometer using NaCl cells with 0.1 mm spacers. All ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature in acetone-d_6 solution with TMS or deuterated solvents as the internal reference using a Varian Mercury 300 spectrometer running at 300 MHz. 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.

Reaction of $[Fe_2(\mu\text{-}CO)(CO)_4(\eta^8\text{-}C_8H_8)]$ (1) with C_6H_5Li To Give $[Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_5\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (2) and $[Fe_2\{\mu\text{-}C(OC_2H_5)\}(COC_6H_5)(CO)_3(\eta^8\text{-}C_8H_8)]$ (5). Compound **1** (1.0 g, 2.80 mmol) was suspended in 100 mL of ether at −78 °C, to which was added 4.20 mmol of the freshly prepared C_6H_5Li[8] ether solution. The mixture was stirred at −78 to −40 °C for 4 h, during which time the solid compound **1** dissolved gradually to give a dark red solution. The reaction solution was then evaporated under high vacuum at −40 °C to dryness. To the dark red solid residue obtained was added Et_3OBF_4[12] (ca. 5 g). This solid mixture was dissolved in 40 mL of N_2-saturated water at 0 °C with vigorous stirring, and the mixture was covered with petroleum ether (30−60 °C). Immediately afterward, Et_3OBF_4 was added portionwise to the aqueous solution, with strong stirring, until it became acidic. The aqueous solution was extracted with petroleum ether/CH_2Cl_2 (5:1). After removal of the solvent under vacuum, the residue was chromatographed on a neutral alumina column at −20 to −25 °C with petroleum ether followed by petroleum ether/CH_2Cl_2 (5:1) as the eluant. A brown-red band which eluted first was collected, and then a deep brown band was eluted with petroleum ether/CH_2Cl_2 (2:1). The solvents were removed from the above two eluates in vacuo, and the residues were recrystallized from petroleum ether/CH_2Cl_2 (5:1) at −80 °C. From the first fraction, 0.770 g (60%, based on **1**) of dark red crystals of **2**[5a] was obtained: mp 95−97 °C dec; IR (CH_2Cl_2) ν(CO) 2022 (m), 1986 (s), 1966 (m), 1936 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 8.04−7.33 (m, 5H, C_6H_5), 4.48 (s, 8H, C_8H_8), 3.48 (q, 2H, J = 6.8 Hz, OCH_2CH_3), 1.12 (t, 3H, J = 6.8 Hz, OCH_2CH_3); ^{13}C NMR (CD_3COCD_3) δ 217.8 (br, CO), 159.8 (μ-C), 128.1, 127.7, 127.0 (C_6H_5), 71.6 (C_8H_8), 67.9 (OCH_2CH_3), 14.9 (OCH_2CH_3); MS m/e 462 (M^+), 434 ($M^+ - CO$), 406 ($M^+ - 2CO$), 378 ($M^+ - 3CO$), 350 ($M^+ - 4CO$). From the second fraction, 0.050 g (4%, based on **1**) of purple-red crystalline **5** was obtained: mp 110−112 °C dec; IR (CH_2Cl_2) ν(CO) 2004 (s), 1942 (s, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.18 (m, 5H, C_6H_5), 5.60 (m, 1H, CH_2Cl_2), 5.17 (q, 2H, J = 6.8 Hz, OCH_2CH_3), 4.81 (s, 8H, C_8H_8), 1.75 (t, 3H, J = 6.8 Hz, OCH_2CH_3); ^{13}C NMR (CD_3COCD_3) δ 376.3 (μ-C$_{\text{carbyne}}$), 259.3, 222.2, 217.9, 217.2 (CO), 147.0, 130.7, 128.5, 126.8 (C_6H_5), 85.5 (OCH_2CH_3), 77.1 (C_8H_8), 15.5 (OCH_2CH_3); MS m/e 462 (M^+), 406 ($M^+ - 2CO$), 378 ($M^+ - 3CO$), 273 ($M^+ - 3CO - C_6H_5CO$), 84 ($CH_2Cl_2^+$). Anal. Calcd for $C_{21}H_{18}Fe_2O_5\cdot 0.5CH_2Cl_2$: C, 51.18; H, 3.80. Found: C, 50.64; H, 3.74.

Reaction of 1 with $p\text{-}CH_3C_6H_4Li$ To Give $[Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CH_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (3) and $[Fe_2\{\mu\text{-}C(OC_2H_5)\}(COC_6H_4CH_3\text{-}p)(CO)_3(\eta^8\text{-}C_8H_8)]$ (6). Similar to the procedures used in the reaction of **1** with C_6H_5Li, 1.0 g (2.80 mmol) of **1** was treated with 4.00 mmol of freshly prepared p-$CH_3C_6H_4Li$[9] at −78 to −40 °C for 4 h, followed by alkylation and further treatment of the resulting solution as described for the preparation of **2** and **5** to produce deep red crystalline **3**[5a] (0.938 g, 62% based on **1**) and purple-red crystalline **6** (0.075 g, 5% based on $[Fe_2(CO)_5(\eta^8\text{-}C_8H_8)]$). **3**: 77−78 °C dec; IR (CH_2Cl_2) ν(CO) 2014 (m), 1976 (s), 1957 (m), 1922 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.93 (d, 2H, J = 8.0 Hz, p-$CH_3C_6H_4$), 7.10 (d, 2H, J = 8.0 Hz, p-$CH_3C_6H_4$), 4.48 (s, 8H, C_8H_8), 3.49 (q, 2H, J = 6.8 Hz, OCH_2CH_3), 2.43 (s, 3H, p-$CH_3C_6H_4$), 1.11 (t, 3H, J = 6.8 Hz, OCH_2CH_3); ^{13}C NMR (CD_3COCD_3) δ 217.9 (CO), 157.3 (μ-C), 136.4, 128.2, 128.1 (Ar C), 71.6 (C_8H_8), 67.9 (OCH_2CH_3), 21.0 (p-$CH_3C_6H_4$), 14.9 (OCH_2CH_3); MS m/e 476 (M^+), 448 ($M^+ - CO$), 420 ($M^+ - 2CO$), 392 ($M^+ - 3CO$), 364 ($M^+ - 4CO$). **6**: mp 82−84 °C dec; IR (CH_2Cl_2) ν(CO) 2007 (s), 1945 (vs, br), cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.25 (d, 2H, J = 8.0 Hz, p-$CH_3C_6H_4$), 7.10 (d, 2H, J = 8.0 Hz, p-$CH_3C_6H_4$), 5.13 (q, 2H, J = 7.2 Hz, OCH_2CH_3), 4.78 (s, 8H, C_8H_8), 2.30 (s, 3H, p-$CH_3C_6H_4$), 1.71 (t, 3H, J = 7.2 Hz, OCH_2CH_3); ^{13}C NMR (CD_3COCD_3) δ 376.3 (μ-C$_{\text{carbyne}}$), 258.1, 222.3, 217.3 (CO), 144.6, 140.9, 129.1, 127.3 (Ar C), 85.5 (OCH_2CH_3), 77.2 (C_8H_8), 21.2 (p-$CH_3C_6H_4$), 15.6 (OCH_2CH_3); MS m/e 432 ($M^+ - CH_3CHO$), 199 ($CH_3C_6H_4CO^+$). Anal. Calcd for $C_{22}H_{20}Fe_2O_5$: C, 55.50; H, 4.23. Found: C, 55.23; H, 4.36.

Reaction of 1 with $p\text{-}CF_3C_6H_4Li$ To Give $[Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (4) and $[Fe_2\{\mu\text{-}C(OC_2H_5)\}(COC_6H_4CF_3\text{-}p)(CO)_3(\eta^8\text{-}C_8H_8)]$ (7). Compound **1** (0.500 g, 1.40 mmol) was treated, in a manner similar to that described in the reaction of **1** with C_6H_5Li, with fresh p-$CF_3C_6H_4Li$[10] prepared by the reaction of p-$CF_3C_6H_4Br$ (0.34 mL, 2.40 mmol) and n-C_4H_9Li[11] (2.40 mmol). The solution was stirred at −78 to −40 °C for 4 h. After vacuum removal of the solvent at −40 °C to dryness, the dark red oil residue obtained was dissolved in 40 mL of CH_2Cl_2 at −65 °C, to which was added dropwise 0.430 g (2.26 mmol) of Et_3OBF_4 in 10 mL of CH_2Cl_2. The solution was stirred at −65 to −30 °C for 1.5 h. The following workup was similar to the preparation of **2** and **5**, giving 0.550 g (74%, based on **1**) of **4**[5a] as deep red crystals and 0.061 g (8%, based on **1**) of purple-red crystals of **7**. **4**: mp 108−110 °C dec; IR (CH_2Cl_2) ν(CO) 2018 (m), 1980 (s), 1963 (m), 1927 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 8.11 (d, 2H, J = 8.0 Hz, p-$CF_3C_6H_4$), 7.50 (d, 2H, J = 8.0 Hz, p-$CF_3C_6H_4$), 4.53 (s, 8H, C_8H_8), 3.47 (q, 2H, J = 7.2 Hz, OCH_2CH_3), 1.14 (t, 3H, J = 7.2 Hz, OCH_2CH_3); ^{13}C NMR (CD_3COCD_3) δ 218.1 (br), 215.6 (br), 197.9 (br, CO), 163.6 (μ-C), 128.4, 127.7 (q), 126.5, 124.8, 71.6 (C_8H_8), 68.0 (OCH_2CH_3), 14.8 (OCH_2CH_3); MS m/e 530 (M^+), 502 ($M^+ - CO$), 474 ($M^+ - 2CO$), 446 ($M^+ - 3CO$), 418 ($M^+ - 4CO$). **7**: mp 130−132 °C dec; IR (CH_2Cl_2) ν(CO) 2007 (s), 1945 (vs, br), cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.63 (d, 2H, J = 8.0 Hz, p-$CF_3C_6H_4$), 7.44 (d, 2H, J = 8.0 Hz, p-$CF_3C_6H_4$), 5.17 (m, 2H, OCH_2CH_3), 4.82 (s, 8H, C_8H_8), 1.73 (t, 3H, J = 7.2 Hz, OCH_2CH_3); ^{13}C NMR (CD_3COCD_3) 376.7 (μ-C$_{\text{carbyne}}$), 260.2, 221.9, 217.7, 217.0 (CO), 149.5, 130.9, 126.9, 125.7(q) (Ar C), 85.9 (OCH_2CH_3), 77.1 (C_8H_8), 15.5 (OCH_2CH_3); MS m/e 474 ($M^+ - 2CO$), 446 ($M^+ - 3CO$), 418 [$M^+ - Fe(CO)_2$], 306 [$M^+ - 2Fe(CO)_2$]. Anal. Calcd for $C_{22}H_{17}Fe_2F_3O_5$: C, 49.85; H, 3.23. Found: C, 49.35; H, 3.42.

Transformation of 5 into 2. A solution of **5** (0.045 g, 0.097 mmol) in 25 mL of THF was stirred at −30 to 0 °C for 24 h, during which time the deep red solution gradually turned purple-red, and the strong IR absorption peaks at 2004 and 1942 cm^{-1} disappeared. The solvent was removed in vacuo, and the residue was chromatographed at −20 °C on Al_2O_3 (neutral) with petroleum/CH_2Cl_2 (10:1) as the eluant. The brown-red band was eluted and collected. After removal of the solvent, the residue was recrystallized from petroleum/CH_2Cl_2 (5:1) at −80 °C to give 0.033 g (73%) as deep red crystals of **2**, which was identified by its melting point and IR, ^{1}H NMR, and mass spectra.

Transformation of 6 into 3. A solution of **6** (0.045 g, 0.095 mmol) in 25 mL of THF was stirred at −30 to 0 °C for 24 h, during which time the deep red solution gradually turned purple-red, and the strong IR absorption peaks at 2005 and 1944 cm^{-1} disappeared. The solvent was removed in vacuo, and the residue was chromatographed at −20 °C on Al_2O_3 (neutral) with petroleum/CH_2Cl_2 (10:1) as the eluant. The brown-red band was eluted and collected. After removal of the solvent, the residue was recrystallized from

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Table 1. Crystal Data and Experimental Details for Complex 6

empirical formula	$C_{22}H_{20}O_5Fe_2$
formula wt	476.08
space group	$P2_1/c$ (No. 14)
a (Å)	9.4554(8)
b (Å)	26.142(2)
c (Å)	8.0859(7)
β (deg)	90.709(2)
V (Å^3)	1998.5(3)
Z	4
D_{calcd} (g/cm^3)	1.582
F(000)	976
μ(Mo Kα) (cm^{-1})	14.83
radiation	Mo Kα (λ = 0.710 73 Å)
diffractometer	Bruker Smart
temp (°C)	20
orientation rflns: no.; range (2θ), deg	2136; 4.581−50.830
scan type	ω−2θ
data collecn range, 2θ (deg)	3.12−49.0
no. of unique data, total with $I > 2.00\sigma(I)$	3317, 2733
no. of params refined	304
R^a	0.0756
$R_w{}^b$	0.1772
quality-of-fit indicator[c]	1.163
largest shift/esd final cycle	0.076
max peak, e/Å^3	0.676
min peak, e/Å^3	−0.749

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

petroleum/CH_2Cl_2 (5:1) at −80 °C to give 0.031 g (69%) as deep red crystals of **3**, which was identified by its melting point and IR, ^{1}H NMR, and mass spectra.

Transformation of 7 into 4. A solution of **7** (0.045 g, 0.085 mmol) in 25 mL of THF was stirred at −30 to 0 °C for 24 h, during which time the deep red solution gradually turned purple-red, and the strong IR absorption peaks at 2007 and 1945 cm^{-1} disappeared. A workup similar to that described above gave 0.030 g (67%) of deep red crystals of **4**, which was identified by its melting point and IR, ^{1}H NMR, and mass spectra.

X-ray Crystal Structure Determination of Complex 6. Single crystals of **6** suitable for X-ray diffraction analysis were obtained by recrystallization from petroleum ether/CH_2Cl_2 solution at −80 °C. A single crystal was mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for 3317 independent reflections, of which 2733 with $I > 2.00\sigma(I)$ were observable, were collected with a Bruker Smart diffractometer at 20 °C using Mo Kα radiation with an ω−2θ scan mode.

The structure of **6** was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2733 observed reflections and 304 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.0756$ and $R_w = 0.1772$.

The details of the crystallographic data and the procedures used for data collection and reduction information for complex **6** are given in Table 1. Selected bond lengths and angles are given in Table 2. The atomic coordinates and B_{iso}/B_{eq} values, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **6** are given in the Supporting Information. The molecular structure of **6** is given in Figure 1.

Table 2. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complex 6

Fe(1)−Fe(2)	2.6728(12)	Fe(1)−C(9)	1.759(7)
Fe(1)−C(8)	1.826(7)	Fe(2)−C(10)	1.798(8)
Fe(2)−C(8)	1.886(6)	Fe(2)−C(11)	1.762(8)
Fe(1)−C(13)	2.403(7)	C(12)−C(13)	1.429(10)
Fe(2)−C(13)	2.82(7)	C(13)−C(14)	1.401(11)
Fe(1)−C(14)	2.179(7)	C(14)−C(15)	1.425(11)
Fe(1)−C(15)	2.148(7)	C(15)−C(16)	1.371(11)
Fe(1)−C(16)	2.142(7)	C(16)−C(17)	1.464(11)
Fe(1)−C(17)	2.462(7)	C(17)−C(18)	1.415(10)
Fe(2)−C(17)	2.271(7)	C(18)−C(19)	1.377(11)
Fe(2)−C(18)	2.097(7)	C(19)−C(12)	1.427(10)
Fe(2)−C(19)	2.095(7)	C(8)−O(5)	1.269(8)
Fe(2)−C(12)	2.123(7)	C(21)−O(5)	1.482(9)
Fe(1)−C(1)	1.961(7)	C(1)−O(1)	1.226(8)
Fe(1)−C(8)−Fe(2)	92.1(3)	C(17)−Fe(2)−Fe(1)	59.07(19)
C(8)−Fe(1)−Fe(2)	44.8(2)	Fe(1)−C(8)−O(5)	141.7(5)
C(8)−Fe(2)−Fe(1)	43.1(2)	Fe(2)−C(8)−O(5)	126.2(5)
Fe(1)−C(17)−Fe(2)	68.62	Fe(1)−C(1)−O(1)	123.8(5)
C(17)−Fe(1)−Fe(2)	52.31(18)	Fe(1)−C(1)−C(2)	121.4(5)

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

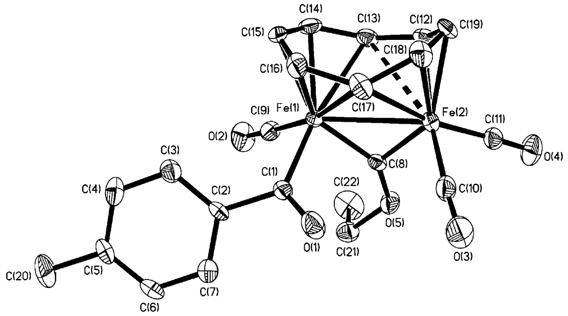
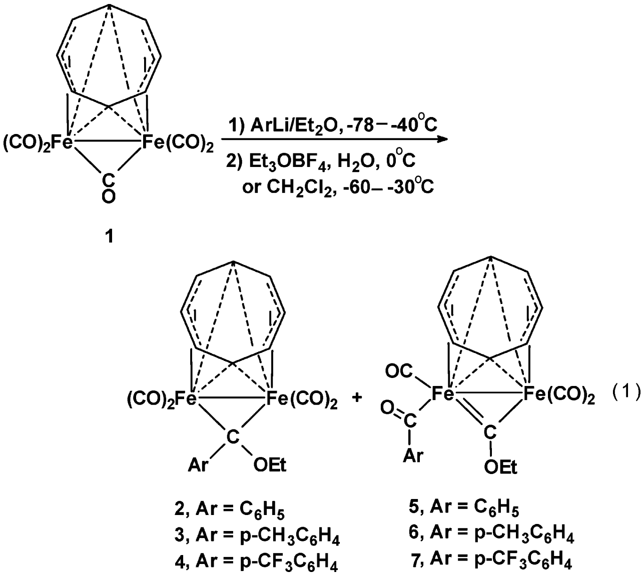


Figure 1. Molecular structure of **6**, showing the atom-numbering scheme with 45% thermal ellipsoids.

Results and Discussion

Pentacarbonyl(cyclooctatetraene)diiron, $[Fe_2(CO)_5(\eta^8\text{-}C_8H_8)]$ (**1**), was treated with about a 50% molar excess of aryllithium reagents, ArLi (Ar = C_6H_5, p-$CH_3C_6H_4$, p-$CF_3C_6H_4$), in ether at low temperature (−78 to −40 °C), followed by alkylation with Et_3OBF_4 in aqueous or CH_2Cl_2 solution at low temperature. After workup as described in the Experimental Section, not only the expected COT-coordinated diiron bridging alkoxycarbene complexes $[Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**2**, Ar = C_6H_5; **3**, Ar = p-$CH_3C_6H_4$; **4**, Ar = p-$CF_3C_6H_4$) but also the novel COT-coordinated diiron bridging carbyne complexes $[Fe_2\{\mu\text{-}C(OC_2H_5)\}(COAr)(CO)_3(\eta^8\text{-}C_8H_8)]$ (**5**, Ar = C_6H_5; **6**, Ar = p-$CH_3C_6H_4$; **7**, Ar = p-$CF_3C_6H_4$) were obtained in 60−74% and 4−8% isolated yields, respectively (eq 1).



Complexes **5**−**7** are more polar than complexes **2**−**4**. On the basis of elemental analysis and IR, ^{1}H and ^{13}C NMR, and mass spectroscopy, as well as X-ray crystallography, complexes **5**−**7** are formulated as possessing a μ-C(OC_2H_5) carbyne ligand bridging the two Fe atoms and an acyl (ArC═O) ligand bound to an Fe atom, which could be formally formed via transfer of the aryl group from the carbene carbon of complexes **2**−**4** to a terminal carbonyl of an $Fe(CO)_2$ moiety. Thus, products **5**−**7** can be regarded as the isomers of complexes **2**−**4**, respectively.

The IR spectrum of complexes **2**−**4** showed four absorption bands in the ν(CO) region. For complexes **5**−**7**, there are only two strong broad ν(CO) bands at about 2007 and 1945 cm^{-1}. The ^1H NMR and ^{13}C NMR spectral data for complexes **2**−**4** and complexes **5**−**7** are given in the Experimental Section, from which it can be seen that the above two types of complexes differ significantly in the chemical shift of the μ-carbon. In complexes **5**−**7**, the ^{13}C NMR signal at 376 ppm is consistent with the resonance region of bridging carbyne carbon,[13] whereas the chemical shifts of the bridging carbene carbons of complexes **2**−**4** are in the range of 157−163 ppm. Another obvious distinction is the ^1H NMR signals for ethoxy groups. The methenyl resonances of complexes **2**−**4** are at about 3.48 ppm, while in complexes **5**−**7**, the corresponding signals shift significantly downfield to about 5.17 ppm. These indicate that the bridging carbyne ligand is more electron deficient than the bridging carbene ligand. This effect is also apparent in the different NMR data of the COT ligand and methyl group for complexes **2**−**4** (at ca. 1.12 ppm) and complexes **5**−**7** (at ca. 1.73 ppm).

The molecular structure of complex **6**, established by its single-crystal X-ray diffraction study, is shown in Figure 1. As anticipated from the IR and ^1H NMR spectra, one of the Fe atoms is attached with two terminal CO groups, and the other is attached with one terminal CO group and an acyl ($CH_3C_6H_4C$═O) group, while the bridging carbyne carbon is attached with an ethoxy group. In complex **6**, the distance (2.6728(12) Å) of the Fe−Fe bond bridged by C(OC_2H_5) is the same within experimental error as that found in the bridging carbene complex **4** (2.686(1) Å).[5a] In comparison with complex **4**, the μ-C−Fe distances (average 1.856 Å) are significantly shorter (by 0.20 Å) than those in **4**, which indicates that the interaction between the μ-$C_{carbyne}$ carbon and the Fe atoms is stronger than that between the μ-$C_{carbene}$ carbon and the Fe atoms. Moreover, the alkylidyne carbon in **6** nearly symmetrically bridges the Fe−Fe bond (C(8)−Fe(1) = 1.826(7) Å, C(8)−Fe(2) = 1.886(6) Å), indicating that the d−π conjugation effect between the bridging carbyne carbon C(8) and Fe(1) is similar to that between C(8) and Fe(2). Another feature is the shorter bond distance of the μ-carbyne carbon to the oxygen atom of the ethoxy group. The μ-C(8)−O(5) distance of **6** (1.269(8) Å) is shorter than that of **4** by ca. 0.14 Å, which could be attributed to the different hybridizations of the two bridging carbons; the μ-$C_{carbyne}$ carbon is an sp^2-hybridized carbon in the former, while the μ-$C_{carbene}$ carbon is an sp^3-hybridized carbon in the latter.

It is documented that there are two coordination models between the COT ligand and the metals in the COT-coordinated dimetal complexes, as shown in Chart 1; i.e., in model I there are two η^4 bonds between the COT ligand and the two coordinated metal atoms,[14] and in model II there are two η^3-allyl bonds and two "two-electron−three-center" (Fe−C−Fe) bonds between the COT ligand and the two coordinated metal atoms.[5a,15] The X-ray crystallographic data of complex **6** show that it possesses the COT−Fe_2 coordination of model II. Furthermore, in complex **6** such a coordination interaction becomes unsymmetrical, since the ligands on the two Fe atoms are different (Fe(1) is bound to a carbonyl and an acyl groups, while Fe(2) is bound to two carbonyl groups). Hence, the lengths of the two-electron−three-center bonds appear to be in accordance with the unsymmetrical coordination properties of **6**. The bond length of Fe(1)−C(13) (2.403(7) Å) is much shorter (by 0.42 Å) than that of Fe(2)−C(13) (2.82(7) Å), while the bond distance of Fe(1)−C(17) (2.462(7) Å) is significantly longer (by ca. 0.19 Å) than that of Fe(2)−C(17) (2.271(7) Å), indicating that the coordination between the COT ring and the two Fe atoms highly deviates from the symmetric position, as shown in model II of Chart 1.

Chart 1

I **II**

Although the reaction pathway to complexes **2**−**4** and **5**−**7** has not yet been fully established, it appears that the major products **2**−**4** were formed via nucleophilic attack on the bridging CO, while the minor products **5**−**7** were formed via nucleophilic attack on the terminal CO of **1**.

In general, however, the nucleophilic attack on the terminal CO should be favored due to its lower electron density:[16] e.g., in the study of the hydridic reduction of carbonyl ligands on various diiron carbonyl complexes, Atwood, Nelson, et al.[17] and Paolessoe et al.[18] have demonstrated that the presence of terminal carbonyls is necessary for the reduction of carbonyl ligands, indicating that the initial step is the hydride anion attack on the terminal carbonyls. It should be pointed out that, in our previous research, only the bridging alkoxycarbene complexes, the products of apparent nucleophilic attack on bridging CO, were obtained from a similar nucleophilic addition and subsequent alkylation reactions[5b,c] of the diiron complexes [$Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2$] and [$Fe_2(\mu\text{-}CO)_2(CO)_2SiMe_2(\eta\text{-}C_5H_5)_2$], bearing both bridging and terminal CO groups. These experimental results are in apparent contradiction with the fact that the terminal carbonyls have higher reactivity toward nucleophiles than the bridging carbonyls. In the present study, the isolation of complexes **5**−**7** (the products of apparent nucleophilic attack on a terminal CO), though as the minor products, is very important and helpful in understanding the reaction mechanism, which leads us to further investigate their reactivity.

Of special interest is the thermal sensitivity of the carbyne bridging complexes **5**−**7**. The solutions of **5**−**7** in THF were stirred at −30 to 0 °C for 24 h. As detected by ^1H NMR, the ethoxy signals at ca. 5.17−5.13 ($-OCH_2CH_3$) and 1.73−1.71 ($-OCH_2CH_3$) ppm assigned to complexes **5**−**7** were gradually changed to the signals that appear at ca. 3.49−3.47 ($-OCH_2CH_3$) and 1.14−1.11 ($-OCH_2CH_3$) ppm of complexes **2**−**4**, respectively, which indicated that complexes **5**−**7** isomerized

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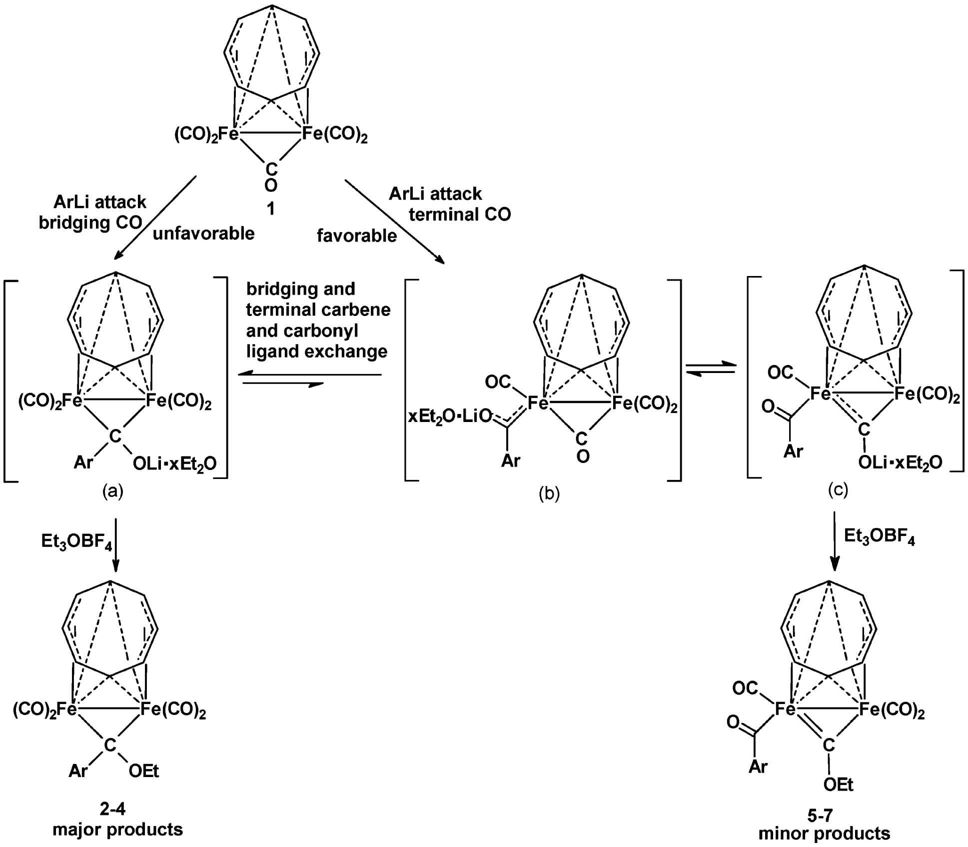
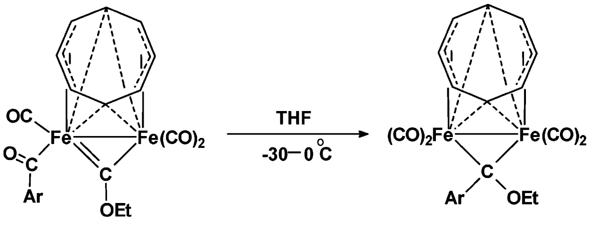
Scheme 1



to complexes **2**−**4** in this duration. After workup as described in the Experimental Section, deep red crystals of **2**−**4** were obtained in 67−73% yields (eq 2).



(2)

5, Ar = C$_6$H$_5$
6, Ar = p-CH$_3$C$_6$H$_4$
7, Ar = p-CF$_3$C$_6$H$_4$

2, Ar = C$_6$H$_5$
3, Ar = p-CH$_3$C$_6$H$_4$
4, Ar = p-CF$_3$C$_6$H$_4$

The transformation of complexes **5**−**7** to complexes **2**−**4** indicates that the latter is the thermodynamically more stable isomers than the former. More importantly, the experimental result in eq 1 that complexes **2**−**4** are major products while complexes **5**−**7** are minor products is understandable by considering the thermodynamic difference between them.

The isolation of the “unusual” products **5**−**7** and their thermal isomerization to the “normal” products **2**−**4** give us further understanding of the nucleophilic addition to CO ligands in the dimetal carbonyl complexes. Hence, we proposed that the formation of complexes **2**−**4** and **5**−**7**, as shown in Scheme 1, might proceed by the following possible reaction pathways. (1) The aryllithium reagents attack the bridging CO group of **1** to form the acylmetalate intermediates (a), which are subsequently alkylated with Et$_3$OBF$_4$ to give the bridging alkoxycarbene complexes **2**−**4**. This attack is unfavorable, due to the higher electron density of the bridging carbonyl. (2) The aryllithium reagents attack the terminal CO group of **1** to produce the acylmetalate intermediates (b). This is a favorable attack due to the lower electron density on the terminal carbonyls. The intermediates (b) could be converted into the intermediates (a)[19] or another isomer (c), which are subsequently alkylated with Et$_3$OBF$_4$ to afford the bridging alkoxycarbene complexes **2**−**4** and bridging alkoxycarbyne complexes **5**−**7**, respectively. Because complexes **2**−**4** are thermodynamically more stable, the equilibrium between intermediates (a) and (b) in Scheme 1 should favor intermediate (a), and the major products are complexes **2**−**4** in the reactions.

Since intermediates (a)−(c) are anionic isomers, their relative ratios might be solvent and /or temperature dependent, which will determine the distribution of the products. To explore the influence of solvent and temperature on the product distribution following the ethylation of the acylmetal intermediates, the alkylations by changing conditions were attempted. When the acylmetal intermediate formed by reaction of compound **1** with C_6H_5Li (or p-$CH_3C_6H_4Li$) was subsequently alkylated in CH_2Cl_2, and the acylmetal intermediate formed from **1** and p-$CF_3C_6H_4Li$ was alkylated in water at 0 °C, major products **2** (or **3**) and **4** were obtained, respectively, in yields lower (ca. 30−40%) than those under optimum conditions (Experimental Section) and no minor products **5** (or **6**) and **7** were obtained, indicating that the solvent used and temperature in the alkylation step exert great influence on the final results.

A possible alternative explanation for the result that complexes **2**−**4** were major products and complexes **5**−**7** were minor products in the reactions is as follows: the alkylating

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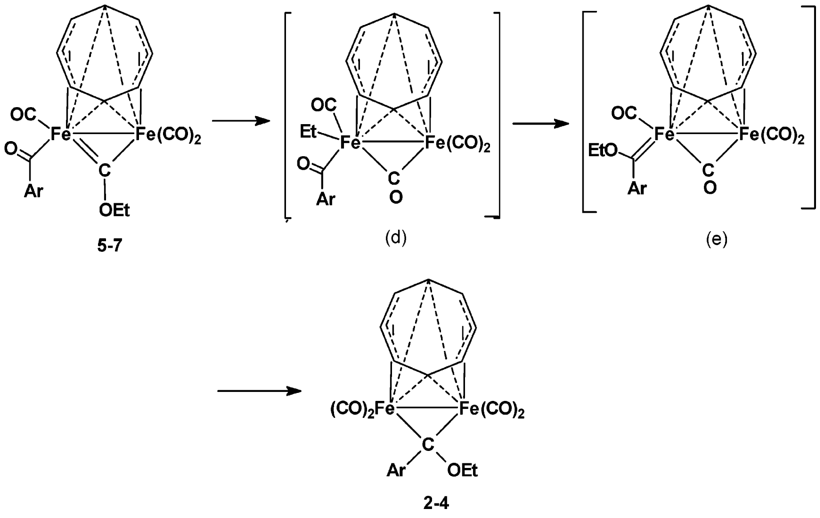
[19] According to the properties of di- or polymetal bridging carbene complexes, the intermediates (a) and (b) could be converted to each other, i.e., the monometal carbene ligand and dimetal bridging carbene ligand can be converted to each other, accompanied by a conversion between the terminal CO group and the bridging CO group. For a detailed review on fluxional metal carbonyls, see: Cotton, F. A. *Inorg. Chem.* **2002**, *41*, 643.

Scheme 2



reaction is a rate-determining step, so that the distribution of the two types of products depends on the rates of electrophilic attack of the alkylation reagent on the different sites of the anionic intermediates formed from the nucleophilic reaction. Once an acyl is formed from the reaction of compound **1** with aryllithium reagent, by attack on either bridging or terminal carbonyls, the corresponding anionic intermediate formed will quickly rearrange before the addition of the electrophile. The electrophilic attack can occur at the acyl oxygen or at a carbonyl oxygen, either terminal or bridging. In the synthesis of Fischer-type carbene complexes, it has been well demonstrated that in such an anionic intermediate the acyl oxygen is a stronger nucleophile than the carbonyl oxygen.[20] Thus, the nucleophilic attack on the acyl is favorable. Because of the lability of the terminal carbene complexes and their easy transformation to the corresponding bridging carbene complexes (which is discussed below), the bridging carbene complexes **2**−**4** are the major products.

In addition, as for the thermal conversion of **5**−**7** into **2**−**4** shown in eq 2, a possible mechanism is illustrated in Scheme 2. In complexes **5**−**7**, first ethyl migration from the ethoxycarbyne ligand to the iron atom which bears an acyl group to forming a CO ligand occurs to give intermediates (d),[21] which subsequently undergoes a further 1,3-ethyl migration from the iron atom to the acyl oxygen to afford terminal carbene intermediates (e). The carbene species (e) might be thermally unstable and isomerizes to the corresponding bridging carbene complexes **2**−**4** via an exchange between the terminal and bridging ligands under the reaction conditions (at −30 to 0 °C). It has been observed in our recent studies[6b,22] that the terminal carbene complexes $[\mathrm{Fe_2({=}CArNHAr')(\mu\text{-}CO)(CO)_3(\eta^8\text{-}C_8H_8)}]$ ($\mathrm{Ar = C_6H_5}$, p-$\mathrm{CH_3C_6H_4}$, p-$\mathrm{CF_3C_6H_4}$; $\mathrm{Ar' = C_6H_5}$, 2-naphthyl), the analogues of the intermediates (e), are highly thermally unstable in solution and very easily isomerize to the corresponding chelated iron-carbene complexes (over −40 °C).

In summary, we have isolated the COT-coordinated diiron bridging alkoxycarbene complexes **2**−**4** and the novel COT-coordinated diiron bridging alkoxycarbyne complexes **5**−**7** from the reaction of the COT-coordinated pentacarbonyl diiron complex **1** with aryllithium reagents. To the best of our knowledge, this is the first example of isolating both of the products that result from apparent nucleophilic attack on either terminal or bridging carbonyl ligands in a dimetal carbonyl compound. The comparison of the thermodynamic stabilities between the bridging carbene complex **2**−**4** and bridging carbyne complexes **5**−**7** reveals more details of the chemistry of the nucleophilic attack on CO groups of dimetal carbonyl complexes.

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Supporting Information Available: Tables of positional parameters and temperature factors, H atom coordinates, anisotropic displacement parameters, all bond angles, and least-squares planes for complex **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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