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Thermolytic Products Derived from Thermolysis of Cycloolefin-Coordinated Diiron Bridging Carbene Complexes[†]

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Heating a benzene solution of the COT-coordinated diiron bridging alkoxycarbene complexes $[Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**1**, Ar = C_6H_5; **2**, Ar = p-$CH_3C_6H_4$; **3**, Ar = p-$CF_3C_6H_4$) in a sealed tube at 85−90 °C for 72 h gave the bicycloolefin-coordinated tricarbonyliron dimers $[Fe\{\eta^4\text{-}C_9H_8(Ar\}(CO)_3]_2$ (**10**, Ar = C_6H_5; **12**, Ar = p-$CH_3C_6H_4$; **14**, Ar = p-$CF_3C_6H_4$) and bridging arylcarbene complexes $[Fe_2\{\mu\text{-}C(H)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**11**, Ar = C_6H_5; **13**, Ar = p-$CH_3C_6H_4$; **15**, Ar = p-$CF_3C_6H_4$). A similar thermolysis of 7*H*-indene-coordinated diiron bridging alkoxycarbene complex $[Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_5\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (**4**) yielded the ring addition product $[Fe_2\{C(OC_2H_5)C_6H_5(\eta^2,\eta^5\text{-}C_9H_8)\}(CO)_5]$ (**16**). The 7*H*-indene-coordinated diiron bridging arylthiocarbene complexes $[Fe_2\{\mu\text{-}C(Ar)SC_6H_4CH_3\text{-}p\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (**8**, Ar = C_6H_5; **9**, Ar = p-$C_6H_5C_6H_4$) were heated similarly to afford the isomerized 7*H*-indene-coordinated diiron bridging carbene complexes with a μ-$SC_6H_4CH_3$-p ligand, $[Fe_2\{\mu\text{-}C(Ar)(\eta^2,\eta^5\text{-}C_9H_8)\}(\mu\text{-}SC_6H_4CH_3\text{-}p)(CO)_3]$ (**17**, Ar = C_6H_5; **19**, Ar = p-$C_6H_5C_6H_4$), and the acyliron compounds $[Fe(CO)_2(C{=}O)\{C(H)Ar(\eta^5\text{-}C_9H_8)\}]$ (**18**, Ar = C_6H_5; **20**, Ar = p-$C_6H_5C_6H_4$). The structures of complexes **14**, **16**, **17**, and **18** have been established by X-ray diffraction studies.

Introduction

Our interest in the synthesis, structure, and chemistry of alkene−metal carbene and carbyne complexes stems from the possible involvement of these species in many reactions catalyzed by organometallic compounds.[1,2] The chemistry of di- and polynuclear metal bridging carbene and carbyne complexes has been receiving considerable current attention, largely because of the interesting chemical properties exhibited by such complexes. A number of di- and polymetal complexes containing bridging carbene and carbyne ligands have been synthesized by Stone et al.[3] and Keister,[4] and a series of diiron bridging carbene and carbyne complexes have also been reported.[5−8] However, a few examples of olefin-coordinated dimetal bridging carbene or carbyne complexes are known[9,10] In a continuation of our interest in developing the methodologies of the synthesis of olefin-coordinated metal carbene and carbyne complexes, we have found a facile method for the preparation of dimetal bridging carbene and carbyne complexes, that is, to conduct the reactions of olefin-ligated dimetal carbonyl compounds, such as $[Fe_2(\mu\text{-}CO)(CO)_4(\eta^8\text{-}C_8H_8)]$, with aryllithium reagents followed by alkylation with Et_3OBF_4 to give cyclooctatetraene (COT)-coordinated diiron bridging alkoxycarbene complexes $[Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (**1**, Ar = C_6H_5; **2**, Ar = p-$CH_3C_6H_4$; **3**, Ar = p-$CF_3C_6H_4$) (eq 1).[10]

To develop a new synthetic method for the preparation of olefin-coordinated dimetallic bridging carbene and carbyne complexes and to explore the reactivity of the olefin-coordinated

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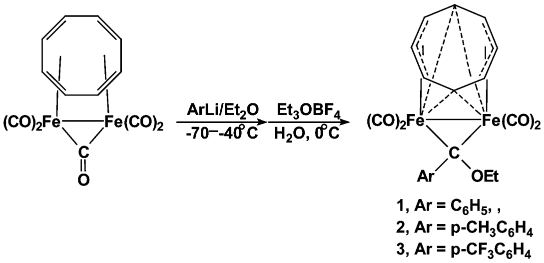
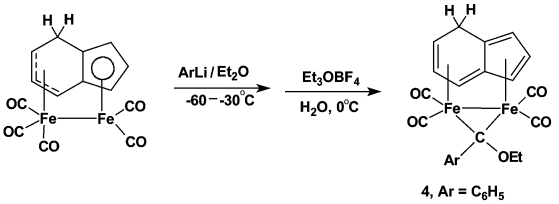


1, Ar = C_6H_5, ,
2, Ar = p-$CH_3C_6H_4$
3, Ar = p-$CF_3C_6H_4$

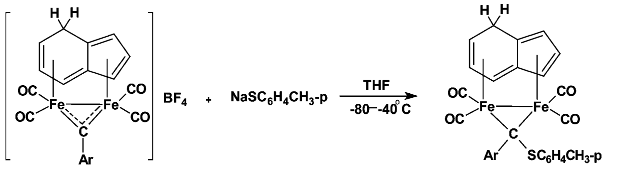
(1)

diiron cationic bridging carbyne complexes containing different cycloolefin ligands toward nucleophiles, we investigated the reactions of pentacarbonyl-7*H*-indenediiron, [$Fe_2(CO)_5(\eta^3,\eta^5\text{-}C_9H_8)$], a dimetal compound bearing only terminal CO ligands, with aryllithium reagents, which gave a new type of 7*H*-indene-coordinated diiron bridging alkoxycarbene complexes [$Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)$] (**4**, Ar = C_6H_5; **5**, Ar = p-$C_6H_5C_6H_4$) (eq 2),[11] and carried out the study of the reactivities of their cationic bridging carbyne complexes [$Fe_2(\mu\text{-}CAr)(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)$]$BF_4$ (**6**, Ar = C_6H_5; **7**, Ar = p-$C_6H_5C_6H_4$), prepared by the reactions[11] of diiron bridging alkoxycarbene complexes **4** and **5** with HBF_4, respectively, toward nucleophiles involving carbonylmetal anions. These reactions afforded a series of novel dimetal bridging carbene complexes. For instance, cationic **6** and **7** react with $NaSC_6H_4CH_3$-p at low temperature to produce the bridging arylthiocarbene complexes [$Fe_2\{\mu\text{-}C(Ar)SC_6H_4CH_3\text{-}p\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)$] (**8**, Ar = C_6H_5; **9**, Ar = p-$C_6H_5C_6H_4$) (eq 3).[11]



4, Ar = C_6H_5
5, Ar = p-$C_6H_5C_6H_4$

(2)



6, Ar = C_6H_5
7, Ar = p-$C_6H_5C_6H_4$

8, Ar = C_6H_5
9, Ar = p-$C_6H_5C_6H_4$

(3)

It is well-known that the thermal decomposition of carbene complexes usually results in dimerization of the carbene ligand to produce alkene derivatives[12] and that heating a Fischer-type carbene complex with an olefin generally results in addition of the double bond of the olefin to the carbene ligand to form cyclopropane products.[13,14] Recently, we have shown a number of thermolysis reactions of the olefin-coordinated monoiron alkoxycarbene complexes or their isomerized products and the COT-coordinated diiron Fischer-type carbene complexes, which produced a series of novel thermolytic products.[15,16] What happens when the cycloolefin-coordinated diiron bridging carbene complexes containing a bridging carbene ligand and a cycloolefin ligand are subjected to thermolysis? To explore thermolysis reactivity of such bridging carbene complexes and to compare their thermolysis reactivities with that of COT-coordinated diiron Fischer-type carbene complexes, we chose COT-coordinated diiron bridging alkoxycarbene complexes [$Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)$] (**1**, Ar = C_6H_5; **2**, Ar = p-$CH_3C_6H_4$; **3**, Ar = p-$CF_3C_6H_4$), 7*H*-indene-coordinated diiron bridging alkoxycarbene complex [$Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_5\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)$] (**4**), and analogous bridging arylthiocarbene complexes [$Fe_2\{\mu\text{-}C(Ar)SC_6H_4CH_3\text{-}p\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)$] (**8**, Ar = C_6H_5; **9**, Ar = p-$C_6H_5C_6H_4$) as starting materials for the thermolysis reactions, which afforded a series of novel thermal decomposition products. In this paper, we report these unusual thermolysis reactions and the structures of the novel thermolytic products.

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. Benzene was distilled from sodium, while petroleum ether (30 to 60 °C) and CH_2Cl_2 were distilled from CaH_2. The neutral SiO_2 (Scientific Adsorbents Incorporated, 40 μm flash) used for chromatography was deoxygenated at room temperature under high vacuum for 12 h, and 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 [$Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)$] (**1**−**3**),[10] [$Fe_2\{\mu\text{-}C(OC_2H_5)\text{-}Ar\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)$] (**4**, **5**),[11] and [$Fe_2\{\mu\text{-}C(Ar)SC_6H_4CH_3\text{-}p\}\text{-}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)$] (**8**, **9**)[11] were prepared as previously described.

The IR spectra were measured on a Nicolet AV-360 spectrophotometer using NaCl cells with 0.1 mm spacers. The ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature in acetone-d_6 or $CDCl_3$ solution with TMS 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. The HRMS spectrum was measured on a Finnigan MAT 8430 spectrometer. Melting points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

Thermolysis of 1 to Give [$Fe\{\eta^4\text{-}C_9H_8(C_6H_5)\}(CO)_3]_2$ (10) and [$Fe_2\{\mu\text{-}C(H)\text{-}C_6H_5\}(CO)_4(\eta^8\text{-}C_8H_8)$] (11). A 0.300 g (0.65 mmol) amount of compound **1** was dissolved in benzene (20 mL) in a quartz tube. The tube was cooled at −80 °C to freeze the benzene solution and sealed under high vacuum. The sealed tube was heated to 85−90 °C for 72 h, during which time the deep red solution turned dark and turbid. After cooling, the dark solution was evaporated *in vacuo* to dryness. The residue was chromatographed on SiO_2 with petroleum ether as the eluant. The yellow band which eluted first was collected, then a brown-red band was eluted with petroleum ether/CH_2Cl_2/Et_2O (10:2:1). After vacuum removal of the solvent from the above two eluates, the residues were recrystallized from petroleum ether/CH_2Cl_2 at −80 °C. From the first fraction, 0.065 g (30%) of orange-yellow crystals of **10** was obtained: mp 132−134 °C dec; IR (CH_2Cl_2) ν(CO) 2046 (s), 2034 (m), 1975 (vs, br) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.32−7.09 (m, 10H, C_6H_5), 5.88 (d, 2H, J = 4.5 Hz, C_9H_8), 5.70 (t, 2H, J = 5.1 Hz, C_9H_8), 5.47 (t, 2H, J = 6.3 Hz, C_9H_8), 3.71−3.56 (m, 4H, C_9H_8), 3.35 (d, 2H, J = 9.3 Hz, C_9H_8), 2.28 (d, 2H, J = 4.5 Hz, C_9H_8), 2.18 (d, 2H, J = 3.6 Hz, C_9H_8); ^{13}C NMR (CD_3COCD_3) δ

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211.2 (CO), 140.6, 128.6, 126.6, 125.1 (C_6H_5), 96.7, 90.4, 90.1, 77.5, 66.6, 63.3, 59.3, 58.1, 34.2; MS *m/e* 610 ($M^+ - 2CO$), 582 ($M^+ - 3CO$), 554 ($M^+ - 4CO$), 498 ($M^+ - 6CO$), 386 [$M^+ - 2Fe(CO)_3$]. Anal. Calcd for $C_{36}H_{26}O_6Fe_2$: C, 64.90; H, 3.93. Found: C, 64.35; H, 4.31. From the second fraction, 0.110 g (40%) of purple-red crystalline **11**[17] was obtained: mp 210−212 °C dec; IR (CH_2Cl_2) ν(CO) 2007 (m), 1978 (vs), 1944 (m) cm^{-1}; ^{1}H 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); MS *m/e* 362 ($M^+ - 2CO$), 306 ($M^+ - 2CO - Fe$), 194 [$M^+ - 2Fe(CO)_2$].

Thermolysis of 2 to Give [Fe{η^4-$C_9H_8(C_6H_4CH_3$-*p*)}$(CO)_3]_2$ (12) and [Fe_2{μ-C(H)$C_6H_4CH_3$-*p*}$(CO)_4(\eta^8$-C_8H_8)] (13). As described above for the thermolysis of **1**, compound **2** (0.350 g, 0.74 mmol) in benzene in a quartz tube was heated to 85−90 °C for 72 h. Subsequent treatment as described for the thermolysis of **1** afforded 0.098 g (38%) of orange-yellow crystalline **12** and 0.109 g (35%) of purple-red crystals of **13**.[17] **12**: mp 126−128 °C dec; IR (CH_2Cl_2) ν(CO) 2045 (s), 2033 (m), 1975 (vs, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.35−7.02 (m, 8H, *p*-$CH_3C_6H_4$), 5.83 (d, 2H, *J* = 4.8 Hz, C_9H_8), 5.69 (t, 2H, *J* = 4.5 Hz, C_9H_8), 5.63 (s, 1H, CH_2Cl_2), 5.46 (t, 2H, *J* = 5.1 Hz, C_9H_8), 3.70−3.52 (m, 4H, C_9H_8), 3.34 (d, 2H, *J* = 10.5 Hz, C_9H_8), 2.26 (d, 2H, *J* = 4.6 Hz, C_9H_8), 2.22 (s, 6H, *p*-$CH_3C_6H_4$), 2.19 (d, 2H, *J* = 3.6 Hz, C_9H_8); MS *m/e* 638 ($M^+ - 2CO$), 582 ($M^+ - 4CO$), 414 [$M^+ - 2Fe(CO)_3$], 84 [$CH_2Cl_2^+$]. Anal. Calcd for $C_{38}H_{30}O_6Fe_2 \cdot 0.5CH_2Cl_2$: C, 62.76; H, 4.24. Found: C, 62.31; H, 4.67. **13**: mp 201−203 °C dec; IR (CH_2Cl_2) ν(CO) 2006 (m), 1976 (s), 1942 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 9.42 (s, 1H, μ-CH), 7.14−6.91 (d, 4H, *p*-$CH_3C_6H_4$), 4.49 (s, 8H, C_8H_8), 2.19 (s, 3H, *p*-$CH_3C_6H_4$); MS *m/e* 376 ($M^+ - 2CO$), 320 ($M^+ - 2CO - Fe$), 208 [$M^+ - 2Fe(CO)_2$].

Thermolysis of 3 to Give [Fe{η^4-$C_9H_8(C_6H_4CF_3$-*p*)}$(CO)_3]_2$ (14) and [Fe_2{μ-C(H)$C_6H_4CF_3$-*p*}$(CO)_4(\eta^8$-C_8H_8)] (15). As described above for the thermolysis of **1**, compound **3** (0.320 g, 0.60 mmol) in benzene in a quartz tube was heated to 85−90 °C for 72 h. Subsequent treatment as described for the thermolysis of **1** afforded 0.087 g (37%) of orange-yellow crystalline **14** and 0.120 g (41%) of **15**[17] as purple-red crystals. **14**: mp 141−143 °C dec; IR (CH_2Cl_2) ν(CO) 2048 (s), 2036 (m), 1978 (vs, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.77−7.49 (m, 8H, *p*-$CF_3C_6H_4$), 5.97 (d, 2H, *J* = 4.5 Hz, C_9H_8), 5.72 (t, 2H, *J* = 7.2 Hz, C_9H_8), 5.50 (t, 2H, *J* = 6.3 Hz, C_9H_8), 3.72−3.54 (m, 4H, C_9H_8), 3.36 (d, 2H, *J* = 9.9 Hz, C_9H_8), 2.40 (d, 2H, *J* = 14.8 Hz, C_9H_8), 2.30 (d, 2H, *J* = 4.8 Hz, C_9H_8); MS *m/e* 690 ($M^+ - 4CO$), 634 ($M^+ - 6CO$), 522 [$M^+ - 2Fe(CO)_3$]. Anal. Calcd for $C_{38}H_{24}O_6F_6Fe_2$: C, 56.89; H, 3.02. Found: C, 56.38; H, 3.37. **15**: mp 220 °C dec; IR (CH_2Cl_2) ν(CO) 2010 (m), 1981 (s), 1947 (m) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 9.17 (s, 1H, μ-CH), 7.44−7.38 (d, 4H, *p*-$CF_3C_6H_4$), 4.55 (s, 8H, C_8H_8); MS *m/e* 374 [$M^+ - Fe(CO)_2$], 346 [$M^+ - Fe(CO)_2 - CO$], 318 [$M^+ - Fe(CO)_2 - 2CO$], 262 [$M^+ - 2Fe(CO)_2$].

Thermolysis of 3 in Benzene-d_6 to Give 14 and 15. As described above for the thermolysis of **1**, 0.100 g (0.19 mmol) of compound **3** dissolved in benzene-d_6 (7 mL) in a quartz tube was heated to 85−90 °C for 72 h. Further treatment as described for the thermolysis of **1** gave 0.025 g (34%) of **14** and 0.036 g (39%) of **15**, which were identified by their IR and ^{1}H NMR spectra.

Thermolysis of 4 to Give [Fe_2{C(OC_2H_5)C_6H_5(η^2,η^5-C_9H_8)}$(CO)_5$] (16). Using the same procedures as those for the thermolysis of **1**, 0.200 g (0.42 mmol) of **4** in benzene in a quartz tube was heated to 85−90 °C for 72 h. After cooling, the dark red solution was evaporated *in vacuo* to dryness. The residue was chromatographed on Al_2O_3 with petroleum ether/CH_2Cl_2 (10:1) as the eluant. The brown-red band was collected. After vacuum removal of the solvent, the residue was recrystallized from petroleum ether or petroleum ether/CH_2Cl_2 at −80 °C to afford 0.084 g (45%) of brown-red crystals of **16**: mp 144−146 °C; IR (CH_2Cl_2) ν(CO) 2031 (s), 1986 (vs), 1963 (m), 1936 (m) cm^{-1}; ^{1}H NMR δ 7.39−7.04 (m, 5H, C_6H_5), 5.13 (t, 2H, C_9H_8), 5.01 (d, 1H, C_9H_8), 4.81 (d, 1H, C_9H_8), 4.27 (t, 1H, C_9H_8), 3.60 (t, 1H, C_9H_8), 3.11 (td, 1H, C_9H_8), 2.44 (q, 2H, OCH_2CH_3), 1.61 (d, 1H, C_9H_8), 0.96 (t, 3H, OCH_2CH_3); ^{13}C NMR (CD_3COCD_3) δ 220.96, 217.05, 206.41, 154.77, 129.24, 124.92, 92.13, 86.59, 78.89, 73.37, 68.37, 61.83, 61.42, 46.61, 35.30, 20.98, 14.89; MS *m/e* 446 ($M^+ - 2CO$), 418 ($M^+ - 3CO$), 362 ($M^+ - 5CO$), 317 ($M^+ - 5CO - OC_2H_5$), 261 [$M^+ - 3CO - OC_2H_5 - Fe(CO)_2$], 205 [$C_9H_8C(C_6H_5)^+$]. Anal. Calcd for $C_{23}H_{18}O_6Fe_2$: C, 55.02; H, 3.61. Found: C, 54.71; H, 3.60.

Thermolysis of 8 to Give [Fe_2{μ-C(C_6H_5)(η^2,η^5-C_9H_8)}(μ-$SC_6H_4CH_3$-*p*)$(CO)_3$] (17) and [$Fe(CO)_2$(C=O){C(H)C_6H_5(η^5-C_9H_8)}] (18). Compound **8** (0.104 g, 0.19 mmol) was dissolved in benzene (20 mL) in a quartz tube. The tube was cooled at −80 °C to freeze the benzene solution and sealed under high vacuum. The sealed tube was heated to 85−90 °C for 48 h. After cooling, the dark red solution was evaporated *in vacuo* to dryness. The residue was chromatographed on Al_2O_3 with petroleum ether/CH_2Cl_2 (10:1) as the eluant. The blackish band that eluted first was collected, then a brown-yellow band was eluted with petroleum ether/CH_2Cl_2 (5:1). After vacuum removal of the solvent from the above three eluates, the residues were recrystallized from petroleum ether or petroleum ether/THF at −80 °C. From the first fraction, 0.067 g (56%) of green crystals of **17** was obtained: mp 158−160 °C dec; IR (CH_2Cl_2) ν(CO) 1984 (m), 1965 (vs), 1927 (s) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.10−6.91 (m, 9H, C_6H_5 + *p*-$CH_3C_6H_4$), 6.23 (s, 1H, C_9H_8), 5.64 (d, 1H, C_9H_8), 5.60 (m, 4H, CH_2Cl_2), 5.51 (t, 1H, C_9H_8), 3.41−3.37 (m, 2H, C_9H_8), 3.15 (t, 1H, C_9H_8), 2.21 (*p*-$CH_3C_6H_4$), 1.90 (dd, 1H, C_9H_8), 1.76 (dd, 1H, C_9H_8); ^{13}C NMR (CD_3COCD_3) δ 224.9, 220.4, 218.1, 157.8, 142.3, 138.2, 136.9, 132.2, 129.3, 128.5, 125.8, 124.9, 101.0, 98.3, 90.7, 78.9, 78.1, 62.1, 58.5, 42.4, 32.7, 23.0; MS *m/e* 316 ($M^+ - 3CO -$ *p*-$CH_3C_6H_4S$), 204 ($M^+ - 3CO - Fe -$ *p*-$CH_3C_6H_4S$), 115 ($C_9H_8 - 1)^+$, 84 ($CH_2Cl_2^+$). Anal. Calcd for $C_{26}H_{19}O_3SFe_2 \cdot 2CH_2Cl_2$: C, 48.52; H, 3.35. Found: C, 48.35; H, 3.60. From the second deep red fraction, 0.015 g (12%) of orange crystalline **18** was obtained: mp 130−132 °C dec; IR (CH_2Cl_2) ν(CO) 2021 (vs), 1962 (s) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.24−6.98 (m, 5H, C_6H_5), 6.56 (d, 1H, C_9H_8), 6.08 (dd, 1H, C_9H_8), 5.44 (s, 1H, C_9H_8), 5.33 (s, 1H, C_9H_8), 4.60 (t, 1H, C_9H_8), 3.25 (d, 1H, C_9H_8), 2.91 (t, 1H, C_9H_8), 2.77−2.68 (m, 2H, C_9H_8 + CHC_6H_5); ^{13}C NMR (CD_3COCD_3) δ 255.4, 216.2, 214.4, 143.9, 131.2, 129.5, 126.5, 121.8, 96.9, 94.2, 86.4, 84.9, 78.4, 63.9, 39.5; MS *m/e* 345 ($M^+ - 1$), 318 ($M^+ - CO$), 290 ($M^+ - 2CO$), 262 ($M^+ - 3CO$), 234 ($M^+ - 3CO - Fe$), 206 [$C_9H_8C(H)C_6H_5^+$]. Anal. Calcd for $C_{19}H_{14}O_3Fe$: C, 65.92; H, 4.08. Found: C, 66.06; H, 4.26.

Thermolysis of 9 to Give [Fe_2{μ-C($C_6H_4C_6H_5$-*p*)(η^2,η^5-C_9H_8)}(μ-$SC_6H_4CH_3$-*p*)-*p*)$(CO)_3$] (19) and [$Fe(CO)_2$(C=O){C(H)-$C_6H_4C_6H_5$-*p*(η^5-C_9H_8)}] (20). As the same procedures described above, 0.130 g (0.21 mmol) of **9** in 25 mL of benzene in a quartz tube was heated to 85−90 °C for 24 h. Subsequent treatment of the dark resulting solution as described for the thermolysis of **8** afforded 0.055 g (44%) of green crystalline **19** and 0.016 g (17%) of **20** as orange crystals. **19**: mp 74−76 °C; IR (CH_2Cl_2) ν(CO) 1984 (m), 1966 (vs), 1928 (s) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.64−6.92 (m, 9H, C_6H_5 + *p*-$CH_3C_6H_4$), 6.28 (s, 1H, C_9H_8), 5.67 (d, 1H, C_9H_8), 5.54 (t, 1H, C_9H_8), 3.44 (t, 2H, C_9H_8), 3.19 (t, 1H, C_9H_8), 2.21 (s, 3H, *p*-$CH_3C_6H_4$), 1.93 (dd, 1H, C_9H_8), 1.78 (d, 1H, C_9H_8); ^{13}C NMR (CD_3COCD_3) δ 228.1, 224.6, 223.1(CO), 157.8 (μ-C), 141.9, 141.3, 137.5, 136.6, 131.9, 129.4, 127.4, 126.7, 126.5, 125.2, 119.6 (C_6H_5 + *p*-$CH_3C_6H_4$), 101.8, 98.0, 90.6, 83.7, 81.3, 78.6, 77.9, 63.8, 62.1, 61.3, 58.2, 58.0, 42.4 (C_9H_8), 23.0 (*p*-$CH_3C_6H_4$); MS *m/e* 362 [$M^+ - 3CO - C_6H_5C_6H_4$], 239 [$M^+ - 3CO - C_6H_5C_6H_4 - CH_3C_6H_4S$], 115 ($C_9H_8 - 1)^+$. Anal. Calcd for $C_{32}H_{23}O_3SFe_2$: C, 64.14; H, 3.87. Found: C, 64.55; H, 3.48. **20**: mp 58−60 °C; IR (CH_2Cl_2) ν(CO) 2021 (vs), 1962 (s) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.58−7.08 (m, 9H, *p*-$C_6H_5C_6H_4$), 6.56 (d, 1H, C_9H_8), 6.14 (dd, 1H, C_9H_8), 5.45 (s, 1H, C_9H_8), 5.36 (d,

Table 1. Crystal Data and Experimental Details for Complexes 14, 16, 17, and 18

	14	**16**	**17**·2THF	**18**
formula	$C_{38}H_{24}O_6F_6Fe_2$	$C_{23}H_{18}O_6Fe_2$	$C_{34}H_{35}O_5SFe_2$	$C_{19}H_{14}O_3Fe$
fw	802.27	502.07	667.38	346.15
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)
a (Å)	9.0696(10)	10.6638(10)	10.054(7)	7.163(3)
b (Å)	13.3537(13)	12.0300(10)	10.371(7)	11.724(6)
c (Å)	14.4026(15)	16.6822(14)	16.115(11)	36.548(17)
α (deg)			76.906(13)	90
β (deg)	99.971(2)	105.890(2)	77.329(11)	90
γ (deg)			74.356(12)	90
V (Å^3)	1718.0(3)	2058.3(3)	1553.5(17)	3069(3)
Z	2	4	2	8
D_{calcd} (g /cm^3)	1.551	1.620	1.427	1.498
F(000)	812	1024	694	1424
μ(Mo Kα) (cm^{-1})	9.24	14.48	10.41	9.94
orientation reflns: no.; range (2θ) (deg)	1259; 4.560−38.667	1502; 5.708−40.203	1933; 4.497−43.133	997; 4.458−33.920
data coll. range, 2θ (deg)	4.18−54.00	3.98−54.00	2.64−51.00	4.46−54.00
no. of unique data, total	3746	4487	5703	3346
with $I > 2.00\sigma(I)$	2044	2465	3865	1380
no. of params refined	283	305	330	208
correct. factors, max. min.	0.66444−1.00000	0.81279−1.00000	0.81417−1.00000	0.77491−1.00000
R^a	0.0629	0.0461	0.0790	0.0498
$R_w{}^b$	0.1124	0.0673	0.2040	0.0903
quality of fit indicator^c	0.925	0.790	1.022	0.795
max. shift/esd. final cycle	0.001	0.024	0.001	0.000
largest peak (e$^-$/Å^3)	0.416	0.469	0.655	0.451
min. peak (e$^-$/Å^3)	−0.351	−0.353	−0.658	−0.355

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

1H, C_9H_8), 4.61 (t, 1H, C_9H_8), 3.31 (d, 1H, C_9H_8), 2.78 (t, 1H, C_9H_8), 2.64−2.62 (m, 2H, C_9H_8 + C*H*$C_6H_4C_6H_5$-*p*), 1.20−1.12 (m, 8H, $CH_3(CH_2)_4CH_3$), 0.86 (t, 6H, $CH_3(CH_2)_4CH_3$); MS *m*/*e* 393 ($M^+ - CO - H$), 365 ($M^+ - 2CO - H$), 337 ($M^+ - 3CO - H$), 282 [$M^+ - Fe(CO)_3$], 281 [$M^+ - Fe(CO)_3 - H$], 116 ($C_9H_8^+$), 86 ($C_6H_{14}^+$). Anal. Calcd for $C_{25}H_{18}O_3Fe\cdot C_6H_{14}$ (hexane): C, 73.23; H, 6.34. Found: C, 73.56; H, 6.42.

X-ray Crystal Structure Determinations of Complexes 14, 16, 17, and 18. The single crystals of complexes **14**, **16**, **17**, and **18** suitable for X-ray diffraction studies were obtained by recrystallization from petroleum ether/CH_2Cl_2 or petroleum ether/THF at −80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for the nine complexes were collected with a Bruker Smart diffractometer at 20 °C using Mo Kα radiation with an $\omega-2\theta$ scan mode.

The structures of **14**, **16**, **17**, and **18** were solved by the direct methods and expanded using Fourier techniques. For the 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 the agreement factors listed in Table 1.

The details of the crystallographic data and the procedures used for data collection and reduction information for **14**, **16**, **17**, and **18** are given in Table 1. The selected bond lengths and angles for complexes **16**−**18** are listed in Table 2, and the principal bond lengths and angles for complex **14** are presented in Figure 1. The molecular structures of **14**, **16**, **17**, and **18** are given in Figures 1−4, respectively. The atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **14**, **16**, **17**, and **18** are given in the Supporting Information.

Table 2. Selected Bond Lengths (Å)^a and Angles (deg)^a of Complexes 16−18

	16	**17**	**18**
Fe(1)−Fe(2)	2.7521(8)	2.531(2)	
Fe(1)−C(5)	2.157(3)	2.020(6)	
Fe(2)−C(5)		2.046(5)	
Fe(2)−C(1)			1.965(5)
Fe(1)−S		2.231(2)	
Fe(2)−S		2.2284(19)	
Fe(1)−C(11)	2.212(3)	2.129(7)	
Fe(1)−C(12)	2.208(4)	2.135(7)	
C(1)−C(5)			1.569(6)
C(5)−C(13)	1.529(4)	1.558(8)	1.582(5)
C(1)−O(1)	1.142(4)	1.159(8)	1.198(5)
C(6)−C(10)	1.430(5)	1.424(9)	1.415(6)
C(10)−C(11)	1.433(5)	1.445(10)	1.434(6)
C(11)−C(12)	1.366(5)	1.359(9)	1.342(5)
C(12)−C(13)	1.499(5)	1.510(9)	1.473(6)
C(13)−C(14)	1.552(4)	1.526(9)	1.511(5)
C(6)−C(14)	1.490(4)	1.458(9)	1.493(5)
Fe(1)−Fe(2)−C(5)		51.05(16)	
Fe(1)−C(5)−Fe(2)		77.0(2)	
Fe(2)−Fe(1)−C(5)	93.18(9)	51.97(16)	
Fe(1)−Fe(2)−S		55.48(6)	
Fe(2)−Fe(1)−S		49.63(14)	
Fe(1)−S−Fe(2)		55.37(5)	
C(5)−Fe(1)−S		85.15(16)	
C(5)−Fe(2)−S		84.63(17)	
Fe(1)−C(5)−C(13)	94.1(2)	97.4(4)	
Fe(2)−C(5)−C(13)		109.1(4)	
Fe(2)−C(1)−C(5)			126.5(3)
Fe(2)−C(1)−O(1)			121.8(3)
C(5)−C(1)−O(1)			111.3(4)
C(6)−C(10)−C(11)	121.2(4)	119.9(6)	120.2(4)
C(10)−C(11)−C(12)	118.8(4)	116.0(7)	117.9(5)
C(11)−C(12)−C(13)	124.2(4)	118.7(6)	122.3(5)
C(12)−C(13)−C(14)	112.4(3)	110.2(6)	112.7(4)
C(13)−C(14)−C(6)	112.5(3)	103.7(5)	109.2(4)
C(14)−C(6)−C(10)	120.0(3)	120.1(6)	119.5(4)
C(13)−C(5)−C(17)	115.6(3)	116.9(5)	112.2(4)

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

Results and Discussion

An orange-red benzene solution of complex **1** in a sealed quartz tube was heated with stirring to 85−90 °C for 72 h. After workup as described in the Experimental Section, a bicycloolefin-coordinated tricarbonyliron dimer [Fe{η^4-$C_9H_8(C_6H_5)$}-$(CO)_3]_2$ (**10**) and a bridging arylcarbene complex [Fe_2{μ-

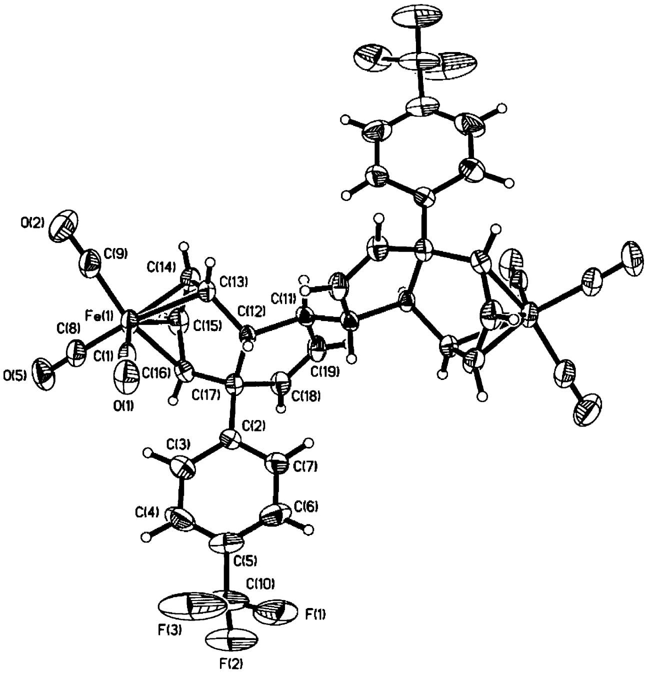


Figure 1. ORTEP diagram of **14**. Selected bond lengths (Å): Fe(1)−C(13) = 2.110(4), Fe(1)−C(14) = 2.037(5), Fe(1)−C(15) = 2.039(5), Fe(1)−C(16) = 2.094(5), C(11)−C(12) = 1.555(5), C(12)−C(13) = 1.513(5), C(13)−C(14) = 1.409(6), C(14)−C(15) = 1.370(7), C(15)−C(16) = 1.399 (6), C(16)−C(17) = 1.518(5), C(17)−C(18) = 1.511(5), C(18)−C(19) = 1.315(6), C(11)−C(19) = 1.485(6).

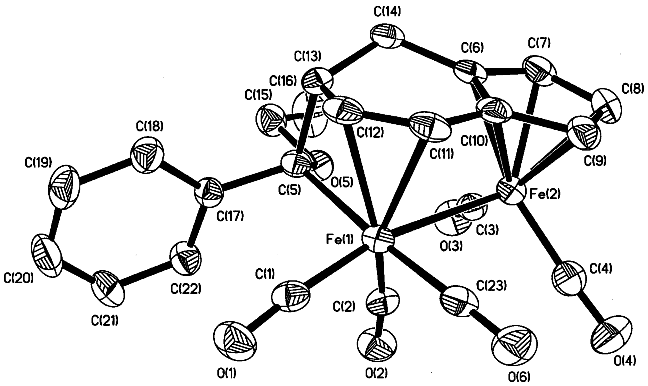


Figure 2. Molecular structure of **16**, showing the atom-numbering scheme with 45% thermal ellipsoids.

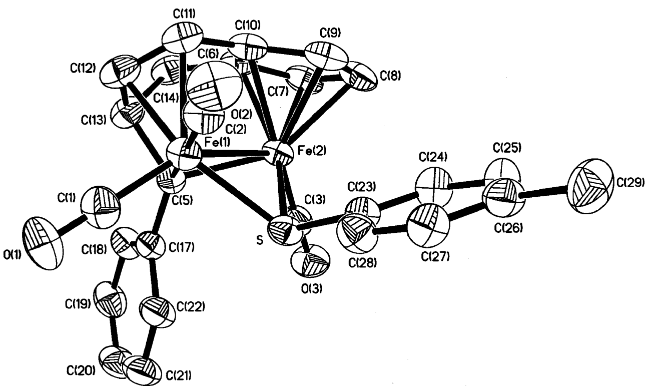


Figure 3. Molecular structure of **17**, showing the atom-numbering scheme with 45% thermal ellipsoids.

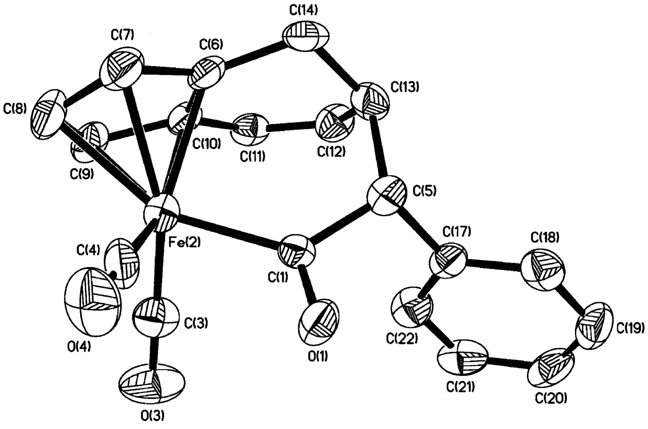
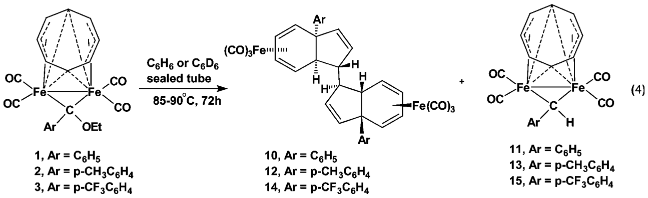


Figure 4. Molecular structure of **18**, showing the atom-numbering scheme with 40% thermal ellipsoids.

$C(H)C_6H_5\}(CO)_4(\eta^8-C_8H_8)]$ (**11**) (eq 4) were obtained in 23% and 40% isolated yields, respectively. The analogous thermolyses of complexes **2** and **3** gave the corresponding dimers $[Fe\{\eta^4-C_9H_8(Ar)\}(CO)_3]_2$ (**12**, Ar = $p-CH_3C_6H_4$; **14**, Ar = $p-CF_3C_6H_4$) in 30−37% yields and bridging arylcarbene complexes $[Fe_2\{\mu-C(H)Ar\}(CO)_4(\eta^8-C_8H_8)]$ (**13**, Ar = $p-CH_3C_6H_4$; **15**, Ar = $p-CF_3C_6H_4$) in 35−41% yields (eq 4).



The purple-red products **11**, **13**, and **15** are known compounds[17] whose structures have been established by X-ray crystallography; they have been obtained by the reactions of COT-coordinated diiron cationic bridging carbyne complexes $[Fe_2(\mu-CAr)(CO)_4(\eta^8-C_8H_8)]BF_4$ (Ar = C_6H_5, $p-CH_3C_6H_4$, $p-CF_3C_6H_4$),[17] prepared by treating bridging alkoxycarbene complexes **1**−**3** with HBF_4, with $NaBH_4$ in THF at low temperature. The yellow dimer products **10**, **12**, and **14** shown in eq 4 are the centrically symmetric compounds established by microanalytical data and IR, ^1H NMR, and mass spectra, as well as X-ray crystallography. The IR spectra of complexes **10**, **12**, and **14** containing two $Fe(CO)_3$ units showed only three CO absorption bands at about 2045−2048, 2033−2036, and 1942−1947 cm^{-1} in the $\nu(CO)$ region, which are consistent with their symmetry structures. In the ^1H NMR spectra of complexes **10**, **12**, and **14**, the proton signals of the bicycloolefin ligand showed seven sets of peaks and the protons of the olefin coordinated to the metal shift greatly upfield (at 3.72−3.34 ppm) as compared with that of uncoordinated olefin protons (at 5.97−5.46 ppm) (see Experimental Section). The structures of products **10**, **12**, and **14** were further confirmed by the single-crystal X-ray diffraction study of complex **14**. The results of the X-ray diffraction work for **14** are summarized in Table 1, and its structure is shown in Figure 1. Thus, the spectroscopic data and the results of the X-ray diffraction analysis indicate that the formation of products **10**, **12**, and **14** was highly stereoselective and only one stereoisomer was obtained (eq 4), presumably due to the steric control.

The structure of **14** (Figure 1) confirmed that it is a bicycloolefin-coordinated tricarbonyliron dimer having a symmetric center. The original bridging carbene carbon in **3** has inserted into the COT ring and an annelation reaction occurred

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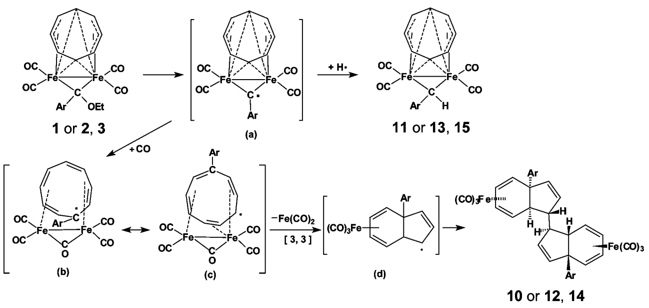
[17] Zhang, S.; Xu, Q.; Sun, J.; Chen, J.-B. *Organometallics* **2003**, *22*, 1816.

Scheme 1



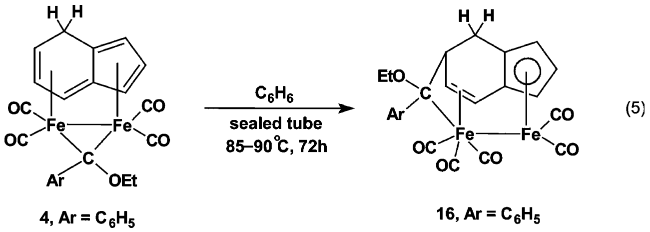
to form a bicyclic olefin ligand consisting of a six-membered ring and a five-membered ring, an indene derivative. In complex **14**, the two double bonds (C(13)═C(14) and C(5)═C(16)) of the cyclohexadiene moiety are in η^4-bonding coordination to the $Fe(CO)_3$ moiety, while the C(18)═C(19) double bond of the five-membered ring is retained. The two identical bicycloolefin-coordinated tricarbonyliron species were connected by each carbon atom (C(11)) of the five-membered ring moiety to construct dimer **14**.

In the six-membered ring moiety of the bicycloolefin ligand, the C(13), C(14), C(15), and C(16) atoms lie in one plane, and the C(12), C(13), C(16), and C(17) atoms lie in another plane. The dihedral angle between the two planes is 40.71°. In the five-membered ring moiety, the C(11), C(12), C(17), C(18), and C(19) carbon atoms lie in the same plane. The dihedral angle between the C(12)C(13)C(16)C(17) and C(11)C(12)C(17)C(18)C(19) planes is 63.12°. The benzene ring plane comprised of C(2) though C(7) is oriented at an angle of 84.28° with respect to the five-membered ring C(11)C(12)C(17)C(18)C(19) plane.

The formation mechanism for the products **10**, **12**, and **14** and products **11**, **13**, and **15** is not clear. A presumedly possible thermolysis pathway is shown in Scheme 1. Under heating, the cleavage of the μ-C−O bond of the μ-$C(OC_2H_5)Ar$ ligand in **1** (or **2**, **3**) occurred to form a bridging carbene free radical intermediate (a), which could either abstract a hydrogen to produce bridging arylcarbene complex **11**, **13**, or **15** or undergo an insertion reaction of the μ-carbene carbon into the coordinated COT ring aided by the metal iron accompanied by abstraction of a CO ligand generated from the decomposition of starting **1** (or **2**, **3**) or intermediate (a) to form a diiron-coordinated nine-membered-ring free radical intermediate (b). The free radical electron of the intermediate (b) could undergo delocalization to yield intermediate (c). The latter, under the heating, underwent an annulation reaction, similar to [3, 3]-σ rearrangement, to form a bicyclic free radical intermediate (d) consisting of a six-membered ring and a five-membered ring. Two bicyclic free radicals (d) could form the dimer **10** (or **12**, **14)** by dimerization.

Evidently, complexes **10**, **12**, and **14** were first obtained from the expanded ring products formed by insertion of the bridging carbene carbon into the cycloolefin ligand in the dimetal bridging carbene complexes. The source of the hydrogen atom at the μ-carbene carbon in products **11**, **13**, and **15** could be the solvent benzene or the cleaved OC_2H_5 from the starting compounds **1**−**3**. However, the solvent benzene can be excluded due to the fact that the thermolysis of compound **3** in deuterated benzene (C_6D_6) under the same conditions as those in benzene also afforded the bridging arylcarbene complex **15** in similar yield (39%) (eq 4). Thus, the most possible source of the H atom at the μ-C atom of complexes **11**, **13**, and **15** is the cleaved OC_2H_5. The intermediate (a) might abstract a methylene hydrogen from the OCH_2CH_3 group to produce products **11**, **13**, and **15**. Due to no relative reference and lack of further experimental evidence, the proposed mechanism above is only a speculation.

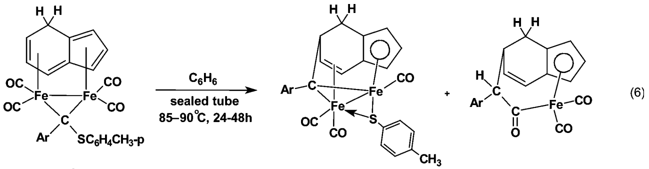
To examine the effect of different cycloolefin ligands of the diiron bridging carbene complexes on the thermolysis reactions, we investigated the thermolysis reaction of 7*H*-indene-coordinated diiron bridging alkoxycarbene complex **4** under conditions similar to those in the thermolysis of **1**−**3**. A deep red benzene solution of **4** in a sealed tube was heated with stirring at 85−90 °C for 72 h to give a novel ring addition product, $[Fe_2\{C(OC_2H_5)C_6H_5(\eta^2,\eta^5\text{-}C_9H_8)\}(CO)_5]$ (**16**), in 45% yield (eq 5). An analogous ring addition product, $[Fe_2\{C(OC_2H_5)C_6H_4C_6H_5\text{-}p(\eta^2,\eta^5\text{-}C_9H_8)\}(CO)_5]$,[11] a biphenyl analogue of **16**, has been obtained by stirring a CH_2Cl_2 solution of $[Fe_2\{\mu\text{-}C(OC_2H_5)\text{-}C_6H_4C_6H_5\text{-}p\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)\}]$ (**5**) at room temperature for 12 h.



The structure of product **16** was supported by its elemental analysis, IR and ^1H and ^{13}C NMR spectroscopies, and X-ray single-crystal diffraction. The crystallographic investigation of **16** reveals an unusual structure (Figure 2), which is quite different from that of precursor **4**, arising from the μ-C−Fe(2) bond in **4** being cleaved and the μ-carbene carbon (C(5)) being linked to a ring carbon (C(13)) of the 7*H*-indene ligand, forming a new carbon−carbon bond (C(5)−C(13)) and leading to formation of an η^2-bonding to coordinate to the $Fe(CO)_3$ moiety in **16**. Thus, the six-membered ring of the 7*H*-indene ligand carries a $C(OC_2H_5)C_6H_5$ group on C(13), and its configuration and bond lengths have been changed due to the migration of the μ-carbene ligand $C(OC_2H_5)C_6H_5$ from Fe(2) to C(13) of the C_6 ring. In **16**, the ring carbons C(11) and C(12) are coordinated to Fe(1) in an η^2-bonding, C(5) is σ bound to Fe(2), and a CO group, generated from the decomposition of **4** or an intermediate, is also coordinated to the Fe(1) atom. The Fe−Fe distance (2.7521(8) Å) is the same within experimental error as that of $[Fe_2\{C(OC_2H_5)C_6H_4C_6H_5\text{-}p(\eta^2,\eta^5\text{-}C_9H_8)\}(CO)_5]$ (2.7512(7) Å).[11] The Fe(1)−C bond lengths of C(11) and C(12) are 2.212(3) and 2.208(4) Å, respectively. The structure of the six-membered ring moiety of the 7*H*-indene ligand in **16** is also similar to that in $[Fe_2\{C(OC_2H_5)C_6H_4C_6H_5\text{-}p\text{-}(\eta^2,\eta^5\text{-}C_9H_8)\}(CO)_5]$.[11]

The formation pathway of thermolysis product **16** is similar to that of $[Fe_2\{C(OC_2H_5)C_6H_4C_6H_5\text{-}p(\eta^2,\eta^5\text{-}C_9H_8)\}(CO)_5]$.[11] Under higher temperature (80−90 °C), the μ-carbene ligand in **4** migrated from Fe(2) to a carbon atom (C(13)) of the six-membered-ring moiety of the 7*H*-indene ligand, forming an η^2-bonding to coordinate to the Fe atom in **16**. This indicates that complex **4** is thermodynamically more stable than complex $[Fe_2\{C(OC_2H_5)C_6H_4C_6H_5\text{-}p(\eta^2,\eta^5\text{-}C_9H_8)\}(CO)_5]$ and that the different aryl substituents on the bridging carbene ligand exert a great influence on the thermal stability of the diiron bridging alkoxycarbene complexes.

To explore the effect of different bridging carbene ligands of the diiron bridging carbene complexes on thermolysis reactions and the resulting products, we studied the thermolysis of 7*H*-indene-coordinated diiron bridging arylthiocarbene complexes **8** and **9**. The dark red benzene solution of compounds **8** and **9**, respectively, in a sealed tube was heated with stirring at 85−90 °C for 24 to 48 h. After workup as described in the Experimental Section, the green, crystalline complexes [Fe_2{μ-C(Ar)(η^2,η^5-C_9H_8)}(μ-$SC_6H_4CH_3$-*p*)$(CO)_3$] (**17**, Ar = C_6H_5; **19**, Ar = *p*-$C_6H_5C_6H_4$) and the orange compounds [$Fe(CO)_2$(C═O){C(H)Ar(η^5-C_9H_8)}] (**18**, Ar = C_6H_5; **20**, Ar = *p*-$C_6H_5C_6H_4$) were obtained in 44−56% and 12−17% yields, respectively (eq 6).



8, Ar = C_6H_5
9, Ar = p-$C_6H_5C_6H_4$

17, Ar = C_6H_5
19, Ar = p-$C_6H_5C_6H_4$

18, Ar = C_6H_5
20, Ar = p-$C_6H_5C_6H_4$

The structures proposed in eq 6 were based on their elemental analyses and spectroscopic evidence, as well as X-ray crystallography. Products **17** and **19** are formulated as the isomerized 7*H*-indene-coordinated diiron bridging carbene complexes with a μ-$SC_6H_4CH_3$-*p* ligand. In both products, the original bridging carbene ligand C(Ar)$SC_6H_4CH_3$-*p* (Ar = C_6H_5 or *p*-$C_6H_5C_6H_4$) is now a μ-CAr ligand bonded to a carbon of the C_6 ring of the 7*H*-indene ligand, which was formed by migration of the *p*-$CH_3C_6H_4S$ group from the bridging carbene ligand to the two Fe atoms accompanied by loss of a CO ligand from the iron atom (Fe(2)). The orange products **18** and **20** are formulated as acyliron compounds in which the C_6 ring moiety of the 7*H*-indene ligand now carries a C(H)Ar(C═O) group. The structures of products **17** and **19** and products **18** and **20** were further confirmed by X-ray diffraction studies of complex **17** and complex **18**, respectively.

The X-ray structure of **17** (Figure 3) shows a highly unusual structure, which contains a capping μ-C(C_6H_5) ligand and a thio-bridged *p*-$C_6H_5C_6H_4S$ ligand. The μ-C(5) is 2.020(6) Å from Fe(1), 2.046(5) Å from Fe(2), and 1.558(8) Å from C(13). The structural features of the six-membered-ring portion in **17** are very similar to those of the same unit in **16**, except the carrying substituent is a μ-CC_6H_5 carbene ligand in the former but a C(OC_2H_5)C_6H_5 group in the latter.

The Fe−Fe bond is bridged by a μ-$SC_6H_4C_6H_5$-*p* ligand with the following dimensions: Fe(1)−Fe(2) 2.531(2) Å, μ-S−Fe(1) 2.231(2) Å, μ-S−Fe(2) 2.2284(19) Å. The Fe−Fe distance in **17** is significantly shorter than that in the analogous complex [Fe_2{μ-C(OC_2H_5)C_6H_5}$(CO)_4$(η^4,η^4-C_9H_8)] (2.6663(8) Å)[11] and precursor compound **8** (2.6754(8) Å),[11] arising from the bridging μ-$SC_6H_4CH_3$-*p* group.

The molecular structure of **18** (Figure 4) shows that the configuration and bond distances of the 7*H*-indene ligand have been changed by comparison with parent **8**, caused by the loss of the $Fe(CO)_2$ moiety and the transfer of the bridging carbene carbon with a phenyl from the lost Fe(1) atom to the C(13) atom of the indene ring. In the six-membered-ring moiety, only C(10), C(11), C(12), and C(13) are in a plane (±0.0014 Å); C(14) is out of the C(10)C(11)C(12)C(13) plane by 0.7767 Å. In contrast to the nearly equal distances in C(10) to C(13) of the C_6 ring in **8**, in **18** the C(10)−C(11) (1.434(6) Å) and C(12)−C(13) (1.473(6) Å) bonds are obviously longer than C(11)−C(12) (1.342(5) Å), indicating that the latter is a double bond.

The thermolysis pathway to products **17** and **19** and products **18** and **20** is not yet clear. We speculate that the formation of **17** and **19** could be via a migration of the *p*-$CH_3C_6H_4S$ group from the μ-carbene carbon (C(5)) to Fe(2) accompanied by loss of a CO ligand from the Fe(2)$(CO)_2$ moiety and bonding of the μ-carbene carbon to a carbon (C(13)) of the six-membered ring of the 7*H*-indene ligand to form the new carbon−carbon bond (C(5)−C(13)). Then the *p*-$CH_3C_6H_4S$ group coordinates to Fe(1) to produce product **17** or **19**. Products **18** and **20** would be the further thermodynamic product of **17** and **19**, respectively, by losing both the *p*-$CH_3C_6H_4S$ ligand and Fe(1)$(CO)_2$ moiety from **17** or **19** accompanied by bonding of an acyl group and a CO ligand, generated from the loss of the $Fe(CO)_2$ species, to the C(5) and Fe(2) atoms, respectively. Prolonging the heating time or raising the thermolysis temperature leads to a decrease in the yield of product **17** or **19** but an increase in the yield of product **18** or **20**. The origin of the H atom on the C(H)Ar(C═O) group in products **18** and **20** could be the 7*H*-indene ligand or water, which is a contaminant in benzene or from glassware. Compounds **8** and **9** and thermolysis products **17** and **19** all showed a strong ion peak at *m*/*e* 115 (C_9H_8 − 1) in their mass spectra, which suggests that the methylene hydrogen (−CH_2−) of the 7*H*-indene ligand could be dissociated and indicates that it could provide a H^- for the formation of the C(H)Ar(C═O) group under the thermolysis conditions. Thus, the most probable source of the H atom on the C(H)Ar(C═O) group is the 7*H*-indene ligand of products **17** and **19** or starting compounds **8** and **9**.

In summary, we have found the remarkable thermolysis reactions of the COT- and 7*H*-indene-coordinated diiron bridging carbene complexes, and a series of novel thermolytic products were obtained. The thermolysis results indicate that the different cycloolefin ligands and different bridging carbene ligands exert a great influence on the thermolysis behavior of the dimetal bridging carbene complexes and resulting products. Further studies on the scope of these thermolysis reactions and applications in organic and organometallic synthesis are being carried out in our laboratory.

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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 **14, 16, 17**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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