Unusual Reactions of Pentacarbonyl(cyclooctatetraene)diiron with Nucleophiles. Synthesis and Structure of Cyclooctatetraene-Coordinated Diiron Bridging Carbene Complexes[†]

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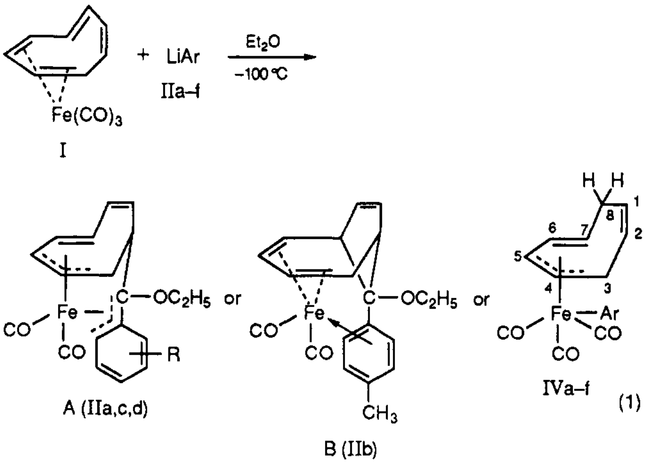
The reaction of pentacarbonyl(cyclooctatetraene)diiron (1) with aryllithium reagents, ArLi (Ar = C_6H_5, *o*-, *m*-, and *p*-$CH_3C_6H_4$, *p*-ClC_6H_4, *p*-$CF_3C_6H_4$), in ether at low temperature afforded acylmetalate intermediates. Subsequent alkylation with Et_3OBF_4 in aqueous solution at 0 °C gave the six new dimetal bridging carbene complexes $C_8H_8(CO)_2Fe\{\mu\text{-}C(OC_2H_5)Ar\}Fe(CO)_2$ (**2**, Ar = C_6H_5; **3**, Ar = *o*-$CH_3C_6H_4$; **4**, Ar = *m*-$CH_3C_6H_4$; **5**, Ar = *p*-$CH_3C_6H_4$; **6**, Ar = *p*-ClC_6H_4; **7**, Ar = *p*-$CF_3C_6H_4$); the structure of **7** has been established by X-ray diffraction analysis. Complex **7** crystallized in the monoclinic system, space group $P2_1/n$, with a = 8.766(2) Å, b = 23.404(5) Å, c = 10.270(2) Å, β = 94.25(2)°, V = 2101.27(7) Å^3, Z = 4, D_{calcd} = 1.68 g/cm^3, R = 0.0347, and R_w = 0.0330 for 2496 reflections with $F_o^2 > 3\sigma(F_o^2)$.

Introduction

In recent years, olefin-coordinating transition-metal carbene complexes and/or their isomerized products have been examined extensively in our laboratory.[2-13] We have previously observed several novel isomerizations of olefin ligands, and a series of isomerized carbene complexes with novel structures were isolated by the reactions of olefin-ligated monometal carbonyls with nucleophiles.[2-11] For instance, the reaction of (cyclooctatetraene)tricarbonyliron with aryllithium and subsequent alkylation with Et_3OBF_4 results in the formation of novel isomerized carbene complexes with two types of structures, A and B, or (8,8-dihydro-(3-5-η)-cyclooctatrienyl)tricarbonyliron complexes depending on the alkylation conditions[3] (eq 1).



(1)

II, IV: a, Ar = C_6H_5; b, Ar = *p*-$CH_3C_6H_4$; c, Ar = *o*-$CH_3C_6H_4$; d, Ar = *m*-$CH_3C_6H_4$; e, Ar = *p*-$CF_3C_6H_4$; f, Ar = C_6Cl_5
III: a, R = H; c, R = *o*-CH_3; d, R = *m*-CH_3

In an extension of our research on olefin-coordinating metal carbene complexes, we have now studied the reaction of olefin-ligated dimetal carbonyls with nucleophiles in order to investigate the effect of binuclear central metals on the isomerization of olefin ligands and the reaction products. Herein we report an unusual reaction of pentacarbonyl(cyclooctatetraene)diiron (**1**),[14-17] where a μ-CO group bridges to the Fe–Fe bond and two terminal carbonyl groups are attached to each of the two iron atoms, with aryllithium reagents at low temperature, followed by alkylation with Et_3OBF_4 to form the cyclooctatetraene-coordinated dimetal bridging carbene complexes and the structural characterization of the resulting products.

[†] Dedicated to Professor Ernst Otto Fischer on the occasion of his 75th birthday and in recognition of his brilliant contributions to organometallic chemistry.

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Experimental Section

All manipulations were carried out under a prepurified N_2 atmosphere with standard Schlenk techniques. All solvents employed were dried by reflux over appropriate drying agents and stored over 4-Å molecular sieves under an N_2 atmosphere. Diethyl ether (Et_2O) was distilled from sodium-benzophenone ketyl, petroleum ether (30–60 °C) from CaH_2, and CH_2Cl_2 from P_2O_5. The neutral alumina (Al_2O_3) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% w/w N_2-saturated water, and stored under N_2. Compound 1,[14-16] Et_3OBF_4,[18] and aryllithium reagents[19-23] were prepared by literature methods.

The IR spectra were measured on a Zeiss Specord-75 spectrophotometer. All ^1H NMR spectra were recorded at ambient temperature in acetone-d_6 solution with TMS as the internal reference using a Varian 200 spectrometer. Electron ionization mass spectra (EIMS) were run on a Finnigan 4021 GC/MS/DS spectrometer. The melting points were determined in sealed, nitrogen-filled capillaries and are not corrected.

(i) Preparation of $C_8H_8(CO)_2Fe\{\mu\text{-}C(OC_2H_5)C_6H_5\}Fe(CO)_2$ (2). To a suspended solution of 1 (0.50 g, 1.40 mmol) in 50 mL of ether was added dropwise 1.96 mmol of C_6H_5Li[19] in 15 mL of ether at −78 °C within 15 min. The reaction mixture was stirred at −70 to −45 °C for 3.5 h, during which time the red solution gradually turned dark red. The solution was then evaporated under high vacuum at −30 to −40 °C to dryness. The dark red solid residue obtained was dissolved in 50 mL of N_2-saturated water at 0 °C and covered with petroleum ether (30–60 °C). Immediately afterward Et_3OBF_4 was added portionwise, with strong stirring, to the aqueous solution until it became acidic. The aqueous solution was extracted with petroleum ether. The combined extract was dried over anhydrous Na_2SO_4. After removal of solvent in vacuo, the residue was chromatographed on an alumina (neutral, 100–200 mesh) column (1.6 × 15 cm) at −20 °C with petroleum ether followed by petroleum ether/CH_2Cl_2 (10:1) as the eluant. A brown-red band was eluted and collected. Removal of solvent under vacuum and recrystallization of crude product from petroleum ether/CH_2Cl_2 solution at −80 °C gave 0.42 g (42%, based on 1) of dark red crystals of 2, mp 95–96 °C dec. Anal. Calcd for $C_{21}H_{18}O_5Fe_2$: C, 54.59; H, 3.93. Found: C, 54.66; H, 4.04. MS: *m/e* 462 (M^+), 434 ($M^+ - CO$), 406 ($M^+ - 2CO$), 378 ($M^+ - 3CO$), 350 ($M^+ - 4CO$), 249 ($M^+ - 4CO - Fe - OC_2H_5$), 190 ($M^+ - 4CO - Fe - C_8H_8$), 134 ($C_6H_5COC_2H_5$).

(ii) Preparation of $C_8H_8(CO)_2Fe\{\mu\text{-}C(OC_2H_5)C_6H_4CH_3\text{-}o\}Fe(CO)_2$ (3). Similar to the preparation of 2, the reaction of 0.50 g (1.40 mmol) of 1 with 2.10 mmol of o-$CH_3C_6H_4Li$[20] at −70 to −40 °C for 3.5 h, followed by alkylation and further treatment, afforded 0.47 g (71%, based on 1) of dark red crystalline 3, mp 115 °C dec. Anal. Calcd for $C_{22}H_{20}O_5Fe_2$: C, 55.50; H, 4.23. Found: C, 55.42; H, 4.17. MS: *m/e* 476 (M^+), 448 ($M^+ - CO$), 420 ($M^+ - 2CO$), 392 ($M^+ - 3CO$), 364 ($M^+ - 4CO$), 263 ($M^+ - 4CO - Fe - OC_2H_5$), 204 ($M^+ - 4CO - Fe - C_8H_8$), 148 ($CH_3C_6H_4COC_2H_5$).

(iii) Preparation of $C_8H_8(CO)_2Fe\{\mu\text{-}C(OC_2H_5)C_6H_4CH_3\text{-}m\}Fe(CO)_2$ (4). The reaction of 0.30 g (0.84 mmol) of 1 with 1.26 mmol of m-$CH_3C_6H_4Li$[20] was as described in (i) at −70 to −40 °C for 4 h. The subsequent alkylation and further treatment as described for the preparation of 2 gave 0.25 g (63%, based on 1) of 4 as dark red crystals, mp 87–89 °C dec. Anal. Calcd for $C_{22}H_{20}O_5Fe_2$: C, 55.50; H, 4.23. Found: C, 55.67; H, 4.02. MS: *m/e* 476 (M^+), 448 ($M^+ - CO$), 420 ($M^+ - 2CO$), 392 ($M^+ - 3CO$), 364 ($M^+ - 4CO$), 263 ($M^+ - 4CO - Fe - OC_2H_5$), 204 ($M^+ - 4CO - Fe - C_8H_8$), 148 ($CH_3C_6H_4COC_2H_5$).

(iv) Preparation of $C_8H_8(CO)_2Fe\{\mu\text{-}C(OC_2H_5)C_6H_4CH_3\text{-}p\}Fe(CO)_2$ (5). Compound 1 (0.40 g, 1.12 mmol) was treated, in a manner similar to that described in (i), with 1.60 mmol of p-$CH_3C_6H_4Li$[20] at −70 to −45 °C for 3.5 h, followed by alkylation and further treatment as described above in the preparation of 2, to yield 0.35 g (66%, based on 1) of dark red crystals of 5, mp 76–78 °C dec. Anal. Calcd for $C_{22}H_{20}O_5Fe_2$: C, 55.50; H, 4.23. Found: C, 55.68; H, 3.86. MS: *m/e* 476 (M^+), 448 ($M^+ - CO$), 420 ($M^+ - 2CO$), 392 ($M^+ - 3CO$), 364 ($M^+ - 4CO$), 263 ($M^+ - 4CO - Fe - OC_2H_5$), 204 ($M^+ - 4CO - Fe - C_8H_8$), 148 ($CH_3C_6H_4COC_2H_5$).

(v) Preparation of $C_8H_8(CO)_2Fe\{\mu\text{-}C(OC_2H_5)C_6H_4Cl\text{-}p\}Fe(CO)_2$ (6). To a solution of 2.55 mmol of n-C_4H_9Li[21] in 15 mL of ether, cooled to 0 °C, was added dropwise 0.48 g (2.52 mmol) of p-ClC_6H_4Br in 25 mL of ether. After it was stirred at room temperature for 30 min, the resulting solution of p-ClC_6H_4Li[22] was added dropwise to a suspended solution of 0.60 g (1.69 mmol) of 1 in 80 mL of ether at −78 °C within 20 min. The reaction mixture was stirred at −70 to −40 °C for 3–4 h. Subsequent alkylation and further treatment in a manner similar to that described in the preparation of 2 afforded 0.56 g (67%, based on 1) of dark red crystalline 6, mp 52–54 °C dec. Anal. Calcd for $C_{21}H_{17}O_5ClFe_2$: C, 50.79; H, 3.45. Found: C, 50.81; H, 3.41. MS: *m/e* 496 (M^+), 468 ($M^+ - CO$), 440 ($M^+ - 2CO$), 412 ($M^+ - 3CO$), 384 ($M^+ - 4CO$), 284 ($M^+ - 4CO - Fe - OC_2H_5$), 224 ($M^+ - 4CO - Fe - C_8H_8$), 168 ($ClC_6H_4COC_2H_5$).

(vi) Preparation of $C_8H_8(CO)_2Fe\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}Fe(CO)_2$ (7). Compound 1 (0.60 g, 1.69 mmol) was treated, in a manner similar to that described in (i), with fresh p-$CF_3C_6H_4Li$[23] prepared by the reaction of 0.57 g (2.52 mmol) of p-$CF_3C_6H_4Br$ with 2.52 mmol of n-C_4H_9Li, in ether solution at −70 to −40 °C for 3–4 h. Subsequent alkylation and further treatment similar to the procedures described in (i) gave 0.66 g (74%, based on 1) of dark red crystals of 7, mp 108–109 °C dec. Anal. Calcd for $C_{22}H_{17}O_5F_3Fe_2$: C, 49.85; H, 3.23. Found: C, 49.60; H, 3.30. MS: *m/e* 530 (M^+), 502 ($M^+ - CO$), 474 ($M^+ - 2CO$), 446 ($M^+ - 3CO$), 418 ($M^+ - 4CO$), 317 ($M^+ - 4CO - Fe - OC_2H_5$), 259 ($M^+ - 4CO - Fe - C_8H_8$), 202 ($CF_3C_6H_4COC_2H_5$).

(vii) X-ray Crystal Structure Determination of Complex 7. Single crystals of 7 suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH_2Cl_2 solution at −80 °C. A single crystal of approximate dimensions 0.12 × 0.46 × 0.50 mm³ was sealed in a capillary under a N_2 atmosphere. The X-ray diffraction intensity data of 3819 independent reflections, of which 2496 with $F_o^2 > 3\sigma(F_o^2)$ were observable, were collected with a R_3M/E four-circle diffractometer at room temperature using Mo Kα radiation with a $\theta/2\theta$ scan mode within the range $3° \le 2\theta \le 50°$. The intensity data were corrected for Lorentz and polarization factors. An absorption correction was also made.

Compound 7 crystallizes in the monoclinic system. The space group was determined to be $P2_1/n$ according to the following systematic absences: $h0l$ reflections, $h + l = 2n + 1$; $0k0$ reflections, $k = 2n + 1$. Crystal data for 7: $a = 8.766(2)$ Å, $b = 23.404(5)$ Å, $c = 10.270(2)$ Å, $\beta = 94.25(2)°$, $V = 2101.17(7)$ Å³, $Z = 4$, $D_{calcd} = 1.68$ g/cm³, μ(Mo Kα) = 14.8 cm⁻¹.

The structure was solved by using the Patterson function method. After the positions of the Fe atoms were determined, the coordinates of the other non-hydrogen atoms were located by the Fourier synthesis. The coordinates of all hydrogen atoms were located from the difference Fourier map. The coordinates and thermal parameters of all the atoms were refined by a block-diagonal matrix least-squares method to give the final discrepancy indices $R = 0.0347$ and $R_w = 0.0330$. The atomic coordinates and temperature factors of non-hydrogen atoms for 7 are given in

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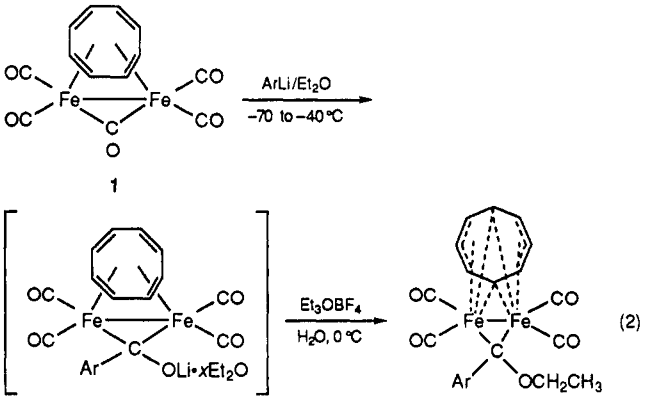
Table I. IR Spectra of Complexes 2–7 in the ν(CO) Region

complex	ν(CO), cm^{-1}				medium
1[14]	2022 s	1992 s	1959 s	1802 s	CS_2
2	2002 w	1990 s	1970 s	1940 s	*n*-hexane
3	2001 w	1995 vs	1969 s	1949 s	*n*-hexane
4	2000 m	1989 vs	1970 s	1940 s	*n*-hexane
5	2001 w	1982 vs	1960 s	1930 s	*n*-hexane
6	2002 m	1994 vs	1978 s	1942 s	*n*-hexane
7	2004 m	1993 vs	1978 s	1945 s	*n*-hexane

Table III, and the bond lengths and angles are presented in Tables IV and V, respectively.

Results and Discussion

Pentacarbonyl(cyclooctatetraene)diiron (1) was treated with a 10–30% molar excess of aryllithium reagents, ArLi (Ar = C_6H_5, *o*-, *m*-, and *p*-$CH_3C_6H_4$, *p*-ClC_6H_4, *p*-$CF_3C_6H_4$), in diethyl ether at −75 to −40 °C for 3–4 h, and the acylmetalate intermediates formed were subsequently alkylated with Et_3OBF_4 in aqueous solution at 0 °C. After removal of the solvents under a high vacuum at low temperature, the solid residue was chromatographed on an alumina column at −20 °C, and the crude product was recrystallized from petroleum ether/CH_2Cl_2 solution at −80 °C to afford dark red crystalline complexes (2–7) with the compositions $C_8H_8(CO)_2\overline{Fe\{\mu\text{-}C(OC_2H_5)Ar\}Fe}(CO)_2$ (eq 2) in 65–74% yields.



2, Ar = C_6H_5
3, Ar = *o*-$CH_3C_6H_4$
4, Ar = *m*-$CH_3C_6H_4$
5, Ar = *p*-$CH_3C_6H_4$
6, Ar = *p*-ClC_6H_4
7, Ar = *p*-$CF_3C_6H_4$

Complexes 2–7 are formulated as the cyclooctatetraene-coordinated bridging carbene complexes on the basis of their elemental analyses and spectroscopic studies and the single-crystal X-ray diffraction study of 7. Complexes 2–7 are the first examples of olefin-bridged dimetal complexes with a bridging carbene ligand, where the olefin ligand bridges the two metal atoms. There are only a few examples of bridging carbene complexes containing an olefin ligand in which a olefin binds only to one metal atom.[24–28]

Table II. ^{1}H NMR Spectra of Complexes 2–7 in Acetone-d_6 at 20 °C[a]

complex	$\delta(C_8H_8)$	δ(aryl)	$\delta(OCH_2CH_3)$
1[14]	4.78 (s)		
2	4.48 (s, 8H)	8.04 (m, 2H), 7.33 (m, 3H)	3.48 (q, 2H), 1.12 (t, 3H)
3	4.46 (s, 8H)	7.36–7.23 (m, 4H), 2.14 (s, 3H)	3.90 (q, 2H), 1.34 (t, 3H)
4	4.47 (s, 8H)	7.85 (m, 2H), 7.20 (m, 2H), 2.39 (s, 3H)	3.46 (q, 2H), 1.13 (t, 3H)
5	4.48 (s, 8H)	7.93 (m, 2H), 7.10 (m, 2H), 2.43 (s, 3H)	3.49 (q, 2H), 1.11 (t, 3H)
6	4.50 (s, 8H)	8.06 (m, 2H), 7.31 (m, 2H)	3.45 (q, 2H), 1.13 (t, 3H)
7	4.53 (s, 8H)	8.26 (m, 2H), 7.63 (m, 2H)	3.47 (q, 2H), 1.14 (t, 3H)

[a] TMS was the internal reference.

Complexes 2–7 are soluble in polar organic solvents but only slightly soluble in nonpolar solvents. They are sensitive to air and temperature in solution but stable for short periods on exposure to air at room temperature in the crystalline state. The IR spectra and the solution ^{1}H NMR spectra, as well as the mass spectra, are consistent with the proposed structure. The IR spectra (Table I) of complexes 2–7 showed three strong and one moderate or weak CO absorption band in the ν(CO) region, in accordance with a $(CO)_2Fe–Fe(CO)_2$ moiety in these complexes. The absorption band at ca. 1800 cm^{-1} attributed to the bridging carbonyl group disappears from each of the complexes, caused by the nucleophilic addition of the aryllithium reagents. In the ^{1}H NMR spectra (Table II) of complexes 2–7, resonances at δ 3.45–3.50 and 1.11–1.34 ppm attributed to ethoxy group (OCH_2CH_3) proton signals and at δ 7.10–8.26 ppm assigned to aryl group proton signals were observed, in addition to the expected proton signal of the cyclooctatetraene ligand. As compared with starting material 1, the chemical shift of the proton signal of the cyclooctatetraene ligand moved upfield, which indicated that the extent of back-donation of d electrons from the central metal iron to the π back-bonding orbital of the coordinated olefin increased, owing to the formation of the bridging carbene ligand. The results of the X-ray single-crystal diffraction study (see below) showed that, in complexes 2–7, the eight-membered ring of the cyclooctatetraene ligand has an approximately planar configuration and is fluxional, thus giving a single-line NMR spectrum at room temperature.[29] The characteristic mass spectral peaks (*m*/*e*) of complexes 2–7 are given in the Experimental Section. All of the complexes showed, besides their molecular ions, the principal fragments produced by successive loss of CO ligands and the feature ion peaks from fragmentation generated by further cleavage of these principal fragments.

The molecular structure of complex 7 is shown in Figure 1. As anticipated from the IR and ^{1}H NMR spectra, of the four terminal carbonyl ligands, two are attached to one iron atom and two to the other iron atom, and the ethoxy and aryl groups are attached to the bridging carbene carbon atom (C). The distance (2.686(1) Å) of the Fe–Fe bond bridged by $C(OC_2H_5)C_6H_4CF_3$-*p* is somewhat longer than that found (2.533(1) Å) in $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)NHPh\}]$.[30] The alkylidene carbon symmetrically

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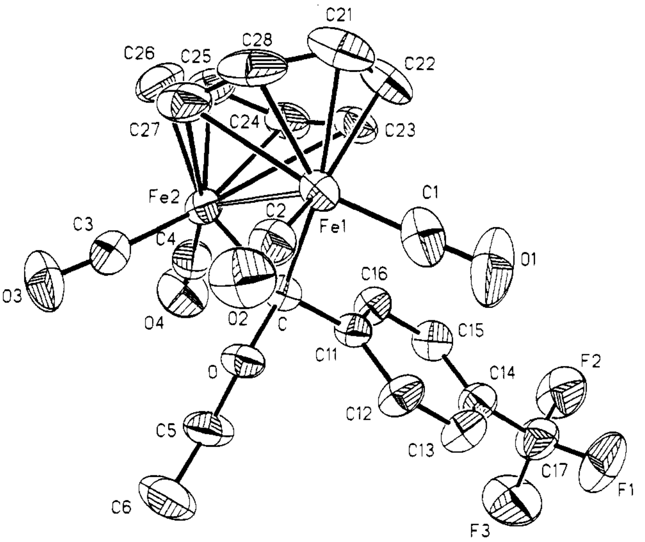

Figure 1. Molecular structure of 7, showing the atom-numbering scheme.

Table III. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for 7

atom	x	y	z	U^a
Fe(1)	11179(1)	1160(1)	6744(1)	38(1)
Fe(2)	9089(1)	1992(1)	6896(1)	36(1)
F(1)	5918(3)	-1190(1)	7878(3)	92(1)
F(2)	4338(3)	-759(1)	6550(3)	81(1)
F(3)	4200(4)	-665(1)	8598(3)	107(1)
O	9869(3)	1305(1)	9197(2)	39(1)
O(1)	11388(4)	-64(1)	7077(4)	97(2)
O(2)	13410(3)	1278(1)	8981(3)	72(1)
O(3)	10060(3)	2729(1)	9085(3)	69(1)
O(4)	5939(3)	2145(1)	7477(3)	69(1)
C	9338(4)	1249(1)	7868(3)	33(1)
C(1)	11275(4)	419(2)	6946(4)	58(2)
C(2)	12516(4)	1242(2)	8120(4)	47(1)
C(3)	9584(4)	2422(2)	8242(4)	43(1)
C(4)	7182(4)	2079(2)	7226(3)	45(1)
C(5)	8727(5)	1428(2)	11097(3)	59(2)
C(6)	9488(6)	1472(2)	11426(4)	80(2)
C(11)	8202(4)	756(2)	7756(3)	36(1)
C(12)	8483(4)	281(2)	8568(4)	49(1)
C(13)	7522(5)	-185(2)	8542(4)	53(1)
C(14)	6225(4)	-197(2)	7678(3)	44(1)
C(15)	5919(4)	268(2)	6864(3)	45(1)
C(16)	6895(4)	735(2)	6908(3)	40(1)
C(17)	5173(5)	-693(2)	7679(4)	60(2)
C(21)	12276(5)	1294(2)	4976(4)	71(2)
C(22)	10877(5)	1023(2)	4685(4)	64(2)
C(23)	9380(5)	1188(2)	4949(3)	48(1)
C(24)	8532(4)	1701(2)	4931(3)	48(1)
C(25)	8949(5)	2280(2)	4954(4)	56(2)
C(26)	10242(5)	2506(2)	5610(4)	61(2)
C(27)	11498(5)	2181(2)	6232(4)	62(2)
C(28)	12521(5)	1765(2)	5769(4)	67(2)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

bridges the Fe–Fe bond (C–Fe(1) = 2.063(3) Å, C–Fe(2) = 2.010(3) Å). This asymmetry is very similar to that in $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)NHPh\}]$ (C(4)–Fe(1) = 2.004(2) Å, C(4)–Fe(2) = 2.028(2) Å).[30] The μ-C–Fe distance in 7 is much longer than that found in $[(\eta^5\text{-}C_5H_5)(CO)Fe(\mu\text{-}CO)(\mu\text{-}COEt)Mn(CO)(\eta^5\text{-}MeC_5H_4)]$ (C(1)–Fe = 1.843(4) Å)[31] but similar to that found in $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)NHPh\}]$ and $[MoFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$.[32]

Table IV. Bond Lengths (Å)[a] for 7

Fe(1)–Fe(2)	2.686(1)	Fe(2)–C	2.010(3)
Fe(1)–C(1)	1.746(4)	Fe(2)–C(4)	1.742(4)
Fe(1)–C(21)	2.140(4)	Fe(2)–C(25)	2.100(4)
Fe(1)–C(23)	2.335(4)	Fe(2)–C(27)	2.309(4)
Fe(1)–C(28)	2.137(5)	F(2)–C(17)	1.333(5)
Fe(2)–C(3)	1.757(4)	O–C	1.415(4)
Fe(2)–C(24)	2.151(3)	O(1)–C(1)	1.144(5)
Fe(2)–C(26)	2.100(5)	O(3)–C(3)	1.154(4)
F(1)–C(17)	1.342(5)	C–C(11)	1.523(5)
F(3)–C(17)	1.320(5)	C(11)–C(12)	1.399(5)
O–C(5)	1.441(5)	C(12)–C(13)	1.378(5)
O(2)–C(2)	1.140(4)	C(13)–C(14)	1.390(5)
O(4)–C(4)	1.148(5)	C(14)–C(15)	1.386(5)
C(5)–C(6)	1.478(5)	C(15)–C(16)	1.387(5)
C(11)–C(16)	1.387(5)	C(21)–C(28)	1.377(7)
C(14)–C(17)	1.483(6)	C(22)–C(23)	1.413(6)
C(21)–C(22)	1.393(6)	C(23)–C(24)	1.412(6)
Fe(1)–C	2.063(3)	C(24)–C(25)	1.405(6)
Fe(1)–C(2)	1.779(4)	C(25)–C(26)	1.379(6)
Fe(1)–C(22)	2.135(4)	C(26)–C(27)	1.447(6)
Fe(1)–C(27)	2.468(5)	C(27)–C(28)	1.429(6)
Fe(2)–C(23)	2.771(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Bond Angles (deg)[a] for 5

Fe(2)–Fe(1)–C	47.9(1)	Fe(2)–Fe(1)–C(1)	137.7(1)
C–Fe(1)–C(1)	93.8(2)	Fe(2)–Fe(1)–C(2)	106.7(1)
C–Fe(1)–C(2)	92.3(1)	C(1)–Fe(1)–C(2)	89.4(2)
Fe(2)–Fe(1)–C(21)	107.1(1)	C–Fe(1)–C(21)	151.6(1)
C(1)–Fe(1)–C(21)	103.1(2)	C(2)–Fe(1)–C(21)	110.3(2)
Fe(2)–Fe(1)–C(22)	97.5(1)	C–Fe(1)–C(22)	121.7(2)
C(1)–Fe(1)–C(22)	88.3(2)	C(2)–Fe(1)–C(22)	146.0(2)
C(21)–Fe(1)–C(22)	38.0(2)	Fe(2)–Fe(1)–C(23)	66.6(1)
C–Fe(1)–C(23)	85.9(1)	C(1)–Fe(1)–C(23)	98.4(2)
C(2)–Fe(1)–C(23)	172.1(2)	C(21)–Fe(1)–C(23)	69.3(1)
C(22)–Fe(1)–C(23)	36.5(2)	Fe(2)–Fe(1)–C(27)	53.0(1)
C–Fe(1)–C(27)	97.3(1)	C(1)–Fe(1)–C(27)	168.8(2)
C(2)–Fe(1)–C(27)	89.2(2)	C(21)–Fe(1)–C(27)	67.1(2)
C(22)–Fe(1)–C(27)	86.6(2)	C(23)–Fe(1)–C(27)	83.4(1)
Fe(2)–Fe(1)–C(28)	87.0(1)	C–Fe(1)–C(28)	132.5(2)
C(1)–Fe(1)–C(28)	133.6(2)	C(2)–Fe(1)–C(28)	87.0(2)
C(21)–Fe(1)–C(28)	37.6(2)	C(22)–Fe(1)–C(28)	70.5(2)
C(23)–Fe(1)–C(28)	88.5(1)	C(27)–Fe(1)–C(28)	35.2(2)
Fe(1)–Fe(2)–C	49.6(1)	Fe(1)–Fe(2)–C(3)	107.3(1)
C–Fe(2)–C(3)	95.2(1)	Fe(1)–Fe(2)–C(4)	139.8(1)
C–Fe(2)–C(4)	94.3(2)	C(3)–Fe(2)–C(4)	90.8(2)
Fe(1)–Fe(2)–C(24)	79.8(1)	C–Fe(2)–C(24)	101.6(1)
C(3)–Fe(2)–C(24)	162.3(2)	C(4)–Fe(2)–C(24)	93.7(2)
Fe(1)–Fe(2)–C(25)	99.8(1)	C–Fe(2)–C(25)	138.3(1)
C(3)–Fe(2)–C(25)	123.8(2)	C(4)–Fe(2)–C(25)	99.1(2)
C(24)–Fe(2)–C(25)	38.6(2)	Fe(1)–Fe(2)–C(26)	90.9(1)
C–Fe(2)–C(26)	140.2(2)	C(3)–Fe(2)–C(26)	92.2(2)
C(4)–Fe(2)–C(26)	124.7(2)	C(24)–Fe(2)–C(26)	71.2(2)
C(25)–Fe(2)–C(26)	38.3(2)	Fe(1)–Fe(2)–C(27)	58.6(1)
C–O–C(5)	116.2(2)	Fe(1)–C–Fe(2)	82.5(1)
Fe(1)–C–O	109.5(2)	Fe(2)–C–O	114.5(2)
Fe(1)–C–C(11)	114.5(2)	Fe(2)–C–C(11)	124.9(2)
O–C–C(11)	108.1(3)	Fe(1)–C(1)–O(1)	177.8(4)
Fe(1)–C(2)–O(2)	177.2(3)	Fe(2)–C(3)–O(3)	176.4(3)
Fe(2)–C(4)–O(4)	177.9(3)	O–C(5)–C(6)	108.6(3)
C–C(11)–C(12)	118.1(3)	C–C(11)–C(16)	125.3(3)
C(13)–C(14)–C(17)	119.6(3)	C(15)–C(14)–C(17)	121.5(3)
C–Fe(2)–C(27)	104.2(1)	C(3)–Fe(2)–C(27)	84.2(2)
C(4)–Fe(2)–C(27)	161.2(2)	C(21)–C(22)–C(23)	130.6(4)
C(22)–C(21)–C(28)	125.9(4)	C(23)–C(24)–C(25)	133.2(4)
C(22)–C(23)–C(24)	136.4(4)	C(25)–C(26)–C(27)	125.8(4)
C(24)–C(25)–C(26)	125.5(4)	C(21)–C(28)–C(27)	131.9(4)
C(26)–C(27)–C(28)	133.4(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

As compared to cyclopolyene-coordinated carbene complex, the μ-C–Fe distance of 7 is longer than the $Fe–C_{carbene}$

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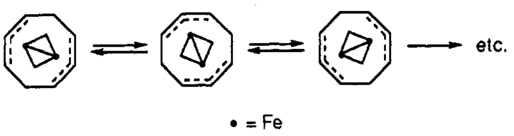
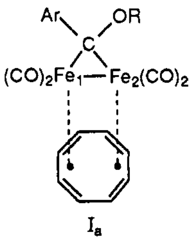
Scheme I. Valence Tautomerism



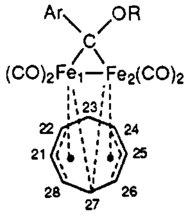
distance (1.89(2) Å) of the (1,3-cyclohexadiene)dicarbonyl[ethoxy(aryl)carbene]iron complex $C_6H_8(CO)_2FeC(OC_2H_5)C_6H_4CH_3$-*o*[33] but is similar to the corresponding Fe–C distance (2.03(1) Å) in the isomerized carbene complex $C_6H_8(CO)_2FeC(OC_2H_5)C_6H_5$.[34]

The bridging carbon atom, C, lies essentially in the plane of the benzene ring (±0.0024 Å). The benzene ring plane is at an angle of 112.0° to the plane comprised of Fe(1), Fe(2), and C, 112.3° to the plane defined by C(21), C(22), C(27), and C(28), and 34.2° to the plane comprised of C(23), C(24), C(25), and C(26). The angles between the Fe(1)Fe(2)C and C(21)C(22)C(27)C(28) planes and the Fe(1)Fe(2)C and C(23)C(24)C(25)C(26) planes are 68.3 and 114.3°, respectively.

When the bond length data of the central metals Fe(1) and Fe(2) to the eight carbon atoms of the cyclooctatetraene ring are compared, it is seen that the average distance (2.14 Å) of Fe(1) to the three η^3-allyl carbon atoms (C(21), C(22), and C(28)) is approximately equal to that (2.22 Å) of Fe(2) to the other three η^3-allyl carbon atoms C(24), C(25), and C(26)). Also, the bond distances of Fe(1)–C(27) (2.468(5) Å) and Fe(2)–C(27) (2.309(4) Å) are nearly equal to that of Fe(1)–C(23) (2.335(4) Å), except the Fe(2)–C(23) distance of 2.771(4) Å is somewhat longer. Hence, we considered that complex 7 does not have the structure shown schematically as I_a, in which the cyclooctatetraene ligand has two η^4 bonds to the two central Fe atoms, but has the structure shown as I_b, in which each Fe atom is coordinated to three ring carbon atoms in a kind of η^3-allyl bonding. Because of the short Fe–Fe bond distance (2.686(1) Å), which is slightly shorter than that found (2.742 Å) in 1,[17] a metal–metal single bond is apparent. After allowance for the metal–CO bonds, each Fe atom has one half-occupied orbital in its valence shell, and the two ring carbon atoms (C(23) and C(27)) which have not been included in the η^3-allyl group each have a half-occupied orbital. These four atoms, four oritals, and four electrons combined to produce a four-center–four-electron delocalized bonding system, thus giving each Fe atom in 18-electron configuration.



I_a



I_b

The cyclooctatetraene ring is not exactly planar but has a slightly twisted configuration, with an angle of 146.4° between the planes C(21)C(22)C(27)C(28) and C(23)C(24)C(25)C(26). The structure shown as I_b seems to have five nonequivalent hydrogen environments in the cyclooctatetraene ligand. However, the ^1H NMR spectrum of complex 7 showed only a single peak attributed to the proton signal of the cyclooctatetraene ring, which may be explained on the basis of rapid degenerate valence tautomerism involving rotation of the Fe–Fe bond about the ring as shown in Scheme I.[17] The structure I_a may be one of the intermediate transition states generated in the course of the valence tautomerism.

A series of dimetal bridging carbene complexes has been synthesized by Stone et al. by reactions[24–26,35] of carbene complexes with low-valent metal species or by reactions[36,37] of neutral carbyne complexes with metal hydrides. Most recently, we reported an unusual reaction of a cationic carbyne complex of rhenium with carbonyl dianion, which also afforded a bridging carbene complex.[38] However, complexes 2–7 are the first dimetal complexes with a bridging carbene ligand synthesized by the reaction of an olefin-ligated dimetal carbonyl compound with nucleophiles followed by alkylation with Et_3OBF_4 in a one-pot reaction. Undoubtedly, this is a direct, simple, and convenient method for the preparation of dimetal bridging carbene complexes.

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Supplementary Material Available: Tables of anisotropic thermal parameters, H atom coordinates and isotropic thermal parameters, least-squares planes, and additional bond angles for 7 (7 pages). Ordering information is given on any current masthead page.

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