Unexpected reactions of (cyclooctatetraene)diiron hexacarbonyl with aryllithium reagents: crystal structures of [(CO)₃Fe(1-4-η:5-7-η-C₈H₉)(CO)₂Fe(COC₆H₅)] and [(CO)₃Fe(1-4-η:5-8-η-C₈H₈)(CO)₂FeC(OC₂H₅)C₆H₅]

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Abstract

The reaction of (cyclooctatetraene)diiron hexacarbonyl (1) with aryllithium reagents ArLi (Ar = C₆H₅, o-, m-, p-CH₃C₆H₄, p-CH₃OC₆H₄) in ether at low temperature afforded acylmetalate intermediates. Subsequent alkylation with Et₃OBF₄ in aqueous solution at 0 °C gave the (8,8-dihydro-1-4-η:5-7-η-cyclooctatrienyl)tricarbonylirondicarbonyl(arylformacyl)iron complexes [(CO)₃Fe(1-4-η:5-7-η-C₈H₉)(CO)₂Fe(COAr)] (2a–e) (2a, Ar = C₆H₅; 2b, Ar = o-CH₃C₆H₄; 2c, Ar = m-CH₃C₆H₄; 2d, Ar = p-CH₃C₆H₄; 2e, Ar = p-CH₃OC₆H₄) and (1-4-η:5-8-η-cyclooctatetraene)tricarbonylirondicarbonyl[ethoxy(aryl)carbene]iron complexes [(CO)₃Fe(1-4-η:5-8-η-C₈H₈)(CO)₂FeC(OC₂H₅)Ar] (3a–e) (3a, Ar = C₆H₅; 3b, Ar = o-CH₃C₆H₄; 3c, Ar = m-CH₃C₆H₄; 3d, Ar = p-CH₃C₆H₄; 3e, Ar = p-CH₃OC₆H₄). The structures of 2a and 3a have been established by X-ray diffraction studies, which indicate that the Fe(CO)₃ unit and the (CO)₂Fe(COC₆H₅) moiety in 2a and the (CO)₂FeC(OC₂H₅)C₆H₅ moiety in 3a are on opposite sides of the cyclooctatetraene ring.

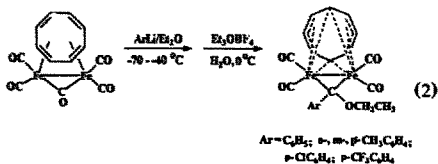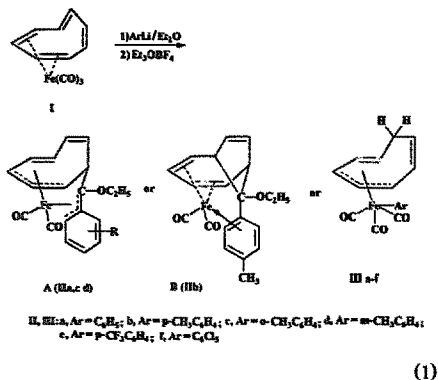*Keywords:* (Cyclooctatetraene)diiron hexacarbonyl; Reaction; Crystal structure

1. Introduction

The current interest in the synthesis, structure, and chemistry of alkene–metal carbene complexes stems from the possible involvement of these species in various reactions of metal carbene complexes with alkenes [1–3]. In the previous papers [4–15] we showed that a series of novel olefin-coordinated transition metal carbene complexes and/or isomerized products have been isolated and several novel isomerizations of olefin ligands have been observed by the reaction of olefin-ligated metalcarbonyls with nucleophiles, followed by alkylation with Et₃OBF₄. We found that the isomerizations and resulting products depend not only on the olefin ligands but also on the central metals [5–10,16,17]. For instance, the reaction of (cycloocta-

tetraene)tricarbonyliron with aryllithium reagents and subsequent alkylation with Et₃OBF₄ results in the formation of novel isomerized carbene complexes with two types of structure, A and B, or (8,8-dihydro-3-5-η-cyclooctatrienyl)tricarbonyliron complexes, depending on the alkylation conditions [5] (Eq. (1)); while pentacarbonyl(cyclooctatetraene)diiron, where the two iron atoms are directly bonded to each other, reacts with aryllithium reagents under the analogous conditions to give dimetal bridging carbene complexes [9] (Eq. (2)). As an extension of our research on the olefin-coordinated metal carbene complexes, we have now studied the reaction of (cyclooctatetraene)diiron hexacarbonyl, C₈H₈[Fe(CO)₃]₂ (1), where the two iron atoms are not directly bonded to each other, for the reaction in order to further investigate the effect of different binuclear central metals on the isomerization of the olefin ligands and reaction products. Several unexpected products, (1-4-η:5-7-η-cyclooctatrienyl)tricarbonylirondicarbonyl(arylformacyl)iron and (1-4-η:5-8-η-cycloocta-

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tetraene)tricarbonylirondicarbonyl[ethoxy(aryl)carbene]-iron complexes, were obtained by the reactions of compound 1 with aryllithium reagents, in a similar manner as previously described [5–9]. Herein we describe the syntheses and structural characterizations of these new complexes.

II, III: a, Ar = C₆H₅; b, Ar = p-CH₃C₆H₄; c, Ar = o-CH₃C₆H₄; d, Ar = m-CH₃C₆H₄; e, Ar = p-CF₃C₆H₄; f, Ar = C₆Cl₅

$$\tag{1}$$

$$\tag{2}$$

2. Experimental section

All procedures were performed under a dry, oxygen-free N_2 atmosphere using standard Schlenk techniques. Solvents were reagent grade and dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under N_2. Diethyl ether (Et₂O) was distilled from sodium benzophenone ketyl, while petroleum ether (30–60 °C) was distilled from CaH₂, and CH₂Cl₂ from P₂O₅. The neutral alumina (Al₂O₃) 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 [18–20], Et₃OBF₄ [21], and aryllithium reagents [22–26] were prepared by literature methods.

The IR spectra were measured on a Zeiss Specord-75 spectrophotometer. All ^{1}H NMR spectra were recorded at ambient temperature in acetone-d_6 solution with TMS as internal reference using a Varian 200 spectrometer. Electron ionization mass spectra (EIMS) were run on a Finnigan 4021 GC/MS/DS spectrometer. Melting points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

2.1. Reaction of $C_8H_8[Fe(CO)_3]_2$ (1) with C_6H_5Li to give $[(CO)_3Fe(1\text{-}4\text{-}\eta\text{:}5\text{-}7\text{-}\eta\text{-}C_8H_9)(CO)_2Fe(COC_6H_5)]$ (2a) and $[(CO)_3Fe(1\text{-}4\text{-}\eta\text{:}5\text{-}8\text{-}\eta\text{-}C_8H_8)\text{-}(CO)_2FeC(OC_2H_5)C_6H_5]$ (3a)

To a solution of 0.40 g (1.04 mmol) of 1 dissolved in 50 ml of ether at −65 °C was added dropwise 2.10 mmol of C_6H_5Li [22] with stirring for 15 min. The reaction mixture was stirred at −60 to −50 °C for 4.5 h, during which time the yellow solution gradually turned dark brown–yellow. The resulting solution then evaporated under high vacuum at −40 to −50 °C to dryness. To the dark brown solid residue obtained was added Et₃OBF₄ [21] (ca. 5 g). This solid mixture was dissolved in 50 ml of N_2-saturated water at 0 °C with vigorous stirring, and the mixture covered with petroleum ether (30–60 °C). Immediately afterwards, Et₃OBF₄ (ca. 10 g) was added portionwise to the aqueous solution, with strong stirring, until it became acidic. The aqueous solution was extracted with petroleum ether. The combined extract was dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was chromatographed on an alumina (neutral, 100–200 mesh) column (1.6 × 15 cm²) at −25 °C with petroleum ether as eluant. After elution of a small yellow band which contains $C_8H_8Fe(CO)_3$, the brown–yellow band was eluted and collected and then an orange–yellow band was eluted with petroleum ether/Et₂O (10:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from petroleum ether/CH₂Cl₂ at −80 °C. From the first fraction, 0.21 g (43% based on 1) of dark red crystals of 2a was obtained, m.p. 62–64 °C decomp. IR (ν_{CO}) (hexane): 2002 (s), 1991 (vs), 1979 (vs), 1940 (w), 1625 (s) cm⁻¹. MS: m/e 462 (M⁺), 434 (M⁺ − CO), 406 (M⁺ − 2CO), 378 (M⁺ − 3CO), 350 (M⁺ − 4CO), 322 (M⁺ − 5CO), 217 (M⁺ − 5CO−COC₆H₅), 104 $(C_8H_9\text{-}H)^+$. Anal. Found: C, 52.25; H, 3.11. $C_{20}H_{14}O_6Fe_2$ Calc.: C, 51.99; H, 3.05%. From the second fraction, 0.20 g (39% based on 1) of orange–red crystalline 3a was obtained, m.p. 69–70 °C decomp. IR (ν_{CO}) (hexane): 2050 (vs), 1990 (vs), 1980 (sh), 1960 (m), 1944 (s) cm⁻¹. MS: m/e 490 (M⁺), 462 (M⁺ − CO), 434 (M⁺ − 2CO), 406 (M⁺ − 3CO), 378 (M⁺ − 4CO), 350 (M⁺ − 5CO), 216 (M⁺ − 5CO−C(OC₂H₅)−C₆H₅), 104 $(C_8H_8)^+$. Anal. Found: C, 54.37; H, 3.64. $C_{22}H_{18}O_6Fe_2$ Calc.: C, 53.92; H, 3.70%.

2.2. Reaction of 1 with o-CH₃C₆H₄Li to give [(CO)₃Fe(1-4-η:5-7-η-C₈H₉)(CO)₂Fe(COC₆H₄CH₃-o)] (2b) and [(CO)₃Fe(1-4-η:5-8-η-C₈H₈)-(CO)₂FeC(OC₂H₅)C₆H₄CH₃-o] (3b)

Similar to the procedures described above in Section 2.1, the reaction of 1 (0.70 g, 1.82 mmol) with 3.70 mmol of o-CH₃C₆H₄Li [23] at −60 to −50°C for 4 h, followed by alkylation and further treatment, afforded 0.35 g (40% based on 1) of dark red crystalline 2b and 0.39 g (42% based on 1) of 3b as orange–red crystals. 2b: m.p. 38–90°C decomp. IR (ν_{CO}) (hexane): 2004 (s), 1994 (vs), 1982 (vs), 1942 (w), 1620 (s) cm⁻¹. MS: m/e 476 (M⁺), 448 (M⁺ − CO), 420 (M⁺ − 2CO), 392 (M⁺ − 3CO), 364 (M⁺ − 4CO), 336 (M⁺ − 5CO), 217 (M⁺ − 5CO–COC₆H₄CH₃), 104 (C₈H₉–H)⁺. Anal. Found: C, 52.85; H, 3.02. C₂₁H₁₆O₆Fe₂ Calc.: C, 52.98; H, 3.39%. 3b: m.p. 82–83°C decomp. IR (ν_{CO}) (hexane): 2030 (vs), 1995 (s), 1978 (s), 1960 (m), 1942 (s) cm⁻¹. MS: m/e 504 (M⁺), 476 (M⁺ − CO), 448 (M⁺ − 2CO), 420 (M⁺ − 3CO), 392 (M⁺ − 4CO), 364

(M⁺ − 5CO), 216 (M⁺ − 5CO–C(OC₂H₅)C₆H₄CH₃), 104 (C₈H₈)⁺. Anal. Found: C, 54.85; H, 3.90. C₂₃H₂₀O₆Fe₂ Calc.: C, 54.80, H, 4.00%.

2.3. Reaction of 1 with m-CH₃C₆H₄Li to give [(CO)₃Fe(1-4-η:5-7-η-C₈H₉)(CO)₂Fe(COC₆H₄CH₃-m)] (2c) and [(CO)₃Fe(1-4-η:5-8-η-C₈H₈)-(CO)₂FeC(OC₂H₅)C₆H₄CH₃-m] (3c)

The reaction of 0.70 g (1.82 mmol) of 1 with 3.70 mmol of m-CH₃C₆H₄Li [23] was as described above in Section 2.1 at −60 to −50°C for 5 h. After evaporation of the solvent in vacuo, further treatment of the resulting residue in a manner similar to that described in Section 2.1 gave 0.36 g (41% based on 1) of dark red crystals of 2c and 0.40 g (43% based on 1) of 3c as orange–red crystals. 2c: m.p. 86–88°C decomp. IR (ν_{CO}) (hexane): 2003 (s), 1990 (vs), 1980 (vs), 1944 (w), 1622 (s) cm⁻¹. MS: m/e 476 (M⁺), 448 (M⁺ − CO), 420 (M⁺ − 2CO), 392 (M⁺ − 3CO), 364 (M⁺ −

Table 1
Crystal data and experimental details for complexes 2a and 3a

	2a	3a
formula	C₂₀H₁₄O₆Fe₂	C₂₂H₁₇O₆Fe₂
formula weight	462.02	489.07
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	8.229(6)	10.997(4)
b (Å)	6.891(4)	14.532(9)
c (Å)	32.949(6)	7.044(4)
α (°)	90	99.78(5)
β (°)	94.89(4)	93.89(4)
γ (°)	90	112.04(3)
V (Å³)	1861(1)	1017(1)
Z	4	2
d_{calc} (g cm⁻³)	1.648	1.596
crystal size (cm³)	0.20 × 0.20 × 0.30	0.20 × 0.10 × 0.20
μ (Mo Kα) (cm⁻¹)	15.91	14.61
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
diffractometer	Rigaku AFC7R	Rigaku AFC7R
temperature (°C)	20	20
orientation reflections: no.; range 2θ (°)	25; 18.5–21.2	24; 13.5–23.0
scan method	ω–2θ	ω–2θ
data collection range 2θ (°)	5–45	5–45
No. of unique data, total	2506	2539
with $I > 3.00\sigma(I)$	1354	1166
No. of parameters refined	253	271
correction factors: max., min. (DIFABS)	1.0000, 0.8426	1.0000, 0.8266
R [a]	0.038	0.068
R_w [b]	0.039	0.065
quality-of-fit indicator [c]	1.50	2.40
largest shift/e.s.d. final cycle	0.00	0.01
largest peak (e Å⁻³)	0.32	0.78
minimum peak (e Å⁻³)	−0.31	−0.54

[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 $[\Sigma_w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

4CO), 336 (M$^+$ − 5CO), 217 (M$^+$ − 5CO–COC$_6$H$_4$CH$_3$), 104 (C$_8$H$_9$–H)$^+$. Anal. Found: C, 52.51; H, 3.75. C$_{21}$H$_{16}$O$_6$Fe$_2$ Calc.: C, 52.98; H, 3.39. **3c**: m.p. 62–64 °C decomp. IR: (ν_{CO}) (hexane): 2015 (vs), 1988 (vs), 1975 (sh), 1955 (m), 1938 (s) cm^{-1}. MS: m/e 504 (M$^+$), 476 (M$^+$ − CO), 448 (M$^+$ − 2CO), 420 (M$^+$ − 3CO), 392 (M$^+$ − 4CO), 364 (M$^+$ − 5CO), 216 (M$^+$ − 5CO–C(OC$_2$H$_5$)C$_6$H$_4$CH$_3$), 104 (C$_8$H$_8$)$^+$. Anal. Found: C, 54.45; H, 3.80. C$_{23}$H$_{20}$O$_6$Fe$_2$ Calc.: C, 54.80; H, 4.00%.

2.4. Reaction of 1 with p-CH$_3$C$_6$H$_4$Li to give [(CO)$_3$Fe(1-4-η:5-7-η-C$_8$H$_9$)(CO)$_2$Fe(COC$_6$H$_4$CH$_3$-p] (2d) and [(CO)$_3$Fe(1-4-η:5-8-η-C$_8$H$_8$)-(CO)$_2$FeC(OC$_2$H$_5$)C$_6$H$_4$CH$_3$-p] (3d)

Compound **1** (0.70 g, 1.82 mmol) was treated, in a manner similar to that described in Section 2.1, with 3.70 mmol of *p*-CH$_3$C$_6$H$_4$Li [23] at − 60 to − 50 °C for 5 h, followed by alkylation and further treatment as described above for the preparation of **2a** and **3a** to yield 0.33 g (38% based on **1**) of dark red crystals of **2d**

and 0.42 g (46% based on **1**) of orange–red crystalline **3d**. **2d**: m.p. 76–78 °C decomp. IR (ν_{CO}) (hexane): 2002 (s), 1990 (vs), 1979 (vs), 1942 (m), 1624 (s) cm^{-1}. MS: m/e 476 (M$^+$), 448 (M$^+$ − CO), 420 (M$^+$ − 2CO), 392 (M$^+$ − 3CO), 364 (M$^+$ − 4CO), 336 (M$^+$ − 5CO), 217 (M$^+$ − 5CO–COC$_6$H$_4$CH$_3$), 104 (C$_8$H$_9$–H)$^+$. Anal. Found: C, 52.84; H, 3.77. C$_{21}$H$_{16}$O$_6$Fe$_2$ Calc.: C, 52.98; H, 3.39. **3d**: m.p. 54–56 °C decomp. IR (ν_{CO}) (hexane): 2010 (vs), 1981 (vs), 1970 (sh), 1952 (m), 1938 (s) cm^{-1}. MS: m/e 504 (M$^+$), 476 (M$^+$ − CO), 448 (M$^+$ − 2CO), 420 (M$^+$ − 3CO), 392 (M$^+$ − 4CO), 364 (M$^+$ − 5CO), 216 (M$^+$ − 5CO–C(OC$_2$H$_5$)C$_6$H$_4$CH$_3$), 104 (C$_8$H$_8$)$^+$. Anal. Found: C, 55.16; H, 4.06. C$_{23}$H$_{20}$O$_6$Fe$_2$ Calc.: C, 54.80; H, 4.00%.

2.5. Reaction of 1 with p-CH$_3$OC$_6$H$_4$Li to give [(CO)$_3$Fe(1-4-η:5-7-η-C$_8$H$_9$)(CO)$_2$Fe(COC$_6$H$_4$OCH$_3$-p] (2e) and [(CO)$_3$Fe(1-4-η:5-8-η-C$_8$H$_8$)-(CO)$_2$FeC(OC$_2$H$_5$)C$_6$H$_4$OCH$_3$-p] (3e)

A solution of 0.70 g (3.74 mmol) of *p*-CH$_3$OC$_6$H$_4$Br in 20 ml of ether was mixed with 3.74 mmol of *n*-

Table 2
Positional parameters and their estimated standard deviations [a] for **2a** and **3a**

Atom	**2a**				**3a**			
	x	y	z	B_{eq} (Å^2)	x	y	z	B_{eq} (Å^2)
Fe(1)	0.1057(1)	0.3234(2)	0.93467(3)	3.54(3)	0.8196(3)	0.0973(2)	0.3401(5)	2.88(10)
Fe(2)	0.4313(1)	0.1985(2)	0.85274(3)	2.90(3)	0.7132(3)	0.3262(2)	0.1138(4)	2.77(9)
O(1)	0.3365(8)	0.406(1)	1.0048(2)	8.8(2)	0.940(2)	0.256(1)	0.689(3)	6.5(6)
O(2)	−0.0892(8)	0.6772(10)	0.9202(2)	6.3(2)	1.030(2)	0.030(1)	0.282(3)	6.2(6)
O(3)	−0.1552(7)	0.162(10)	0.9787(2)	6.8(2)	0.675(1)	−0.063(1)	0.539(2)	5.1(5)
O(4)	0.3059(8)	−0.1768(9)	0.8235(2)	6.6(2)	0.610(1)	0.165(1)	−0.225(2)	4.2(5)
O(5)	0.3735(6)	0.4244(8)	0.7773(2)	4.4(2)	0.841(2)	0.489(1)	−0.094(3)	6.6(6)
O(6)	0.7005(7)	−0.0342(8)	0.8411(2)	6.1(2)	0.450(1)	0.331(1)	0.126(2)	5.0(5)
C(1)	0.202(1)	0.039(1)	0.9326(2)	4.0(2)	0.882(2)	0.190(2)	0.126(3)	4.4(7)
C(2)	0.1103(9)	0.094(1)	0.8960(2)	3.4(2)	0.776(2)	0.089(2)	0.051(3)	3.0(6)
C(3)	0.1535(8)	0.260(1)	0.8742(2)	2.9(2)	0.661(20	0.062(2)	0.130(3)	3.3(6)
C(4)	0.2695(9)	0.412(1)	0.8890(2)	3.0(2)	0.648(2)	0.126(2)	0.292(4)	3.8(7)
C(5)	0.4500(10)	0.415(1)	0.8982(2)	3.4(2)	0.652(2)	0.234(2)	0.320(3)	2.5(6)
C(6)	0.5517(10)	0.258(1)	0.9091(2)	4.1(2)	0.762(2)	0.333(2)	0.406(3)	4.1(7)
C(7)	0.5015(10)	0.064(1)	0.9099(2)	3.9(2)	0.877(2)	0.361(2)	0.315(3)	3.2(6)
C(8)	0.3775(10)	−0.016(1)	0.9368(2)	4.7(2)	0.887(2)	0.294(2)	0.149(3)	3.2(6)
C(9)	0.245(1)	0.380(1)	0.9770(3)	5.4(3)	0.896(2)	0.197(2)	0.548(4)	4.7(7)
C(10)	−0.012(1)	0.542(3)	0.9346(3)	4.2(2)	0.945(30)	0.061(2)	0.315(4)	5.6(9)
C(11)	−0.535(10)	0.227(1)	0.9613(2)	4.8(3)	0.732(2)	0.000(2)	0.465(4)	4.9(8)
C(12)	0.3574(10)	−0.031(1)	0.8340(2)	3.9(2)	0.652(3)	0.233(2)	−0.085(3)	4.2(8)
C(13)	0.3937(8)	0.343(1)	0.8074(2)	3.2(2)	0.791(3)	0.427(1)	−0.007(3)	2.6(6)
C(14)	0.6476(10)	0.130(1)	0.8350(2)	3.7(2)	0.587(2)	0.381(2)	0.163(3)	3.4(7)
C(15)	0.7541(9)	0.274(1)	0.8149(2)	3.3(2)	0.600(2)	0.485(2)	0.259(3)	3.4(6)
C(16)	0.8559(8)	0.196(1)	0.7865(2)	3.2(2)	0.731(2)	0.551(2)	0.356(3)	4.7(7)
C(17)	0.9635(9)	0.320(1)	0.7695(2)	3.7(2)	0.756(3)	0.648(2)	0.455(4)	5.3(8)
C(18)	0.9754(9)	0.514(1)	0.7800(2)	3.9(2)	0.661(3)	0.685(2)	0.459(4)	5.0(7)
C(19)	0.8738(9)	0.589(1)	0.8076(2)	3.7(2)	0.536(3)	0.624(2)	0.350(4)	5.4(9)
C(20)	0.7618(9)	0.469(1)	0.8247(2)	3.1(2)	0.504(2)	0.523(2)	0.252(3)	3.0(6)
C(21)					0.384(2)	0.226(2)	0.021(3)	4.4(7)
C(22)					0.233(2)	0.206(2)	0.001(4)	6.9(8)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $8/3\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^* bb^* \cos\gamma + 2U_{13}aa^* cc^* \cos\beta + 2U_{23}bb^* cc^* \cos\alpha]$.

C_4H_9Li [24]. After 30 min stirring at room temperature, the resulting ether solution of p-$CH_3OC_6H_4Li$ [25] was reacted, as described in Section 2.1, with 0.70 g (1.82 mmol) of **1** at -60 to $-50°C$ for 5 h, followed by alkylation; further treatment as described for the preparation of **2a** and **3a** gave 0.37 g (41% based on **1**) of dark red crystalline **2e** and 0.38 g (40% based on **1**) of **3e** as orange–red crystals. **2e**: m.p. 71–73°C decomp. IR (ν_{CO}) (hexane): 2005 (s), 1992 (vs), 1980 (vs), 1938 (m), 1602 (s) cm^{-1}. MS: m/e 492 (M$^+$), 464 (M$^+$ – CO), 436 (M$^+$ – 2CO), 408 (M$^+$ – 3CO), 380 (M$^+$ – 4CO), 352 (M$^+$ – 5CO), 217 (M$^+$ – 5CO– $COC_6H_4OCH_3$), 104 (C_8H_9–H)$^+$. Anal. Found: C, 51.70; H, 3.58. $C_{21}H_{16}O_7Fe_2$ Calc.: C, 51.26; H, 3.28%. **3e**: m.p. 80–82°C decomp. IR (ν_{CO}) (hexane): 2030 (vs), 1987 (vs), 1976 (sh), 1961 (s), 1945 (s) cm^{-1}. MS: m/e 520 (M$^+$), 492 (M$^+$ – CO), 464 (M$^+$ – 2CO), 436 (M$^+$ – 3CO), 408 (M$^+$ – 4CO), 380 (M$^+$ – 5CO), 216 (M$^+$ – 5CO–$C(OC_2H_5)C_6H_4OCH_3$), 104 (C_8H_8)$^+$. Anal. Found: C, 52.92; H, 3.80. $C_{23}H_{20}O_7Fe_2$ Calc.: C, 53.11; H, 3.88%.

2.6. Reaction of **1** with p-$CF_3C_6H_4Li$ to give $C_8H_8Fe(CO)_3$, (4) and (p-$CF_3C_6H_4$)$CO(C_2H_5)$ (5)

Compound **1** (0.70 g, 1.82 mmol) was reacted, in a manner similar to that described in Section 2.1, with fresh p-$CF_3C_6H_4Li$ [26] prepared by the reaction of 0.86 g (3.80 mmol) of p-$CF_3C_6H_4Br$ with 3.80 mmol of

n-C_4H_9Li in ether solution at -60 to $-50°C$ for 4 h. Subsequent alkylation took place, similar to that chromatographed on Al_2O_3 (neutral) with petroleum ether as eluant. A red band which eluted first was collected, and then a light yellow band was eluted with petroleum ether/Et$_2$O (20:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from petroleum ether solution at $-80°C$. From the first fraction, 0.21 g (48% based on **1**) of bright red crystals of **4** [18] was obtained, m.p. 91–92°C (lit. 93–95°C [18]). IR (ν_{CO}) (hexane): 2050 (s), 1995 (vs), 1982 (s) cm^{-1} (lit. [18] (CS$_2$): 2058, 1992 cm^{-1}). ^{1}H NMR (acetone-d_6): δ 5.35 (s) (lit. (CS$_2$): δ 5.18 (s) [18]). MS: m/e 244 (M$^+$). Anal. Found: C, 54.38; H, 3.24. $C_{11}H_8O_3Fe$ Calc.: C, 54.14; H, 3.30%. From the second fraction, 0.15 g (41% based on **1**) of white crystals of **5** [27] was obtained, m.p. 29–31°C (lit. 32–33°C [27]). IR: ($\nu_{C=O}$) (KCl): 1612 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.00 (dd, 4H, CF$_3$C$_6$H$_4$), 3.18 (q, 2H, CH_2CH$_3$), 1.18 (t, 3H, CH$_2$CH_3). MS: m/e 202 (M$^+$). Anal. Found: C, 59.07; H, 4.36. $C_{10}H_9OF_3$ Calc.: C, 59.41; H, 4.49%.

2.7. X-ray crystal structure determinations of complexes **2a** and **3a**

Single crystals of **2a** and **3a** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH$_2$Cl$_2$ solution at $-80°C$. Single

Table 3
Bond lengths (Å) [a] for complexes **2a** and **3a**

	2a	3a		2a	3a
Fe(1)–C(1)	2.116(9)	2.17(2)	Fe(1)–C(2)	2.033(8)	2.04(2)
Fe(1)–C(3)	2.111(7)	2.05(2)	Fe(1)–C(4)	2.191(7)	2.10(2)
Fe(1)–C(9)	1.771(10)	1.78(3)	Fe(1)–C(10)	1.805(10)	1.66(2)
Fe(1)–C(11)	1.769(9)	1.79(3)	Fe(2)–C(5)	2.100(7)	2.12(2)
Fe(2)–C(6)	2.071(8)	2.06(2)	Fe(2)–C(7)	2.135(8)	2.06(2)
Fe(2)–C(8)		2.14(2)	Fe(2)–C(12)	1.788(9)	1.67(2)
Fe(2)–C(13)	1.799(9)	1.79(2)	Fe(2)–C(14)	1.977(8)	1.87(2)
O(1)–C(9)	1.149(9)	1.14(2)	O(2)–C(10)	1.132(9)	1.20(2)
O(3)–C(11)	1.145(8)	1.13(2)	O(4)–C(12)	1.131(9)	1.20(2)
O(5)–C(13)	1.140(8)	1.15(2)	O(6)–C(14)	1.221(9)	1.39(2)
O(6)–C(21)		1.46(2)	C(1)–C(2)	1.421(10)	1.47(3)
C(1)–C(8)	1.49(1)	1.46(3)	C(2)–C(3)	1.408(10)	1.36(3)
C(3)–C(4)	1.477(10)	1.40(3)	C(4)–C(5)	1.490(10)	1.53(3)
C(5)–C(6)	1.38(1)	1.48(3)	C(6)–C(7)	1.40(1)	1.41(3)
C(7)–C(8)	1.51(1)	1.43(3)	C(14)–C(15)	1.518(10)	1.49(3)
C(15)–C(16)	1.416(10)	1.44(3)	C(15)–C(20)	1.38(1)	1.35(3)
C(16)–C(17)	1.38(1)	1.38(3)	C(17)–C(18)	1.38(1)	1.34(3)
C(18)–C(19)	1.389(10)	1.41(3)	C(19)–C(20)	1.395(10)	1.41(3)
C(21)–C(22)		1.56(3)			

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

crystals of approximate dimensions $0.20 \times 0.20 \times 0.30\,mm^3$ for **2a** and $0.20 \times 0.10 \times 0.20\,mm^3$ for **3a** were sealed in capillaries under an N_2 atmosphere. The X-ray diffraction intensity data for 2506 and 2539 independent reflections, of which 1354 and 1166 with $I > 3.00\sigma(I)$ were observable, were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo Kα radiation with an ω–2θ scan mode within the ranges $5° \le 2\theta \le 45°$ for **2a** and **3a** respectively. The intensity data were corrected for Lorentz and polarization factors. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in

transmission factors ranging from 0.84 to 1.00 for **2a** and 0.83 to 1.00 for **3a**.

The crystal structures of **2a** and **3a** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. For **2a**, the final cycle of full-matrix least-squares refinement was based on 1354 observed reflections ($I > 3.00\sigma(I)$) and 253 variable parameters and converged (largest parameter 0.00 times its e.s.d.) with unweighted and weighted agreement factors of $R = 0.038$ and $R_w = 0.039$. For **3a**, the final cycle of full-matrix least-squares

Table 4
Bond angles (°) [a] for complexes **2a** and **3a**

	2a	3a		2a	3a
C(1)–Fe(1)–C(2)	40.0(3)	40.8(8)	C(1)–Fe(1)–C(3)	71.1(3)	70.9(8)
C(1)–Fe(1)–C(4)	89.0(3)	82.1(8)	C(1)–Fe(1)–C(9)	90.5(4)	96(1)
C(1)–Fe(1)–C(10)	164.3(4)	90(1)	C(1)–Fe(1)–C(11)	87.9(4)	164.5(10)
C(2)–Fe(1)–C(3)	39.7(3)	39.0(8)	C(2)–Fe(1)–C(4)	75.0(3)	70.9(8)
C(2)–Fe(1)–C(9)	128.3(4)	135(1)	C(2)–Fe(1)–C(10)	124.8(4)	94(1)
C(2)–Fe(1)–C(11)	94.2(4)	123(1)	C(3)–Fe(1)–C(4)	40.1(3)	39.3(8)
C(3)–Fe(1)–C(9)	129.0(3)	133(10)	C(3)–Fe(1)–C(10)	98.1(3)	125(1)
C(3)–Fe(1)–C(11)	126.6(3)	94.3(9)	C(4)–Fe(1)–C(9)	94.8(3)	96(1)
C(4)–Fe(1)–C(10)	89.5(3)	164(1)	C(4)–Fe(1)–C(11)	166.3(3)	89.4(9)
C(9)–Fe(1)–C(10)	105.2(4)	97(1)	C(9)–Fe(1)–C(11)	98.6(4)	97(1)
C(10)–Fe(1)–C(11)	89.8(4)	94(1)	C(5)–Fe(2)–C(6)	38.7(3)	41.6(8)
C(5)–Fe(2)–C(7)	71.3(3)	72.8(7)	C(5)–Fe(2)–C(8)		83.1(8)
C(5)–Fe(2)–C(12)	150.7(3)	97.1(9)	C(5)–Fe(2)–C(13)	101.6(3)	165.4(9)
C(5)–Fe(2)–C(14)	111.5(3)	91.4(8)	C(6)–Fe(2)–C(7)	39.0(3)	39.99(8)
C(6)–Fe(2)–C(8)		71.5(8)	C(6)–Fe(2)–C(12)	127.5(4)	135.0(10)
C(6)–Fe(2)–C(13)	132.1(4)	123.9(9)	C(6)–Fe(2)–C(14)	86.5(3)	92.5(9)
C(7)–Fe(2)–C(8)		39.8(8)	C(7)–Fe(2)–C(12)	88.7(4)	128(1)
C(7)–Fe(2)–C(13)	170.9(3)	95.2(9)	C(7)–Fe(2)–C(14)	88.5(3)	121.5(9)
C(8)–Fe(2)–C(12)		90.1(10)	C(8)–Fe(2)–C(13)		93.0(9)
C(8)–Fe(2)–C(14)		161.3(9)	C(12)–Fe(2)–C(13)	100.0(4)	97.0(10)
C(12)–Fe(2)–C(14)	88.5(3)	108(1)	C(13)–Fe(2)–C(14)	89.0(3)	87.9(9)
C(14)–O(6)–C(12)		122(1)	Fe(1)–C(1)–C(2)	66.8(5)	64(10)
Fe(1)–C(1)–C(8)	126.7(6)	123(1)	C(2)–C(1)–C(8)	126.0(7)	133(10)
Fe(1)–C(2)–C(1)	73.2(5)	74(1)	Fe(1)–C(2)–C(3)	73.2(4)	71(1)
C(1)–C(2)–C(3)	120.6(7)	119(1)	Fe(1)–C(3)–C(2)	67.1(4)	69(1)
Fe(1)–C(3)–C(4)	72.8(4)	72(1)	C(2)–C(3)–C(4)	126.3(7)	120(1)
Fe(1)–C(4)–C(3)	67.1(4)	68(1)	Fe(1)–C(4)–C(5)	121.6(5)	122(1)
C(3)–C(4)–C(5)	132.3(7)	131(2)	Fe(2)–C(5)–C(4)	81.0(4)	123(1)
Fe(2)–C(5)–C(6)	69.5(5)	67(1)	C(4)–C(5)–C(6)	128.4(8)	130(1)
Fe(2)–C(6)–C(5)	71.8(4)	71(1)	Fe(2)–C(6)–C(7)	73.0(5)	69(1)
C(5)–C(6)–C(7)	124.6(8)	118(1)	Fe(2)–C(7)–C(6)	68.1(5)	70(1)
Fe(2)–C(7)–C(8)	122.0(5)	73(1)	C(6)–C(7)–C(8)	125.0(8)	120(1)
Fe(2)–C(8)–C(1)		122(1)	Fe(2)–C(8)–C(7)		66(1)
C(1)–C(8)–C(7)	123.5(6)	130(1)	Fe(1)–C(9)–O(1)	176(1)	174(2)
Fe(1)–C(10)–O(2)	176.3(8)	174(2)	Fe(1)–C(11)–O(3)	179.0(9)	178(2)
Fe(2)–C(12)–O(4)	176.9(8)	178(1)	Fe(2)–C(13)–O(5)	175.6(7)	176(1)
Fe(2)–C(14)–O(6)	119.4(6)	127(1)	Fe(2)–C(14)–C(15)	122.7(6)	131(1)
O(6)–C(14)–C(15)	117.9(7)	100(1)	C(14)–C(15)–C(16)	115.6(7)	114(1)
C(14)–C(15)–C(20)	123.5(7)	126(2)	C(16)–C(15)–C(20)	120.7(7)	119(2)
C(15)–C(16)–C(17)	117.7(8)	120(2)	C(15)–C(17)–C(18)	122.1(7)	121(2)
C(17)–C(18)–C(19)	119.5(8)	117(2)	C(18)–C(19)–C(20)	119.9(8)	122(2)
C(15)–C(20)–C(19)	120.1(7)	118(2)	O(6)–C(21)–C(22)		104(1)

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

refinement was based on 1166 observed reflections ($I > 3.00\sigma(I)$) and 271 variable parameters and converged (largest parameter 0.01 times its e.s.d.) with unweighted and weighted agreement factors of $R = 0.068$ and $R_w = 0.065$.

The standard deviations of an observation of unit weight were 1.50 and 2.40 for **2a** and **3a** respectively. The weighting scheme was based on counting statistics and included a factor ($p = 0.020$) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.32 and $-0.31\,e\,\text{Å}^{-3}$ for **2a** and 0.78 and $-0.54\,e\,\text{Å}^{-3}$ for **3a** respectively. All the calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation.

Details of the crystallographic data and the procedures used for data collection and reduction information for **2a** and **3a** are given in Table 1. The positional parameters and temperature factors of the non-hydrogen atoms for **2a** and **3a** are presented in Table 2. The bond lengths and bond angles for **2a** and **3a** are listed in Tables 3 and 4 respectively.

3. Results and discussion

Similar to the reaction of pentacarbonyl(cyclooctatetraene)diiron with aryllithium reagents [9], (cyclooctatetraene)diiron hexacarbonyl $C_8H_8[Fe(CO)_3]_2$ (1) was treated with two molar equivalents of aryllithium reagents ArLi (Ar = C_6H_5, o-, m-, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$) in ether at -60 to $-50\,°C$ for 4 to 5 h, and the acyimetalate intermediates formed were subsequently alkylated with Et_3OBF_4 in an aqueous solution at 0 °C. After removal of the solvents under high vacuum at low temperature, the residues were chromatographed on an alumina column at -20 to $-25\,°C$, and the crude products were recrystallized from petroleum ether/CH_2Cl_2 solution at $-80\,°C$ to give dark red crystalline complexes **2a–e** with compositions [(CO)$_3$Fe(1-4-η:5-7-η-C_8H_9)(CO)$_2$Fe(COAr)] and orange–red crystalline complexes **3a–e** with compositions [(CO)$_3$Fe(1-4-η:5-8-η-C_8H_8)(CO)$_2$-FeC(OC$_2H_5$)Ar] (Eq. (3)) in 38–43% and 39–46% yield respectively.

(3)
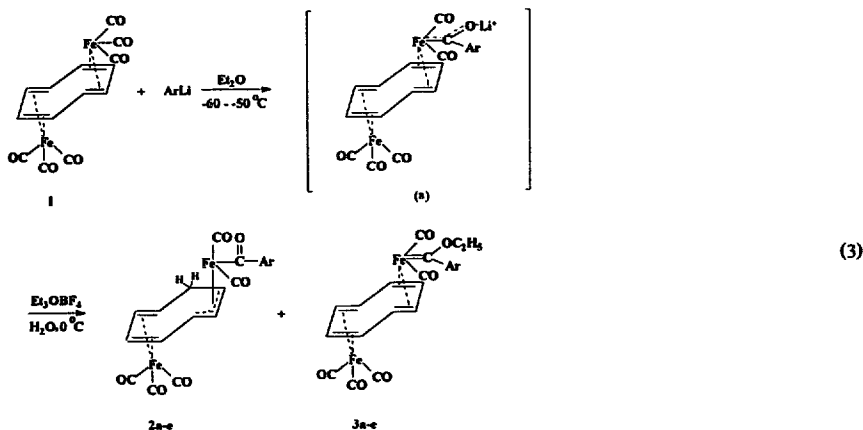
2, 3: a, Ar = C_6H_5; b, Ar = o-$CH_3C_6H_4$; c, Ar = m-$CH_3C_6H_4$;
d, Ar = p-$CH_3C_6H_4$; e, Ar = p-$CH_3OC_6H_4$

When only one, instead of two, equivalents of aryllithium reagents was used for the reaction under the same conditions, the same products **2a–e** (35–40%) and **3a–e** (36–42%) were obtained in somewhat lower yields. However, when p-$CF_3C_6H_4$Li was used for the reaction with **1** under the same conditions, no analogous

products of **2** or **3** were obtained, but (cyclooctatetraene)tricarbonyliron, $C_8H_8Fe(CO)_3$, (4), [18] and p-trifluoromethylpropiophenone, (p-$CF_3C_6H_4$)$CO(C_2H_5)$ (5), [27] were isolated (Eq. (4)) in 48% and 41% yield respectively.

$$(4)$$
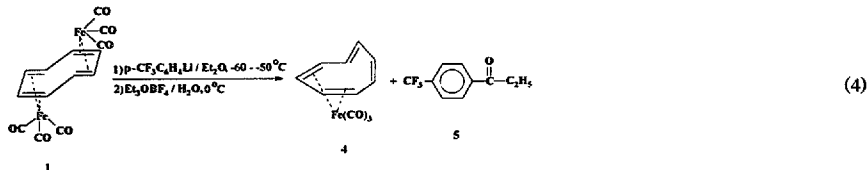
Complexes **2a–e** and **3a–e** are formulated as (8,8-dihydro-1-4-η:5-7-η-cyclooctatrienyl)tricarbonylirondicarbonyl(arylformacyl)iron and (1-4-η:5-8-η-cyclooctatraene)tricarbonylirondicarbonyl[ethoxy(aryl)carbene]iron complexes respectively, on the basis of their elemental analyses, and IR, ^{1}H NMR and mass spectra, as well as the single crystal X-ray diffraction studies of complexes **2a** and **3a**. Since there are two Fe(CO)$_3$ units in the starting material **1**, there should exist dialkoxycarbeneiron complexes and/or diacyliron complexes in the resulting products when treating **1** with aryllithium reagents. However, no expected dialkoxycarbeneiron and/or diacyliron complexes were obtained from the reactions, even though more than two molar equivalents of the aryllithium reagents were used for the reaction.

A possible mechanism for the formation of complexes **2a–e** and **3a–e** might involve the acylmetalate intermediates (a) formed by attack of aryllithium nucleophiles on one of the two Fe(CO)$_3$ units. That the acylmetalate intermediate (a) formed upon subsequent alkylation with Et$_3$OBF$_4$ in aqueous solution gave the carbene complexes **3a–e** accompanied by acyliron complexes **2a–e** having a 16-electron configuration for the acyliron moiety suggests that an isomerization of hydroxycarbene iron complexes generated from hydrolysis of intermediate (a) in the alkylation step occurred simultaneously to yield products **2a–e** and **3a–e**, as shown in Eq. (3). Meanwhile, the mechanism of the reaction of compound **1** with p-CF$_3$C$_6$H$_4$Li in Eq. (4) is not clear, but it could proceed via analogous acylmetalate intermediate (a) which was then converted into an unstable alkoxycarbene complex upon subsequent alkylation with Et$_3$OBF$_4$. The latter undergoes decomposition to lose the carbeneiron moiety, leading to the formation of complexes **4** and **5** owing to its extreme lability, caused by the strong electron-withdrawing effect of the p-CF$_3$C$_6$H$_4$ group.

Complexes **2a–e** and **3a–e** are soluble in polar organic solvents, but slightly soluble in non-polar solvents. They are very sensitive to air and temperature in solution, but stable for a short period on exposure to air at room temperature in the crystalline state. The IR spectra, the solution ^{1}H NMR spectra, and mass spectra are consistent with the proposed structure show in Eq. (3). The IR spectra of **2a–e** in hexane solution (Section 2) showed an absorption band at 1630–1602 cm^{-1},

Table 5
^{1}H NMR spectra of complexes **2a–e** and **3a–e** in acetone-d_6 at 20 °C [a]

| Complex	δ (Cycloolefin proton)	δ (Aryl proton)	δ (OCH$_2$CH$_3$)
2a	5.82 (m, 1H), 5.60 (m, 1H), 5.36 (m, 2H), 5.12 (m, 1H), 3.75 (m, 1H), 3.53 (m, 1H), 3.35 (m, 2H)	7.60–7.20 (m, 5H)	
2b	5.77 (m, 1H), 5.52 (m, 1H), 5.38 (m, 2H), 5.25 (m, 1H), 3.81 (m, 1H), 3.58 (m, 1H), 3.38 (m, 2H)	7.38 (m, 2H), 7.30 (m, 1H), 7.22 (m, 1H), 2.28 (s, 3H)	
2c	5.76 (m, 1H), 5.62 (m, 1H), 5.39 (m, 2H), 5.02 (m, 1H), 3.74 (m, 1H), 3.56 (m, 1H), 3.30 (m, 2H)	7.38–7.10 (m, 4H), 2.34 (s, 3H)	
2d	5.74 (m, 1H), 5.54 (m, 1H), 5.40 (m, 2H), 5.22 (m, 1H), 3.54 (m, 1H), 3.40 (m, 1H), 3.22 (m, 2H)	7.48 (m, 2H), 7.26 (m, 2H), 2.38 (s, 3H)	
2e	5.80 (m, 1H), 5.65 (m, 1H), 5.38 (m, 2H), 5.15 (m, 1H), 3.68 (m, 1H), 3.36 (m, 1H), 3.24 (m, 2H)	7.45 (m, 2H), 6.94 (m, 2H), 3.82 (s, 3H)	
3a	6.36 (m, 1H), 5.64 (m, 1H), 5.36 (m, 2H), 3.80 (m, 1H), 3.60 (m, 1H), 2.88 (m, 1H)	7.62–7.18 (m, 5H)	1.28 (t, 3H), 4.34 (q, 2H)
3b	6.75 (m, 1H), 5.64 (m, 1H), 5.42 (m, 1H), 3.38 (m, 1H), 3.20 (m, 2H), 2.86 (m, 1H)	7.40–7.06 (m, 4H), 2.36 (s, 3H)	1.44 (t, 3H), 4.46 (q, 2H)
3c	6.34 (m, 1H), 5.57 (m, 1H), 5.33 (m, 2H), 3.72 (m, 1H), 3.30 (m, 2H), 2.87 (m, 1H)	7.42–7.04 (m, 4H), 2.34 (s, 3H)	1.26 (t, 3H), 4.30 (q, 2H)
3d	6.35 (m, 1H), 5.60 (m, 1H), 5.34 (m, 2H), 3.54 (m, 1H), 3.26 (m, 2H), 2.88 (m, 1H)	7.41 (m, 2H), 7.15 (m, 2H), 2.32 (s, 3H)	1.28 (t, 3H), 4.32 (q, 2H)
3e	6.38 (m, 1H), 5.70 (m, 1H), 5.30 (m, 2H), 3.84 (m, 1H), 3.24 (m, 2H), 2.76 (m, 1H)	7.44 (m, 2H), 6.90 (m, 2H), 3.80 (s, 3H)	1.49 (t, 3H), 4.50 (q, 2H)

[a] TMS as internal reference.
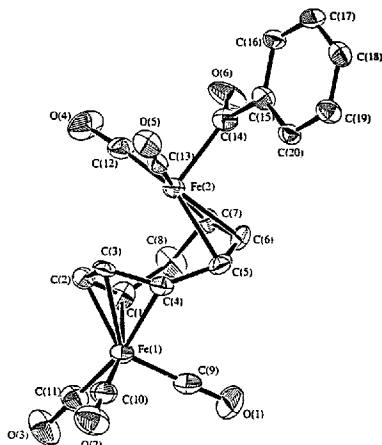
Fig. 1. Molecular structure of 2a showing the atom labeling scheme.

which is characteristic of the acyl ligand, besides the four absorption bands in the $\nu(CO)$ region. In the IR spectra of 3a–e, five CO absorption bands at 2050–1938 cm^{-1} were observed from each of the complexes, which indicates the presence of five terminal CO ligands in these complexes.

The ^{1}H NMR spectra of complexes 2a–e and 3a–e, given in Table 5, showed complex proton signals attributed to the cycloolefin ligand arising from the destruction of the conjugate system of the cyclooctatetraene ligand in 2a–e or the conversion of a CO ligand into a carbene ligand, leading to a change of the chemical environment of the cyclooctatetraene ring in 3a–e. As a result, the structure of the cycloolefin ligand consists of an η^3-allyl and the addition of a hydrogen abstracted front solvent to the C-8 ring position (see Fig. 1) in 2a–e. Thus, the proton signals of the original cycloolefin ligand shifted accordingly. In the ^{1}H NMR spectra of 3a–e, a triplet (ca. 1.35 ppm) and a quartet (ca. 4.38 ppm) and a set of multiplet (ca. 7.10–7.40 ppm) bands were observed for each of the complexes, which showed characteristically the presence of the ethoxy and aryl groups.

The mass spectra of complexes 2a–e and 3a–e, given in Section 2, show the expected molecular ion peaks and the principal fragments produced by successive loss of CO ligands and the carbene ligand or acyl group, as well as the featured ions bearing useful structural information from the fragments generated by further cleavage of these principal fragments.

The molecular structures of complexes 2a and 3a, established by X-ray diffraction studies, are shown in

Figs. 1 and 2 respectively. Both complexes have approximately the same steric configuration. The Fe(CO)$_3$ unit and the (CO)$_2$Fe(COC$_6$H$_5$) moiety in 2a and the (CO)$_2$FeC(OC$_2$H$_5$)C$_6$H$_5$ moiety in 3a are on opposite sides of the cyclooctatetraene ring, as can be visualized in the ORTEP diagrams of 2a and 3a represented in Figs. 1 and 2.

The X-ray diffraction studies of 2a show that it has a structure (Fig. 1) in which one of the CO groups of an Fe(CO)$_3$ unit was converted into an acyl group. As in analogous allyl complexes C$_8$H$_9$(CO)$_3$FeC$_6$H$_5$ and C$_8$H$_9$(CO)$_3$FeC$_6$H$_4$CF$_3$-p [5], the C$_8$H$_9$ moiety in 2a is coordinated to the Fe(2) atom through the three carbon atoms (C(5), C(6), C(7)), which form an η^3-allyl group. The C(5)–C(6) (1.38(1) Å) and C(6)–C(7) (1.40(1) Å) distances of this group are the same within experimental error. In fact, the bond lengths and angles in the η^3-allyl portion of 2a are the same within experimental error as those in C$_8$H$_9$(CO)$_3$FeC$_6$H$_5$ [5] and C$_8$H$_9$(CO)$_3$-FeC$_6$H$_4$CF$_3$-p [5]. The average distance of the Fe(2) atom to the three η^3-allyl carbon atoms (C(5), C(6), C(7)) is 2.102 Å, which is slightly shorter than that of the Fe atom to the corresponding η^3-allyl carbon atoms in C$_8$H$_9$(CO)$_3$FeC$_6$H$_5$ (2.173 Å) [5] and C$_8$H$_9$(CO)$_3$-FeC$_6$H$_4$CF$_3$-p (2.165 Å) [5]. The distance from the Fe(2) atom to the least-squares plane of the η^3-allyl portion is 1.5740 Å, while the distance from Fe(1) to the least-squares plane of the η^4-butadiene residue portion in 2a is 1.5272 Å. The dihedral angle between the η^3-allyl C(5)C(6)C(7) and the η^4-butadiene C(1)C(2)C(3)C(4) planes is 44.67°. The benzene ring plane defined by C(15)-through-C(20) is respectively oriented at an angle

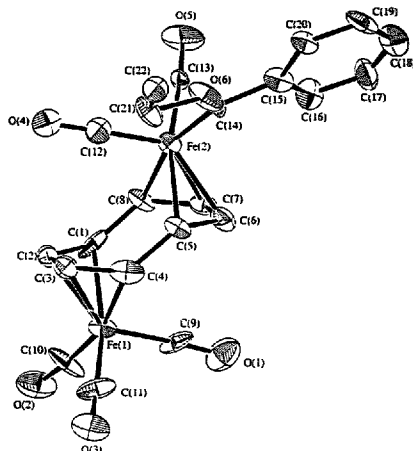Fig. 2. Molecular structure of 3a showing the atom labeling scheme.

of 120.68 and 77.57° with respect to the C(5)C(6)C(7) plane and the C(1)C(2)C(3)C(4) plane. The Fe(2)–C(14) bond length of 1.977(8) Å, which is the same within experimental error as that in the analogous acyliron complex Fe(COC$_6$H$_4$CF$_3$-p)(η-C$_5$H$_5$)(CO)$_2$ (1.972(4) Å) [15], is shorter than that of a normal Fe–C bond. This could be attributed to the formation of a conjugated system of Fe(2), C(14), and O(6). However, this system does not involve the benzene ring since the structural data reveal that the atoms Fe(2), C(14), and O(6) are not in the benzene ring plane, which might be ascribed to the intramolecular steric hindrance.

2a is a 16-electron species for the acyliron moiety, in which the 16 electrons participating in the central atom valence configuration consist of the eight electrons of the Fe atom, two pairs of electrons provided by the two carbonyl ligands, and the other four electrons, one of which is a σ-electron, provided by the acyl group ligating the Fe atom in an end-on mode, and three of which are the π-electrons provided by an allyl-type η^3-bonding orbital of the cycloolefin ligand, bonded side-on to the Fe atom.

The structure of **3a** (Fig. 2) resembles that of C$_8$H$_8$[Fe(CO)$_3$]$_2$ (1) [28], except that the substituent on the Fe(2) atom is a carbene ligand (C(OC$_2$H$_5$)C$_6$H$_5$) in **3a** but a CO ligand on the Fe atom in **1**. The geometries of the cyclooctatetraene C$_8$H$_8$ ring in both complexes are the chair form. The dihedral angle between the plane defined by C(1)-through-C(4) and the plane comprised of C(5)-through-C(8) is 2.38°; thus the C(1)C(2)C(3)C(4) and C(5)C(6)C(7)C(8) planes are essentially parallel to each other. While the angles between the C(1)C(4)C(5)C(8) and C(1)C(2)C(3)C(4) planes and the C(1)C(4)C(5)C(8) and C(5)C(6)C(7)C(8) planes are 38.61 and 40.950° respectively. The benzene ring plane is oriented respectively at 132.31, 128.18 and 131.360° with respect to the C(1)C(2)C(3)C(4) plane, the C(1)C(4)C(5)C(8) plane, and the C(5)C(6)C(7)C(8) plane. The average C–C bond length (1.44 Å) of the C$_8$H$_8$ ring is the same as that in **1**. The Fe(CO)$_3$ unit is located (1.5998 Å) below the C(1)C(2)C(3)C(4) plane, and the (CO)$_2$FeC(OC$_2$H$_5$)C$_6$H$_5$ moiety is located (1.5896 Å) above the C(5)C(6)C(7)C(8) plane. The average distance of the Fe(1) atom to carbon atoms C(1), C(2), C(3) and C(4) is 2.09 Å, which is very close to that of the Fe(2) atom to atoms C(5), C(6), C(7) and C(8) (2.095 Å) and that of the Fe atoms to the carbon atoms of the butadiene-like residues (average 2.10 Å) [28] in **1** but is slightly shorter than the corresponding distance found (2.113 Å) in **2a**. The Fe(2)–C(14) distance of 1.87(2) Å signifies a high double bond character, and is slightly shorter than that found in analogous carbene complexes C$_6$H$_8$(CO)$_2$FeC(OC$_2$H$_5$)-C$_6$H$_4$CH$_3$-o (1.89(2) Å) [29] and (η^4-C$_{10}$H$_{16}$)(CO)$_2$-FeC(OC$_2$H$_5$)C$_6$H$_4$CH$_3$-o (1.915(15) Å) [13]. The sum of the three bond angles around the C(14) atom (O(6)–

C(14)–C(15) 117.9(7)°, Fe(2)–C(14)–O(6) 119.4(6)°, Fe(2)–C(14)–C(15) 122.7(6)°) is exactly 360°, which demonstrates that these atoms are coplanar. The C(14)–O(6) bond length of 1.39(2) Å is comparable with that found in C$_6$H$_8$(CO)$_2$FeC(OC$_2$H$_5$)C$_6$H$_4$CH$_3$-o (1.34(2) Å) [29], but slightly longer than that in (η^4-C$_{10}$H$_{16}$)(CO)$_2$FeC(OC$_2$H$_5$)C$_6$H$_4$CH$_3$-o (1.324(17) Å) [13], which shows the partial delocalization of the π-electron on the O(6) atom owing to the effect of the Fe(2)–C(14) π bond.

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