

Studies on Olefin-co-ordinating Transition Metal Carbene Complexes. Part 12.† Novel Synthesis and Structural Characterization of (η^6 -Arene)dicarbonyliron Complexes, and Their Oxidation Products

Jiabi Chen,* Jianguo Yin, Zhaochang Fan, and Weihua Xu

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai, China

The complexes $[\text{Fe}(\text{CO})_2\{\eta^6\text{-RC}_6\text{H}_4\text{C}(\text{OX})(\text{C}_8\text{H}_{12})\}]$ [$\text{X} = \text{SiMe}_3$, $\text{R} = \text{H}$ (**2**), *m*-Me (**3**), *p*-Me (**4**), or *p*-Ph (**5**); $\text{X} = \text{Et}$, $\text{R} = \text{H}$ (**6**) or *p*-Me (**7**)] have been prepared by the novel reaction of tricarbonyl(cyclo-octa-1,5-diene)iron (**1**) with aryl-lithium reagents in diethyl ether at low temperature, followed by alkylation of the adducts formed with SiMe_3Cl or Et_3OBF_4 . The oxidation of (**2**) and (**4**) with $[\text{NH}_4]_2[\text{Ce}(\text{NO}_3)_6]$ in ethanol solution at low temperature led to dissociation of the $\text{Fe}(\text{CO})_2$ moiety to give 9-aryl-9-trimethylsiloxybicyclo[4.2.1]non-2-ene (aryl = Ph or *p*-MeC₆H₄) in high yields. The new compounds were characterized by elemental analyses, i.r., ¹H n.m.r., and mass spectra. In addition, the structure of complex (**4**) was confirmed unambiguously by X-ray diffraction analyses: triclinic, space group $P\bar{1}$, with $a = 9.689(3)$, $b = 9.801(2)$, $c = 13.185(7)$ Å, $\alpha = 75.20(3)$, $\beta = 68.19(3)$, $\gamma = 64.47(2)^\circ$, $Z = 2$; $R = 0.036$ and $R' = 0.026$ for 3 166 reflections with $I \geq 3\sigma(I)$.

In recent years, the preparation and characterization of olefin-co-ordinated metal carbene complexes have been studied extensively in this laboratory.¹⁻⁶ We discovered that different cyclopolyene-ligated carbonyliron compounds reacted with aryl-lithium reagents, followed by alkylation of the resulting acylmetalate intermediates with Et_3OBF_4 , to give different products. For instance, reaction of tricarbonyl(cyclohexa-1,3-diene)- and tricarbonyl(cyclo-octatetraene)-iron gave a series of novel isomerized olefin-metal-carbene complexes,^{4,5} in which the cyclo-olefin ligand was bonded to the 'carbene' carbon atom to form diallyldicarbonyliron complexes without opening the ring, while in the case of tricarbonyl(cycloheptatriene)iron, ring opening occurred to generate novel ring-opened diallyl complexes.⁶ In an extension of our research, we have chosen tricarbonyl(cyclo-octa-1,5-diene)iron (**1**) as the starting material, where the olefin ligand is a non-conjugated cyclodiene, in order further to investigate the reaction of different cyclopolyene ligands and to reveal the reaction mechanism. Compound (**1**) adopts a quite interesting route to give novel (η^6 -arene)dicarbonyliron complexes which are difficult to prepare by other methods.

Results and Discussion

Preparation of (η^6 -Arene)dicarbonyliron Complexes, (2)–(7).—Compound (**1**) reacts with a ca. 20% molar excess of $\text{Li}(\text{C}_6\text{H}_4\text{R})$ ($\text{R} = \text{H}$, *m*-Me, *p*-Me, or *p*-Ph), in diethyl ether at -60°C to -35°C for 3–4 h to yield the acylmetalate intermediates as yellow crystalline precipitates. Alkylation of the intermediates could be effected either by direct addition of SiMe_3Cl to the reaction mixture at -30 to -20°C or by addition of Et_3OBF_4 to their aqueous solution at 0°C . After removal of solvent in a high vacuum, the solid residue was chromatographed on an alumina column at -20°C , and the crude product recrystallized from light petroleum at -80°C to give the cyclo-olefin substituted complexes $[\text{Fe}(\text{CO})_2\{\eta^6\text{-RC}_6\text{H}_4\text{C}(\text{OX})(\text{C}_8\text{H}_{12})\}]$ [$\text{X} = \text{SiMe}_3$, $\text{R} = \text{H}$ (**2**), *m*-Me (**3**), *p*-Me (**4**), or *p*-Ph (**5**); $\text{X} = \text{Et}$, $\text{R} = \text{H}$ (**6**), or *p*-Me (**7**)] (Scheme 1). The diamagnetic compounds (**2**)–(**7**) are orange to red in

colour and readily soluble in both polar and non-polar solvents. In the solid state, substantial oxidative decomposition occurs on exposure to air at room temperature for several hours. Attempted isolation of the intermediate (**A**) failed since it is extremely sensitive both to air and temperature.

Spectra Analyses and Structures of Complexes (2)–(7).—The elemental analyses of (**2**)–(**7**) were closely consistent with the expected compositions. By means of specific spectra, their structures might be supposed. The ¹H n.m.r. spectral data given in Table 1 show that there are no absorption signals in the normal region of aromatic proton resonances. Unexpectedly, there are several peaks in the region 5–6 p.p.m. The co-ordination of an alkene to a metal always results in the chemical shift of the olefinic protons moving upfield dramatically.⁷ Would it therefore be possible that the aryl group in (**2**)–(**7**) is co-ordinated to the iron atom as a η^6 -arene ligand and so cause the chemical shifts of the aromatic protons to move to δ 5–6 p.p.m.? After comparing the ¹H n.m.r. spectra of (**2**)–(**7**) with those of $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_5\text{R})]$ ($\text{R} = \text{alkyl}$)⁸ we believe that this argument seems to be true. Furthermore, the i.r. spectra of (**2**)–(**7**) in the $\nu(\text{CO})$ region showed two strong stretching vibration bands with nearly identical intensity (see Table 2). This indicated the existence of only two CO ligands and conversion of the third into the carbene ligand upon treatment of (**1**) with aryl-lithium and alkylation reagents. However, the co-ordination of an arene ligand and two CO ligands to the iron atom can already satisfy the 18-electron rule, and there might not be a carbene ligand bonded directly to the iron atom. Therefore, it is possible that cycloaddition of the carbene ligand to the cyclodiene ligand occurred. This supposition was supported by the mass spectra of (**2**)–(**7**) (see Experimental section). The strongest fragment peak for each complex is $[M - \text{Fe}(\text{CO})_2]^+$, which seems to show bonding of the carbene ligand not to the iron atom but to the cyclodiene ligand. If this assumption is true, it could be concluded that the arene ligand replaced the diene and carbene ligands to co-ordinate to the iron atom during the reaction. Thus, (**2**)–(**7**) seem to be η^6 -arene-co-ordinated dicarbonyliron complexes.

Although i.r., ¹H n.m.r., and mass spectra studies revealed the possible structure for (**2**)–(**7**), an unambiguous structural assignment is still rather difficult. In order to corroborate our

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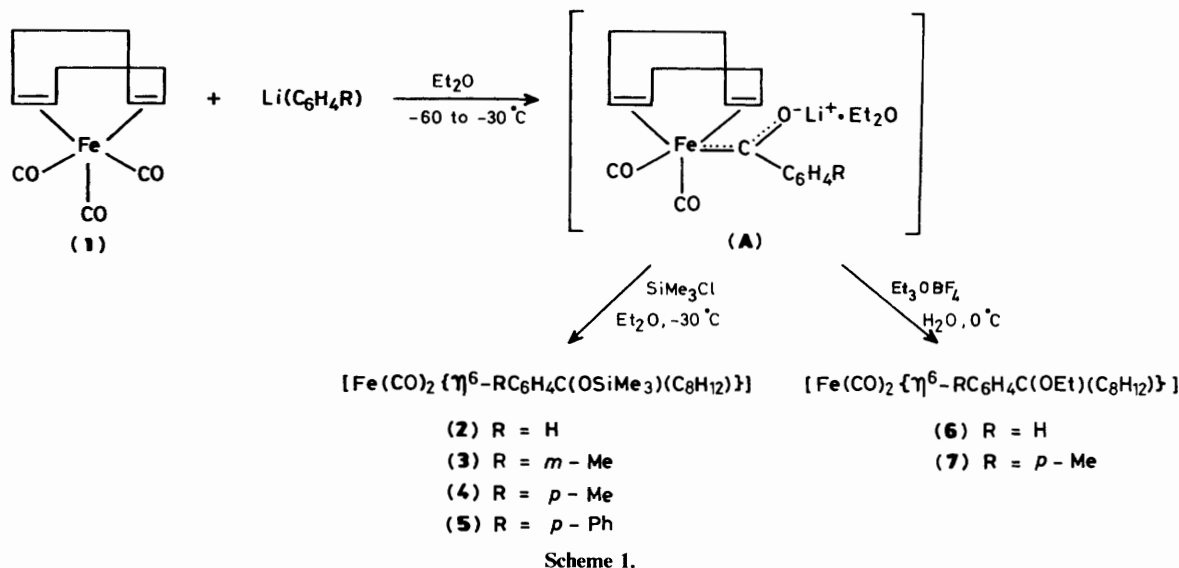


Table 1. ¹H N.m.r. data for complexes (2)–(9) at 20 °C (δ/p.p.m., SiMe₄ as internal reference)^a

Complex	η^6 -Arene and olefin protons	Bicyclo protons	Others
(2)	5.22 (m, 2 H), 5.70 (m, 2 H), 5.85 (m, 1 H), 6.00 (m, 1 H), 6.40 (m, 1 H)	1.50 (m, 2 H), 1.81 (m, 2 H), 2.35 (m, 2 H), 2.76–3.20 (m, 4 H)	–0.13 (s, 9 H)
(3)	5.26 (m, 1 H), 5.50 (m, 1 H), 5.72 (m, 2 H), 6.02 (m, 1 H), 6.30 (m, 1 H)	1.50 (m, 2 H), 1.78 (m, 2 H), 2.20 (m, 2 H), 2.74–3.30 (m, 4 H)	2.32 (s, 3 H), –0.12 (s, 9 H)
(4)	5.20 (m, 2 H), 5.64–6.12 (m, 4 H)	1.50 (m, 2 H), 1.80 (m, 2 H), 2.34 (m, 2 H), 2.98 (m, 2 H), 3.40 (m, 2 H)	2.45 (s, 3 H), –0.12 (s, 9 H)
(5)	5.40 (m, 1 H), 5.68 (m, 2 H), 5.92–6.22 (m, 3 H)	1.52 (m, 2 H), 1.80 (m, 2 H), 2.36 (m, 2 H), 2.82–3.12 (m, 4 H)	7.74 (m, 2 H), 7.42 (m, 3 H), –0.14 (s, 9 H)
(6)	5.16 (m, 1 H), 5.28 (m, 1 H), 5.46 (m, 1 H), 5.58 (m, 2 H), 5.90 (m, 1 H), 6.26 (m, 1 H)	1.50 (m, 2 H), 1.74 (m, 2 H), 2.22 (m, 2 H), 2.35 (m, 1 H), 2.86 (m, 2 H), 3.14 (m, 1 H)	3.50 (q, 2 H), 1.0 (t, 3 H)
(7)	5.30 (m, 2 H), 5.60 (m, 2 H), 5.96 (m, 2 H)	1.48 (m, 2 H), 1.72 (m, 2 H), 2.24 (m, 2 H), 2.30 (m, 1 H), 2.90 (m, 2 H), 3.10 (m, 1 H)	3.50 (q, 2 H), 2.40 (s, 3 H), 1.0 (t, 3 H)
(8) ^b	5.70 (m, 1 H), 6.20 (m, 1 H)	1.16 (m, 2 H), 1.52 (m, 1 H), 1.60–1.90 (m, 1 H), 2.08 (m, 2 H), 2.62 (m, 2 H), 3.20 (m, 1 H), 3.34 (m, 1 H)	7.70–7.54 (m, 5 H), 0.22 (s, 9 H)
(9) ^b	5.61 (m, 1 H), 6.12 (m, 1 H)	1.10 (m, 2 H), 1.64 (m, 2 H), 1.98 (m, 2 H), 2.54 (m, 2 H), 3.08 (m, 1 H), 3.24 (m, 1 H)	7.62 (m, 2 H), 7.40 (m, 2 H), 2.47 (s, 3 H), 0.14 (s, 9 H)

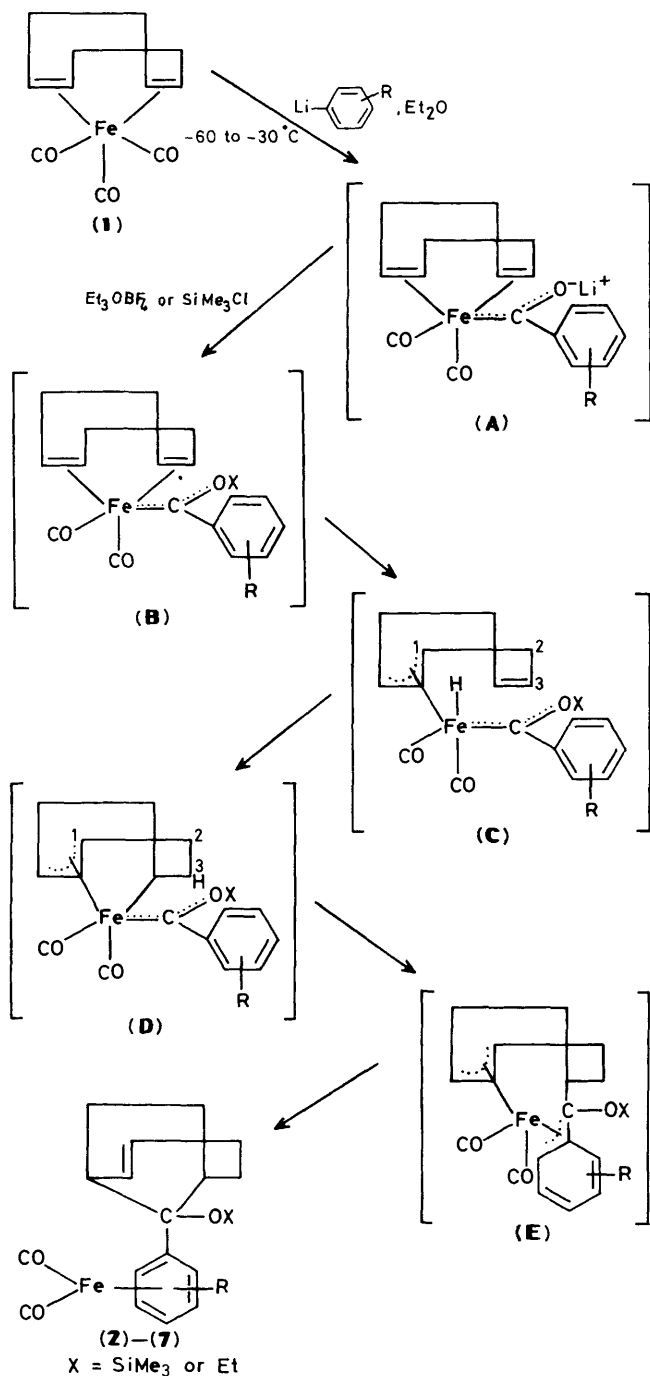
^a In [²H₆]acetone unless otherwise stated. ^b In CDCl₃.

Table 2. I.r. data (cm^{–1}) for complexes (2)–(9)

Complex	v(CO)	v(C=C) (arene)	v(C=C) (cyclo-olefin)	Medium
(2)	1 962vs, 1 890vs 1 980vs, 1 917vs	1 440m	1 650w	KCl Hexane
(3)	1 960vs, 1 888vs 1 980vs, 1 915vs	1 438m	1 630w	KCl Hexane
(4)	1 960vs, 1 892vs 1 980vs, 1 915vs	1 442m	1 650w,br	KCl Hexane
(5)	1 958vs, 1 880vs 1 977vs, 1 915vs	1 440w	1 630w,br	KCl Hexane
(6)	1 960vs, 1 885vs 1 980vs, 1 919vs	1 440w	1 650w,br	KCl Hexane
(7)	1 950vs, 1 877vs 1 979vs, 1 916vs	1 440m	1 640m	KCl Hexane
(8)			1 650m	Film
(9)			1 650w,br	KCl

suggested structure, we determined the crystal and molecular structure of complex (4) by X-ray diffraction. The results show that complexes (2)–(7) are indeed (η^6 -arene)dicarbonyliron complexes.

Based on the structural information obtained we can postulate the reaction mechanism for their formation. As mentioned above, the reaction process should involve a 1,3- σ -shift of a hydrogen atom of the cyclodiene ligand and 1,4-addition of the carbene ligand to the eight-membered ring. Thus, a possible reaction mechanism is proposed in Scheme 2. Alkylation of the acylmetalate intermediates (A), formed by reaction of (1) with aryl-lithium, gave the unstable diene \acute{e} thoxycarbene or trimethylsilyloxycarbene intermediates (B), which transformed into the hydride intermediates (C) via a 16-electron species. (C) Then isomerized to (D). The 1,3-hydrogen atom shift occurs on the transformation of (B) to (D). The further isomerization of (D) gave the diallyl compounds (E) which are transformed subsequently into the final products (2)–(7) via a reduction–elimination reaction and a replacement reaction. The yields of (2)–(7) varied considerably depending on the alkylation conditions used; for example, the acylmetalate compound (A), formed by reaction of (1) with Li(C₆H₄Me-*p*), converted into (4) on addition of SiMe₃Cl at –30 to –20 °C in 45% yield, while alkylation of (A) with Et₃OBF₄ in aqueous solution at 0 °C gave only 19% of (7) possibly due to the thermal stability of the intermediate (A) to temperature and its rapid decomposition during alkylation in aqueous solution.

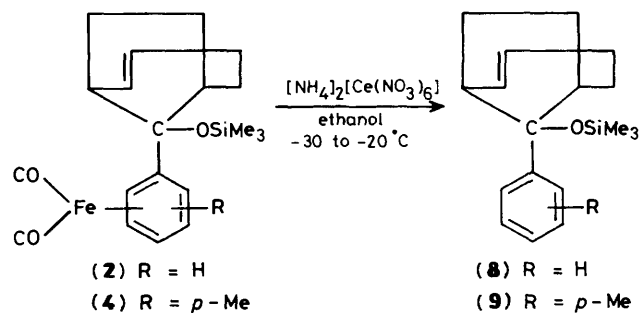


Scheme 2.

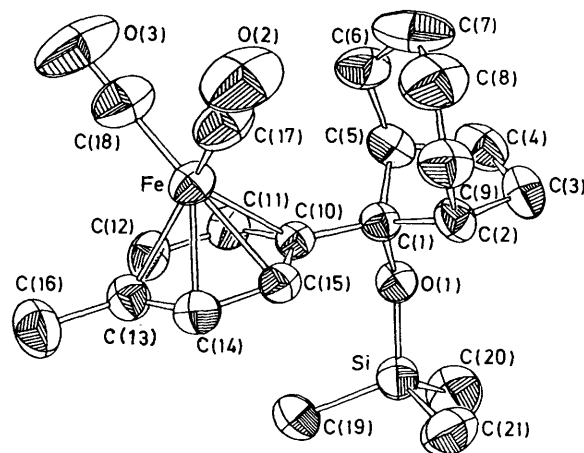
The reported synthesis of (η^6 -arene)iron carbonyl complexes are very few^{9,10} compared with those of chromium, molybdenum, and tungsten.

Oxidation of Complexes (2) and (4).—Interestingly, the oxidation of (2) and (4) with $[\text{NH}_4]_2[\text{Ce}(\text{NO}_3)_6]$ in ethanol solution at -30°C led to the dissociation of the $\text{Fe}(\text{CO})_2$ moiety to give the 9-aryl-9-trimethylsilyloxybicyclo[4.2.1]non-2-enes (8) and (9) in high yield (Scheme 3). Both are well characterized by elemental analyses, i.r., ^1H n.m.r. and mass spectra.

Crystal Structure and Bonding Description of Complex (4).—



Scheme 3.

Figure. Structure of $[\text{Fe}(\text{CO})_2\{\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{C}(\text{OSiMe}_3)(\text{C}_8\text{H}_{12})\}]$ (4)

The molecular structure of (4) is illustrated in the Figure. To our knowledge, there are no related structural data of other (η^6 -arene)dicarbonyliron complexes available for comparison. A comparison of the structural data available for η^6 -arene metal complexes of Fe, Co, and Ni is listed in Table 3. The Fe-CO bond distance (av. 1.74 Å) of (4) is the shortest and slightly shorter than that of $[\text{Fe}(\text{CO})_5]$ (1.79 Å).¹¹ The perpendicular distance from the metal atom to the arene ligand in (4) is shorter than those of the Co and Ni complexes $[\text{M}(\text{C}_6\text{F}_5)_2(\eta^6\text{-C}_6\text{H}_5\text{Me})]$.¹² The Fe-C₆H₄Me-*p* distance in (4) is slightly longer than that of $[\text{Fe}(\text{bipy})(\eta^6\text{-C}_6\text{H}_5\text{Me})]$ (bipy = 2,2'-bipyridyl).¹³ The framework of the arene ligand in (4) is planar, which differs from the Ni complex.¹²

The plane of $\text{Fe}(\text{CO})_2$ is almost perpendicular to the plane of the arene ring, the dihedral angle being 91.6° . The bond angle C(17)-Fe-C(18) (84.7°) shows that both Fe-CO bonds are approximately perpendicular to each other, which is similar to the other complexes given in Table 3. Furthermore, C(17)-Fe-C₆H₄Me-*p* (138.9°) is nearly equivalent to that of C(18)-Fe-C₆H₄Me-*p* (136.4°) (see Table 6). The bond angles C(5)-C(6)-C(7), C(6)-C(7)-C(8), and C(2)-C(9)-C(8) are 118.1(2), 119.7(2), and 127.1(2) respectively, which shows a substantial deviation from the normal values (109° for sp^3 and 120° for sp^2 hybridized carbon atoms). This may be ascribed to the tension of the ring.

Experimental

All experiments were performed under a prepurified N_2 atmosphere using standard Schlenk techniques. All solvents

Table 3. A comparison of X-ray structural data for Fe, Co, and Ni π -arene complexes; distances in Å, angles in °

Complex	M-C(arene)		C-C(arene)		L-M-L
	(av.)	M-CO (av.)	M- π arene*	(av.)	
(4) $[\text{Fe}(\text{CO})_2\{\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{C}(\text{OSiMe}_3)(\text{C}_8\text{H}_{12})\}]$	2.12	1.736	1.586	1.404	84.7 (L = CO)
$[\text{Fe}(\text{bipy})(\eta^6\text{-C}_5\text{H}_5\text{Me})]$	2.09		1.545	1.413	81.9 (L = bipy)
$[\text{Co}(\text{C}_6\text{F}_5)_2(\eta^6\text{-C}_6\text{H}_5\text{Me})]$	2.14	1.931	1.627	1.391	88.3 (L = C_6F_5)
$[\text{Ni}(\text{C}_6\text{F}_5)_2(\eta^6\text{-C}_6\text{H}_5\text{Me})]$	2.19	1.891	1.681	1.387	87.7 (L = C_6F_5)

* M- π Arene represents the perpendicular distance from metal atom to the arene ring.

Table 4. Crystallographic data and experimental details for complex (4)

Formula	$\text{C}_{21}\text{H}_{28}\text{FeO}_3\text{Si}$
<i>M</i>	412.38
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> /Å	9.689(3)
<i>b</i> /Å	9.801(2)
<i>c</i> /Å	13.185(7)
α /°	75.20(3)
β /°	68.19(3)
γ /°	64.47(2)
<i>U</i> /Å ³	1 042.1
<i>D_c</i> /g cm ⁻³	1.314
<i>Z</i>	2
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	7.9
Radiation	Mo-K α
$\lambda(\text{Mo-K}\alpha)/\text{Å}$	0.710 69
Scan mode	$\omega/2\theta$
Scan rate/° min ⁻¹	5.5
Standard reflections	3 every 130
Variation in standards	7.5%
Max. 2 θ /°	54
Total reflections	4 818
Unique observed reflections	3 166 [$I \geq 3\sigma(I)$]
Computer	Vax 780
Solution method	Direct and difference Fourier
Refinement	Full-matrix least-squares
Anisotropic convergence	$R = 0.036$, $R' = 0.026$ [$w = 1/\sigma^2(F)$]
Data parameter	3 166:347 (9:1)
Max. residual electron density in final difference map/e Å ⁻³	0.3

employed were dried and deoxygenated by refluxing and keeping over Na, CaH₂, and P₂O₅ under N₂. Alumina (neutral) was deoxygenated in a high vacuum for 16 h, deactivated with 5% w/w N₂-saturated water, and stored under N₂. Compound (1),¹⁴ Et₃OBf₄,¹⁵ and the aryl-lithium reagents¹⁶⁻¹⁸ were prepared by literature methods.

I.r., ¹H n.m.r., and mass spectra were recorded on Perkin-Elmer 683, Varian XL-200, and Finnigan 4021 GC/MS/DS spectrometers, respectively.

Preparation of $[\text{Fe}(\text{CO})_2\{\eta^6\text{-C}_6\text{H}_5\text{C}(\text{OSiMe}_3)(\text{C}_8\text{H}_{12})\}]$ (2).—To a solution of (1) (2.0 g, 8.1 mmol) in diethyl ether (50 cm³) was added dropwise LiPh (9.8 mmol)¹⁶ in diethyl ether (20 cm³) at -60 °C. After stirring at -50 to -35 °C for 3-4 h, a considerable amount of orange-red acylmetalate (A) precipitated from the dark red reaction solution. To this mixture was added dropwise SiMe₃Cl (1.5 g, 14 mmol) in diethyl ether (15 cm³) at -35 °C and the reaction mixture stirred at -30 to -20 °C for 1.5 h to give a dark red solution. The solvent and excess of SiMe₃Cl was evaporated under vacuum at -15 °C and the residue chromatographed on an alumina column at -20 °C with light petroleum (b.p. 30-60 °C), followed by light petroleum-diethyl ether (10:1) as

eluant. After removal of solvent in vacuum, the crude product was recrystallized from light petroleum at -80 °C to afford orange-red crystals, m.p. 72-74 °C (decomp.), yield 1.20 g [37.2%, based on (1)]. Mass spectra: *m/e* 286 {[*M* - Fe(CO)₂]⁺, 62%}, 73 ([SiMe₃]⁺, 100%) (Found: C, 60.50; H, 6.45. Calc. for C₂₀H₂₆FeO₃Si: C, 60.30; H, 6.60%).

Preparation of $[\text{Fe}(\text{CO})_2\{\eta^6\text{-}m\text{-MeC}_6\text{H}_4\text{C}(\text{OSiMe}_3)(\text{C}_8\text{H}_{12})\}]$ (3).—Similar to the procedures described in the preparation of (2), the reaction of (1) (0.80 g, 3.2 mmol) with LiC₆H₄Me-*m* (3.9 mmol)¹⁷ and subsequent alkylation of the adduct formed with SiMe₃Cl (0.51 g, 4.7 mmol) gave 0.38 g [21%, based on (1)] of orange-red crystals, m.p. 70-72 °C (decomp.). Mass spectra: *m/e* 300 {[*M* - Fe(CO)₂]⁺, 32%}, 73 ([SiMe₃]⁺, 100%) (Found: C, 60.80; H, 6.35. Calc. for C₂₁H₂₈FeO₃Si: C, 61.15; H, 6.85%).

Preparation of $[\text{Fe}(\text{CO})_2\{\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{C}(\text{OSiMe}_3)(\text{C}_8\text{H}_{12})\}]$ (4).—Analogous to the procedures described above for (2), complex (1) (0.40 g, 1.6 mmol) was reacted with LiC₆H₄Me-*p* (2.0 mmol),¹⁷ followed by alkylation with SiMe₃Cl (0.43 g, 4.0 mmol) to give 0.30 g [45%, based on (1)] of orange crystals, m.p. 67-69 °C (decomp.). Mass spectra: *m/e* 300 {[*M* - Fe(CO)₂]⁺, 16%}, 73 ([SiMe₃]⁺, 70%) (Found: C, 60.95; H, 6.8. Calc. for C₂₁H₂₈FeO₃Si: C, 61.15; H, 6.85%).

Preparation of $[\text{Fe}(\text{CO})_2\{\eta^6\text{-}p\text{-PhC}_6\text{H}_4\text{C}(\text{OSiMe}_3)(\text{C}_8\text{H}_{12})\}]$ (5).—Complex (1) (0.40 g, 1.6 mmol) was reacted with LiC₆H₄Ph-*p* (2.0 mmol)¹⁸ in a similar manner as described for (2). The acylmetalate formed was alkylated with SiMe₃Cl (0.50 g, 4.6 mmol) to give 0.19 g [25%, based on (1)] of red crystals, m.p. 74-75 °C (decomp.). Mass spectra: *m/e* 362 {[*M* - Fe(CO)₂]⁺, 53%}, 73 ([SiMe₃]⁺, 100%) (Found: C, 65.75; H, 6.55. Calc. for C₂₆H₃₀FeO₃Si: C, 65.80; H, 6.35%).

Preparation of $[\text{Fe}(\text{CO})_2\{\eta^6\text{-C}_6\text{H}_5\text{C}(\text{OEt})(\text{C}_8\text{H}_{12})\}]$ (6).—Analogous to the procedures described for (2), complex (1) (0.40 g, 1.6 mmol) was reacted with LiPh (2.2 mmol). After evaporation of solvent in a high vacuum at -30 °C, the residue was dissolved in N₂-saturated water (20 cm³) at 0 °C. Immediately afterwards Et₃OBf₄ was added portionwise, with vigorous stirring, to the aqueous solution until it became acidic. The solution was extracted repeatedly with light petroleum. The combined extracts were evaporated in vacuum to dryness. The residue was chromatographed on alumina at -25 °C with light petroleum-diethyl ether (10:1) as eluant. After removal of solvent the crude product was recrystallized from light petroleum at -80 °C to give 0.05 g [9%, based on (1)] of orange-red crystals, m.p. 66-68 °C (decomp.). Mass spectra: *m/e* 326 ([*M* - CO]⁺, 1.3%), 298 ([*M* - 2CO]⁺, 4.3%), 242 {[*M* - Fe(CO)₂]⁺, 38%}, 105 ([PhCO]⁺, 100%) (Found: C, 64.45; H, 6.15. Calc. for C₁₉H₂₂FeO₃: C, 64.40; H, 6.25%).

Preparation of $[\text{Fe}(\text{CO})_2\{\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{C}(\text{OEt})(\text{C}_8\text{H}_{12})\}]$ (7).—The reaction of (1) (0.40 g, 1.6 mmol) with LiC₆H₄Me-*p*

(2.1 mmol) and subsequent alkylation with Et_3OBF_4 in a similar manner as described for (6) gave 0.11 g [19%, based on (1)] of red crystals, m.p. 81–83 °C (decomp.). Mass spectra: m/e 256 $\{[M - \text{Fe}(\text{CO})_2]^+, 2.0\%\}$, 211 $\{[M - \text{Fe}(\text{CO})_2 - \text{OEt}]^+, 55\%\}$ (Found: C, 64.95; H, 6.45. Calc. for $\text{C}_{20}\text{H}_{24}\text{FeO}_3$: C, 65.25; H, 6.55%).

Reaction of (2) with $[\text{NH}_4]_2[\text{Ce}(\text{NO}_3)_6]$. Formation of (8).—To a solution of (2) (0.30 g, 0.75 mmol) in ethanol (30 cm^3) was

added dropwise $[\text{NH}_4]_2[\text{Ce}(\text{NO}_3)_6]$ (1.0 g, 1.82 mmol) in ethanol (15 cm^3) at -30 °C. Gas evolution and a colour change of the reaction solution from orange-red to yellowish were observed. After stirring at -30 to -20 °C for 1 h, the reaction solution was poured into 50 cm^3 of NaCl-saturated water. The solution was extracted three times with 100 cm^3 of light petroleum. The combined extracts were washed with water (50 cm^3) and dried with CaCl_2 . After evaporation of the solvent under vacuum, the residue was chromatographed on an alumina column with light petroleum as eluant to give 0.19 g [89%, based on (2)] of (8) as a colourless oil. Mass spectra: m/e 286 (M^+ , 80%), 271 ($[M - \text{Me}]^+$, 30%), 197 ($[M - \text{OSiMe}_3]^+$, 47%), 73 ($[\text{SiMe}_3]^+$, 100%) (Found: C, 75.35; H, 9.40. Calc. for $\text{C}_{18}\text{H}_{26}\text{OSi}$: C, 75.45; H, 9.15%).

Table 5. Positional parameters and their estimated standard deviations for the non-hydrogen atoms of (4)

Atom	x	y	z
Fe	0.019 11(4)	0.747 12(4)	0.145 71(3)
Si	0.285 82(8)	0.193 94(8)	0.342 89(6)
O(1)	0.098 7(2)	0.312 3(2)	0.375 0(1)
O(2)	-0.188 5(2)	0.803 3(2)	0.015 5(2)
O(3)	-0.171 1(3)	1.060 6(2)	0.181 6(2)
C(1)	-0.011 0(2)	0.422 0(2)	0.316 4(2)
C(2)	-0.056 3(3)	0.332 7(3)	0.260 9(2)
C(3)	-0.149 2(3)	0.252 0(3)	0.361 7(2)
C(4)	-0.218 0(3)	0.350 4(3)	0.455 6(2)
C(5)	-0.167 2(3)	0.487 7(3)	0.408 0(2)
C(6)	-0.297 3(3)	0.628 2(3)	0.372 2(2)
C(7)	-0.385 3(3)	0.607 9(4)	0.305 8(2)
C(8)	-0.295 3(3)	0.534 7(3)	0.206 9(2)
C(9)	-0.153 3(3)	0.427 0(3)	0.183 2(2)
C(10)	0.070 9(2)	0.529 0(2)	0.243 1(2)
C(11)	0.088 0(3)	0.632 9(2)	0.289 1(2)
C(12)	0.184 2(3)	0.717 2(3)	0.224 7(2)
C(13)	0.266 8(3)	0.702 4(3)	0.112 7(2)
C(14)	0.249 9(3)	0.599 3(3)	0.066 9(2)
C(15)	0.154 9(3)	0.514 8(2)	0.131 0(2)
C(16)	0.367 4(3)	0.796 2(3)	0.045 7(2)
C(17)	-0.105 2(3)	0.777 4(3)	0.067 2(2)
C(18)	-0.093 3(3)	0.934 1(3)	0.168 4(2)
C(19)	0.423 1(3)	0.293 7(3)	0.310 9(2)
C(20)	0.296 2(4)	0.060 3(3)	0.469 9(2)
C(21)	0.345 1(3)	0.084 9(3)	0.226 6(2)

Reaction of (4) with $[\text{NH}_4]_2[\text{Ce}(\text{NO}_3)_6]$. Formation of (9).—Similar to the reaction of (2), complex (4) (0.40 g, 0.97 mmol) reacted with $[\text{NH}_4]_2[\text{Ce}(\text{NO}_3)_6]$ (0.90 g, 1.64 mmol) to give 0.27 g [93%, based on (4)] of (9) as colourless crystals, m.p. 57 °C. Mass spectra: m/e 300 (M^+ , 36%), 285 ($[M - \text{Me}]^+$, 100%), 211 ($[M - \text{OSiMe}_3]^+$, 63%), 73 ($[\text{SiMe}_3]^+$, 87%) (Found: C, 76.10; H, 9.70. Calc. for $\text{C}_{19}\text{H}_{28}\text{OSi}$: C, 75.95; H, 9.40%).

Collection of X-Ray Diffraction Data and Structure Determination.—Single crystals of complex (4) were obtained by recrystallization from light petroleum at -30 °C. A single crystal suitable for X-ray diffraction study was sealed in a capillary under a N_2 atmosphere. The diffraction data were collected on a CAD4 automatic four-circle diffractometer at 20–22 °C. The crystal was centred with 25 reflections. The crystallographic data and experimental details are listed in Table 4.

The structure was solved by direct methods and Fourier syntheses, and refined with anisotropic full-matrix least squares to convergence. The hydrogen atoms, located on a difference map, were refined isotropically. The fractional atomic co-

Table 6. Selected bond distances (Å) and angles (°) for (4)

Fe–C(10)	2.150(2)	Fe–C(11)	2.118(2)	Fe–C(12)	2.099(2)
Fe–C(13)	2.134(2)	Fe–C(14)	2.105(2)	Fe–C(15)	2.099(2)
Fe–C(17)	1.753(2)	Fe–C(18)	1.718(2)	Si–O(1)	1.637(1)
Si–C(19)	1.844(2)	Si–C(20)	1.850(3)	Si–C(21)	1.865(3)
O(1)–C(1)	1.444(2)	O(2)–C(17)	1.151(2)	O(3)–C(18)	1.159(2)
C(1)–C(2)	1.547(2)	C(1)–C(5)	1.538(2)	C(1)–C(10)	1.514(2)
C(2)–C(3)	1.546(3)	C(2)–C(9)	1.507(2)	C(3)–C(4)	1.532(3)
C(4)–C(5)	1.536(3)	C(7)–C(8)	1.439(4)	C(8)–C(9)	1.304(3)
C(10)–C(11)	1.403(2)	C(10)–C(15)	1.407(2)	C(11)–C(12)	1.410(2)
C(12)–C(13)	1.405(2)	C(13)–C(14)	1.393(2)	C(13)–C(16)	1.515(3)
C(14)–C(15)	1.403(2)	Fe–C(0)*	1.586		
C(1)–C(2)–C(3)	101.6(2)	C(1)–C(5)–C(4)	102.0(2)	C(1)–C(5)–C(6)	115.9(2)
C(1)–C(2)–C(9)	115.7(2)	C(1)–C(10)–C(11)	120.2(1)	C(1)–C(10)–C(15)	122.9(1)
C(1)–O(1)–Si	136.6(1)	C(2)–C(3)–C(4)	106.4(2)	C(3)–C(4)–C(5)	106.4(2)
C(4)–C(5)–C(6)	113.0(2)	C(5)–C(6)–C(7)	118.1(2)	C(5)–C(1)–C(10)	118.0(1)
C(6)–C(7)–C(8)	119.7(2)	C(7)–C(8)–C(9)	129.1(3)	C(2)–C(9)–C(8)	127.1(2)
C(2)–C(1)–C(10)	117.9(1)	O(1)–C(1)–C(2)	107.6(1)	C(10)–C(11)–C(12)	120.8(2)
C(11)–C(12)–C(13)	122.4(2)	C(12)–C(13)–C(14)	116.8(2)	C(12)–C(13)–C(16)	121.0(2)
C(14)–C(13)–C(16)	122.2(2)	C(13)–C(14)–C(15)	120.8(2)	C(10)–C(15)–C(14)	123.0(2)
Fe–C(17)–O(2)	177.3(2)	Fe–C(18)–O(3)	178.1(2)	C(17)–Fe–C(18)	84.7(1)
C(10)–Fe–C(17)	113.47(8)	C(13)–Fe–C(17)	135.76(9)	C(13)–Fe–C(18)	109.8(1)
C(10)–Fe–C(18)	137.10(9)	Fe–C(11)–C(10)	72.07(9)	Fe–C(11)–C(12)	69.8(1)
Fe–C(14)–C(13)	72.0(1)	Fe–C(14)–C(15)	70.3(1)	Fe–C(15)–C(10)	72.63(9)
Fe–C(15)–C(14)	70.7(1)	C(10)–Fe–C(11)	38.37(6)	C(10)–Fe–C(12)	70.28(7)
C(17)–Fe–C(0)*	138.9	C(18)–Fe–C(0)*	136.4		

* C(0) Represents the centre of the arene ring.

ordinates are listed in Table 5. Selected bond lengths and angles are given in Table 6.

Additional material available from the Cambridge Crystallographic data centre comprises thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

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