Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 20.[1] Oxidative and Thermolytic Cyclopropane Ring-opening Reactions; *X*-Ray Crystal Structure of $[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{18})]$*

Neil G. Connelly, Andrew R. Lucy, Rona M. Mills, John B. Sheridan, and Peter Woodward
Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS

Oxidation of $[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{18})]$ (**1**) with ferrocenium hexafluorophosphate results in regioselective cyclopropane ring-opening and the formation of $[Fe_2(CO)_6(\eta^5:\eta'^5\text{-}C_{16}H_{18})]^{2+}$ (**2**), a derivative of *trans*-1,2-bis(cycloheptadienyl)ethylene. The same hydrocarbon ligand is formed when (**1**) is thermolysed to give the insoluble polymer $[\{Fe_2(CO)_2(\mu\text{-}CO)_2(\eta^5:\eta'^5\text{-}C_{16}H_{18})\}_n]$ (**3**). An *X*-ray diffraction study has shown that the regio- and stereo-specificity observed in the formation of (**2**) and (**3**) derives from the stereochemistry of (**1**). The molecule (**1**) as a whole has near two-fold symmetry, but this is not crystallographically required. Two ring systems comprising fused cyclopropane and cyclohepta-1,3-diene fragments are joined by a single bond between the two apical cyclopropane atoms. Four atoms of each C_7 ring are essentially co-planar, giving an 'envelope' conformation to the ring, and are bonded to an $Fe(CO)_3$ fragment; the remainder of the C_7 ring is also planar, and incorporates the two C atoms shared with the C_3 ring and the CH_2 group. The C_7 ring folds away from the metal atom, and there are further folds at the junction with the C_3 ring and again at the apex of the C_3 ring, all in the same sense. The C_2 symmetry thus confers an overall S shape on the dimeric species when viewed along the two-fold axis. Along the Fe ··· Fe vector, by contrast, the C_3 rings are seen nearly edgewise and the two C_7 rings are almost eclipsed. Crystals of $[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{18})]$ (**1**) are triclinic, space group $P\bar{1}$, and the structure has been refined to *R* 0.043 for 3 468 reflections measured at 293 K. Complex (**3**) undergoes metal–metal bond cleavage with iodine to yield $[Fe_2I_2(CO)_4(\eta^5:\eta'^5\text{-}C_{16}H_{18})]$ (**4**) which may also be prepared from the reaction of (**2**) and iodide ion. Triphenylphosphine adds to the terminal carbon atoms, adjacent to the CH_2 groups, of the dienyl units of (**2**), giving the bis(phosphonium) salt $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{18}(PPh_3)_2\}][PF_6]_2$ (**5**).

The stereospecific oxidative dimerisation[2] of $[Fe(CO)_3(\eta^4\text{-}cot)]$ (cot = cyclo-octatetraene) gives $[Fe_2(CO)_6(\eta^5:\eta'^5\text{-}C_{16}H_{16})]^{2+}$ which reacts with $[BH_4]^-$ to yield $[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{18})]$ (**1**) (Scheme 1). We now report details[3] of the oxidation and thermolysis of (**1**), to yield $[Fe_2(CO)_6(\eta^5:\eta'^5\text{-}C_{16}H_{18})]^{2+}$ (**2**) and $[\{Fe_2(CO)_2(\mu\text{-}CO)_2(\eta^5:\eta'^5\text{-}C_{16}H_{18})\}_n]$ (**3**), respectively; an *X*-ray diffraction study of (**1**) has shown that the stereochemistry of the *trans*-1,2-bis(cycloheptadienyl)ethylene ligands of (**2**) and (**3**) derives from that of the 8,8′-bi(bicyclo[5.1.0]octa-2,4-diene) ligand of (**1**). The reactions of (**2**) with iodide ion and with PPh_3, and the reaction of (**3**) with iodine, are also reported.

Results and Discussion

The addition of two equivalents of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ to a solution of $[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{18})]$ (**1**) in CH_2Cl_2 gave a white precipitate which, on recrystallisation from nitromethane–diethyl ether, was characterised as $[Fe_2(CO)_6(\eta^5:\eta'^5\text{-}C_{16}H_{18})][PF_6]_2$ (**2**) (Table 1).

The structure of the hydrocarbon skeleton of (**2**) (Scheme 1) was readily established by n.m.r. spectroscopy (Table 2). The ^{13}C n.m.r. spectrum shows eight peaks, with chemical shifts typical of one *sp*^{3}-hybridised carbon, one uncomplexed olefinic carbon, one bridgehead carbon, and five pentadienyl carbon atoms; the ^1H n.m.r. spectrum shows the presence of five dienyl protons, two inequivalent CH_2 protons, one bridgehead proton, and one ethylenic proton [H(8)]‡ resonating at δ 5.36.

The signal centred at δ 5.36 is particularly informative, defining the *trans* geometry of the exocyclic ethylenic bond. Thus, H(8) shows a second order $[AX]_2$ spectrum with $J(AA') = 15$, $J(AX) = 8$, $J(AX') = -1$, and $J(XX') = 0$ Hz.

The coupling between the ethylenic protons H(8) and H(9), $J(AA')$, is consistent with *trans* disubstitution,[4] and the allylic coupling, $J(AX')$, is similar to those of substituted propenes (which range[5] from −0.4 to −1.8 Hz). Homoallylic couplings are normally small and positive, and greatest when the β-C–H bonds are orthogonal to the plane of the alkene.[5] Thus, $J(XX')$ for (**2**) indicates that H(1) and H(16) lie in, or close to, the plane of *trans* H(8)C=CH(9).

The proposed mechanism for the formation of (**2**) from (**1**) is shown in Scheme 2. The first step in the reaction, namely one-electron oxidation at each of the two metal centres, has been verified by cyclic voltammetry. Thus, in CH_2Cl_2 (**1**) undergoes irreversible oxidation at a platinum bead electrode, with a peak potential, E_{ox}, of 0.70 V (*vs.* a saturated calomel electrode) at a scan rate, v, of 200 mV s^{-1}; the electron-transfer process is diffusion-controlled ($i_{ox}/\sqrt{v}$ constant for v = 50—500 mV s^{-1}). The number of electrons involved in the redox reaction could not be determined directly, by controlled potential electrolysis and coulometry, due to the coating of the electrode by the insoluble oxidation product (**2**). However, a comparison

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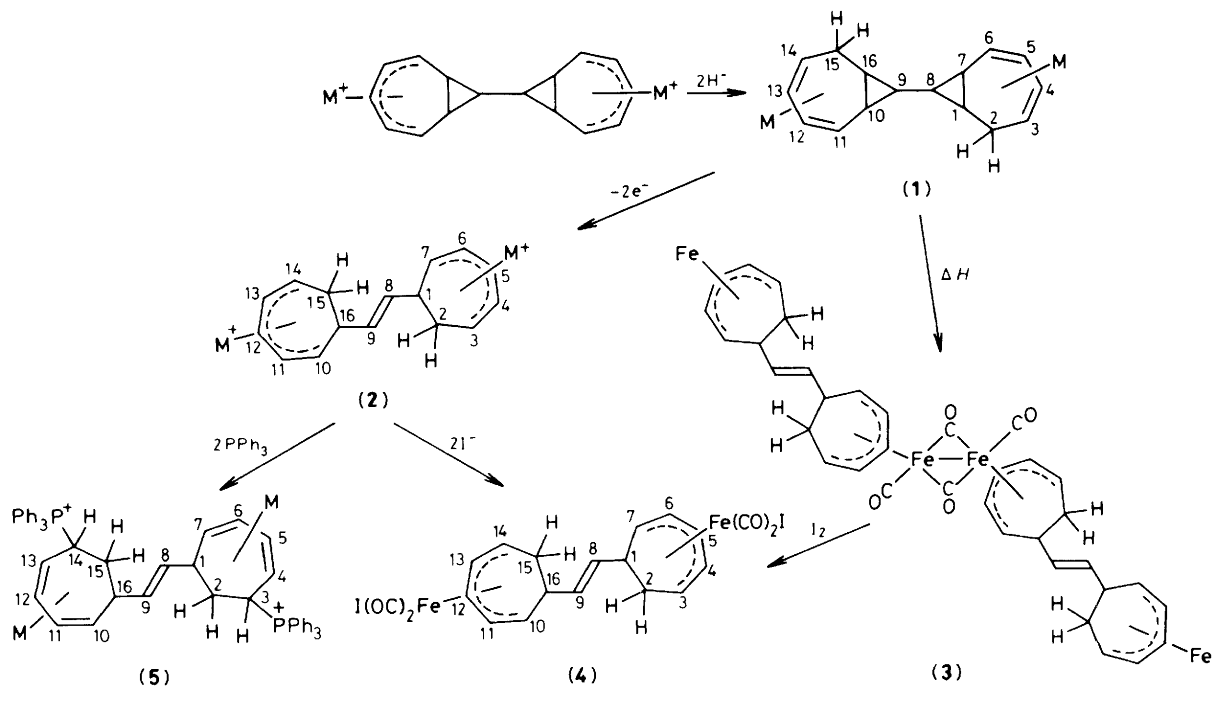
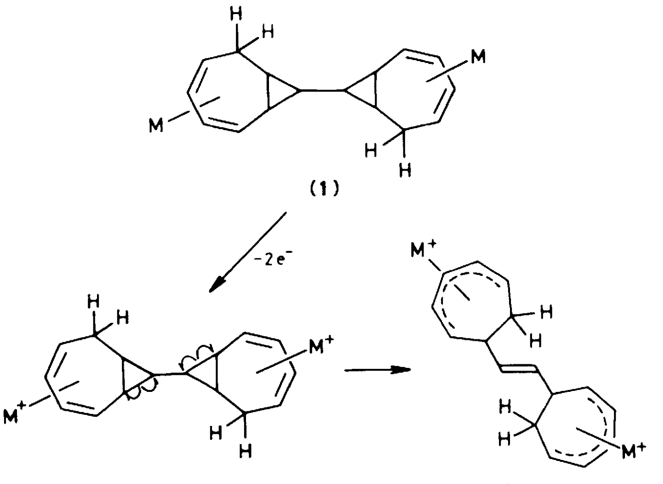
* *trans*-μ-{2—5-η:2′—5′η-8,8′-Bi(bicyclo[5.1.0]octa-2,4-diene)}-hexacarbonyldi-iron.

Supplementary data available (No. SUP 56138, 7 pp.): complete bond lengths and angles, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

‡ For consistency, the atom-numbering scheme for the n.m.r. spectra of the complexes (**1**), (**2**), (**4**), and (**5**), given in Scheme 1, is the same as that used for the *X*-ray structural study of (**1**). Although pairs of carbon atoms, for example, 8 and 9; 7 and 10; 1 and 16, *etc.* (and the appropriate attached hydrogen atoms) are equivalent in the n.m.r. spectra, they are not so in the solid state. Each atom is, therefore, uniquely numbered.



Scheme 1. M = Fe(CO)$_3$



Scheme 2. M = Fe(CO)$_3$

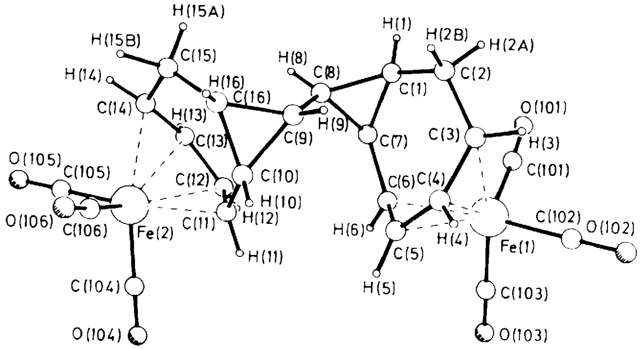


Figure 1. Molecular structure of [Fe$_2$(CO)$_6$(η^4:η'^4-C$_{16}$H$_{18}$)] (1) showing the crystallographic numbering

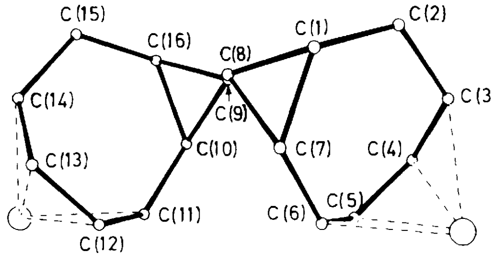


Figure 2. The molecule [Fe$_2$(CO)$_6$(η^4:η'^4-C$_{16}$H$_{18}$)] (1) seen along the single bond [C(8)–C(9)] which joins the two fused-ring systems. The carbonyl ligands and hydrogen atoms are omitted for clarity

of the wave-heights for the oxidations of [Fe(CO)$_3$(η^4-cot)] and (**1**) shows that of the latter to be approximately twice that of the former. It is noteworthy that although E_{ox} for (**1**) is more positive than E° for the reduction of the ferrocenium ion (0.48 V), the electron-transfer reaction occurs, albeit slowly, because of the irreversible formation of (**2**).

For mononuclear tricarbonyl(η^4-diene)iron complexes, there is ample evidence[6] from photoelectron spectroscopy that the highest occupied molecular orbital has a large degree of metal character; a similar situation is very likely for the binuclear complex (**2**). On electron loss, the 17-electron metal centres may attain the extra stability of the 18-electron configuration *via* bonding to a carbon atom adjacent to the η^4-diene group, thereby forming a cationic tricarbonyl(dienyl)iron moiety. Thus, on oxidising (**1**), regiospecific cyclopropane ring-opening occurs *via* the cleavage of bonds C(7)–C(8) and C(9)–C(10), and coupling of the radical centres C(8) and C(9) generates the exocyclic olefinic bond of (**2**). The cleavage of C(1)–C(8), and of C(9)–C(16), does not allow the formation of an η^5-dienyl group [due to the saturation at C(2) and C(15)], and breaking C(1)–C(7), and C(10)–C(16), with the subsequent coupling of C(1) and C(16) to form a cyclobutane ring, is clearly less favourable than the formation of (**2**).

Table 1. I.r. spectroscopic and analytical data

	Complex	Yield (%)	ν(CO)/cm^{-1}	Analysis/(%)^a C	Analysis/(%)^a H
(**1**-D)	$[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{16}D_2)]$	30	2 043, 1 981, 1 972^b	53.8(53.7)	3.5(4.0)^c
(**2**)	$[Fe_2(CO)_6(\eta^5:\eta'^5\text{-}C_{16}H_{18})][PF_6]_2$	76	2 108, 2 063^d	33.6(33.8)	2.3(2.3)
(**2**-D)	$[Fe_2(CO)_6(\eta^5:\eta'^5\text{-}C_{16}H_{16}D_2)][PF_6]_2$	75	2 114, 2 067^d	33.7(33.8)	1.9(2.5)^c
(**3**)	$[\{Fe_2(CO)_2(\mu\text{-}CO)_2(\eta^5:\eta'^5\text{-}C_{16}H_{18})\}_n]$	53	1 968, 1 754^e		
(**4**)	$[Fe_2I_2(CO)_4(\eta^5:\eta'^5\text{-}C_{16}H_{18})]$	72	2 036, 1 997^d	34.9(35.1)	2.6(2.5)
(**5**)	$[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{18}(PPh_3)_2\}][PF_6]_2$	77	2 057, 1 990^d	53.0(53.4)	3.8(3.7)
(**5**-D)	$[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}D_2(PPh_3)_2\}][PF_6]_2$	78	2 057, 1 990^d	53.5(53.3)	3.8(3.8)^c

^{a} Calculated values in parentheses. ^{b} In n-hexane. ^{c} Deuterium added to hydrogen in calculated value. ^{d} In CD_2Cl_2. ^{e} In Nujol.

Table 2. ^1H, ^{13}C, and $^{31}P^a$ n.m.r. spectroscopic data

Compound	^1H (δ)	^{13}C (p.p.m.)^b
(**1**-D) $[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{16}D_2)]$	0.08 (1 H, m, H^8), 1.10 (1 H, ddd, H^1), 1.63 [1 H, m, $J(H^7H^1)$ 9, H^7], 2.23 [1 H, dd, $J(H^2_{endo}H^1)$ 9, H^2_{endo}], 3.04 [1 H, t, $J(H^3H^2)$ 5, $J(H^3H^4)$ 7, H^3], 3.31 [1 H, ddd, $J(H^6H^7)$ 8, H^6], 5.04 [1 H, ddd, $J(H^4H^6)$ 1.5, H^4], 5.26 [1 H, ddd, $J(H^5H^6)$ 8, $J(H^5H^4)$ 5, $J(H^5H^3)$ 1, H^5]^c	18.1, 18.8 (C^1, C^8), 20.0 (C^7), 21.1 [t, $J(C^2D)$ 20, C^2], 60.6, 63.0 (C^3, C^6), 85.8, 90.6 (C^4, C^5), 211.7 (CO)^{c,d}
(**2**) $[Fe_2(CO)_6(\eta^5:\eta'^5\text{-}C_{16}H_{18})][PF_6]_2$	1.23 [1 H, m, $J(H^2_{exo}H^2_{endo})$ 14, $J(H^2_{exo}H^3)$ 6, $J(H^2_{exo}H^1)$ 6, H^2_{exo}], 2.56 [1 H, m, $J(H^2_{endo}\text{-}H^2_{exo})$ 14, $J(H^2_{endo}H^3)$ 9, $J(H^2_{endo}H^1)$ 9, H^2_{endo}], 4.00 [1 H, m br, $J(H^1H^7)$ 4, $J(H^1H^8)$ 8, $J(H^1H^2)$ 6, $J(H^1H^2_{endo})$ 9, H^1], 4.97 [1 H, dd, $J(H^7H^6)$ 7, $J(H^7H^1)$ 4, H^7], 5.09 [1 H, dd, $J(H^3H^4)$ 7, $J(H^3H^2_{exo})$ 6, $J(H^3H^2_{endo})$ 9, H^3], 5.36 [1 H, sextet,^{g} $J(H^8H^9)$ 15, $J(H^8H^1)$ 8, $J(H^8H^{16})$ −1, H^8], 6.15 [1 H, dd, $J(H^6H^5)$ 7, $J(H^6H^7)$ 7, H^6], 6.52 [1 H, dd, $J(H^4H^5)$ 7, $J(H^4H^3)$ 7, H^4], 7.37 [1 H, dd, $J(H^5H^4)$ 7, $J(H^5H^6)$ 7, H^5]^e	31.6 (C^2), 55.0 (C^1), 90.3, 94.0 (C^3, C^7), 101.5 (C^5), 103.9, 104.0 (C^4, C^6), 134.2 (C^8), 202.6 (CO)^{e,f}
(**2**-D) $[Fe_2(CO)_6(\eta^5:\eta'^5\text{-}C_{16}H_{16}D_2)][PF_6]_2$	2.50 (1 H, t, H^2_{endo}), 3.93 (1 H, m, H^1), 4.80 (1 H, dd, H^7), 4.90 (1 H, dt, H^3), 5.25 (1 H, sextet^g, H^8), 5.96 (1 H, dd, H^6), 6.30 (1 H, dd, H^4), 7.20 (1 H, dd, H^5)^{h,i}	31.4 [t, $J(C^2D)$ 20, C^2], 55.7 (C^1), 90.8, 94.5 (C^3, C^7), 101.6 (C^5), 104.2, 104.4 (C^4, C^6), 134.5 (C^8), 202.7 (CO)^{f,h}
(**4**) $[Fe_2I_2(CO)_4(\eta^5:\eta'^5\text{-}C_{16}H_{18})]$	0.47 [1 H, m, $J(H^2_{exo}H^2_{endo})$ 14, $J(H^2_{exo}H^3)$ 10, $J(H^2_{exo}H^1)$ 10, H^2_{exo}], 1.94 [1 H, m, $J(H^2_{endo}\text{-}H^2_{exo})$ 14, $J(H^2_{endo}H^3)$ 10, $J(H^2_{endo}H^1)$ 10, H^2_{endo}], 3.70 [3 H, m, $J(H^7H^6)$ 6, $J(H^3H^4)$ 6, $J(H^3H^2_{exo})$, $J(H^3H^2_{endo})$ 10, $J(H^1H^8)$ 8, $J(H^1\text{-}H^2_{endo})$, $J(H^1H^2_{exo})$ 10, H^7, H^1, H^3], 4.86 [1 H, sextet^g, $J(H^8H^1)$ 8, $J(H^8H^9)$ 14, $J(H^8H^{16})$ −1, H^8], 5.37 [1 H, dd, $J(H^4H^5)$ 6, $J(H^4H^3)$ 6, H^4], 5.84 [1 H, dd, $J(H^6H^5)$ 6, $J(H^6H^7)$ 6, H^6], 6.88 [1 H, dd, $J(H^5H^6)$ 6, $J(H^5H^4)$ 6, H^5]^{c,n}	55.2 (C^1), 74.9 (br), 85.5 (br) (C^3, C^7), 98.8 (C^5), 103.0 (br, C^4, C^6), 134.1 (C^8), 215.2 (CO)^{e,f,j} 30.7 (br, C^2), 73.6, 84.8 (br, C^3, C^7), 97.6 (C^5), 102.3 (br, C^4, C^6), 133.4 (C^8)^{f,k,l} 28.5 (C^2), 67.6, 89.8 (C^7, C^3), 93.4, 108.6 (C^4, C^6), 97.1 (C^5), 132.7 (C^8), 217.3 (CO)^{f,k,l,m} 29.5 (C^2), 76.1, 78.8 (C^3, C^7), 92.4, 110.2 (C^4, C^6), 97.1 (C^5), 132.4 (C^8), 210.3 (CO)^{f,k,l,o}
(**5**) $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{18}(PPh_3)_2\}]\text{-}[PF_6]_2{}^p$	1.02 (1 H, m, H^2_{exo}), 1.71 [1 H, m br, $J(H^2_{endo}H^3)$ 3, $J(H^2_{endo}P)$ 8, H^2_{endo}], 2.68 [1 H, dd, $J(H^4H^5)$ 7, $J(H^4P)$ 15, H^4], 2.75 (1 H, m br, H^1), 2.94 [1 H, d, $J(H^7H^6)$ 7.5, H^7], 3.85 [1 H, ddd, $J(H^3H^2_{exo})$ 10, $J(H^3P)$ 13, $J(H^3H^2_{endo})$ 3, H^3], 4.92 [1 H, dd, $J(H^5H^6)$ 5, $J(H^5H^4)$ 7, H^5], 5.25 [1 H, sextet^g, $J(H^8H^9)$ 15, $J(H^8H^1)$ 9, $J(H^8H^{16})$ −2, H^8], 5.30^q (1 H, dd, H^6), 7.7 (15 H, m, PPh_3)^k	29.4 (s br, C^2), 35.5 [d, $J(C^3P)$ 36, C^3], 42.1 [d, $J(C^1P)$ 14, C^1], 48.2 [d, $J(C^4P)$ 5, C^4], 61.9 (C^7), 87.1 (C^5), 90.6 (C^4), 117.2 [d, $J(C^\alpha P)$ 80, $C^\alpha(PPh_3)$], 131 (d, PPh_3), 134 (d, PPh_3), 135.7 (PPh_3), 135.8 (C^8), 209.7 (CO)^{f,k}
(**5**-D) $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}D_2(PPh_3)_2\}]$ $[PF_6]_2{}^p$	1.70 (1 H, m br, H^2_{endo}), 2.68 (1 H, dd, H^4), 2.75 (1 H, m br, H^1), 2.94 (1 H, d, H^7), 3.85 [1 H, dd, $J(H^3H^2_{endo})$ 3, $J(H^3P)$ 13, H^3], 4.92 (1 H, dd, H^5), 5.25 (1 H, sextet^g, H^8), 5.30^q (1 H, dd, H^6), 7.7 (15 H, m, PPh_3)^k	29.1 [t br, $J(C^2D)$ 18, C^2], 35.5 [d br, $J(C^3P)$ 36, C^3], 42.1 [d, $J(C^1P)$ 14, C^1], 48.2 [d, $J(C^4P)$ 5, C^4], 61.9 (C^7), 87.1 (C^5), 90.6 (C^4), 117.2 [d, $J(C^\alpha P)$ 80, $C^\alpha(PPh_3)$], 131 (d, PPh_3), 134 (d, PPh_3), 135.7 (PPh_3), 136.3 (C^8), 209.7 (CO)^{f,k}

^{a} 36-MHz spectra with chemical shifts to high frequency of 85% H_3PO_4. ^{b} The numbering is as in Scheme 1 (for consistency this numbering is the same as that used in the *X*-ray crystallographic study). For the n.m.r. spectra, however, $H^8 = H^9$, $H^7 = H^{10}$, $H^6 = H^{11}$ *etc.*; *J* values in Hz. 200-MHz spectra, at room temperature, unless stated otherwise. ^{c} In $CDCl_3$. ^{d} 22.5-MHz spectrum. ^{e} In $[^2H_6]$acetone. ^{f} 50-MHz spectrum. ^{g} $[AX]_2$ spectrum, $J(XX') \cong 0.0$ Hz. ^{h} In CD_3NO_2. ^{i} *J* values as for $C_{16}H_{18}$ analogue. ^{j} Signal due to C^2 obscured by solvent. ^{k} In C^1 obscured D_2Cl_2. ^{l} Signal due to C^1 obscured by solvent. ^{m} Major rotamer at −70 °C. ^{n} 100-MHz spectrum. ^{o} Minor rotamer at −70 °C. ^{p} ^{31}P N.m.r. (CD_2Cl_2): 26.4 (PPh_3), −144 (septet, PF_6). ^{q} Signal partially obscured by solvent.

Table 3. Interatomic distances (Å) and angles (°) for [$Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{18})$] (**1**) with estimated standard deviations in parentheses. Those values related by pseudo-two-fold symmetry are listed side by side

Fe(1)–C(101)	1.785(3)	Fe(2)–C(106)	1.789(3)	C(1)–C(2)	1.500(4)	C(16)–C(15)	1.502(4)
C(101)–O(101)	1.129(4)	C(106)–O(106)	1.139(4)	C(2)–C(3)	1.512(5)	C(15)–C(14)	1.519(4)
Fe(1)–C(102)	1.806(3)	Fe(2)–C(105)	1.796(3)	C(3)–C(4)	1.427(5)	C(14)–C(13)	1.429(4)
C(102)–O(102)	1.126(4)	C(105)–O(105)	1.132(4)	C(4)–C(5)	1.394(4)	C(13)–C(12)	1.393(4)
Fe(1)–C(103)	1.788(4)	Fe(2)–C(104)	1.797(4)	C(5)–C(6)	1.415(3)	C(12)–C(11)	1.424(3)
C(103)–O(103)	1.138(5)	C(104)–O(104)	1.137(5)	C(6)–C(7)	1.488(4)	C(11)–C(10)	1.479(4)
Fe(1)–C(3)	2.121(3)	Fe(2)–C(14)	2.117(3)	C(7)–C(8)	1.523(4)	C(10)–C(9)	1.534(5)
Fe(1)–C(4)	2.051(3)	Fe(2)–C(13)	2.050(3)	C(1)–C(7)	1.508(4)	C(16)–C(10)	1.502(5)
Fe(1)–C(5)	2.061(3)	Fe(2)–C(12)	2.067(3)	C(1)–C(8)	1.514(4)	C(16)–C(9)	1.519(4)
Fe(1)–C(6)	2.138(3)	Fe(2)–C(11)	2.144(3)	C(8)–C(9)	1.492(4)		

C(101)–Fe(1)–C(102)	100.4(2)	C(106)–Fe(2)–C(105)	100.0(1)	C(3)–C(4)–C(5)	120.1(2)	C(14)–C(13)–C(12)	120.4(2)
C(101)–Fe(1)–C(103)	101.9(1)	C(106)–Fe(2)–C(104)	104.5(2)	C(4)–C(5)–C(6)	120.4(3)	C(13)–C(12)–C(11)	120.3(3)
C(102)–Fe(1)–C(103)	92.2(2)	C(105)–Fe(2)–C(104)	92.6(2)	C(5)–C(6)–C(7)	128.4(2)	C(12)–C(11)–C(10)	128.6(3)
Fe(1)–C(101)–O(101)	176.5(3)	Fe(2)–C(106)–O(106)	175.4(4)	C(6)–C(7)–C(1)	123.8(2)	C(11)–C(10)–C(16)	124.2(2)
Fe(1)–C(102)–O(102)	178.6(3)	Fe(2)–C(105)–O(105)	178.6(3)	C(7)–C(1)–C(2)	122.6(2)	C(10)–C(16)–C(15)	122.3(3)
Fe(1)–C(103)–O(103)	178.5(2)	Fe(2)–C(104)–O(104)	179.4(4)	C(1)–C(8)–C(7)	59.6(2)	C(16)–C(9)–C(10)	59.6(2)
C(1)–C(2)–C(3)	120.7(3)	C(16)–C(15)–C(14)	121.0(3)	C(9)–C(8)–C(1)	120.3(2)	C(8)–C(9)–C(16)	121.1(2)
C(2)–C(3)–C(4)	128.5(3)	C(15)–C(14)–C(13)	126.8(3)	C(9)–C(8)–C(7)	121.6(2)	C(8)–C(9)–C(10)	121.7(2)

Torsion angles

C(8)–C(7)–C(1)–C(2)	113.5(3)	C(9)–C(10)–C(16)–C(15)	116.4(3)	C(4)–C(5)–C(6)–C(7)	−54.6(5)	C(13)–C(12)–C(11)–C(10)	−54.3(5)
C(8)–C(1)–C(7)–C(6)	−110.6(3)	C(9)–C(16)–C(10)–C(11)	−109.7(3)	C(5)–C(6)–C(7)–C(1)	42.7(5)	C(12)–C(11)–C(10)–C(16)	39.2(5)
C(1)–C(2)–C(3)–C(4)	−47.6(5)	C(16)–C(15)–C(14)–C(13)	−48.8(5)	C(6)–C(7)–C(1)–C(2)	2.9(4)	C(11)–C(10)–C(16)–C(15)	6.7(5)
C(2)–C(3)–C(4)–C(5)	57.8(5)	C(15)–C(14)–C(13)–C(12)	58.5(5)	C(7)–C(1)–C(2)–C(3)	−0.6(5)	C(10)–C(16)–C(15)–C(14)	−1.7(5)
C(3)–C(4)–C(5)–C(6)	0.0(5)	C(14)–C(13)–C(12)–C(11)	0.2(5)	C(1)–C(8)–C(9)–C(16)	149.0(3)	C(7)–C(8)–C(9)–C(10)	−69.9(4)

The source of the *trans* geometry of H(8)C(8)=C(9)H(9) in (**2**), revealed by ^1H n.m.r. spectroscopy (see above), is not obvious from the line drawings given in Schemes 1 and 2, but derives from the stereochemistry of (**1**) which has been determined by *X*-ray crystallography. The results of the diffraction study on (**1**) are illustrated in Figure 1 which also shows the crystallographic numbering. A second view of the molecule (Figure 2), taken along the direction of the C(8)–C(9) bond, quite clearly shows that the oxidative cleavage of bonds C(7)–C(8) and C(9)–C(10) must, of necessity, give rise to a *trans*-disubstituted double bond between C(8) and C(9).

The molecule of (**1**) shows nearly perfect two-fold symmetry which (because the structure is triclinic) is not required crystallographically. Two ring systems comprising fused cyclopropane and cyclohepta-1,3-diene fragments are joined by a single bond between the two apical cyclopropane atoms. Within the C_7 rings, atoms C(3)—C(6) and C(11)—C(14) are η^4-co-ordinated respectively to Fe(1) and Fe(2). The sets of four carbon atoms so co-ordinated are coplanar; indeed, the C_7 ring is folded into an envelope conformation along C(3) ⋯ C(6) or along C(11) ⋯ C(14) at a dihedral angle of some 122°. There is a further fold in the same sense, along the junction of the C_7 and C_3 rings, *i.e.* along the C(1)–C(7) and the C(10)–C(16) bonds. Here the dihedral angle is some 115° (for details see Table 3, which gives relevant bond lengths, bond angles, and torsion angles). The single bond joining the two ring systems, C(8)–C(9), bends yet again in the same sense to give an angle of *ca.* 121° with each of the adjacent bonds in the C_3 ring. When, therefore, the molecule is viewed along the two-fold axis it shows an approximately S-shaped profile, with the metal atoms attached on the outer convex side of the ring system. Each metal atom carries three carbonyl groups with inter-carbonyl angles slightly larger than 90°.

When complex (**1**) was heated under reflux in toluene a red-brown precipitate (**3**), insoluble in all common solvents and usually pyrophoric in air (due to finely-divided iron metal contaminant), was rapidly formed. The precipitate shows two carbonyl bands in the Nujol mull i.r. spectrum due to terminal (1 968 cm^{-1}) and bridging (1 754 cm^{-1}) carbonyl ligands, absorptions very similar in energy to those observed for the metal–metal bonded complexes [$\{Fe(CO)(\mu\text{-}CO)(\eta^5\text{-}C_{5+n}H_{5+2n})\}_2$] ($n = 1$ or 2).[7] It is likely, therefore, that the skeleton (OC)Fe(μ-CO)$_2$Fe(CO) is also present in (**3**), with each metal atom also co-ordinated to an η^5-pentadienyl unit within the $C_{16}H_{18}$ ligand.

Although no further spectroscopic characterisation of (**3**) was possible, its reaction with iodine in CH_2Cl_2, which readily gave red-brown [$Fe_2I_2(CO)_4(\eta^5:\eta'^5\text{-}C_{16}H_{18})$] (**4**) (Table 1), indirectly verified the presence of the *trans*-1,2-bis(cycloheptadienyl)ethylene ligand, previously found in (**2**).

Complex (**4**), which also results from the reaction between (**2**) and iodide ion, has a ^1H n.m.r. spectrum (Table 2) virtually identical to that of (**2**), with the couplings to H(8) again defining the *trans* geometry at the exocyclic alkene bond.

The room-temperature ^{13}C n.m.r. spectrum of (**4**) (Table 2), is, however, very different from that of (**2**) in showing only broad resonances for the carbon atoms of the η^5-dienyl moiety [Figure 3(*a*)]. At −70 °C in CH_2Cl_2, however, the spectrum [Figure 3(*b*)] is well resolved showing two sets of dienyl resonances (Table 2), in the approximate ratio 2:1, due to two of the three possible rotational isomers shown in Figure 4. Clearly, heating (**4**) to room temperature overcomes the barrier to rotation; the thermodynamics of the processes have not been quantified.

Provided that no hydrocarbon rearrangement occurs when (**3**) reacts with iodine, the *trans*-1,2-bis(cycloheptadienyl)ethylene ligand of (**2**) and (**4**) is also present in (**3**). The insolubility of (**3**), and its i.r. carbonyl spectrum, support a polymeric structure (Scheme 1) which undergoes metal–metal bond cleavage on iodination to give (**4**).

The formation of (**3**) from (**1**) again involves cyclopropane ring-opening, a mechanism for which is presented in Scheme 3. Simple cyclopropanes undergo thermolytic ring-opening by radical C–C bond fission, usually with very high activation energies (*ca.* 255 kJ mol^{-1}), but vinyl derivatives isomerise to cyclopentenes at much lower (by *ca.* 100 °C) temperatures, *via* allylically stabilised biradicals.[8] Metal-complex mediated cyclopropane ring openings are relatively facile.[9] Thus, for example, 1-aryl-1-cyclopropylethylene,[10] 1,1-bis(cyclopropyl)ethylene,[11] and spiro[2.4]hepta-4,6-diene[12] readily react with [Fe(CO)$_5$] to give tricarbonyl(diene)iron derivatives. The formation of these iron complexes, and the thermal isomerisation of (η^4-bicyclo[5.1.0]octadiene)tricarbonyliron to tricarbonyl(η^4-cyclo-octatriene)iron,[13] require hydrogen-atom migration, and the postulated intermediacy of allylhydrides[13] would seem reasonable. However, the formation of (**3**) from (**1**) does not require C–H bond cleavage, and an allylhydride intermediate need not be postulated. It is interesting to note that such intermediates are not possible when the polycyclic, vinylcyclopropane derivatives bullvalene (tricyclo[3.3.2.0^{2,8}]-

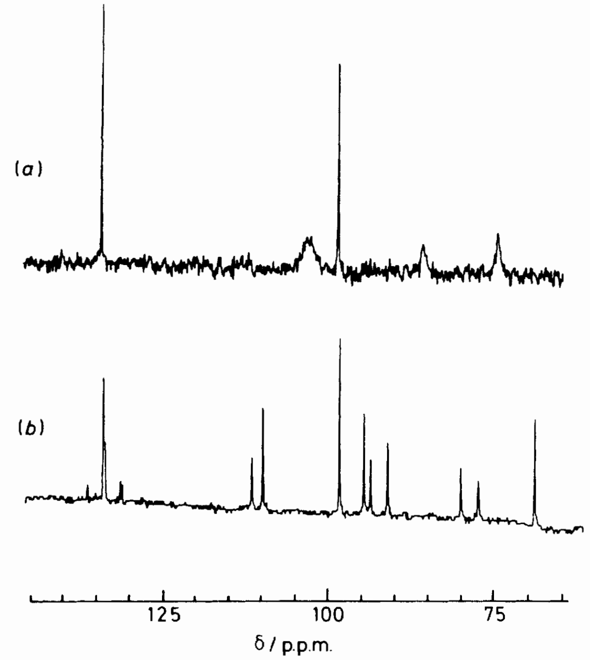


Figure 3. The ^{13}C n.m.r. spectrum in CH$_2$Cl$_2$ of [Fe$_2$I$_2$(CO)$_4$(η^5:η'^5-C$_{16}$H$_{18}$)] (**4**), in the region of the η^5-dienyl carbon atoms, (*a*) at 25 °C, and (*b*) at −70 °C

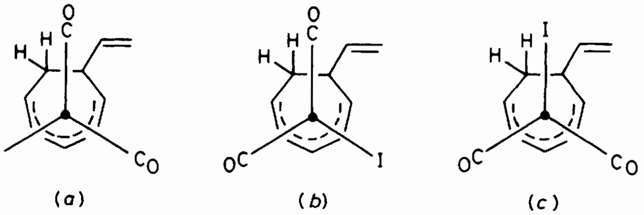
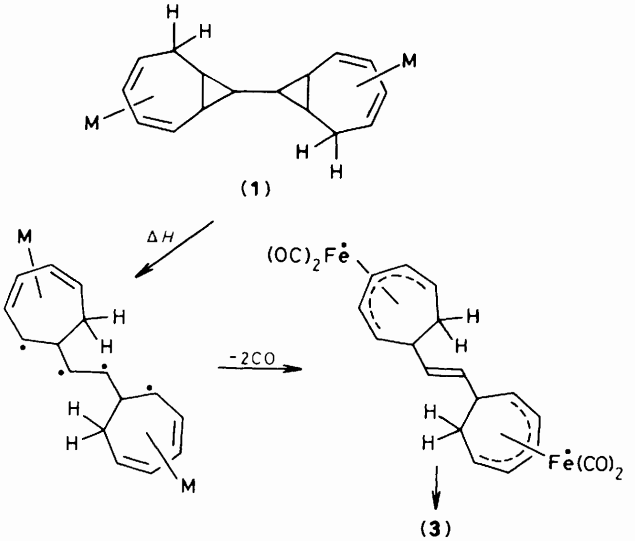
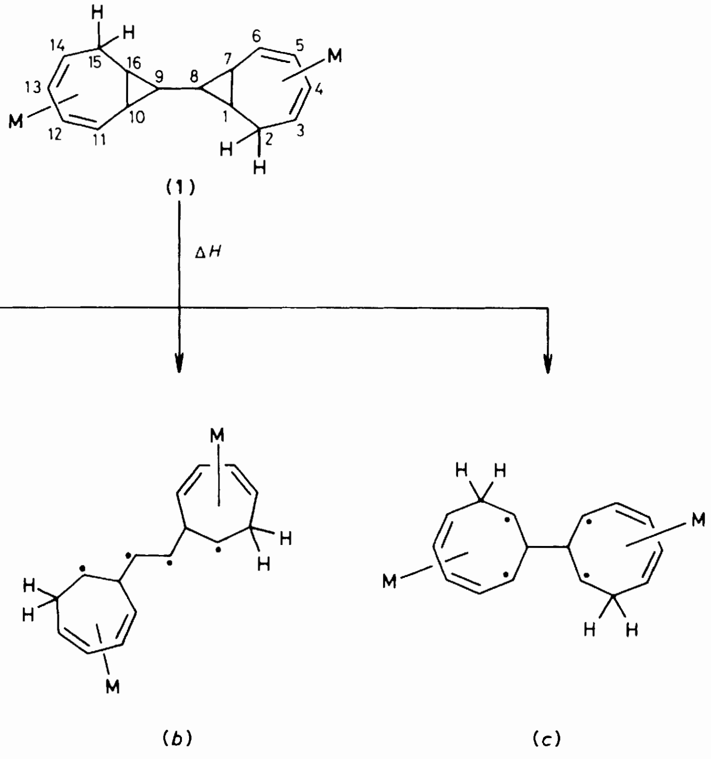


Figure 4. The rotational isomers of [Fe$_2$I$_2$(CO)$_4$(η^5:η'^5-C$_{16}$H$_{18}$)] (**4**), showing one half of the molecule only



Scheme 3. M = Fe(CO)$_3$



Scheme 4. M = Fe(CO)$_3$

deca-3,6,9-triene) and isobullvalene (tricyclo[4.3.1.$0^{7,10}$]deca-2,4,8-triene) react with $[Fe(CO)_5]$ or $[Fe_2(CO)_9]$ to give ring-opened, $\sigma{:}\eta^3$-bonded iron tricarbonyls.[14]

The regioselective formation of the *trans*-1,2-bis(cycloheptadienyl)ethylene ligand of (**3**) may be rationalised in terms of the probable stabilities of the various biradical intermediates (Scheme 4) which might be formed by the thermolysis of (**1**). Clearly, that shown by (*a*) is likely to be the most stable. It is also noteworthy that bonds C(7)–C(8) and C(9)–C(10) in (**1**) are significantly longer than the remaining C–C bonds of the cyclopropane rings C(1)–C(7)–C(8) and C(9)–C(10)–C(16), and are presumably the weakest and most readily cleaved by thermolysis.

The reaction between (**2**) and PPh_3 in CH_2Cl_2 results in the isolation of high yields of the white, crystalline, bis(phosphonium) salt $[Fe_2(CO)_6\{\eta^4{:}\eta'^4\text{-}C_{16}H_{18}(PPh_3)_2\}][PF_6]_2$ (**5**) (Table 1). The ^1H and ^{13}C n.m.r. spectra of (**5**) (Table 2) show that the basic hydrocarbon skeleton of (**2**) is retained on addition of the phosphine ligands. A full assignment of the spectra, which showed nucleophilic attack at C(3) and C(14), rather than C(7) and C(10), was verified by partial deuteriation; the complexes $[Fe_2(CO)_6(\eta^4{:}\eta'^4\text{-}C_{16}H_{16}D_2)]$ (**1-D**), $[Fe_2(CO)_6(\eta^5{:}\eta'^5\text{-}C_{16}H_{16}D_2)][PF_6]_2$ (**2-D**), and $[Fe_2(CO)_6\{\eta^4{:}\eta'^4\text{-}C_{16}H_{16}D_2(PPh_3)_2\}][PF_6]_2$ (**5-D**) (Tables 1 and 2), bearing *exo*-D substituents at C(2) and C(15), were prepared in the same way as their protonated analogues.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless otherwise stated, products were purified by dissolution in CH_2Cl_2, filtration, addition of n-hexane, and partial evaporation of the solvent mixture *in vacuo* to induce precipitation. Unless otherwise stated, the complexes are air-stable, dissolving in polar solvents such as acetone and CH_2Cl_2 to give solutions which slowly decompose in air.

The complexes $[Fe_2(CO)_6(\eta^4{:}\eta'^4\text{-}C_{16}H_{18})]$ (**1**)[2] and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$[15] were prepared by published methods, and $[Fe_2(CO)_6(\eta^4{:}\eta'^4\text{-}C_{16}H_{16}D_2)]$ (**1-D**) was prepared similarly to (**1**) using $NaBD_4$. The compound $NaBD_4$ was purchased from the Aldrich Chemical Co. Ltd.

Infrared spectra were recorded on a Perkin-Elmer PE257 spectrophotometer or a Nicolet MX-1 FT instrument, and were calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Proton n.m.r. spectra were recorded on JEOL PS 100 or FX 200 instruments, and ^{13}C n.m.r. spectra on JEOL FX 200 or FX 90Q spectrometers; both were calibrated against $SiMe_4$ as an internal reference. Phosphorus-31 n.m.r. spectra were recorded on a JEOL FX 90Q instrument and calibrated against 85% H_3PO_4 as an external reference.

Electrochemical studies were performed as previously described.[16] Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

trans-μ-[2′—6′-η:2″—6″-η-1,2-*Bis(cycloheptadienyl)ethylene]hexacarbonyldi-iron Bis(hexafluorophosphate)*, $[Fe_2(CO)_6(\eta^5{:}\eta'^5\text{-}C_{16}H_{18})][PF_6]_2$ (**2**).—To a stirred solution of $[Fe_2(CO)_6(\eta^4{:}\eta'^4\text{-}C_{16}H_{18})]$ (**1**) (0.62 g, 1.3 mmol) in CH_2Cl_2 (50 cm^3) was added $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.80 g, 2.5 mmol). After 1.5 h the white precipitate was filtered off and purified from CH_3NO_2–diethyl ether as a white solid, yield 0.75 g (76%).

The complex is sparingly soluble in CH_2Cl_2 but very soluble in CH_3NO_2 and acetone. The salt $[Fe_2(CO)_6(\eta^5{:}\eta'^5\text{-}C_{16}H_{16}D_2)][PF_6]_2$ (**2-D**) was prepared similarly, from $[Fe_2(CO)_6(\eta^4{:}\eta'^4\text{-}C_{16}H_{16}D_2)]$ (**1-D**).

Thermolysis of $[Fe_2(CO)_6(\eta^4{:}\eta'^4\text{-}C_{16}H_{18})]$ (**1**); *Synthesis of the Polymer* $[\{Fe_2(CO)_2(\mu\text{-}CO)_2(\eta^5{:}\eta'^5\text{-}C_{16}H_{18})\}_n]$ (**3**).—A solution of $[Fe_2(CO)_6(\eta^4{:}\eta'^4\text{-}C_{16}H_{18})]$ (**1**) (0.58 g, 1.20 mmol) in toluene (100 cm^3) was heated under reflux for 5 min. The resulting red precipitate was filtered off, washed well with n-hexane, and air-dried, yield 0.27 g (53%).

The product $[\{Fe_2(CO)_2(\mu\text{-}CO)_2(\eta^5{:}\eta'^5\text{-}C_{16}H_{18})\}_n]$ (**3**) is insoluble in all common solvents and is often pyrophoric in air because of finely-divided metal contaminant.

trans-μ-[2′—6′-η:2″—6″-η-1,2-*Bis(cycloheptadienyl)ethylene]tetracarbonyldi-iododi-iron*, $[Fe_2I_2(CO)_4(\eta^5{:}\eta'^5\text{-}C_{16}H_{18})]$ (**4**).—*Method* (a). To a suspension of crude $[\{Fe_2(CO)_2(\mu\text{-}CO)_2(\eta^5{:}\eta'^5\text{-}C_{16}H_{18})\}_n]$ (**3**) (0.38 g, 0.9 mmol) in CH_2Cl_2 (50 cm^3) was added I_2 (0.23 g, 0.9 mmol). After 20 min the deep red solution was filtered and evaporated to dryness. The brown solid was washed with n-hexane (3 × 10 cm^3) and diethyl ether (10 cm^3). Purification from CH_2Cl_2–n-hexane gave the product as a brown powder, yield 0.3 g (51%).

Method (b). To a stirred suspension of $[Fe_2(CO)_6(\eta^5{:}\eta'^5\text{-}C_{16}H_{18})][PF_6]_2$ (**2**) (0.38 g, 0.50 mmol) in CH_2Cl_2 (50 cm^3) was added $[PMePh_3]I$ (0.39 g, 1.00 mmol). After 2.5 h the red solution was filtered and evaporated to dryness and the red residue was extracted with toluene (300 cm^3). Evaporation of the extract to low volume, and addition of n-hexane (150 cm^3) gave $[Fe_2I_2(CO)_4(\eta^5{:}\eta'^5\text{-}C_{16}H_{18})]$ (**4**) as a pale brown solid, yield 0.24 g (72%).

Reaction of $[Fe_2(CO)_6(\eta^5{:}\eta'^5\text{-}C_{16}H_{18})][PF_6]_2$ (**2**) *with Triphenylphosphine*.—To a stirred suspension of (**2**) (0.20 g, 0.25 mmol) in CH_2Cl_2 (50 cm^3) was added PPh_3 (0.13 g, 0.50 mmol). After 30 min the yellow solution was filtered and evaporated to low volume. Addition of diethyl ether gave $[Fe_2(CO)_6\{\eta^4{:}\eta'^4\text{-}C_{16}H_{18}(PPh_3)_2\}][PF_6]_2$ (**5**) as a white solid, yield 0.25 g (77%). The salt $[Fe_2(CO)_6\{\eta^4{:}\eta'^4\text{-}C_{16}H_{16}D_2(PPh_3)_2\}][PF_6]_2$ (**5-D**) was prepared similarly from $[Fe_2(CO)_6(\eta^5{:}\eta'^5\text{-}C_{16}H_{16}D_2)][PF_6]_2$ (**2-D**).

Crystal Structure Determination of $[Fe_2(CO)_6(\eta^4{:}\eta'^4\text{-}C_{16}H_{18})]$ (**1**).—Crystals of (**1**) grow as clear yellow triangular prisms from $CDCl_3$–tetramethylsilane. The data crystal was of dimensions 0.35 × 0.48 × 0.58 mm and was sealed in a capillary tube. Intensities were recorded (at 273 K by ω-scan because of poor crystal quality) in the range $2.9 \leqslant 2\theta \leqslant 55°$, and two reference reflections (4 2 3 and 1 4 5) which were monitored every 48 reflections showed no significant variation during the 69 h of crystal exposure to *X*-rays. Of the total 4 384 unique reflections, 3 468 satisfied the criterion $I \geqslant 2.0\sigma(I)$ and only these were used in the solution and refinement of the structure. A numerical absorption correction was applied, based on the five crystal faces (0 1 0), ($0\,\bar{1}\,0$), ($\bar{1}\,0\,0$), ($0\,0\,\bar{1}$), and ($1\,\bar{1}\,1$). Transmission factors varied between 0.5452 and 0.6877.

Crystal data. $C_{22}H_{18}Fe_2O_6$, $M = 490.1$, triclinic, $a = 7.522(3)$, $b = 11.799(6)$, $c = 12.715(6)$ Å, $\alpha = 105.96(4)$, $\beta = 104.40(4)$, $\gamma = 98.93(4)°$, $U = 1\,020.1(8)$ Å^3, D_m not measured, $Z = 2$, $D_c = 1.60$ g cm^{-3}, $F(000) = 500$, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 14.6$ cm^{-1}.

The structure was solved by heavy-atom methods and refined by least squares; hydrogen atoms were refined with isotropic thermal parameters, non-hydrogen atoms with anisotropic parameters. The final electron-density difference synthesis showed no peaks >0.6 or <-0.4 e Å^{-3}. Refinement converged at R 0.043, R' 0.044. All computations were carried out in the laboratory on an Eclipse (Data General) computer with the SHELXTL system of programs.[17] Scattering factors were from ref. 18. Fractional atomic co-ordinates are listed in Table 4.

Table 4. Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for $[Fe_2(CO)_6(\eta^4:\eta'^4-C_{16}H_{18})]$ (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	0.880 03(5)	0.251 77(4)	0.588 75(3)	C(11)	0.666 1(4)	0.659 3(3)	0.744 7(3)
Fe(2)	0.661 71(5)	0.840 47(4)	0.836 16(3)	C(12)	0.830 9(4)	0.718 5(3)	0.840 8(3)
C(101)	1.051 0(4)	0.229 8(3)	0.702 0(3)	C(13)	0.814 8(4)	0.770 6(3)	0.949 4(3)
O(101)	1.155 1(4)	0.219 1(3)	0.777 6(3)	C(14)	0.632 8(4)	0.764 8(3)	0.965 6(3)
C(102)	0.823 9(5)	0.105 0(4)	0.479 6(3)	C(15)	0.481 0(5)	0.650 8(4)	0.939 0(3)
O(102)	0.785 9(5)	0.012 8(3)	0.412 4(3)	C(16)	0.423 0(4)	0.551 3(3)	0.825 2(3)
C(103)	1.026 2(5)	0.319 9(4)	0.520 4(3)	H(1)	0.863(4)	0.349(3)	0.930(3)
O(103)	1.122 5(4)	0.364 3(3)	0.479 2(3)	H(2A)	0.738(5)	0.170(4)	0.803(3)
C(104)	0.755 6(5)	0.898 2(3)	0.739 2(3)	H(2B)	0.561(5)	0.211(4)	0.778(3)
O(104)	0.815 8(5)	0.933 9(3)	0.677 7(3)	H(3)	0.605(5)	0.101(4)	0.606(3)
C(105)	0.703 3(5)	0.989 8(3)	0.936 5(3)	H(4)	0.532(5)	0.224(4)	0.510(4)
O(105)	0.725 6(4)	1.083 5(3)	0.999 6(3)	H(5)	0.701(4)	0.419(3)	0.545(3)
C(106)	0.410 7(5)	0.808 0(4)	0.774 2(3)	H(6)	0.953(4)	0.492(3)	0.690(3)
O(106)	0.250 1(4)	0.780 9(3)	0.737 4(3)	H(7)	1.008(4)	0.492(3)	0.867(3)
C(1)	0.793 0(4)	0.350 1(3)	0.856 2(3)	H(8)	0.762(4)	0.525(3)	0.935(3)
C(2)	0.679 7(5)	0.226 8(3)	0.776 0(3)	H(9)	0.462(4)	0.383(3)	0.742(3)
C(3)	0.655 6(4)	0.191 8(3)	0.648 7(3)	H(10)	0.429(4)	0.529(3)	0.661(3)
C(4)	0.604 2(4)	0.259 0(4)	0.572 9(3)	H(11)	0.686(5)	0.656(4)	0.679(3)
C(5)	0.713 1(4)	0.374 9(3)	0.595 4(3)	H(12)	0.943(4)	0.741(3)	0.832(3)
C(6)	0.875 1(4)	0.426 8(3)	0.693 3(2)	H(13)	0.911(5)	0.814(4)	1.005(3)
C(7)	0.889 5(4)	0.444 3(3)	0.815 8(2)	H(14)	0.632(4)	0.826(3)	1.034(3)
C(8)	0.725 7(4)	0.465 6(3)	0.862 9(3)	H(15A)	0.506(5)	0.619(4)	0.996(3)
C(9)	0.537 0(4)	0.461 4(3)	0.786 5(3)	H(15B)	0.361(5)	0.684(4)	0.950(3)
C(10)	0.506 8(4)	0.560 1(3)	0.731 3(3)	H(16)	0.297(5)	0.520(3)	0.797(3)

Acknowledgements

We thank the S.E.R.C. for Research studentships (to A. R. L., R. M. M., and J. B. S.), and Drs. R. J. Goodfellow and M. Murray for assistance with n.m.r. spectroscopy.

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Received 20*th June* 1984; *Paper* 4/1054