

Reduction-Oxidation Properties of Organotransition-metal Complexes. Part 12.¹ Formation of Carbon-Carbon Bonds *via* the Oxidative Dimerisation of $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_8\text{H}_8)]$ and the Reduction of $[\text{Fe}_2(\text{CO})_6(\eta^5:\eta^5\text{-C}_{16}\text{H}_{16})]^{2+}$; X-Ray Crystal Structures of $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2(\eta^5:\eta^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$ and $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$ †

By Neil G. Connelly,* Raymond L. Kelly, Maureen D. Kitchen, Rona M. Mills, Robert F. D. Stansfield, Mark W. Whiteley, Susan M. Whiting, and Peter Woodward,* Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS

The complexes $[\text{Fe}(\text{CO})_{3-n}\text{L}_n(\eta^4\text{-cot})]$ [1 : $\text{cot} = \text{cyclo-octatetraene}$; $n = 0-3$, $\text{L} = \text{P}(\text{OMe})_3$; $n = 1$, $\text{L} = \text{P}(\text{NMe}_2)_3$, PPh_3 , $\text{P}(\text{OCH}_2)_3\text{CMe}$, or $\text{P}(\text{OPh})_3$] undergo chemically irreversible one-electron oxidation in CH_2Cl_2 at a platinum electrode. Chemical generation of the highly reactive radical cation $[\text{Fe}(\text{CO})_2\text{L}(\text{C}_8\text{H}_8)]^+$ [2 ; $\text{L} = \text{CO}$ or $\text{P}(\text{OPh})_3$], by oxidation of (1) with silver(I) salts or $[\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3][\text{PF}_6]$, is followed by isomerisation and dimerisation, *via* C-C bond formation, to give $[\text{Fe}_2(\text{CO})_{6-n}\text{L}_n(\eta^5:\eta^5\text{-C}_{16}\text{H}_{16})]^{2+}$ [3 ; $n = 0$ or 2 , $\text{L} = \text{P}(\text{OPh})_3$]. The crystal structure of [3 ; $n = 2$, $\text{L} = \text{P}(\text{OPh})_3$], as the $[\text{PF}_6]^-$ salt, reveals the presence of a dimeric $\text{C}_{16}\text{H}_{16}$ unit comprising two fused ring systems bonded to one another across a two-fold crystallographic axis of symmetry. The five unbridged carbon atoms of the C_7 ring are coplanar and η^5 -bonded to the iron atom, which in turn is orthogonally co-ordinated to the two CO ligands and the $\text{P}(\text{OPh})_3$ 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 dimeric ligand thus has an overall S shape when viewed down the two-fold axis. Along the $\text{Fe} \cdots \text{Fe}$ vector, by contrast, the C_3 rings are seen edgewise and the two C_7 rings are almost eclipsed. Complex (3 ; $n = 0$) reacts with $\text{Na}[\text{BH}_4]$ to give $[\text{Fe}_2(\text{CO})_6(\eta^4:\eta^4\text{-C}_{16}\text{H}_{18})]$ (4). With halide ion, however, (3 ; $n = 0$) affords $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$ (5) *via* reductive C-C coupling. X-Ray analysis shows that in complex (5) a further link between the two halves of the dimer has been formed, in that the fifth C atom of the C_7 ring which in (3) was bonded to the metal atom is now bonded to its counterpart in the other half of the dimer, forming an additional central C_6 ring. As might be expected, the C_7 ring which is not co-ordinated to iron is more nearly planar and the C-C bonds are more localised. With $[\text{Fe}_2(\text{CO})_6]$, complex (5) yields $[\text{Fe}_2(\text{CO})_6(\eta^4:\eta^4\text{-C}_{16}\text{H}_{18})]$ (6), but with $\text{NMe}_3 \cdot 2\text{H}_2\text{O}$ in refluxing benzene, ring detachment results in the isolation of the free polycyclic hydrocarbon, $\text{C}_{16}\text{H}_{16}$ (7).

We have recently shown² that stable, in some cases isolable, radical cations result from the one-electron oxidation of the cyclobutadiene complexes $[\text{M}(\text{CO})_{3-n}\text{L}_n(\eta^4\text{-C}_4\text{Ph}_4)]$ ($\text{M} = \text{Fe}$ or Ru , $n = 1-3$, $\text{L} = \text{P}$ donor). Preliminary studies³ revealed, however, that the radical cations formed from analogous η^4 -cyclo-octatetraene (cot) complexes are highly reactive and, once formed, undergo dimerisation.⁴ We now present details of chemical and electrochemical studies on the one-electron oxidation of $[\text{Fe}(\text{CO})_{3-n}\text{L}_n(\eta^4\text{-cot})]$, of the chemical synthesis, X-ray analysis, and reactions of the dimer $[\text{Fe}_2(\text{CO})_{6-n}\text{L}_n(\eta^5:\eta^5\text{-C}_{16}\text{H}_{16})]^{2+}$, and of the X-ray analysis of $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$, a complex of a dimer of cot.

RESULTS AND DISCUSSION

The red crystalline complexes $[\text{Fe}(\text{CO})_{3-n}\text{L}_n(\eta^4\text{-cot})]$ [1 : $n = 1$; $\text{L} = \text{P}(\text{NMe}_2)_3$, PPh_3 , $\text{P}(\text{OMe})_3$, or $\text{P}(\text{OPh})_3$; $n = 2$, $\text{L} = \text{P}(\text{OMe})_3$] were prepared by u.v. irradiation of a solution of $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$ in tetrahydrofuran (thf) or toluene in the presence of the appropriate ligand. In all cases small quantities of $[\text{Fe}(\text{CO})_3\text{L}_2]$ were also formed; only for $\text{L} = \text{P}(\text{OMe})_3$ was disubstitution observed. The complex $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OCH}_2)_3\text{CMe}\}(\eta^4\text{-cot})]$ was prepared by the thermal reaction of the tricarbonyl with $\text{P}[\{(\text{OCH}_2)_3\text{CMe}\}]$ in refluxing hexane,⁵ and $[\text{Fe}\{\text{P}(\text{OMe})_3\}_3(\eta^4\text{-cot})]$,

† The last two complexes are *trans-u*-{2-6- η :2'-6'- η -8,8'-bi(bicyclo[5.1.0]octadienyl)}-tetracarbonylbis(triphenyl phosphite)di-iron bis(hexafluorophosphate) and tricarbonyl(3-6- η -pentacyclo[9.5.0.0^{2,10}.0^{3,5}.0^{4,10}]hexadeca-3,5,9,11-tetraene)iron, respectively.

prepared from $[\text{Fe}(\text{cot})_2]$ and $\text{P}(\text{OMe})_3$,⁶ was kindly supplied by Dr. M. Green of this Department. All of the new complexes were fully characterised by i.r. spectroscopy and elemental analysis (Table 1) before use.

Electrochemical Studies.—Complex (1) undergoes one-electron oxidation,[†] to the radical cation $[\text{Fe}(\text{CO})_{3-n}\text{L}_n(\text{C}_8\text{H}_8)]^+$ (2), at a platinum-wire electrode in CH_2Cl_2 or in MeCN. The electron-transfer process is, however, chemically irreversible; even at a scan rate of 200 V s^{-1} (in CH_2Cl_2), and at -40°C (in MeCN), no evidence for a peak corresponding to the reduction of $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}(\text{C}_8\text{H}_8)]^+$ could be found in the cyclic voltammogram of $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}(\eta^4\text{-cot})]$.

The peak potential ($E_{p,ox}$) (Table 1), measured for the oxidation of (1) at a scan rate of 100 mV s^{-1} , cannot be directly equated to oxidation potential, and therefore detailed comparisons within the series of complexes cannot be made. There is, however, a general dependence of ($E_{p,ox}$) on the donor ability of L such that an increase in ligand basicity results in a decrease in the potential. In addition there is a striking, and synthetically useful, reliance of ($E_{p,ox}$) on n in that for each CO ligand replaced by $\text{P}(\text{OMe})_3$ the potential is lowered by *ca.* 0.4 V. Thus full substitution of $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$ [$(E_{p,ox}) = 0.88 \text{ V}$] to give $[\text{Fe}\{\text{P}(\text{OMe})_3\}_3(\eta^4\text{-cot})]$ [$(E_{p,ox}) = -0.22 \text{ V}$] results in a change in ($E_{p,ox}$) of *ca.* 1.1 V.

Although reduction of (1) was not observed down to

† That one-electron transfer is involved is confirmed by a comparison of the peak current for the oxidation of (1) with those for the one-electron oxidations of ferrocene and $[\text{Ni}\{\text{S}_2\text{C}_2(\text{CN})_2\}_2]^{2+}$.

TABLE 1
Infrared, analytical, and electrochemical data

Complex	Yield/%	M.p. ($\theta_c/^\circ\text{C}$)	$\bar{\nu}(\text{CO})^a/\text{cm}^{-1}$	Analysis ^b /%		$(E_p)_{\text{ox}}^c/\text{V}$
				C	H	
$[\text{Fe}(\text{CO})_2\{\text{P}(\text{NMe}_2)_3\}(\eta^4\text{-cot})]$	19	81	1 967, 1 918	50.6 (50.7)	6.9 (6.9) ^d	0.36
$[\text{Fe}(\text{CO})_2\{\text{PPh}_3\}(\eta^4\text{-cot})]$	39	154	1 982, 1 925	70.0 (70.3)	4.9 (4.9)	0.47
$[\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}(\eta^4\text{-cot})]$	43	40—44	1 991, 1 937 2 001, 1 951 (sh), 1 941 ^e	45.7 (45.9)	5.3 (5.0)	0.48
$[\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}_2(\eta^4\text{-cot})]$	19	40—42	1 917 1 925 ^e	41.4 (41.3)	6.4 (6.0)	0.12
$[\text{Fe}(\text{CO})_2\{\text{P}(\text{OCH}_3)_2\text{CMe}\}(\eta^4\text{-cot})]$	43	185	2 003, 1 946	49.3 (49.5)	4.7 (4.7)	0.50
$[\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}(\eta^4\text{-cot})]$	28	137	2 004, 1 950	63.7 (63.9)	4.5 (4.4)	0.60
$[\text{Fe}_2(\text{CO})_6(\eta^5:\eta^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$	87	decomp. > 122	2 095, 2 045br ^f	33.6 (33.9)	2.4 (2.1)	
$[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2(\eta^5:\eta^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$	68		2 061, 2 022	50.1 (50.1)	3.6 (3.5)	
$[\text{Fe}_2(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2(\eta^5:\eta^5\text{-C}_{16}\text{H}_{16})]\text{I}_2$	52	decomp. > 200	1 992	31.7 (32.0)	4.6 (4.6)	
$[\text{Fe}_2(\text{CO})_6(\eta^4:\eta^4\text{-C}_{16}\text{H}_{16})]$	23	decomp. > 135	2 037, 1 967 2 039, 1 977, 1 969 ^e	53.5 (53.9)	3.9 (3.7)	
$[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$	54	140—144	2 037, 1 967 2 045, 1 981, 1 971 ^e	65.5 (65.5)	4.8 (4.6)	
$[\text{Fe}_2(\text{CO})_6(\eta^4:\eta^4\text{-C}_{16}\text{H}_{16})]$	46	decomp. > 200	2 035, 1 967 2 041, 1 979, 1 971 ^e	54.2 (54.1)	3.3 (3.3)	

^a In CH_2Cl_2 unless otherwise stated. ^b Calculated values are given in parentheses. ^c vs. a calomel electrode 1 mol dm^{-3} in LiCl; measured at a scan rate of 100 mV s^{-1} . ^d N, 10.9 (11.1%). ^e In hexane. ^f In Nujol.

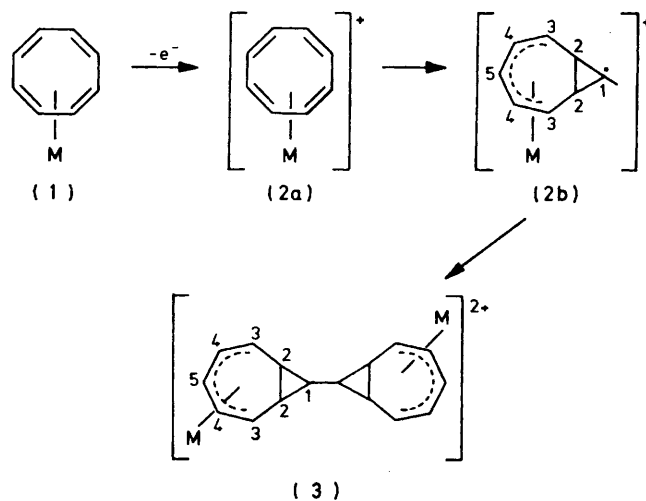
−1.5 V in CH_2Cl_2 , the tricarbonyl undergoes two one-electron reductions, in dimethylformamide⁷ or 1,2-dimethoxyethane,⁸ to $[\text{Fe}(\text{CO})_3(\text{C}_8\text{H}_8)]^Z$ ($Z = -1$ and -2). Chemical reduction with potassium in thf affords solutions of the monoanion, and controlled-potential electrolysis results in the generation of the dianion; the latter reacts with protons to give quantitative yields of $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_8\text{H}_{10})]$ ($\text{C}_8\text{H}_{10} = 1,3,5\text{-cyclo-octatriene}$)⁷ and is said to be a source of other polycyclic hydrocarbon complexes.⁹

Synthetic Studies.—In principle the wide variation of $(E_p)_{\text{ox}}$ with n in $[\text{Fe}(\text{CO})_{3-n}\text{L}_n(\eta^4\text{-cot})]$ allows the selective use of a wide range of chemical oxidants to generate (2). In practice, however, carbonyl substitution by P-donor ligands renders both the metal centre and the co-ordinated cot ligand more susceptible to reaction with electrophiles. Thus, the arenediazonium ion $[\text{N}_2\text{C}_6\text{H}_4\text{R}-p]^+$, a weak one-electron oxidant, undergoes ring addition to $[\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}_2(\eta^4\text{-cot})]$.¹⁰ In this work, therefore, the reactions of the parent tricarbonyl $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$ with suitable strong oxidants have been studied; spectroscopic characterisation of the products is also facilitated by the absence of phosphine or phosphite ligands.

Addition of a deep blue solution of $[\text{N}(\text{C}_6\text{H}_4\text{Br}-p)_3]^-[\text{PF}_6]^+$ {generated by *in situ* oxidation of $\text{N}(\text{C}_6\text{H}_4\text{Br}-p)_3$ with $[\text{NO}][\text{PF}_6]$ } to the red solution of $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$ in CH_2Cl_2 results in the immediate precipitation of quantitative yields of the yellow dimer $[\text{Fe}_2(\text{CO})_{6-n}\text{L}_n(\eta^5:\eta^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$ (3; $n = 0$) (Scheme 1). The salt-like nature of the product is suggested by i.r. carbonyl absorptions above 2 000 cm^{-1} (Table 1) and confirmed by a strong band at 835 cm^{-1} (Nujol) due to the $[\text{PF}_6]^-$ anion; a conductivity measurement ($\Lambda = 270 \text{ S cm}^2 \text{ mol}^{-1}$ in acetone, $10^{-4} \text{ mol dm}^{-3}$) was also consistent with the presence of a 2 : 1 electrolyte in solution.

* E_p for the couple $[\text{N}(\text{C}_6\text{H}_4\text{Br}-p)_3]^+ - \text{N}(\text{C}_6\text{H}_4\text{Br}-p)_3$ is 1.16 V.

The substituted complex [3; $n = 2$, $\text{L} = \text{P}(\text{OPh})_3$] may be prepared by oxidation of $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}(\eta^4\text{-cot})]$ with either $[\text{N}(\text{C}_6\text{H}_4\text{Br}-p)_3][\text{PF}_6]$ or $\text{Ag}[\text{PF}_6]$. In the latter case, however, the dimeric product is formed *via* a silver-containing intermediate. Thus, in toluene the reaction affords a co-precipitate of silver metal and a yellow solid which can be isolated by acetone extraction



SCHEME 1 $\text{M} = \text{Fe}(\text{CO})_{3-n}\text{L}_n$

of the mixture and rapid precipitation with diethyl ether. The presence of co-ordinated silver in the yellow intermediate is suggested by its slow decomposition in acetone, to (3) and metallic silver, and by atomic absorption spectroscopy, which showed 13% silver in one sample. Although no further characterisation of the intermediate was possible, analogy with $[\text{Ag}\{\text{Fe}(\text{CO})_3(\text{PPh}_3)_2\}_2]^+$, detected during the silver(I) oxidation of $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]^+$,¹¹ implies direct Ag-Fe bonding.

One other example of (3) has been isolated, by iodine oxidation of $[\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}_2(\eta^4\text{-cot})]$. Recrystallisation, from CH_2Cl_2 -n-hexane, of the brown precipitate formed in n-hexane gave moderate yields of yellow $[\text{Fe}_2(\text{CO})_2\{\text{P}(\text{OMe})_3\}_4(\eta^5:\eta^5\text{-C}_{16}\text{H}_{16})]\text{I}_2$, characterised by elemental analysis, the i.r. carbonyl spectrum (Table 1), and a poorly resolved ^1H n.m.r. spectrum generally similar to that of (3; $n = 0$).

The ^1H n.m.r. spectra of (3; $n = 0$) and of [3; $n = 2$, $\text{L} = \text{P}(\text{OPh})_3$] (at 60 °C, with ^{31}P decoupling) are closely similar (allowing for high-field shifts due to the presence of the phosphite ligand) and show the $\text{C}_{16}\text{H}_{16}$ ligand to be the same in each complex. Below 60 °C the ^1H n.m.r. spectrum of [3; $n = 2$, $\text{L} = \text{P}(\text{OPh})_3$] is more complex suggesting that restricted rotation of the $\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}$ group leads to further asymmetry in the dication. The ^1H and ^{13}C n.m.r. spectra of (3) (Table 2) are in full agreement with the structure, shown

in Scheme 1, which has been confirmed by a single-crystal X-ray diffraction study (Tables 3 and 4) on $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2(\eta^5:\eta^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$.

The overall molecular configuration is shown in Figure 1 together with the crystallographic atom-numbering scheme. As expected, the iron atom is η^5 -bonded (mean $\text{Fe}-\text{C}$ 2.18, mean $\text{C}-\text{C}$ 1.40 Å) to five coplanar (within 0.04 Å) atoms, $\text{C}(21)-\text{C}(25)$, of a seven-membered ring which in turn is fused to a three-membered ring. The apex of this three-membered ring is directly bonded to an exactly similar moiety related by a crystallographic two-fold axis. This can be clearly seen in Figure 2, which shows the contents of the orthorhombic unit cell. The two carbonyl groups and the $\text{P}(\text{OPh})_3$ ligand are in an approximately orthogonal relationship (Table 4). The $\text{C}_{16}\text{H}_{16}$ ring system is folded along the $\text{C}(21) \cdots \text{C}(25)$ vector away from the $\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}$ group, dividing the C_7 ring into two planar portions at a dihedral angle of 144°, and again

TABLE 2
Proton and ^{13}C n.m.r. data ^a

Compound	^1H (τ)	^{13}C (p.p.m. ^b)
$[\text{Fe}_2(\text{CO})_6(\eta^5:\eta^5\text{-C}_{16}\text{H}_{16})]^{2+}$ (3; $\text{L} = \text{CO}$) ^c	2.32 [1 H, t, $J(\text{H}^4\text{H}^5)$ 6 Hz, H^6], 4.32 [2 H, dd, $J(\text{H}^4\text{H}^5)$ 6, $J(\text{H}^4\text{H}^3)$ 10 Hz, H^4], 4.90 (2 H, m, H^9), 6.86 (2 H, m, H^2), 8.02 [1 H, t, $J(\text{H}^1\text{H}^2)$ 6 Hz, H^1]	42.8 (C^2), 59.4 (C^1), 97.5 (C^5), 101.4, 102.6 (C^3 , C^4)
$[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2(\eta^5:\eta^5\text{-C}_{16}\text{H}_{16})]^{2+}$ [3; $\text{L} = \text{P}(\text{OPh})_3$] ^d	2.63 [15 H, m, $\text{P}(\text{OPh})_3$], 3.31 [1 H, t, $J(\text{H}^4\text{H}^5)$ 5 Hz, H^6], 4.61 (2 H, m, H^4), 5.19 (2 H, m, H^9), 6.97 (2 H, m, H^2), 8.43 [1 H, t, $J(\text{H}^1\text{H}^2)$ 7 Hz, H^1]	41.4 (C^2), 57.1 (C^1), 94.6 (C^5), 101.1 (C^3 , C^4), 121.2, 127.2, 131.2 [$\text{P}(\text{OPh})_3$], 150.6 (d, $J(^{13}\text{C}^{31}\text{P})$ 11 Hz, CO)
$[\text{Fe}_2(\text{CO})_6(\eta^4:\eta^4\text{-C}_{16}\text{H}_{16})]$ (4)	4.72 [1 H, ddd, $J(\text{H}^4\text{H}^3)$ 8, $J(\text{H}^4\text{H}^5)$ 5, $J(\text{H}^6\text{H}^9)$ 1 Hz, H^4], 4.96 [1 H, m, $J(\text{H}^6\text{H}^4)$ 5, $J(\text{H}^6\text{H}^3)$ 1.5 Hz, H^6], 6.69 [1 H, ddd, $J(\text{H}^3\text{H}^4)$ 8, $J(\text{H}^3\text{H}^2)$ 8, $J(\text{H}^3\text{H}^5)$ 1.5 Hz, H^3], 6.94 [1 H, m, $J(\text{H}^6\text{H}^7)$ 5, $J(\text{H}^6\text{H}^9)$ 3, $J(\text{H}^6\text{H}^4)$ 1 Hz, H^6], 7.74 [1 H, ddd, $J(\text{H}^7\text{H}^7')$ 17, $J(\text{H}^7\text{H}^6)$ 10, $J(\text{H}^7\text{H}^9)$ 5 Hz, H^7], 8.15 [1 H, dd, $J(\text{H}^7\text{H}^7')$ 17, $J(\text{H}^7\text{H}^6)$ 3 Hz, H^7], 8.35 [1 H, m, $J(\text{H}^2\text{H}^9)$ 9, $J(\text{H}^2\text{H}^3)$ 8 Hz, H^2], 8.90 [1 H, ddd, $J(\text{H}^8\text{H}^7)$ 10, $J(\text{H}^8\text{H}^2)$ 9 Hz, H^8], 9.92 (1 H, m, H^1)	18.02, 18.69 (C^1 , C^8), 19.97, 21.11 (C^2 , C^7), 60.43, 62.92 (C^3 , C^6), 85.55, 90.46 (C^4 , C^5), 211.62 (CO)
$[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$ (5)	4.12 [1 H, ddd, $J(\text{H}^3\text{H}^4)$ 9, $J(\text{H}^3\text{H}^2)$ 6 Hz, H^3], 4.37 [1 H, m, $J(\text{H}^4\text{H}^3)$ 9 Hz, H^4], 4.45 (2 H, m, H^5 and H^9), 4.81 (2 H, m, H^{12} and H^{13}), 6.72 [1 H, ddd, $J(\text{H}^{11}\text{H}^{12})$ 8, $J(\text{H}^{11}\text{H}^{10})$ 8, $J(\text{H}^{11}\text{H}^{13})$ 2 Hz, H^{11}], 6.93 [1 H, ddd, $J(\text{H}^{14}\text{H}^{13})$ 8, $J(\text{H}^{14}\text{H}^{15})$ 6, $J(\text{H}^{14}\text{H}^{12})$ 2 Hz, H^{14}], 7.10 [1 H, ddd, $J(\text{H}^7\text{H}^8)$ 7, $J(\text{H}^7\text{H}^9)$ 3 Hz, H^7], 7.52 [1 H, ddd, $J(\text{H}^{16}\text{H}^{16})$ 8, $J(\text{H}^{16}\text{H}^{14})$ 6 Hz, H^{16}], 8.07 [1 H, m, $J(\text{H}^2\text{H}^9)$ 7, $J(\text{H}^2\text{H}^3)$ 6 Hz, H^2], 8.38 [1 H, ddd, $J(\text{H}^{10}\text{H}^{11})$ 8, $J(\text{H}^{10}\text{H}^{16})$ 8, $J(\text{H}^{10}\text{H}^9)$ 7 Hz, H^{10}], 8.81 [1 H, ddd, $J(\text{H}^8\text{H}^7)$ 7, $J(\text{H}^8\text{H}^2)$ 7, $J(\text{H}^8\text{H}^3)$ 7 Hz, H^8], 9.12 [1 H, ddd, $J(\text{H}^{18}\text{H}^{18})$ 8, $J(\text{H}^{16}\text{H}^{10})$ 8, $J(\text{H}^{16}\text{H}^9)$ 8 Hz, H^{16}], 9.14 [1 H, ddd, $J(\text{H}^1\text{H}^9)$ 7, $J(\text{H}^1\text{H}^2)$ 6 Hz, H^1], 9.67 [1 H, ddd, $J(\text{H}^9\text{H}^8)$ 8, $J(\text{H}^9\text{H}^{10})$ 7 Hz, H^9]	14.99, 15.35, 17.11, 17.41 (C^1 , C^8 , C^9 , C^{16}), 22.21, 26.21, 33.01, 41.62 (C^2 , C^7 , C^{10} , C^{15}), 60.19, 67.65 (C^{11} , C^{14}), 85.67, 89.13 (C^{12} , C^{13}), 122.50, 124.01, 131.11, 135.72 (C^3 , C^4 , C^5 , C^6), 211.45 (CO)
$[\text{Fe}_2(\text{CO})_6(\eta^4:\eta^4\text{-C}_{16}\text{H}_{16})]$ (6) ^e	4.9 (H^4 , H^5), 6.74 (H^3), 7.00 (H^6), 7.50 (H^7), 8.19 (H^2), 9.25 (H^8), 9.57 (H^1)	15.63, 18.81 (C^1 , C^8), 25.81, 35.32 (C^2 , C^7), 61.42, 66.85 (C^3 , C^6), 85.13, 89.39 (C^4 , C^5)
$\text{C}_{16}\text{H}_{16}$ (7)	4.06 [1 H, dd, $J(\text{H}^3\text{H}^4)$ 12 Hz, H^3], 4.36 (3 H, m, $\text{H}^4\text{-H}^6$), 7.05 [1 H, dd, $J(\text{H}^7\text{H}^6)$ 9 Hz], 8.30 [1 H, ddd, $J(\text{H}^2\text{H}^8)$ 8, $J(\text{H}^2\text{H}^1)$ 8 Hz, H^2], 8.64 [1 H, ddd, $J(\text{H}^8\text{H}^1)$ 8, $J(\text{H}^8\text{H}^2)$ 8 Hz, H^8], 9.18 [1 H, dd, $J(\text{H}^1\text{H}^8)$ 8, $J(\text{H}^1\text{H}^2)$ 8 Hz, H^1]	13.98, 17.67 (C^1 , C^8), 23.54, 39.12 (C^2 , C^7), 122.85, 123.48, 131.20, 136.63 ($\text{C}^3\text{-C}^6$)

^a In CDCl_3 unless stated. Numbering as in Scheme 2. ^b Downfield from SiMe_4 . ^c In CD_3NO_2 . ^d In CD_3NO_2 at 60 °C, ^{31}P -decoupled spectrum. ^e ^{13}C n.m.r. in $[\text{C}_6\text{H}_6]$ toluene; ^1H n.m.r. data from Dr. A. W. Parkins and ref. 13.

TABLE 3

Atomic positional parameters (fractional cell co-ordinates) for $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2(\eta^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$ complex (3), with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	-0.139 5(9)	0.242 1(8)	0.086 7(16)
C(2)	-0.156 2(9)	0.271 3(10)	0.008 8(22)
C(3)	-0.179 5(13)	0.329 4(12)	0.015 1(27)
C(4)	-0.187 0(17)	0.359 0(15)	0.090 0(28)
C(5)	-0.179 8(17)	0.328 3(17)	0.178 1(26)
C(6)	-0.149 0(11)	0.273 4(13)	0.164 2(19)
C(7)	-0.065 3(9)	0.110 1(6)	0.276 4(9)
C(8)	-0.129 1(9)	0.081 0(7)	0.260 5(11)
C(9)	-0.150 4(11)	0.036 7(10)	0.319 7(13)
C(10)	-0.111 3(15)	0.020 9(10)	0.395 3(17)
C(11)	-0.051 0(13)	0.051 8(9)	0.415 1(14)
C(12)	-0.026 6(8)	0.096 2(7)	0.353 1(12)
C(13)	-0.048 8(9)	0.074 1(6)	-0.012 8(10)
C(14)	0.007 9(8)	0.068 5(6)	-0.073 4(11)
C(15)	-0.005 5(11)	0.045 5(7)	-0.162 3(13)
C(16)	-0.071 5(14)	0.030 0(9)	-0.188 5(13)
C(17)	-0.125 0(11)	0.033 5(8)	-0.124 9(17)
C(18)	-0.114 4(9)	0.056 6(7)	-0.036 1(11)
C(19)	0.019 4(7)	0.219 2(7)	-0.048 9(11)
C(20)	0.019 1(7)	0.296 9(8)	0.094 5(10)
C(21)	0.158 5(7)	0.272 5(7)	0.033 1(10)
C(22)	0.158 1(6)	0.211 2(7)	0.011 3(8)
C(23)	0.143 7(6)	0.161 4(6)	0.073 2(10)
C(24)	0.116 6(7)	0.171 2(7)	0.161 0(9)
C(25)	0.107 5(7)	0.227 1(7)	0.205 4(8)
C(26)	0.153 5(7)	0.285 2(6)	0.208 1(10)
C(27)	0.180 9(7)	0.305 7(5)	0.120 7(12)
C(28)	0.231 8(7)	0.281 0(6)	0.193 9(9)
H(2)	-0.147 1	0.249 7	-0.057 4
H(3)	-0.197 6	0.352 0	-0.047 1
H(4)	-0.198 2	0.408 0	0.090 3
H(5)	-0.192 9	0.348 6	0.244 2
H(6)	-0.132 6	0.249 9	0.226 4
H(8)	-0.162 0	0.095 0	0.202 9
H(9)	-0.199 8	0.013 1	0.304 9
H(10)	-0.129 8	-0.016 3	0.439 1
H(11)	-0.021 8	0.041 6	0.477 6
H(12)	0.022 7	0.120 2	0.367 9
H(14)	0.061 1	0.082 2	-0.053 5
H(15)	0.038 7	0.038 4	-0.208 9
H(16)	-0.082 8	0.017 8	-0.259 3
H(17)	-0.177 4	0.016 5	-0.142 7
H(18)	-0.157 6	0.058 9	0.013 0
H(21)	0.140 1	0.302 7	-0.021 4
H(22)	0.167 8	0.198 8	-0.059 8
H(23)	0.155 8	0.114 5	0.052 8
H(24)	0.100 9	0.130 3	0.198 7
H(25)	0.059 2	0.229 7	0.245 8
H(26)	0.121 2	0.304 6	0.262 6
H(27)	0.182 1	0.347 9	0.080 7
H(28)	0.288 3	0.281 9	0.208 4
F(1)	0.234 3(5)	0.072 8(4)	0.479 7(6)
F(2)	0.223 0(4)	0.069 5(4)	0.262 5(6)
F(3)	0.248 6(7)	0.000 2(5)	0.369 8(8)
F(4)	0.215 6(8)	0.142 9(5)	0.372 5(9)
F(5)	0.311 8(6)	0.086 9(7)	0.359 0(8)
F(6)	0.148 0(7)	0.057 0(7)	0.382 6(9)
F(3')	0.165 5(17)	0.013 3(15)	0.376 8(23)
F(4')	0.280 0(23)	0.131 9(17)	0.370 0(25)
F(5')	0.300 4(27)	0.030 1(20)	0.373 7(33)
F(6')	0.162 2(18)	0.122 4(16)	0.361 8(22)
Fe	0.054 2(1)	0.222 0(1)	0.066 6(1)
O(1)	-0.114 0(4)	0.181 2(4)	0.080 1(6)
O(2)	-0.036 5(4)	0.156 3(4)	0.218 6(8)
O(3)	-0.033 9(4)	0.093 2(3)	0.078 8(6)
O(4)	-0.003 4(6)	0.218 9(5)	-0.122 4(7)
O(5)	0.001 4(6)	0.346 4(5)	0.112 8(9)
P(1)	-0.034 7(2)	0.163 3(2)	0.109 4(2)
P(2)	0.228 8(3)	0.070 0(2)	0.371 6(3)

For atoms F(3)—F(6), the population parameter = 0.8; for F(3')—F(6'), the population parameter = 0.2.

TABLE 4

Bond distances (Å) and angles (°) for $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2(\eta^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$ complex (3), with estimated standard deviations in parentheses

(i) Distances			
Fe co-ordination			
Fe—C(21)	2.292(14)	Fe—P(1)	2.186(4)
Fe—C(22)	2.119(11)	Fe—C(19)	1.796(15)
Fe—C(23)	2.132(12)	C(19)—O(4)	1.147(19)
Fe—C(24)	2.109(14)	Fe—C(20)	1.792(17)
Fe—C(25)	2.248(12)	C(20)—O(5)	1.152(20)
C ₁₆ H ₁₆ ligand			
C(21)—C(22)	1.36(2)	C(26)—C(27)	1.44(2)
C(22)—C(23)	1.43(2)	C(26)—C(28)	1.49(2)
C(23)—C(24)	1.39(2)	C(27)—C(21)	1.52(2)
C(24)—C(25)	1.38(2)	C(27)—C(28)	1.52(2)
C(25)—C(26)	1.52(2)	C(28)—C(28')	1.50(2)
Phosphite ligand			
P(1)—O(1)	1.593(9)	O(1)—C(1)	1.40(2)
P(2)—O(2)	1.589(9)	O(2)—C(7)	1.41(2)
P(3)—O(3)	1.578(8)	O(3)—C(13)	1.42(2)
Mean C—C(phenyl) 1.35(2)			
Hexafluorophosphate anion (disordered)			
P(2)—F(1)	1.57(1)		
P(2)—F(2)	1.58(1)		
P(2)—F(3)	1.55(1)	P(2)—F(3')	1.71(3)
P(2)—F(4)	1.60(1)	P(2)—F(4')	1.65(4)
P(2)—F(5)	1.61(1)	P(2)—F(5')	1.60(5)
P(2)—F(6)	1.55(1)	P(2)—F(6')	1.69(3)
(ii) Angles			
Fe co-ordination			
P(1)—Fe—C(19)	88.1(5)	Fe—C(20)—O(5)	175(1)
Fe—C(19)—O(4)	178(1)	C(19)—Fe—C(20)	96.1(7)
P(1)—Fe—C(20)	100.3(5)		
C ₁₆ H ₁₆ ligand			
C(27)—C(21)—C(22)	131(1)	C(27)—C(26)—C(28)	63(1)
C(21)—C(22)—C(23)	126(1)	C(26)—C(27)—C(21)	120(1)
C(22)—C(23)—C(24)	122(1)	C(21)—C(27)—C(28)	126(1)
C(23)—C(24)—C(25)	127(1)	C(26)—C(27)—C(28)	60(1)
C(24)—C(25)—C(26)	131(1)	C(26)—C(28)—C(27)	57(1)
C(25)—C(26)—C(27)	116(1)	C(26)—C(28)—C(28')	121
C(25)—C(26)—C(28)	120(1)	C(27)—C(28)—C(28')	127
Phosphite ligand			
Fe—P(1)—O(1)	119.7(4)	P(1)—O(1)—C(1)	121.9(9)
Fe—P(1)—O(2)	110.7(3)	P(1)—O(2)—C(7)	131.8(8)
Fe—P(1)—O(3)	118.0(3)	P(1)—O(3)—C(13)	122.7(7)
O(1)—C(1)—C(6)	126(2)	O(2)—C(7)—C(12)	116(1)
O(1)—C(1)—C(2)	118(2)	O(3)—C(13)—C(14)	118(1)
O(2)—C(7)—C(8)	124(1)	O(3)—C(13)—C(18)	120(1)
Hexafluorophosphate anion (disordered)			
F(1)—P(2)—F(2)	178.2(5)	F(1)—P(2)—F(3')	91.7(12)
F(1)—P(2)—F(3)	92.2(6)	F(1)—P(2)—F(4')	86.8(13)
F(1)—P(2)—F(4)	88.0(6)	F(1)—P(2)—F(5')	86.9(17)
F(1)—P(2)—F(5)	92.3(6)	F(1)—P(2)—F(6')	96.1(11)
F(1)—P(2)—F(6)	88.2(6)	F(3')—P(2)—F(6')	88.3(16)
F(3)—P(2)—F(6)	93.5(7)	F(3')—P(2)—F(5')	101.4(22)
F(3)—P(2)—F(5)	89.3(7)	F(4')—P(2)—F(6')	83.4(18)
F(4)—P(2)—F(6)	91.5(8)	F(4')—P(2)—F(5')	87.0(24)
F(4)—P(2)—F(5)	85.8(8)	F(4')—P(2)—F(4')	44.6(15)

in the same sense along the C(26)—C(27) bond (dihedral angle 115°) which is the junction between the seven- and three-membered rings. Lastly another bend also in the same sense occurs between the three-membered ring and the bond C(28)—C(28') which connects the two halves of the cation; this bond is at an angle of 140° to the plane of the three-membered ring and is of length 1.50(2) Å

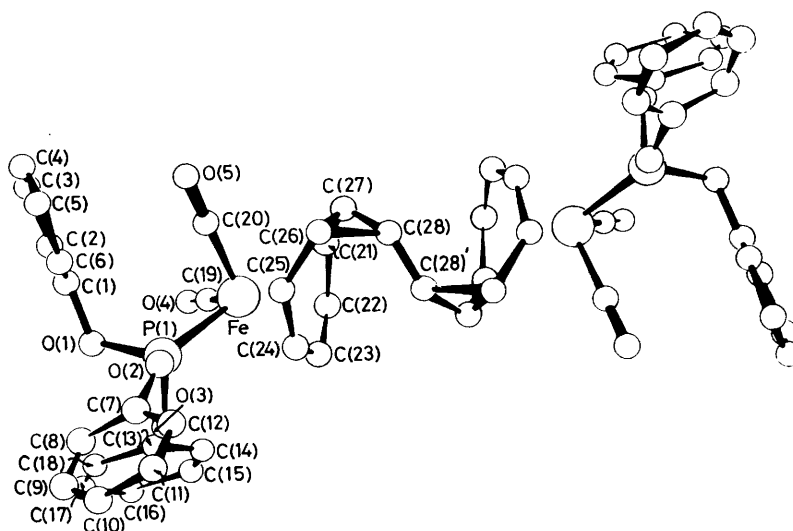


FIGURE 1 Molecular configuration of the dication of complex (3), $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2(\eta^5\text{-}\eta^6\text{-C}_{16}\text{H}_{16})]^{2+}$, showing the crystallographic atom-numbering sequence

(Table 4). A stereoscopic view of the molecular structure is given in Figure 3.

The geometry around the iron atom shows no abnormal features [Fe-C 1.79, C-O 1.15, Fe-P 2.186, P-O 1.59, and O-C 1.41 Å; mean Fe-P-O 116, mean P-O-C 125°]. It should be noted, however, that the estimated standard deviations in the atomic positional parameters

are all relatively high (Table 3), reflecting poor crystal quality. Nearly half of the original data set had $I/\sigma(I) < 1$; see Experimental section. Nevertheless the diffraction results reveal the existence of an unprecedented form of dimeric cyclo-octatetraene. For details about many other forms of cot dimers, including other iron carbonyl complexes, see ref. 12.

The structure of (3) is closely related to that reported¹³ for $[\text{Fe}_2(\text{CO})_6(\eta^4\text{-}\eta^4\text{-C}_{16}\text{H}_{16})]$ in which the atom equivalent to C(21) is bonded across the two-fold axis to its dimeric counterpart (thereby creating a central six-membered ring) instead of to the iron atom.

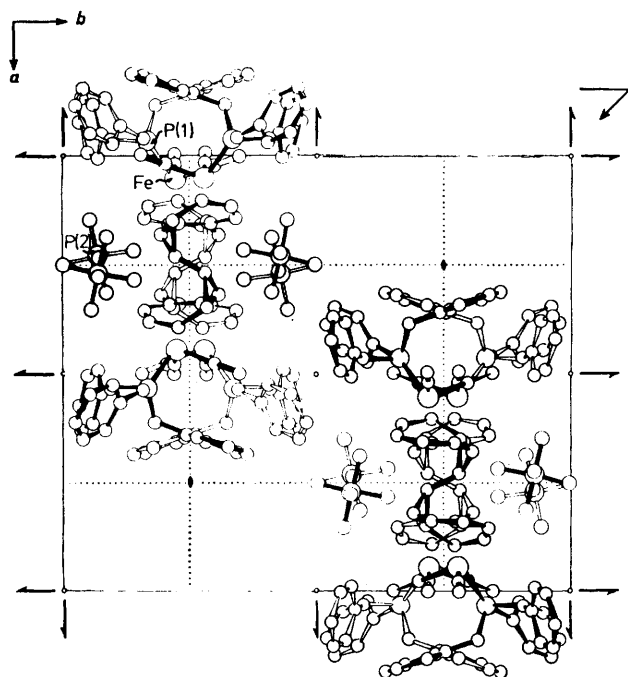


FIGURE 2 Contents of the orthorhombic unit cell of complex (3), $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2(\eta^5\text{-}\eta^6\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$, looking down c towards the origin. The disorder in the equatorial fluorine atoms of the PF_6 anion has not been included. The coordinates of Table 3 refer to the open-line molecule nearest the origin. The full-line molecules are related by the c glide planes and are nearer to the reader

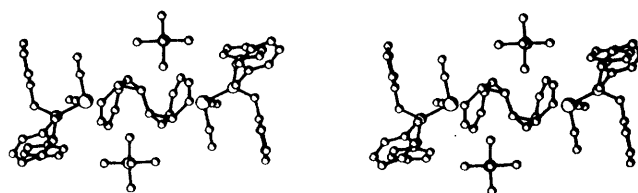


FIGURE 3 Stereoscopic view of the molecular structure of complex (3), $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2(\eta^5\text{-}\eta^6\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$

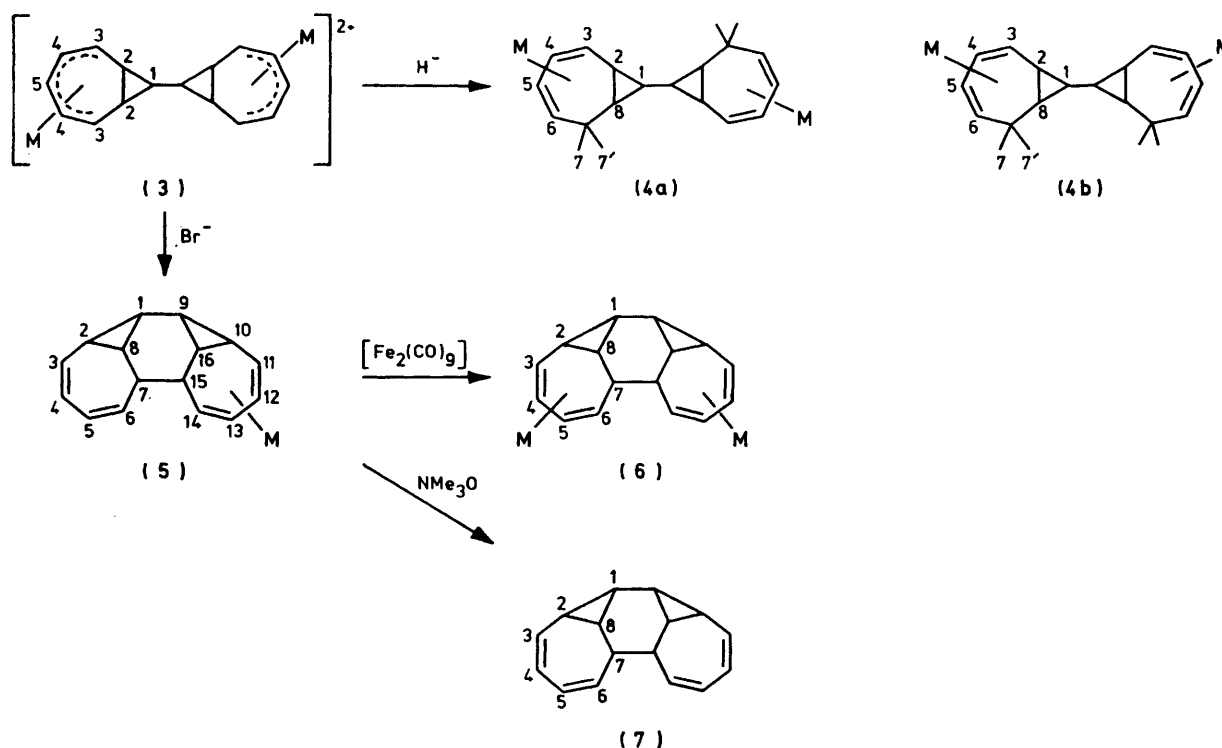
The X-ray diffraction analysis and the electrochemical study on (1) suggest that the dimeric complex (3) is formed *via* the mechanism shown in Scheme 1. Initial oxidation of $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$ affords the cation (2a) which isomerises to the bicyclo[5.1.0]octadienyl complex (2b) before dimerisation, *via* C-C bond formation, to (3). The radical cations (2a) and (2b) have not yet been detected, and the preliminary cyclic voltammetric studies made at a scan rate of 200 V s^{-1} and at -40°C (see above) suggest their lifetimes to be no greater than 2 ms. Nevertheless, the identity of (2b) follows from the structure of (3), and the photoelectron spectrum¹⁴ of $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$ suggests that electron removal is most likely to result in the initial formation of a metal-centred radical cation, *i.e.* complex (2a). The isomerisation

of (2a) to (2b) leads to the separation of the positive charge, on the iron atom, and the free electron, on C¹ (Scheme 1), thereby allowing the unusual dimerisation of a cation radical. It has been noted that silver(I) oxidation of $[\text{Fe}(\sigma\text{-allyl})(\text{CO})_2(\text{cp})]$ also results¹⁵ in dimerisation, to give $[\text{Fe}_2(\text{CO})_4(\eta^2:\eta'^2\text{-C}_6\text{H}_{10})(\text{cp})_2]^{2+}$ (cp = $\eta\text{-C}_5\text{H}_5$). Again the separation of positive and negative charge facilitates carbon-carbon bond formation.

The dimer $[\text{Fe}_2(\text{CO})_6(\eta^5:\eta'^5\text{-C}_{16}\text{H}_{16})]^{2+}$ undergoes reactions with simple anionic nucleophiles to give neutral complexes of polycyclic hydrocarbons. In thf, $\text{Na}[\text{BH}_4]$ acts as a source of hydride ions and forms, with

from which yellow $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$ (5) (Table 1) was isolated by column chromatography; a second product was $[\text{PMePh}_3][\text{FeBr}_4]$. The ¹³C n.m.r. spectrum showed 16 signals (apart from that due to the carbonyl ligands) revealing the asymmetry of the structure of (5), and the complexities of the ¹H n.m.r. spectrum were only unravelled in the light of the results of a single-crystal X-ray diffraction analysis of the structure of (5) (Tables 5 and 6).

The molecular configuration of complex (5), $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$, is shown in Figure 4; the overall linkage of the C₁₆H₁₆ moiety is remarkably similar to that found¹³ in $[\text{Fe}_2(\text{CO})_6(\eta^4:\eta'^4\text{-C}_{16}\text{H}_{16})]$ except for the detailed geometry of the unco-ordinated C₇ ring. Inspection of



SCHEME 2 M = $\text{Fe}(\text{CO})_3$

a suspension of (3; $n = 0$), a yellow solution of $[\text{Fe}_2(\text{CO})_6(\eta^4:\eta'^4\text{-C}_{16}\text{H}_{18})]$ (4); this complex, as a pale yellow solid, has been characterised by elemental analysis and i.r. spectroscopy. The mass spectrum of (4) shows no parent ion but a peak at $m/e = 462 [M - \text{CO}]^+$, and the sequential loss of five carbonyl ligands. The dimeric nature of (4) is, however, confirmed by the ¹H and ¹³C n.m.r. spectra (Table 2) which are consistent with either structure (4a) or (4b) (Scheme 2); no distinction can be made between these two forms on spectroscopic grounds alone.

With halide ions $[\text{Fe}_2(\text{CO})_6(\eta^5:\eta'^5\text{-C}_{16}\text{H}_{16})]^{2+}$ undergoes a reaction in which another C-C bond is formed, apparently by reductive coupling. Addition of $[\text{PMePh}_3]\text{Br}$ to (3; $n = 0$) in acetone at -78°C followed by warming to room temperature gave an orange solution

corresponding bond lengths and angles in Table 6 shows that the central portion of the C₁₆H₁₆ ligand has almost exact two-fold symmetry, and that this extends not only to the three-membered rings adjacent to the central six-membered ring but also to the bonds leading into the seven-membered rings. Moreover, the geometry of the η^4 -bonded half of the ligand, together with that of the $\text{Fe}(\text{CO})_3$ group, does not differ in any significant way from that reported¹³ for $[\text{Fe}_2(\text{CO})_6(\eta^4:\eta'^4\text{-C}_{16}\text{H}_{16})]$. (The same atom-numbering system has been used for both structures.) In $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$ the atoms C(11) and C(14) are at a significantly greater distance from the iron atom [mean 2.135(7) Å] than are C(12) and C(13) [mean 2.070(7) Å] with which they form a coplanar group; this feature, together with alternating C-C bond lengths [C(11)—C(12) 1.437, C(12)—C(13) 1.403, and

TABLE 5

Atomic positional parameters (fractional cell co-ordinates) for $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$, complex (5), with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.193 4(4)	-0.079 6(4)	0.192 6(4)
C(2)	0.072 3(4)	-0.022 8(4)	0.178 5(4)
C(3)	0.036 3(4)	0.100 9(4)	0.126 0(4)
C(4)	-0.071 1(4)	0.166 1(4)	0.140 5(4)
C(5)	-0.149 4(5)	0.099 6(5)	0.185 8(5)
C(6)	-0.133 9(5)	0.076 5(5)	0.294 4(5)
C(7)	-0.034 2(5)	0.117 0(4)	0.400 1(4)
C(8)	0.074 5(4)	0.164 3(4)	0.417 0(4)
C(9)	0.136 0(4)	0.190 5(4)	0.335 8(4)
C(10)	0.237 3(4)	0.089 9(4)	0.352 6(4)
C(11)	0.337 2(4)	0.145 0(4)	0.320 2(4)
C(12)	0.327 6(4)	0.183 8(4)	0.207 9(4)
C(13)	0.296 7(4)	0.097 0(5)	0.118 6(4)
C(14)	0.275 4(4)	-0.028 9(5)	0.139 5(4)
C(15)	0.177 5(4)	-0.028 4(4)	0.297 0(4)
C(16)	0.059 5(4)	0.208 9(4)	0.208 0(4)
C(17)	0.527 0(4)	-0.017 1(4)	0.171 5(4)
C(18)	0.457 3(3)	-0.091 5(5)	0.348 9(4)
C(19)	0.579 7(4)	0.125 4(5)	0.348 8(4)
H(1)	0.190(4)	-0.170(5)	0.189(4)
H(2)	-0.001(5)	-0.079(4)	0.166(4)
H(3)	0.043(4)	0.116(5)	0.052(4)
H(4)	-0.113(5)	0.215(5)	0.080(4)
H(5)	-0.220(5)	0.074(5)	0.127(4)
H(6)	-0.205(5)	0.029(5)	0.311(4)
H(7)	-0.050(5)	0.108(5)	0.464(5)
H(8)	0.121(5)	0.181(5)	0.494(4)
H(9)	0.180(4)	0.271(5)	0.360(4)
H(10)	0.279(4)	0.076(5)	0.436(4)
H(11)	0.372(5)	0.200(5)	0.375(4)
H(12)	0.355(4)	0.258(5)	0.197(4)
H(13)	0.311(4)	0.122(5)	0.046(4)
H(14)	0.278(4)	-0.091(5)	0.080(4)
H(15)	0.167(4)	-0.091(5)	0.350(4)
H(16)	0.077(4)	0.275(5)	0.179(4)
Fe	0.448 9(1)	0.038 6(1)	0.259 3(1)
O(17)	0.576 4(3)	-0.053 9(3)	0.116 8(3)
O(18)	0.458 7(3)	-0.176 0(3)	0.404 1(3)
O(19)	0.664 1(3)	0.179 0(4)	0.409 2(3)

C(13)—C(14) 1.436 Å], occurs exactly as in the Fe_2 analogue. The only significant difference between the two structures, therefore, is in the portion C(5)—C(8) of

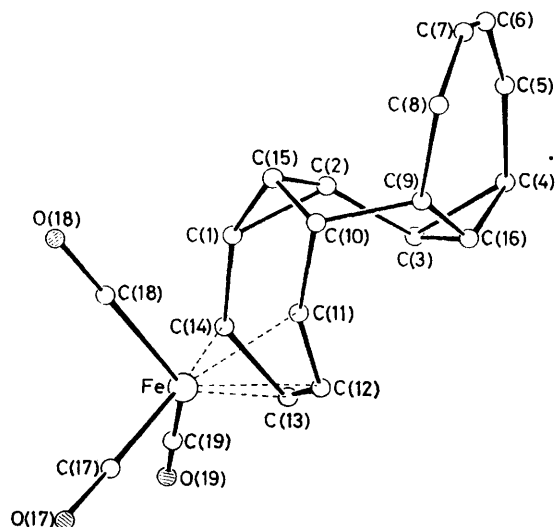


FIGURE 4 Molecular configuration of complex (5), $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$, showing the crystallographic atom-numbering sequence

TABLE 6

Bond distances (Å) and angles ($^\circ$) for $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$, complex (5), with estimated standard deviations in parentheses

(i) Distances			
Fe co-ordination			
Fe—C(11)	2.117(5)	Fe—C(18)	1.788(5)
Fe—C(12)	2.065(5)	Fe—C(19)	1.791(5)
Fe—C(13)	2.076(4)	C(17)—O(17)	1.139(6)
Fe—C(14)	2.153(4)	C(18)—O(18)	1.149(6)
Fe—C(17)	1.803(5)	C(19)—O(19)	1.153(6)
$\text{C}_{16}\text{H}_{16}$ ligand			
C(1)—C(2)	1.511(7)	C(6)—C(7)	1.462(7)
C(1)—C(14)	1.486(7)	C(7)—C(8)	1.327(7)
C(1)—C(15)	1.506(7)	C(8)—C(9)	1.498(7)
C(2)—C(3)	1.487(6)	C(9)—C(10)	1.578(6)
C(2)—C(15)	1.528(6)	C(9)—C(16)	1.521(6)
C(3)—C(4)	1.531(7)	C(10)—C(11)	1.521(7)
C(3)—C(16)	1.516(6)	C(10)—C(15)	1.504(6)
C(4)—C(5)	1.458(7)	C(11)—C(12)	1.437(7)
C(4)—C(16)	1.522(6)	C(12)—C(13)	1.403(7)
C(5)—C(6)	1.330(7)	C(13)—C(14)	1.436(7)
Mean C—H 0.96 Å			
(ii) Angles			
Fe co-ordination			
C(17)—Fe—C(18)	101.9(2)	Fe—C(17)—O(17)	179.0(4)
C(17)—Fe—C(19)	92.0(2)	Fe—C(18)—O(18)	177.7(4)
C(18)—Fe—C(19)	101.5(2)	Fe—C(19)—O(19)	177.9(5)
$\text{C}_{16}\text{H}_{16}$ ligand			
C(2)—C(1)—C(14)	123.8(4)	C(8)—C(9)—C(10)	109.1(4)
C(2)—C(1)—C(15)	60.9(3)	C(8)—C(9)—C(16)	119.9(4)
C(14)—C(1)—C(15)	125.7(4)	C(10)—C(9)—C(16)	110.0(4)
C(1)—C(2)—C(3)	121.2(4)	C(9)—C(10)—C(11)	108.9(4)
C(1)—C(2)—C(15)	59.4(3)	C(9)—C(10)—C(15)	109.5(4)
C(3)—C(2)—C(15)	117.0(4)	C(11)—C(10)—C(15)	119.2(4)
C(2)—C(3)—C(4)	118.4(4)	C(10)—C(11)—C(12)	127.5(4)
C(2)—C(3)—C(16)	117.1(4)	C(11)—C(12)—C(13)	119.1(4)
C(4)—C(3)—C(16)	59.9(3)	C(12)—C(13)—C(14)	120.4(4)
C(3)—C(4)—C(5)	120.3(4)	C(13)—C(14)—C(1)	129.0(4)
C(3)—C(4)—C(16)	59.5(3)	C(1)—C(15)—C(2)	59.7(3)
C(5)—C(4)—C(16)	126.9(4)	C(1)—C(15)—C(10)	121.7(4)
C(4)—C(5)—C(6)	129.9(5)	C(2)—C(15)—C(10)	118.5(4)
C(5)—C(6)—C(7)	128.0(5)	C(3)—C(16)—C(4)	60.5(3)
C(6)—C(7)—C(8)	130.9(5)	C(3)—C(16)—C(9)	119.5(4)
C(7)—C(8)—C(9)	131.8(4)	C(4)—C(16)—C(9)	127.4(4)

the molecule, where the alternation of bond lengths is much more marked: C(5)—C(6) 1.330; C(6)—C(7) 1.462; and C(7)—C(8) 1.327 Å. Also, as might be expected, the unco-ordinated ring is much more nearly planar; only atom C(9) deviates from the mean plane by more than 0.1 Å, and this it does towards C(10) by 0.17 Å. Comparative values of interplanar angles and other geometrical features of the two structures are given in Table 7, those for $[\text{Fe}_2(\text{CO})_6(\eta^4\text{-}\eta^4\text{-C}_{16}\text{H}_{16})]$ having been computed from the set of atomic co-ordinates provided by Professor B. R. Penfold.

The bond between C(9) and C(10) in (5) (Figure 4) is apparently formed by the reduction of (3; $n = 0$) by bromide ion, although oxidation of bromide to bromine does not seem likely on the basis of redox potentials. Nevertheless, the isolation of $[\text{PMePh}_3][\text{FeBr}_4]$ lends some support for the generation of bromine during the reaction.

As shown by the X-ray diffraction study, the $\text{C}_{16}\text{H}_{16}$ organic ligand in (5) is identical to that present in $[\text{Fe}_2(\text{CO})_6(\eta^4\text{-}\eta^4\text{-C}_{16}\text{H}_{16})]$ (6) prepared by Parkins and co-

TABLE 7

Comparative geometry for the two structures $[\text{Fe}_2(\text{CO})_6(\eta^4\text{:}\eta^4\text{-C}_{16}\text{H}_{16})]$, (a),¹³ and $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$, (b)

Distances (Å)	(a)	(b)
Fe—C(12,13) mean	2.06(2)	2.060(7)
Fe—C(11,14) mean	2.14(2)	2.135(7)
C(11)—C(12)	1.45(2)	1.437(7)
C(13)—C(14)	1.44(2)	1.436(7)
C(12)—C(13)	1.40(2)	1.403(7)
Interplanar angles (°)		
Planes: (i) C(11), C(12), C(13), C(14)		
(ii) C(11), C(10), C(15), C(1), C(14)		
(iii) C(15), C(1), C(2)		
(iv) C(16), C(3), C(4)		
(i)—(ii)	39.6	38.8
(ii)—(iii)	112.2	113.7
(iii)—(iv)	141.6	141.7

workers¹³ from $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$ and the olefin-metathesis catalyst $\text{WCl}_6\text{-AlCl}_2\text{Et-EtOH}$ in toluene. Indeed, complex (6) may be simply prepared, in good yield, from (5) and $[\text{Fe}_2(\text{CO})_9]$ in n-hexane under reflux. It is probable, therefore, that the direct formation of (6) from $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$, *via* the metathesis catalyst, involves initial

$\text{C}_{16}\text{H}_{16}]^{2+}$ demonstrates that the activation, by one-electron oxidation, of organotransition-metal complexes is a viable means to high yields of stereospecific organic and organometallic products.

EXPERIMENTAL

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Where appropriate, reactions were monitored by i.r. spectroscopy; unless stated the complexes are air-stable in the solid state but slowly decompose in solution. All of the complexes are soluble in common organic solvents, such as n-hexane, diethyl ether, CH_2Cl_2 , and acetone, unless stated otherwise. The complexes $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$ ¹⁶ and $[\text{Fe}(\text{CO})_2(\text{P}(\text{OCH}_2)_3\text{CMe})(\eta^4\text{-cot})]$ ⁵ and the amine $\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3$ ¹⁷ were prepared by published procedures; silver(I) salts were purchased from Fluorochem Ltd., Glossop, Derbyshire and $\text{NMe}_3\cdot 2\text{H}_2\text{O}$ from Aldrich Chemical Co. Ltd. Infrared spectra were recorded on a Perkin-Elmer PE 457 spectrophotometer and calibrated against the absorption band of polystyrene at 1601 cm^{-1} . Proton n.m.r. spectra were recorded on Varian Associates HA100 or JEOL PS100 or FX200 spectrometers, and ¹³C n.m.r. spectra on JEOL

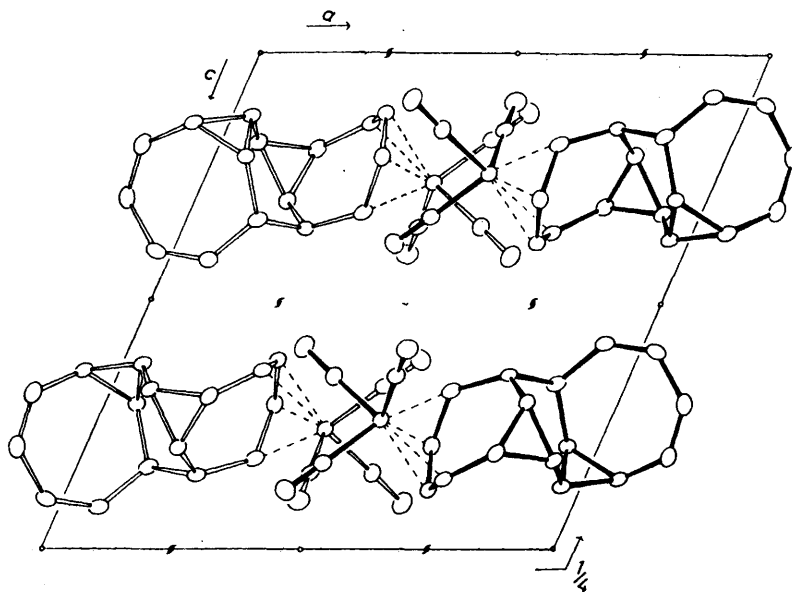


FIGURE 5 Contents of the monoclinic unit cell of complex (5), $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$, looking down b towards the origin

oxidation by WCl_6 followed by reduction of the dimer (3; $n = 0$) with halide ions or the alkylaluminium reagent.

Cleavage of the $\text{C}_{16}\text{H}_{16}$ ligand (7) from (5) is readily achieved, in refluxing benzene, with $\text{NMe}_3\cdot 2\text{H}_2\text{O}$. Air-stable white needles of the hydrocarbon may be isolated from the reaction by evaporation to dryness and recrystallisation of the residue with n-hexane. Detachment of (7) from (5) does not result in thermal rearrangement of the ligand, as evidenced by the close similarities in the ¹H and ¹³C n.m.r. spectra of (5)—(7). Indeed, such similarities have aided the spectral assignments given in Table 2.*

Conclusion.—The synthesis of $[\text{Fe}_2(\text{CO})_6(\eta^5\text{:}\eta^5\text{-}$

PFT100 or FX200 instruments; both were calibrated against tetramethylsilane as internal reference. Mass spectra were recorded on an A.E.I. MS 902 instrument. Cyclic voltammetry was carried out with Beckmann Electroscan 30 and AMEL Electrochemolab instruments using platinum-wire auxiliary and working electrodes and a calomel electrode (1 mol dm^{-3} in LiCl) as reference. Solutions were $10^{-3}\text{ mol dm}^{-3}$ in complex and 0.05 mol dm^{-3} in $[\text{NEt}_4][\text{ClO}_4]$ as supporting electrolyte.

Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol. Melting points are uncorrected.

* The ¹H n.m.r. spectrum for complex (6) was kindly supplied by Dr. A. W. Parkins, Queen Elizabeth College, University of London.

Dicarbonyl(1—2:3—4- η -cyclo-octatetraene)(triphenylphosphine)iron, $[\text{Fe}(\text{CO})_2(\text{PPh}_3)(\eta^4\text{-C}_8\text{H}_8)]$.—A solution of $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_8\text{H}_8)]$ (1.0 g, 4.10 mmol) and PPh_3 (1.08 g, 4.12 mmol) in *n*-hexane (250 cm³) was irradiated (u.v. light) with stirring for 22 d. The red precipitate was dissolved in a minimum of CH_2Cl_2 and chromatographed on an alumina column. Elution with hexane- CH_2Cl_2 (20 : 1) and evaporation of the deep red eluate to low volume gave red crystals of the complex, yield 0.76 g (39%). The $\text{P}(\text{OPh})_3$ (in toluene with a large excess of the ligand) and $\text{P}(\text{NMe}_2)_3$ analogues were prepared similarly. The $\text{P}(\text{NMe}_2)_3$ complex is very soluble in *n*-hexane; the PPh_3 and $\text{P}(\text{OPh})_3$ derivatives are less so.

Dicarbonyl(1—2:3—4- η -cyclo-octatetraene)(trimethyl phosphite)iron and Carbonyl(1—2:3—4- η -cyclo-octatetraene)-bis(trimethyl phosphite)iron, $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}(\eta^4\text{-cot})]$ and $[\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}_2(\eta^4\text{-cot})]$.—A stirred solution of $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$ (3.0 g, 12.30 mmol) and $\text{P}(\text{OMe})_3$ (7.9 g, 63.5 mmol) in thf (450 cm³) was irradiated (u.v. light) for 48 h. The deep red solution was evaporated to dryness and the oily residue was dissolved in diethyl ether (10 cm³). Chromatography on an alumina-hexane column (55 \times 3.5 cm) gave unchanged $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$, eluted with *n*-hexane, followed by $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}(\eta^4\text{-cot})]$ and $[\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}_2(\eta^4\text{-cot})]$ which were separately eluted by slowly increasing the proportion of diethyl ether in a mixture with *n*-hexane. Pure samples of the substituted products, as red solids, were obtained by evaporation of each eluate and recrystallisation from hexane at -78°C . The products $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}(\eta^4\text{-cot})]$, 1.48 g (43%), and $[\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}_2(\eta^4\text{-cot})]$, 0.86 g (19%), slowly decompose at room temperature. The former is stable at 0°C and the latter, for 3—4 d, at -20°C .

trans- μ -{2—6- η :2'—6'- η -8,8'-Bi(bicyclo[5.1.0]octadienyl)-hexacarbonyl}di-iron Bis(hexafluorophosphate), $[\text{Fe}_2(\text{CO})_6(\eta^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$.—A deep blue solution of $[\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3][\text{PF}_6]$ {prepared by stirring $\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3$ (1.52 g, 3.15 mmol) in CH_2Cl_2 (70 cm³) with $[\text{NO}][\text{PF}_6]$ (0.55 g, 3.15 mmol) for 12 min (while passing a rapid stream of nitrogen gas through the mixture)} was filtered into $[\text{Fe}(\text{CO})_3(\eta^4\text{-cot})]$ (0.70 g, 2.87 mmol) in CH_2Cl_2 (20 cm³). After 10 min the yellow precipitate was filtered off, and washed with CH_2Cl_2 (2 \times 10 cm³) and OEt_2 (2 \times 10 cm³); yield 0.96 g (87%). The product may be further purified, if necessary, by recrystallisation from acetone-diethyl ether; it is insoluble in CH_2Cl_2 , *n*-hexane, and diethyl ether, but soluble in acetone and nitromethane.

trans- μ -{2—6- η :2'—6'- η -8,8'-Bi(bicyclo[5.1.0]octadienyl)-tetracarbonyl}bis(triphenyl phosphite)di-iron Bis(hexafluorophosphate), $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2(\eta^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$.—A solution of $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}(\eta^4\text{-cot})]$ (0.50 g, 0.95 mmol) and $\text{Ag}[\text{PF}_6]$ (0.51 g, 2.0 mmol) in toluene (50 cm³) was stirred for 20 min. Extraction of the precipitate with CH_2Cl_2 (40 cm³), removal of silver metal by filtration, addition of *n*-hexane, and partial removal of the solvent *in vacuo* gave an oily yellow solid. Recrystallisation from CH_2Cl_2 -diethyl ether gave orange crystals of the complex, yield 0.43 g (68%). The complex is insoluble in *n*-hexane and diethyl ether.

trans- μ -{2—6- η :2'—6'- η -8,8'-Bi(bicyclo[5.1.0]octadienyl)-dicarbonyl}tetrakis(trimethyl phosphite)di-iron Di-iodide, $[\text{Fe}_2(\text{CO})_2\{\text{P}(\text{OMe})_3\}_4(\eta^5\text{-C}_{16}\text{H}_{16})]\text{I}_2$.—To $[\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}_2(\eta^4\text{-cot})]$ (0.14 g, 0.32 mmol) in *n*-hexane (25 cm³) was added dropwise a solution of I_2 (0.06 g, 0.24 mmol) in *n*-hexane (50 cm³). The resulting pale brown precipitate was recrystallised from CH_2Cl_2 -*n*-hexane to give the product as a

yellow solid, yield 0.09 g (50%). The complex is insoluble in *n*-hexane and diethyl ether.

trans- μ -{2—5- η :2'—5'- η -8,8'-Bi(bicyclo[5.1.0]octa-2,4-diene)-hexacarbonyl}di-iron, $[\text{Fe}_2(\text{CO})_6(\eta^4\text{-C}_{16}\text{H}_{16})]$.—To a stirred cooled (-78°C) suspension of $[\text{Fe}_2(\text{CO})_6(\eta^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$ (1.9 g, 2.45 mmol) in thf (140 cm³) was added an excess of $\text{Na}[\text{BH}_4]$ (1.48 g, 38.8 mmol). After 6 h the yellow solution was filtered and evaporated to dryness. Dissolution of the residue in CH_2Cl_2 (10 cm³) followed by chromatography on a silica-*n*-hexane column (40 \times 4 cm) gave a pale yellow band which was eluted with *n*-hexane-diethyl ether (10 : 1). Partial removal of the solvent *in vacuo* gave the complex as a pale yellow solid, yield 0.28 g (23%). The complex is only moderately soluble in *n*-hexane.

Preparation of Complex (5), $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$.—To a stirred cold (-78°C) solution of $[\text{Fe}_2(\text{CO})_6(\eta^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$ (3.15 g, 4.05 mmol) in acetone (100 cm³) was added $[\text{PMePh}_3]\text{Br}$ (2.89 g, 8.10 mmol). After 4 h the mixture was allowed to warm to room temperature giving a deep orange-red solution. After removing the solvent *in vacuo* the oily residue was dissolved in CH_2Cl_2 (10 cm³) and chromatographed on a silica-hexane column (40 \times 4 cm). A bright yellow band was eluted with hexane-diethyl ether (10 : 1) to give a yellow solid on evaporation to dryness. Recrystallisation from hexane at -78°C gave the complex as yellow crystals, yield 0.76 g (54%).

Synthesis of Complex (6), $[\text{Fe}_2(\text{CO})_6(\eta^4\text{-C}_{16}\text{H}_{16})]$.—A stirred mixture of $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$ (0.75 g, 2.17 mmol) and $[\text{Fe}_2(\text{CO})_6]$ (1.06 g, 2.92 mmol) was heated under reflux in *n*-hexane (75 cm³) to give a green-yellow solution and a pale yellow precipitate. After 1.5 h the precipitate was recrystallised from CH_2Cl_2 -*n*-hexane to give pale yellow crystals of the complex, yield 0.48 g (46%). The complex is only poorly soluble in *n*-hexane, CH_2Cl_2 , or acetone, but is soluble in toluene.

Synthesis of Compound (7), $\text{C}_{16}\text{H}_{16}$.—A mixture of $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$ (0.29 g, 0.82 mmol) and $\text{NMe}_3\text{O}\cdot 2\text{H}_2\text{O}$ (1.85 g, 16.7 mmol) in benzene (100 cm³) was heated under reflux for 7 h. Filtration followed by removal of the solvent *in vacuo* gave a white solid which was recrystallised from *n*-hexane at -78°C to give white needles of the product, yield 0.10 g (51%) (Found: C, 92.1; H, 7.8. $\text{C}_{16}\text{H}_{16}$ requires C, 92.3; H, 7.7%), m.p. = $108\text{--}110^\circ\text{C}$, $m/e = 208$.

Crystal-structure Determinations.—(a) $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2(\eta^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$, Complex (3). Crystals of [3; $n = 2$, $L = \text{P}(\text{OPh})_3$] grow as fine yellow needles from dichloromethane-*n*-hexane at 0°C . Diffracted intensities were recorded at room temperature from a 0.5 mm long crystal cut from a longer needle, on a Syntex P21 four-circle diffractometer in the range $2.9 \leq 2\theta \leq 50^\circ$, according to methods described earlier.¹⁸ Of the total 5 201 independent observations, only 2 186 satisfied the criterion $F \geq 3\sigma(F)$, where $\sigma(F)$ is the estimated standard deviation in the observed structure amplitude. No correction for *X*-ray absorption was made [$\mu(\text{Mo-K}\alpha) = 6.3 \text{ cm}^{-1}$]. The intensities of three standard reflections were remeasured every 50 reflections and showed no significant crystal decay during 153 h of exposure to *X*-rays. The unusually high proportion of weak reflections is indicative of poor crystal quality and has resulted in a relatively poor refinement.

Crystal data. $\text{C}_{56}\text{H}_{46}\text{F}_{12}\text{Fe}_2\text{O}_{10}\text{P}_4$, $M = 1\,342.5$, Orthorhombic, $a = 18.760(15)$, $b = 21.605(10)$, $c = 14.486(4)$ Å, $U = 5\,872(6)$ Å³, D_m (floatation) = 1.52, $Z = 4$, $D_c = 1.52 \text{ g cm}^{-3}$, $F(000) = 2\,728$, space group $Pccn$ (no. 56), $\text{Mo-K}\alpha$ *X*-radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-K}\alpha) = 6.3 \text{ cm}^{-1}$.

The structure was solved by heavy-atom methods which yielded, successively, one iron atom, two phosphorus atoms, and then all other non-hydrogen atoms in the crystallographic asymmetric unit. The dimeric species lies astride a two-fold axis parallel to c in the orthorhombic unit cell (Figure 3). Hydrogen atoms were incorporated at calculated positions with a fixed isotropic thermal parameter $U_{\text{iso}}(\text{H}) = 0.03 \text{ \AA}^2$. All other atoms were allowed anisotropic thermal refinement, but the very large values obtained for atoms F(3), F(4), F(5), and F(6) were suggestive of disorder among these 'equatorial' sites.

The non-disordered axis of the octahedral PF_6 anion lies almost parallel to c in the unit cell and comprises the sequence F(1)–P–F(2). Incorporation of four other equatorial sites for F(3)–F(6) at 45° positions, with isotropic thermal parameters and a population parameter, gave, on refinement, more sensible thermal parameters and a site-occupancy ratio of 0.8 : 0.2. Convergence of the blocked-matrix least-squares refinement was obtained at R 0.116 (R' 0.090) with an optimised weighting scheme $w = 2.852 [\sigma^2(F) + 0.0003|F|^2]^{-1}$ for the individual weights. The high R reflects the poor quality of the data, but the final electron-density difference synthesis showed no peaks >0.6 or $<-0.7 \text{ e \AA}^{-3}$, and all atoms were well defined. Scattering factors were from ref. 19 for all non-hydrogen atoms and from ref. 20 for hydrogen. All computational work was carried out on the South Western Universities' Computer Network with the SHELX system of programs.²¹

(b) $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_{16}\text{H}_{16})]$, Complex (5). Crystals of (5) grow as yellow rhombs from *n*-hexane at -20°C . Diffracted intensities were recorded to $2\theta = 55^\circ$ from a crystal of dimensions *ca.* $0.4 \times 0.3 \times 0.2 \text{ mm}$ at 220 K on a Syntex P3 four-circle diffractometer. Of the total 3 634 independent observations, 2 205 satisfied the criterion $I \geq 2.0\sigma(I)$, and only these were used in the solution and refinement of the structure.

Crystal data. $\text{C}_{19}\text{H}_{16}\text{FeO}_3$, $M = 348.2$, Monoclinic, $a = 11.882(8)$, $b = 10.877(10)$, $c = 12.586(10) \text{ \AA}$, $\beta = 112.98(6)^\circ$, $U = 1 498(2) \text{ \AA}^3$, D_{m} (floatation) = 1.43, $Z = 4$, $D_{\text{c}} = 1.54 \text{ g cm}^{-3}$, $F(000) = 720$, space group $P2_1/c$ (no. 14), $\mu(\text{Mo-K}\alpha) = 9.5 \text{ cm}^{-1}$, $\lambda = 0.710 69 \text{ \AA}$.

The structure was solved by heavy-atom methods and the molecule has no crystallographically imposed symmetry. The hydrogen atoms were located from the electron-density difference maps and were included in the refinement with common isotropic thermal parameters for chemically equivalent atoms. All non-hydrogen atoms were given anisotropic thermal parameters, and because of the relatively small size of the structure a full-matrix least-squares refinement was possible. A few reflections for which $F_{\text{c}} \gg F_{\text{o}}$, presumably because of extinction effects, were omitted

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

from the refinement [202, 313, 415, 315, 413, 323, and 314]. Otherwise conditions were as for (a). Refinement converged at R 0.062 (R' 0.058), with an optimised weighting scheme $w = 5.113[\sigma^2(F) + 0.0015|F|^2]^{-1}$. The results for structure (a) are summarised in Tables 3 and 4, for (b) in Tables 5 and 6. Observed and calculated structure factors for (a) and (b) and all thermal parameters are given in Supplementary Publication No. SUP 23022 (31 pp.).*

We thank the S.R.C. for Research Studentships (to R. L. K. M. D. K., R. M. M., and M. W. W.) and for funds to purchase electrochemical equipment. We also thank Dr. R. J. Goodfellow for invaluable assistance with ^1H n.m.r. spectroscopy.

[0/1663 Received, 31st October, 1980]

REFERENCES

- Part 11, K. L. Amos and N. G. Connelly, *J. Organomet. Chem.*, 1980, **194**, C57.
- N. G. Connelly, R. L. Kelly, and M. W. Whiteley, *J. Chem. Soc., Dalton Trans.*, 1981, 34.
- N. G. Connelly and R. L. Kelly, *J. Organomet. Chem.*, 1976, **120**, C16.
- N. G. Connelly, M. D. Kitchen, R. F. D. Stansfield, S. M. Whiting, and P. Woodward, *J. Organomet. Chem.*, 1978, **155**, C34.
- M. Cooke, Ph.D. Thesis, University of Bristol, 1969.
- B. Lewis, Ph.D. Thesis, University of Bristol, 1973.
- N. El Murr, M. Riveccí, E. Laviron, and G. Deganello, *Tetrahedron Lett.*, 1976, 3339.
- R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, 1966, **88**, 471.
- G. Deganello, 'Transition Metal Complexes of Cyclic Polyolefins,' Academic Press, London, 1979, p. 224.
- N. G. Connelly, A. R. Lucy, and M. W. Whiteley, *J. Chem. Soc., Chem. Commun.*, 1979, 985.
- P. K. Baker, N. G. Connelly, B. M. R. Jones, J. P. Maher, and K. R. Somers, *J. Chem. Soc., Dalton Trans.*, 1980, 579.
- G. I. Fray and R. G. Saxton, 'The Chemistry of Cyclo-octatetraene and its Derivatives,' Cambridge University Press, 1978 and refs. therein.
- H. A. Bockmeulen, R. G. Holloway, A. W. Parkins, and B. R. Penfold, *J. Chem. Soc., Chem. Commun.*, 1976, 298; H. A. Bockmeulen and A. W. Parkins, *J. Chem. Soc., Dalton Trans.*, 1981, 262.
- J. C. Green, P. Powell, and J. van Tilborg, *J. Chem. Soc., Dalton Trans.*, 1976, 1974; M. C. Böhm and R. Gleiter, *Z. Naturforsch., Teil B*, 1980, **35**, 1028.
- P. S. Waterman and W. P. Giering, *J. Organomet. Chem.*, 1978, **155**, C47.
- R. B. King, *Organomet. Synth.*, 1965, **1**, 126.
- T. N. Baker, W. P. Doherty, jun., W. S. Kelley, W. Newmeyer, J. E. Rogers, jun., R. E. Spalding, and R. I. Walter, *J. Org. Chem.*, 1965, **30**, 3714.
- A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1974, 2065.
- D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
- R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
- G. M. Sheldrick, SHELX: A system of crystallographic computer programs, Cambridge, 1975.