Structural Effects of One-electron Oxidation on a Cyclobutadieneiron Derivative: *X*-Ray Crystal Structures of $[Fe(CO)\{P(OMe)_3\}_2(\eta\text{-}C_4Ph_4)]$ and $[Fe(CO)\{P(OMe)_3\}_2(\eta\text{-}C_4Ph_4)]BF_4$†

A. Guy Orpen, Neil G. Connelly, Mark W. Whiteley, and Peter Woodward
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Single-crystal *X*-ray diffraction studies on the tetraphenylcyclobutadiene iron complexes $[Fe(CO)\{P(OMe)_3\}_2(\eta\text{-}C_4Ph_4)]$ (**1**) and $[Fe(CO)\{P(OMe)_3\}_2(\eta\text{-}C_4Ph_4)]^+$ (**2**), the latter as its $[BF_4]^-$ salt, show that significant variations in molecular geometry occur as a consequence of one-electron oxidation. The Fe–P distances increase by 0.115(5) Å and the Fe–CO distance by 0.075(8) Å, while cyclobutadiene ring carbon–iron lengths show a very small increase of 0.021 (8) Å. No significant change in the square-planar geometry of the C_4 ring occurs on oxidation, but the $Fe(CO)\{P(OMe)_3\}_2$ fragment adopts a different conformation relative to the C_4Ph_4 moiety in (**1**) as compared with (**2**). In one of the two distinct cations present in crystals of (**2**) the $Fe(CO)\{P(OMe)_3\}_2$ is strongly tilted so that the pseudo-three-fold axis of this conical fragment is not coincident with the four-fold axis of the C_4 ring. These structural observations have been analyzed in order to test current theories of the electronic structure of $FeL_3(\eta\text{-}C_4R_4)$ complexes. The principal conclusion is that the highest occupied molecular orbital (**1**) is iron based and not strongly involved in bonding to cyclobutadiene. This is in full accord with the results of both photoelectron spectroscopic and generalized molecular orbital studies on $[Fe(CO)_3(\eta\text{-}C_4H_4)]$. The orbital depopulated on oxidation contributes to both $Fe\text{–}P(OMe)_3$ and Fe–CO π back bonding. Oxidation diminishes such π bonding and causes changes in P–O bond lengths consistent with P–O σ^* orbitals contributing to the π-acceptor function of the $P(OMe)_3$ ligand.

The prediction, in 1956,[1] that the anti-aromatic molecule cyclobutadiene might be stabilized by co-ordination to transition-metal fragments such as $Fe(CO_3)$ stimulated the development of a large body of research into the properties of co-ordinated cyclobutadienes. Both experimental[2–4] and theory-based[5] studies have shown that cyclobutadiene (or its derivatives C_4R_4) attains a quasi-aromatic, near-square, C_4 ring structure on co-ordination to $Fe(CO)_3$ [or $Fe(CO)_{3-n}L_n$]. This is in marked contrast to the rectangular geometry predicted for free C_4H_4[6] and observed for $C_4Bu^t{}_4$.[7] The anti-aromatic structural behaviour of singlet C_4R_4 may be viewed as arising from a Jahn–Teller distortion away from a putative square geometry in which the doubly degenerate cyclobutadiene π orbitals (e_u under D_{4h} symmetry) are half-filled. In complexes of C_4R_4 aromaticity is essentially restored, by interaction of these π orbitals with appropriate orbitals on the metal–ligand moiety [*e.g.* $Fe(CO)_3$] leading to approximately equal net occupancy of the two e_u orbitals.[5]

In the course of a general study[8] of the reduction–oxidation chemistry of organotransition-metal complexes we have synthesized and studied[9] the reactivity and electrochemistry of $[Fe(CO)\{P(OMe)_3\}_2(\eta\text{-}C_4Ph_4)]$ (**1**). In addition we have prepared stable, crystalline salts of its paramagnetic monocation $[Fe(CO)\{P(OMe)_3\}_2(\eta\text{-}C_4Ph_4)]^+$ (**2**). In principle if the singly occupied molecular orbital (s.o.m.o.) of (**2**) is substantially derived from a member of the cyclobutadiene e_u set then a Jahn–Teller-like distortion would be expected to ensue [although no first-order effect operates since the symmetry of the complexes (**1**) and (**2**) is at most C_s] leading to a non-square geometry for the cyclobutadiene ring in (**2**). Photoelectron spectroscopy (p.e.s.) studies on $[Fe(CO)_3(\eta\text{-}C_4H_4)]$[10] indicate that the lowest-energy ionization band is associated with essentially localized metal *d* orbitals, and the next lowest with strongly interacting iron–cyclobutadiene bonding orbitals. Molecular orbital studies on $[Fe(CO)_3(\eta\text{-}C_4H_4)]$ have sought to understand its p.e. spectrum[11] as well as its reactivity and structure, including the conformational preferences of the complex.[12] These studies, at various levels of theory, suggest a variety of orbital orderings in $[Fe(CO)_3(\eta\text{-}C_4H_4)]$ and some[10,11,13] have investigated the electronic structure of the paramagnetic monocation $[Fe(CO)_3(\eta\text{-}C_4H_4)]^+$. The balance of theoretical and experimental evidence suggests that the highest occupied molecular orbital (h.o.m.o.) in $[Fe(CO)_3(\eta\text{-}C_4H_4)]$, and by implication in (**1**), is localized primarily on iron (*i.e.* is a t_{2g}-type orbital). In order to test the accuracy of this prediction[11] as to the site of the h.o.m.o. in complex (**1**) and the apparently contradictory suggestion[9] that the cyclobutadiene ring in (**2**) might be non-square we have determined the structures of (**1**) and (**2**), as its $[BF_4]^-$ salt, by *X*-ray single-crystal diffraction methods and report our findings below. This study forms part of a more general series of investigations probing the consequences of oxidation on the structure and bonding of organotransition-metal complexes.[14,15]

Results and Discussion

The structures of complexes (**1**) and (**2**) ($[BF_4]^-$ salt) were determined by conventional single-crystal *X*-ray diffraction methods at room temperature. The crystal structure of (**1**) consists of isolated molecules separated by normal van der Waals distances. In (**2**) there is no apparent tendency to dimerization of the $17e^-$ cation, the shortest Fe $\cdots$ Fe distance being 9.039 Å. The structure of (**2**) contains two crystallographically distinct cations, (**A**) and (**B**), which have very similar gross structures

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† Carbonyl(η-tetraphenylcyclobutadiene)(trimethyl phosphite)-iron and -iron tetrafluoroborate.

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Table 1. Selected bond lengths (Å) and inter-bond angles (°) for complex (**1**)

Fe–P(1)	2.145(1)	Fe–P(2)	2.147(1)	P(1)–Fe–P(2)	98.6(1)	P(1)–Fe–C(5)	94.5(1)
Fe–C(5)	1.743(3)	Fe–C(1)	2.076(3)	P(2)–Fe–C(5)	96.4(1)	P(1)–Fe–C(1)	91.6(1)
Fe–C(2)	2.052(3)	Fe–C(3)	2.051(3)	P(2)–Fe–C(1)	137.6(1)	C(5)–Fe–C(1)	123.9(1)
Fe–C(4)	2.051(3)	P(1)–O(17)	1.605(2)	P(1)–Fe–C(2)	119.2(1)	P(2)–Fe–C(2)	141.2(1)
P(1)–O(18)	1.596(3)	P(1)–O(19)	1.591(2)	C(5)–Fe–C(2)	89.4(1)	C(1)–Fe–C(2)	41.3(1)
P(2)–O(27)	1.611(2)	P(2)–O(28)	1.597(2)	P(1)–Fe–C(3)	151.2(1)	P(2)–Fe–C(3)	100.0(1)
P(2)–O(29)	1.588(2)	O(17)–C(17)	1.410(5)	C(5)–Fe–C(3)	105.0(1)	C(1)–Fe–C(3)	60.0(1)
O(18)–C(18)	1.405(6)	O(19)–C(19)	1.435(4)	C(2)–Fe–C(3)	41.9(1)	P(1)–Fe–C(4)	113.8(1)
O(27)–C(27)	1.440(5)	O(28)–C(28)	1.419(4)	P(2)–Fe–C(4)	97.8(1)	C(5)–Fe–C(4)	145.9(1)
O(29)–C(29)	1.423(6)	C(5)–O(5)	1.154(4)	C(1)–Fe–C(4)	41.5(1)	C(2)–Fe–C(4)	60.8(1)
C(1)–C(2)	1.457(4)	C(1)–C(4)	1.461(4)	C(3)–Fe–C(4)	41.9(1)	Fe–P(1)–O(17)	122.6(1)
C(1)–C(11)	1.472(4)	C(2)–C(3)	1.468(4)	Fe–P(1)–O(18)	121.0(1)	O(17)–P(1)–O(18)	96.7(1)
C(2)–C(21)	1.479(4)	C(3)–C(4)	1.467(4)	Fe–P(1)–O(19)	109.8(1)	O(17)–P(1)–O(19)	103.7(1)
C(3)–C(31)	1.469(4)	C(4)–C(41)	1.487(4)	O(18)–P(1)–O(19)	99.5(1)	Fe–P(2)–O(27)	120.3(1)
C(11)–C(12)	1.383(5)	C(11)–C(16)	1.375(4)	Fe–P(2)–O(28)	116.1(1)	O(27)–P(2)–O(28)	97.3(1)
C(12)–C(13)	1.389(5)	C(13)–C(14)	1.341(6)	Fe–P(2)–O(29)	113.1(1)	O(27)–P(2)–O(29)	102.8(1)
C(14)–C(15)	1.369(6)	C(15)–C(16)	1.379(5)	O(28)–P(2)–O(29)	104.8(1)	P(1)–O(17)–C(17)	125.3(2)
C(21)–C(22)	1.380(4)	C(21)–C(26)	1.394(4)	P(1)–O(18)–C(18)	125.8(3)	P(1)–O(19)–C(19)	123.9(3)
C(22)–C(23)	1.392(5)	C(23)–C(24)	1.368(5)	P(2)–O(27)–C(27)	120.0(2)	P(2)–O(28)–C(28)	129.0(3)
C(24)–C(25)	1.384(5)	C(25)–C(26)	1.379(5)	P(2)–O(29)–C(29)	124.9(2)	Fe–C(5)–O(5)	175.8(3)
C(31)–C(32)	1.380(4)	C(31)–C(36)	1.396(4)	Fe–C(1)–C(2)	68.4(1)	Fe–C(1)–C(4)	68.3(1)
C(32)–C(33)	1.387(4)	C(33)–C(34)	1.366(5)	C(2)–C(1)–C(4)	90.6(2)	Fe–C(1)–C(11)	135.9(2)
C(34)–C(35)	1.378(5)	C(35)–C(36)	1.379(4)	C(2)–C(1)–C(11)	134.1(2)	C(4)–C(1)–C(11)	131.8(2)
C(41)–C(42)	1.387(4)	C(41)–C(46)	1.394(4)	Fe–C(2)–C(1)	70.2(1)	Fe–C(2)–C(3)	69.0(1)
C(42)–C(43)	1.383(4)	C(43)–C(44)	1.377(5)	C(1)–C(2)–C(3)	89.7(2)	Fe–C(2)–C(21)	127.5(2)
C(44)–C(45)	1.367(5)	C(45)–C(46)	1.381(4)	C(1)–C(2)–C(21)	134.3(2)	C(3)–C(2)–C(21)	134.8(2)
				Fe–C(3)–C(2)	69.1(1)	Fe–C(3)–C(4)	69.0(1)
				C(2)–C(3)–C(4)	90.0(2)	Fe–C(3)–C(31)	127.4(2)
				C(2)–C(3)–C(31)	134.4(2)	C(4)–C(3)–C(31)	134.7(2)
				Fe–C(4)–C(1)	70.2(1)	Fe–C(4)–C(3)	69.1(1)
				C(1)–C(4)–C(3)	89.6(2)	Fe–C(4)–C(41)	136.1(2)
				C(1)–C(4)–C(41)	130.7(2)	C(3)–C(4)–C(41)	134.9(2)

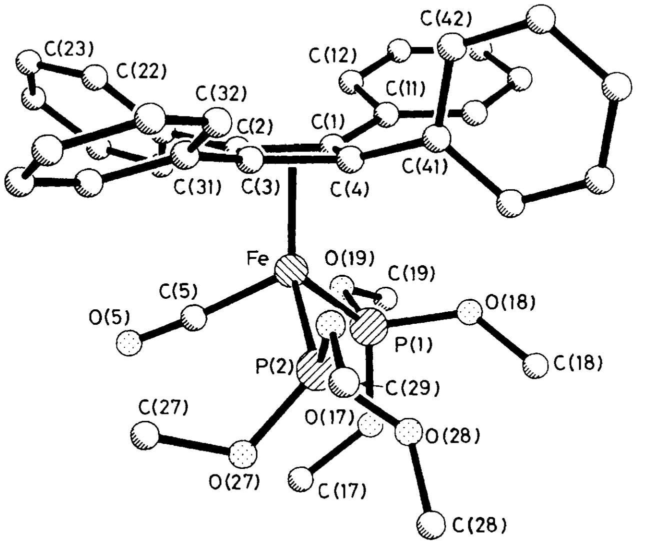

Figure 1. Molecular structure of complex (**1**) showing the labelling scheme; hydrogen atoms are omitted for clarity

differing in the conformations of the phenyl and trimethyl phosphite groups and in other details as discussed below. Anion–cation contacts between (**2**) and $[BF_4]^-$ are not strong, the shortest Fe ··· F distances being between Fe(1) and F(5′) [related to F(5) by *x*, *y* − 1, *z*] at 4.983 Å, and Fe(2) and F(1) at 5.133 Å. In both cases these contacts approximately bisect a P–Fe–CO angle [C(5)–Fe(1)–P(1) and C(55)–Fe(2)–P(3) respectively].

Selected bond lengths and inter-bond angles are listed in Tables 1 and 2 for (**1**) and (**2**) respectively. Perspective views of the molecular structure of $[Fe(CO)\{P(OMe)_3\}_2(\eta\text{-}C_4Ph_4)]$ (**1**) and of (**2**) (both independent cations) are given in Figures 1 and 2 respectively. Figure 3 shows a view approximately perpendicular to the cyclobutadiene ring planes of (**1**) and the two distinct cations in the structure of (**2**).

Some general observations about the molecular geometries of complexes (**1**) and (**2**) may be made first. In each case the iron atom is η^4-bonded to a tetraphenylcyclobutadiene (tpcb) ligand, and further ligated by one linear carbonyl and two trimethyl phosphite ligands. The cyclobutadiene rings are essentially square in each case, deviations from equality of C–C bond lengths within a ring being compatible with the estimated standard deviations (e.s.d.s) and all internal C–C–C angles being 90° to within 3σ. The *ipso* carbons of the phenyl substituents on the tpcb ligands are all displaced from the mean plane through the ring carbons, away from the iron atom, by amounts which vary in an irregular way from 0.152 to 0.515 Å. The C_4 rings themselves show very small deviations from planarity, as reflected in C–C–C–C torsion angles of ±1.4(3), ±2.7(6), and ±0.9(6)° for (**1**), (**A**), and (**B**), respectively. The phenyl group geometries are unremarkable and the C_{ring}–C_{ipso} bond lengths average* 1.477(3), 1.477(5), and 1.488(9) Å respectively. Allowing for the difference in substituents at iron, the bond lengths and geometry of complex (**1**) are broadly similar to those of $[Fe(CO)_3(\eta\text{-}C_4Ph_4)]$ [16] (and of other related derivatives[4]) which shows mean Fe–C_{ring} 2.067(9), Fe–CO 1.751(6), C_{ring}–C_{ring} 1.459(6), and C_{ring}–C_{ipso} 1.468(8) Å.

A variety of changes in the geometry of the [Fe(CO)-

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* Standard deviations quoted for averaged dimensions throughout this paper are calculated as standard errors in the mean value given, whereas for individual values the estimated stardard deviations quoted are derived from least-squares procedures.

Table 2. Selected bond lengths (Å) and inter-bond angles (°) for complex (**2**) ($[BF_4]^-$ salt)

Fe(1)–P(1)	2.250(2)	Fe(1)–P(2)	2.265(2)	P(1)–Fe(1)–P(2)	97.3(1)	P(1)–Fe(1)–C(1)	111.6(2)
Fe(1)–C(1)	2.066(6)	Fe(1)–C(2)	2.093(7)	P(2)–Fe(1)–C(1)	150.4(2)	P(1)–Fe(1)–C(2)	151.1(2)
Fe(1)–C(3)	2.076(7)	Fe(1)–C(4)	2.100(7)	P(2)–Fe(1)–C(2)	108.8(2)	C(1)–Fe(1)–C(2)	41.6(3)
Fe(1)–C(5)	1.814(8)	P(1)–O(6)	1.591(6)	P(1)–Fe(1)–C(3)	124.2(2)	P(2)–Fe(1)–C(3)	97.8(2)
P(1)–O(7)	1.565(5)	P(1)–O(8)	1.566(6)	C(1)–Fe(1)–C(3)	61.1(2)	C(2)–Fe(1)–C(3)	41.6(3)
P(2)–O(9)	1.579(6)	P(2)–O(10)	1.566(6)	P(1)–Fe(1)–C(4)	93.3(2)	P(2)–Fe(1)–C(4)	134.0(2)
P(2)–O(11)	1.569(7)	O(5)–C(5)	1.123(10)	C(1)–Fe(1)–C(4)	41.6(3)	C(2)–Fe(1)–C(4)	59.7(3)
O(6)–C(6)	1.419(11)	O(7)–C(7)	1.431(12)	C(3)–Fe(1)–C(4)	41.9(3)	P(1)–Fe(1)–C(5)	95.4(3)
O(8)–C(8)	1.418(12)	O(9)–C(9)	1.425(10)	P(2)–Fe(1)–C(5)	89.7(2)	C(1)–Fe(1)–C(5)	93.6(3)
O(10)–C(10)	1.409(9)	O(11)–C(11)	1.373(15)	C(2)–Fe(1)–C(5)	96.9(3)	C(3)–Fe(1)–C(5)	138.0(3)
C(1)–C(2)	1.478(9)	C(1)–C(4)	1.479(9)	C(4)–Fe(1)–C(5)	133.7(3)	Fe(1)–P(1)–O(6)	121.3(3)
C(1)–C(12)	1.486(9)	C(2)–C(3)	1.480(9)	Fe(1)–P(1)–O(7)	109.9(2)	O(6)–P(1)–O(7)	105.5(3)
C(2)–C(18)	1.465(10)	C(3)–C(4)	1.493(9)	Fe(1)–P(1)–O(8)	109.2(2)	O(6)–P(1)–O(8)	100.2(3)
C(3)–C(24)	1.473(9)	C(4)–C(30)	1.484(10)	O(7)–P(1)–O(8)	110.3(3)	Fe(1)–P(2)–O(9)	111.0(2)
C(12)–C(13)	1.364(11)	C(12)–C(17)	1.399(11)	Fe(1)–P(2)–O(10)	116.2(2)	O(9)–P(2)–O(10)	105.1(3)
C(13)–C(14)	1.391(10)	C(14)–C(15)	1.362(14)	Fe(1)–P(2)–O(11)	114.5(2)	O(9)–P(2)–O(11)	104.1(3)
C(15)–C(16)	1.369(14)	C(16)–C(17)	1.382(10)	O(10)–P(2)–O(11)	104.8(3)	P(1)–O(6)–C(6)	124.3(6)
C(18)–C(19)	1.387(10)	C(18)–C(23)	1.412(10)	P(1)–O(7)–C(7)	127.4(6)	P(1)–O(8)–C(8)	129.7(6)
C(19)–C(20)	1.409(13)	C(20)–C(21)	1.349(13)	P(2)–O(9)–C(9)	128.5(6)	P(2)–O(10)–C(10)	129.7(6)
C(21)–C(22)	1.372(13)	C(22)–C(23)	1.400(13)	P(2)–O(11)–C(11)	132.1(7)	Fe(1)–C(1)–C(2)	70.1(3)
C(24)–C(25)	1.400(10)	C(24)–C(29)	1.395(10)	Fe(1)–C(1)–C(4)	70.5(3)	C(2)–C(1)–C(4)	89.8(5)
C(25)–C(26)	1.386(11)	C(26)–C(27)	1.401(13)	Fe(1)–C(1)–C(12)	134.2(5)	C(2)–C(1)–C(12)	134.7(6)
C(27)–C(28)	1.388(13)	C(28)–C(29)	1.353(10)	C(4)–C(1)–C(12)	131.3(6)	Fe(1)–C(2)–C(1)	68.2(4)
C(30)–C(31)	1.404(10)	C(30)–C(35)	1.352(11)	Fe(1)–C(2)–C(3)	68.6(4)	C(1)–C(2)–C(3)	90.7(5)
C(31)–C(32)	1.392(12)	C(32)–C(33)	1.360(13)	Fe(1)–C(2)–C(18)	124.8(5)	C(1)–C(2)–C(18)	134.4(6)
C(33)–C(34)	1.378(12)	C(34)–C(35)	1.380(13)	C(3)–C(2)–C(18)	134.7(6)	Fe(1)–C(3)–C(2)	69.8(4)
Fe(2)–P(3)	2.272(2)	Fe(2)–P(4)	2.257(3)	Fe(1)–C(3)–C(4)	69.9(4)	C(2)–C(3)–C(4)	89.2(5)
Fe(2)–C(54)	2.078(7)	Fe(2)–C(53)	2.077(7)	Fe(1)–C(3)–C(24)	130.6(5)	C(2)–C(3)–C(24)	134.1(6)
Fe(2)–C(52)	2.089(7)	Fe(2)–C(51)	2.053(7)	C(4)–C(3)–C(24)	134.4(6)	Fe(1)–C(4)–C(1)	68.0(4)
Fe(2)–C(55)	1.821(7)	P(3)–O(56)	1.571(5)	Fe(1)–C(4)–C(3)	68.2(4)	C(1)–C(4)–C(3)	90.2(5)
P(3)–O(57)	1.593(5)	P(3)–O(58)	1.583(6)	Fe(1)–C(4)–C(30)	132.7(5)	C(1)–C(4)–C(30)	132.3(5)
P(4)–O(59)	1.567(7)	P(4)–O(60)	1.567(6)	C(3)–C(4)–C(30)	135.5(6)	Fe(1)–C(5)–O(5)	176.6(7)
P(4)–O(61)	1.621(7)	O(55)–C(55)	1.122(8)	P(3)–Fe(2)–P(4)	95.6(1)	P(3)–Fe(2)–C(54)	98.5(2)
O(56)–C(56)	1.441(11)	O(57)–C(57)	1.437(9)	P(4)–Fe(2)–C(54)	132.6(2)	P(3)–Fe(2)–C(53)	128.4(2)
O(58)–C(58)	1.462(11)	O(59)–C(59)	1.392(14)	P(4)–Fe(2)–C(53)	96.2(2)	C(54)–Fe(2)–C(53)	41.6(3)
O(60)–C(60)	1.445(12)	O(61)–C(61)	1.347(14)	P(3)–Fe(2)–C(52)	157.1(2)	P(4)–Fe(2)–C(52)	105.0(2)
C(54)–C(53)	1.475(9)	C(54)–C(51)	1.454(9)	C(54)–Fe(2)–C(52)	60.0(3)	C(53)–Fe(2)–C(52)	40.4(3)
C(54)–C(62)	1.483(10)	C(53)–C(52)	1.440(10)	P(3)–Fe(2)–C(51)	117.2(2)	P(4)–Fe(2)–C(51)	146.6(2)
C(53)–C(68)	1.511(9)	C(52)–C(51)	1.472(9)	C(54)–Fe(2)–C(51)	41.2(3)	C(53)–Fe(2)–C(51)	59.4(2)
C(52)–C(74)	1.471(10)	C(51)–C(80)	1.485(9)	C(52)–Fe(2)–C(51)	41.6(3)	P(3)–Fe(2)–C(55)	97.1(2)
C(62)–C(63)	1.383(9)	C(62)–C(67)	1.398(10)	P(4)–Fe(2)–C(55)	92.4(2)	C(54)–Fe(2)–C(55)	129.9(3)
C(63)–C(64)	1.374(12)	C(64)–C(65)	1.396(12)	C(53)–Fe(2)–C(55)	132.3(3)	C(52)–Fe(2)–C(55)	92.1(3)
C(65)–C(66)	1.374(12)	C(66)–C(67)	1.372(12)	C(51)–Fe(2)–C(55)	89.7(3)	Fe(2)–P(3)–O(56)	113.3(2)
C(68)–C(69)	1.395(11)	C(68)–C(73)	1.391(11)	Fe(2)–P(3)–O(57)	118.2(2)	O(56)–P(3)–O(57)	99.9(3)
C(69)–C(70)	1.401(11)	C(70)–C(71)	1.373(18)	Fe(2)–P(3)–O(58)	110.4(2)	O(56)–P(3)–O(58)	108.7(4)
C(71)–C(72)	1.391(16)	C(72)–C(73)	1.400(12)	O(57)–P(3)–O(58)	105.5(3)	Fe(2)–P(4)–O(59)	119.3(3)
C(74)–C(75)	1.382(11)	C(74)–C(79)	1.379(10)	Fe(2)–P(4)–O(60)	114.0(3)	O(59)–P(4)–O(60)	107.8(4)
C(75)–C(76)	1.410(13)	C(76)–C(77)	1.358(13)	Fe(2)–P(4)–O(61)	107.9(3)	O(59)–P(4)–O(61)	99.3(4)
C(77)–C(78)	1.361(15)	C(78)–C(79)	1.400(13)	O(60)–P(4)–O(61)	107.0(3)	P(3)–O(56)–C(56)	125.3(5)
C(80)–C(81)	1.394(11)	C(80)–C(85)	1.363(10)	P(3)–O(57)–C(57)	121.1(5)	P(3)–O(58)–C(58)	125.1(5)
C(81)–C(82)	1.428(12)	C(82)–C(83)	1.383(13)	P(4)–O(59)–C(59)	121.9(7)	P(4)–O(60)–C(60)	125.5(7)
C(83)–C(84)	1.349(16)	C(84)–C(85)	1.376(11)	P(4)–O(61)–C(61)	130.8(8)	Fe(2)–C(54)–C(53)	69.2(4)
B(1)–F(1)	1.256(18)	B(1)–F(2)	1.239(22)	Fe(2)–C(54)–C(51)	68.5(4)	C(53)–C(54)–C(51)	88.6(5)
B(1)–F(3)	1.421(19)	B(1)–F(4)	1.227(20)	Fe(2)–C(54)–C(62)	139.9(5)	C(53)–C(54)–C(62)	132.4(6)
B(2)–F(5)	1.317(15)	B(2)–F(6)	1.286(17)	C(51)–C(54)–C(62)	132.4(6)	Fe(2)–C(53)–C(54)	69.2(4)
B(2)–F(7)	1.312(20)	B(2)–F(8)	1.270(20)	Fe(2)–C(53)–C(52)	70.2(4)	C(54)–C(53)–C(52)	91.2(5)
				Fe(2)–C(53)–C(68)	126.7(5)	C(54)–C(53)–C(68)	129.6(6)
				C(52)–C(53)–C(68)	138.3(6)	Fe(2)–C(52)–C(53)	69.3(4)
				Fe(2)–C(52)–C(51)	67.9(4)	C(53)–C(52)–C(51)	89.3(5)
				Fe(2)–C(52)–C(74)	127.0(5)	C(53)–C(52)–C(74)	136.7(6)
				C(51)–C(52)–C(74)	133.3(6)	Fe(2)–C(51)–C(54)	70.3(4)
				Fe(2)–C(51)–C(52)	70.5(4)	C(54)–C(51)–C(52)	90.8(5)
				Fe(2)–C(51)–C(80)	130.1(5)	C(54)–C(51)–C(80)	132.3(6)
				C(52)–C(51)–C(80)	134.6(6)	Fe(2)–C(55)–O(55)	175.2(6)

$\{P(OMe)_3\}_2(\eta\text{-}C_4Ph_4)]$ unit is apparent on comparison of complex (**1**) with (**A**) and (**B**). In terms of bond lengths the Fe–tpcb bonding is only slightly affected by oxidation, the mean Fe–C distances being 2.058(6), 2.084(8), and 2.074(8) Å respectively. The Fe-ring plane distances show a corresponding small lengthening on oxidation [1.778 Å in (**1**), and 1.800 and 1.798 Å for (**A**) and (**B**)] implying a slight weakening of the Fe–tpcb bond. While the variation in Fe–C distances in (**2**) is no more than expected from e.s.d. values, that in (**1**) is marginally significant, the Fe–C bond eclipsed by Fe–P(1) being uniquely

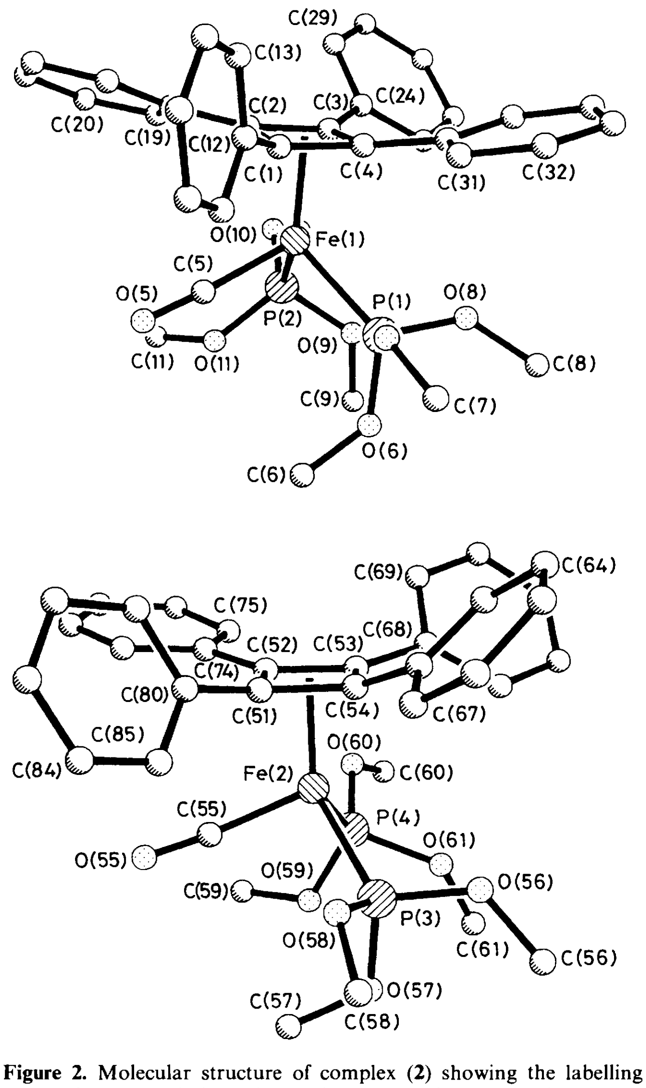

Figure 2. Molecular structure of complex (**2**) showing the labelling scheme for the two independent cations present in the crystal structure; hydrogen atoms are omitted for clarity

Table 3. Structure analyses of complexes (**1**) and (**2**) ($[BF_4]^-$ salt)[a]

	(**1**)	(**2**) ($[BF_4]^-$ salt)
(*a*) Crystal data		
Formula	$C_{35}H_{38}FeO_7P_2$	$C_{35}H_{38}BF_4FeO_7P_2$
M	688.5	775.3
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$(no. 2)	*Pc*(no. 7)
a/Å	13.230(9)	11.315(7)
b/Å	13.446(9)	22.771(14)
c/Å	9.535(7)	14.568(9)
α/°	97.05(6)	90
β/°	94.23(6)	100.08(5)
γ/°	89.71(6)	90
U/Å^3	1 679(2)	3 696(4)
Z	2	4
D_c/g cm^{-3}	1.36	1.39
F(000)	720	1 604
μ(Mo-K_α)/cm^{-1}	5.9	5.6
(*b*) Data collection and reduction		
Crystal dimensions (mm)	0.55 × 0.31 × 0.38	0.8 × 0.4 × 0.35
Scan width (2θ°)	2.2 + $\Delta\alpha_1\alpha_2$	2.0 + $\Delta\alpha_1\alpha_2$
Total data	4 985	5 516
Unique data	4 453	4 683
'Observed' data (N_O) $[F^2 > 2\sigma(F^2)]$	4 198	4 231
(*c*) Refinement[b]		
Least-squares variables (N_V)	462	889
R	0.035	0.045
R'	0.042	0.046
S	1.75	1.51
g	0.000 13	0.0002
Difference map features (e Å^{-3})	+0.35, −0.3	+0.4, −0.4

[a] Details common to both: $T = 295$ K; graphite monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å); 2θ range 4—50°; scan method ω–2θ.
[b] $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = [\Sigma w\Delta^2/\Sigma wF_o^2]^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_O - N_V)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$; $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$, where $\sigma_c^2(F_o)$ = variance in F_o due to counting statistics.

long. The C–C bond lengths within the tpcb ring show no significant variations from (**1**) to (**2**) [mean values in (**1**) and (**2**) are 1.477(4) and 1.471(6) Å respectively]. More notable is the change in conformation that occurs on oxidation (see Figure 3); in (**1**) {as in $[Fe(CO)_3(\eta\text{-}C_4H_4)]$ [3] and $[Fe(CO)_3(\eta\text{-}C_4Ph_4)]$ [16]} one of the terminal ligands, L, of the FeL_3 unit eclipses a carbon of the C_4 ring [P(1), hence P(1)–Fe–C(1)–C(11) torsion angle 3.2(3)°]. In both (**A**) and (**B**) the conformation adopted has the Fe–(CO) vector approximately orthogonal to one of the C–C bonds of the C_4 ring; this corresponds to a rotation of the tpcb ligand of *ca.* 20° about the Fe-ring axis [hence torsion angles are C(5)–Fe–C(2)–C(21) −17.6(3), C(5)–Fe–C(3)–C(31) 59.0(3), C(5)–Fe(1)–C(2)–C(18) −41.9(6), C(5)–Fe(1)–C(1)–C(12) 37.5(7), C(55)–Fe(2)–C(51)–C(80) 39.3(7), and C(55)–Fe(2)– C(52)–C(74) −40.8(6)°].

The largest change in bond lengths between complexes (**1**) and (**2**) involves the trimethyl phosphite ligands, Fe–P distances are 2.145(1) and 2.147(1) Å in (**1**), 2.250(2) and 2.265(2) Å in (**A**) and 2.272(2) and 2.257(3) Å in (**B**). The increase in Fe–P distance of *ca.* 0.12 Å is comparable to the change in Mn–P lengths observed in our structural study [14] of $[Mn(CO)(Ph_2PCH_2CH_2PPh_2)(\eta^5\text{-}C_6H_6Ph)]$ and its paramagnetic monocation; on oxidation the Mn–P lengths increase by 0.118 Å. The P–O bond lengths show a corresponding shift on oxidation, but it is smaller and in the opposite sense, mean P–O in (**1**) is 1.598(4) Å and for (**2**) is 1.578(5) Å. Accompanying the bond-length changes in the $P(OMe)_3$ ligands is a flattening of the PO_3 unit on oxidation of (**1**) [mean O–P–O in (**1**) is 100.8(14) and 104.9(10)° in (**2**)], although the wide range of individual values observed reduces the statistical significance of this change. In addition to the effect on the $P(OMe)_3$ ligands there is an increase in the Fe–CO bond length [1.743(3) Å in (**1**), 1.814(8) and 1.821(7) Å in (**A**) and (**B**)], and a reduction in the C–O length [1.154(4) Å in (**1**) and 1.123(10) and 1.122(10) Å in (**A**) and (**B**)]. As well as these bond-length variations there are significant alterations in bond angles on oxidation. In particular the $Fe(CO)\{P(OMe)_3\}_2$ fragment is tilted so that the C_4 ring centroid lies somewhat off the pseudo-three-fold axis of the FeL_3 moiety in (**2**) but closer to it in (**1**). Thus the ring centroid (cb)–Fe–L angles are cb–Fe–C(5) 118.2, cb–Fe–P(1) 121.2, and cb–Fe–P(2) 122.0° in (**1**), cb–Fe(1)–C(5) 117.9, cb–Fe(1)–P(1) 122.6, cb–Fe–P(2) 125.8° in (**A**), and cb–Fe(2)–C(55) 112.9, cb–Fe(1)–P(1) 128.3, and cb–Fe–P(2) 122.7° in (**A**). The direction of tilt brings the CO slightly towards the tpcb ring and one phosphorus substantially further away; for both (**A**) and (**B**) this phosphorus shows the longer of the two Fe–P distances. In addition the FeL_3 unit undergoes a slight, further, pyramidalization on oxidation, the sum of the P–Fe–P and P–Fe–CO angles decreasing from 289.5(2)° in complex (**1**) to

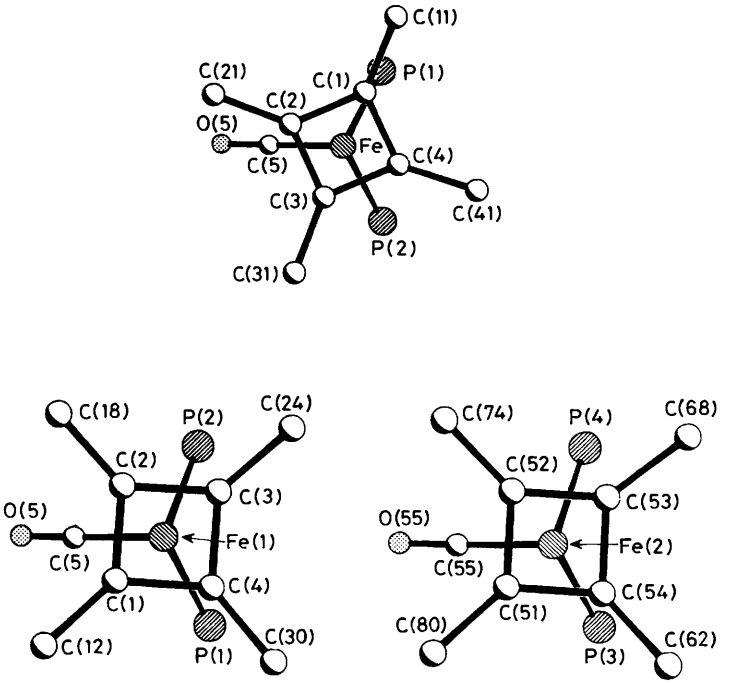

Figure 3. View of complex (**1**), and the two independent cations of (**2**) [(**A**) and (**B**)], each viewed normal to the cyclobutadiene plane. For clarity only *ipso* carbons of the phenyl rings are shown and the methoxy groups have been omitted

Table 4. Atomic co-ordinates (× 10^4) for complex (**1**)

Atom	*x*	*y*	*z*
Fe	7 506(1)	7 204(1)	5 656(1)
P(1)	6 001(1)	7 112(1)	4 644(1)
P(2)	8 276(1)	7 734(1)	3 985(1)
O(17)	5 766(2)	6 672(2)	3 010(2)
O(18)	5 309(2)	8 086(2)	4 609(2)
O(19)	5 304(2)	6 454(2)	5 464(2)
O(27)	8 864(2)	6 961(2)	2 904(2)
O(28)	7 581(2)	8 233(2)	2 823(2)
O(29)	9 119(2)	8 553(2)	4 545(2)
C(17)	6 272(3)	5 859(3)	2 292(4)
C(18)	5 243(4)	8 712(4)	3 530(5)
C(19)	4 222(3)	6 384(4)	5 213(5)
C(27)	9 725(3)	6 415(3)	3 422(4)
C(28)	7 769(4)	8 339(4)	1 403(4)
C(29)	9 795(4)	8 973(4)	3 680(5)
C(5)	7 767(2)	5 937(2)	5 209(3)
O(5)	7 951(2)	5 095(2)	5 000(3)
C(1)	6 973(2)	7 796(2)	7 576(3)
C(2)	7 720(2)	7 013(2)	7 760(3)
C(3)	8 509(2)	7 663(2)	7 354(3)
C(4)	7 748(2)	8 437(2)	7 135(3)
C(11)	5 972(2)	8 022(2)	8 112(3)
C(12)	5 522(3)	7 409(3)	8 953(4)
C(13)	4 612(3)	7 672(3)	9 535(4)
C(14)	4 141(3)	8 527(3)	9 296(4)
C(15)	4 573(3)	9 147(3)	8 469(4)
C(16)	5 473(3)	8 892(3)	7 877(4)
C(21)	7 719(2)	6 060(2)	8 388(3)
C(22)	8 491(2)	5 842(2)	9 355(3)
C(23)	8 491(3)	4 944(2)	9 942(3)
C(24)	7 713(3)	4 273(2)	9 587(4)
C(25)	6 924(3)	4 485(2)	8 634(3)
C(26)	6 935(3)	5 365(2)	8 031(3)
C(31)	9 621(2)	7 625(2)	7 406(3)
C(32)	10 197(2)	8 491(2)	7 597(3)
C(33)	11 246(3)	8 463(3)	7 605(4)
C(34)	11 733(3)	7 563(3)	7 425(4)
C(35)	11 179(2)	6 686(3)	7 250(3)
C(36)	10 137(2)	6 715(2)	7 241(3)
C(41)	7 778(2)	9 540(2)	7 119(3)
C(42)	8 122(2)	10 157(2)	8 332(3)
C(43)	8 105(3)	11 189(2)	8 382(4)
C(44)	7 735(3)	11 624(2)	7 216(4)
C(45)	7 396(3)	11 031(2)	6 006(4)
C(46)	7 417(2)	10 000(2)	5 949(4)

282.4(4)° in (**A**) and 285.1(4)° in (**B**). A comparable change occurs in the ML_3 geometry of [$Mn(CO)(Ph_2PCH_2CH_2PPh_2)$-($\eta^5$-$C_6H_6Ph$)] on one-electron oxidation[14] [the sum of P–Mn–P and P–Mn–CO angles was 265.5(2) and 261.4(2)° for the neutral complex and its cation respectively]. As can be seen in Figures 1 and 2 the $P(OMe)_3$ ligand conformations vary considerably between the three molecules, as do the conformations of the phenyl rings on the tpcb ligands. Presumably these variations, due in part at least to the differing crystal environments of the molecules (**1**), (**A**), and (**B**), are in turn responsible for some of the variation in the values of the softer molecular parameters (*e.g.* bond angles). Some feel for the magnitudes of these 'packing' effects can be gained by comparison of the geometries of ions (**A**) and (**B**).

The main objective of this study was to provide an experimental test of the current theories concerning structure and bonding in [FeL_3(η-C_4R_4)] complexes. The principal structural effects of oxidation on the geometry of (**1**) are focused on the iron atom and the L_3 ligand set, *i.e.* the carbonyl and trimethyl phosphite ligands. There is little disruption of iron–tpcb bonding and no sign of departure from essentially square geometry in the C_4 ring as a consequence of oxidation. The clear implication is that the h.o.m.o. of (**1**) is not an orbital involved in Fe–tpcb bonding. Had such an orbital been depopulated by

Table 5. Atomic co-ordinates ($\times 10^4$) for complex (**2**) ($[BF_4]^-$ salt)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	−598	1 175(1)	3 551	Fe(2)	−1 214(1)	6 227(1)	3 335(1)
P(1)	631(2)	861(1)	2 596(2)	P(3)	−160(2)	5 378(1)	3 334(1)
P(2)	−2 337(2)	838(1)	2 704(2)	P(4)	−2 962(2)	5 794(1)	3 490(2)
O(5)	−438(6)	117(3)	4 719(4)	O(55)	−618(5)	6 504(2)	5 334(3)
O(6)	433(5)	243(3)	2 085(4)	O(56)	−442(6)	5 037(2)	2 383(3)
O(7)	1 957(4)	853(3)	3 129(4)	O(57)	−395(5)	4 869(2)	4 031(3)
O(8)	512(5)	1 279(3)	1 731(4)	O(58)	1 236(5)	5 505(3)	3 568(4)
O(9)	−2 240(5)	786(3)	1 639(4)	O(59)	−3 099(6)	5 521(3)	4 454(4)
O(10)	−3 480(5)	1 222(3)	2 726(4)	O(60)	−4 099(4)	6 180(3)	3 145(4)
O(11)	−2 698(5)	205(3)	2 976(4)	O(61)	−3 100(7)	5 202(3)	2 862(5)
C(1)	306(6)	1 683(3)	4 624(4)	C(54)	−636(6)	6 641(3)	2 222(5)
C(2)	−1 004(6)	1 748(3)	4 575(4)	C(53)	−1 923(6)	6 753(3)	2 208(5)
C(3)	−1 112(6)	2 044(3)	3 660(4)	C(52)	−1 653(6)	7 106(3)	3 038(5)
C(4)	218(6)	2 005(3)	3 733(4)	C(51)	−367(6)	6 990(3)	3 069(5)
C(5)	−484(7)	513(4)	4 252(5)	C(55)	−828(6)	6 374(3)	4 580(5)
C(6)	532(10)	−307(4)	2 551(8)	C(56)	−247(13)	4 419(4)	2 263(7)
C(7)	2 997(8)	650(5)	2 789(8)	C(57)	−199(9)	4 964(4)	5 021(5)
C(8)	1 007(10)	1 226(5)	905(6)	C(58)	2 173(8)	5 055(4)	3 721(9)
C(9)	−2 588(9)	308(4)	1 018(6)	C(59)	−3 471(11)	5 854(6)	5 151(7)
C(10)	−4 459(7)	1 342(5)	2 010(6)	C(60)	−5 327(9)	5 977(6)	3 009(10)
C(11)	−3 693(11)	−6(5)	3 290(10)	C(61)	−3 561(13)	4 673(5)	3 014(8)
C(12)	1 340(6)	1 578(4)	5 388(5)	C(62)	59(6)	6 512(3)	1 472(4)
C(13)	1 667(7)	2 020(4)	6 013(5)	C(63)	−449(7)	6 628(3)	556(5)
C(14)	2 644(7)	1 962(4)	6 733(6)	C(64)	196(7)	6 584(3)	−158(5)
C(15)	3 276(8)	1 450(5)	6 799(7)	C(65)	1 401(8)	6 419(4)	52(6)
C(16)	2 982(8)	1 000(4)	6 179(6)	C(66)	1 904(7)	6 281(4)	954(6)
C(17)	2 010(6)	1 059(3)	5 464(5)	C(67)	1 259(6)	6 333(3)	1 664(5)
C(18)	−1 836(6)	1 617(3)	5 213(5)	C(68)	−2 991(6)	6 614(3)	1 463(5)
C(19)	−3 062(7)	1 546(4)	4 919(6)	C(69)	−3 797(7)	7 062(4)	1 140(5)
C(20)	−3 804(8)	1 387(4)	5 560(7)	C(70)	−4 782(8)	6 957(6)	431(6)
C(21)	−3 332(8)	1 308(4)	6 468(6)	C(71)	−4 972(9)	6 399(6)	79(7)
C(22)	−2 131(9)	1 390(4)	6 795(6)	C(72)	−4 153(10)	5 955(5)	379(7)
C(23)	−1 368(7)	1 526(4)	6 165(5)	C(73)	−3 145(7)	6 057(4)	1 068(5)
C(24)	−2 064(6)	2 389(3)	3 080(5)	C(74)	−2 315(6)	7 501(3)	3 566(5)
C(25)	−2 150(7)	2 405(3)	2 110(5)	C(75)	−3 551(7)	7 554(4)	3 364(5)
C(26)	−2 995(8)	2 751(4)	1 556(6)	C(76)	−4 177(8)	7 967(5)	3 817(7)
C(27)	−3 786(7)	3 087(4)	1 981(6)	C(77)	−3 542(10)	8 307(4)	4 497(7)
C(28)	−3 674(7)	3 082(4)	2 945(6)	C(78)	−2 333(9)	8 237(4)	4 735(6)
C(29)	−2 842(6)	2 744(3)	3 480(5)	C(79)	−1 695(7)	7 838(4)	4 277(5)
C(30)	1 132(6)	2 302(3)	3 278(5)	C(80)	762(6)	7 257(3)	3 568(5)
C(31)	2 345(6)	2 174(4)	3 611(5)	C(81)	913(7)	7 860(4)	3 467(5)
C(32)	3 213(7)	2 471(4)	3 222(6)	C(82)	1 961(8)	8 148(4)	3 950(6)
C(33)	2 908(8)	2 870(4)	2 524(6)	C(83)	2 815(8)	7 807(5)	4 502(7)
C(34)	1 713(8)	3 002(4)	2 232(6)	C(84)	2 666(7)	7 223(5)	4 583(6)
C(35)	836(7)	2 711(4)	2 604(6)	C(85)	1 655(6)	6 950(4)	4 112(5)
B(1)	3 332(15)	5 581(8)	6 197(12)	B(2)	3 770(13)	9 594(7)	4 809(10)
F(1)	2 239(6)	5 711(4)	5 993(7)	F(5)	2 610(5)	9 705(3)	4 620(5)
F(2)	3 978(10)	5 973(4)	5 963(11)	F(6)	4 466(7)	10 044(4)	4 891(6)
F(3)	3 734(10)	5 717(6)	7 153(7)	F(7)	4 123(9)	9 285(4)	4 146(10)
F(4)	3 698(11)	5 086(4)	6 065(8)	F(8)	3 923(8)	9 235(8)	5 487(8)

oxidation more dramatic effects on the Fe–tpcb bond and the C_4 ring geometry would have ensued. This conclusion is in accord with the description given by Bursten and Fenske[5] of the electronic structure of $[Fe(CO)_3(\eta\text{-}C_4H_4)]$ in which the Fe–ring and Fe–CO interactions were considered reasonably separable. The marked increases in Fe–CO and Fe–P bond lengths in (**2**) as compared with (**1**) are consistent with a substantial iron ($d\pi$) contribution to the depopulated orbital which is involved in Fe–CO and Fe–$P(OMe)_3$ π back bonding. If the oxidation is considered to first order to be at iron then the formal oxidation state of the iron atom rises from Fe^{II} in (**1**) to Fe^{III} in (**2**) (assuming the tpcb ligand acts as a dianionic 6π aromatic species), or Fe^0 in (**1**) to Fe^I in (**2**) (assuming the tpcb ligand is neutral). In either event the radius of the iron atom would be expected to decrease and bond lengths Fe–L to fall if the ligand, L, is a simple σ donor. That the reverse is the case here is consistent with Fe–L (π) back bonding being important for both CO and $P(OMe)_3$, and this bonding being diminished by oxidation at iron and in turn leading to longer Fe–CO and Fe–P distances. As we have pointed out[17] the changes in P–O bond lengths that accompany the disruption of Fe–P π bonding are consistent with the view that the π-acceptor function of phosphite is composed, in part, of P–O σ^* orbitals.

The results of this study are consistent with the electronic structure described by Chinn and Hall[11] for $[Fe(CO)_3(\eta\text{-}C_4H_4)]$ in that we have deduced the h.o.m.o. of complex (**1**) is an iron-centred *d* orbital. Several of the structural changes observed on oxidation of (**1**) were not predicted by these or other authors. In particular the tilting and increased pyramidalization of the FeL_3 moiety, and the change that occurs in the relative conformation of C_4 and FeL_3 units, were unexpected. On a cautionary note however, it seems unlikely that the conformational preference in (**2**) is strong despite essentially identical conformations being present in both (**A**) and (**B**). It may well be that given some tilting, non-bonded, steric interactions favour the observed conformation in which the carbonyl tilted toward the tpcb ligand approaches it between the phenyl substituents. In addition we note that the degree of tilting is clearly rather variable, the cb–Fe–CO angle in (**A**) is 117.9 and 112.9° in (**B**). We conclude that it is not safe to assume that the equilibrium geometry of (**2**) is strongly tilted but rather that (**2**) may be readily deformed in this way, and that tilted structures would be easily accessible, in solution for example. Such tilting, in which the pseudo-symmetry of the (tpcb)FeL_3 unit is reduced from C_{3v} to C_s is a mode of Jahn–Teller type distortion that deserves consideration by theoreticians seeking to understand the properties of derivatives of $[Fe(CO)_3(\eta\text{-}C_4H_4)]$. In addition the rehybridization of iron orbitals which must surely accompany such a geometric distortion will have consequences on the details of iron–cyclobutadiene bonding. Among the published structures of FeL_3(cyclobutadiene) derivatives (*e.g.* see ref. 4) only one[18] shows a cb–Fe–L angle <116.5° [in a benzocyclobutadiene derivative in which cb–Fe–CO 113.7° and the $Fe(CO)_3$ orientation is as in (**2**)], more typically cb–Fe–L angles fall close to 120°. This implies that the large tilt observed in (**B**) is unusual and facilitated by the $17e^-$ configuration at iron.

The enhanced reactivity of (**2**) towards nucleophilic attack at iron (*e.g.* by halide anions) as compared with (**1**) follows from the reduced barrier to associative reactions with electron donors, *e.g.* as previously noted[19] for $[Co(PEt_3)_2(\eta\text{-}C_5H_5)]$ and its radical cation (see also ref. 20, p. 155 and refs. therein). As is illustrated by the observation[9] of e.s.r. spectra assignable to species $[Fe(CO)X\{P(OMe)_3\}_2(\eta\text{-}C_4Ph_4)]$ (X = Cl or Br) obtained by treatment of (**2**) with X^-, the presence of a s.o.m.o. centred on iron in (**2**) allows formation of relatively favourable three-electron interactions with nucleophiles. In contrast, attack on the iron atom of (**1**) by an incoming nucleophile will result in a strongly destabilizing four-electron interaction. In addition the readiness of (**2**) to undergo the tilting distortion may facilitate nucleophilic attack at iron by reducing steric barriers. This is in contrast to the reactivity of *e.g.* $[Fe(CO)_3(dienyl)]^+$ cations which generally favour nucleophilic attack at the dienyl rather than at the metal.[21]

Experimental

Structure Determinations for Complexes (**1**) *and* (**2**) ($[BF_4]^-$ *Salt*).—Many of the details of the structure analyses carried out on complexes (**1**) and (**2**) ($[BF_4]^-$ salt) are listed in Table 3. *X*-Ray diffraction measurements were made using Nicolet four-circle P3m diffractometers on single crystals mounted in thin-walled glass capillaries. Cell dimensions for each analysis were determined from the setting angle values of 15 centred reflections.

Intensity data were collected by ω—2θ scans for unique portions of reciprocal space and corrected for Lorentz, polarization, crystal decay (of 0 and 8% respectively, but not for absorption effects. Only those reflections with pre-scan counts above a low threshold [of 30 counts s^{-1} for (**1**) and 20 counts s^{-1} for (**2**)] were measured for $2\theta > 40°$. The structures were solved by heavy-atom (Patterson, direct and Fourier difference) methods, and refined by blocked-cascade least squares against *F*. All non-hydrogen atoms were assigned anisotropic displacement parameters. All hydrogen atoms were constrained to ideal geometries (with C–H 0.96 Å), and were assigned isotropic displacement parameters, those for (**1**) being allowed to refine and those for (**2**) being fixed. Despite the rather low data: variable ratio, the final fully anisotropic model used for (**2**) was preferred because of the improvements in residual index *R*, goodness of fit *S*, and e.s.d.s in bond lengths, *etc.* resulting from the less restricted model (*cf.* a refinement model with isotropic carbon atoms having 540 variables gave *R* 0.059, *S* 1.89, and e.s.d.s in bond lengths 50% greater than those in Table 2).

Final difference syntheses showed no chemically significant features, the largest being close to the metal atoms and the $[BF_4]^-$ anion. The large and highly anisotropic displacement parameters (U_{ij}) observed for the fluorine atoms are probably indicative of disorder in the anion, however it was not possible to resolve multiple atomic sites. Refinements converged smoothly to residuals given in Table 3. The absolute structure of complex (**2**) was assigned by the Rogers η-refinement method[22] [η = 0.65(5)]. Tables 4 and 5 list atomic positional co-ordinates for the non-hydrogen atoms of (**1**) and (**2**).

All calculations were made with programs of the SHELXTL[23] system as implemented on a Nicolet R3m/E structure determination system. Complex neutral-atom scattering factors were taken from ref. 24.

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

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