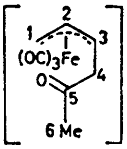
Metal–Carbonyl and Metal–Nitrosyl Complexes. Part XIV.[1] Molecular Structure of the Allyltricarbonyliron Cation Intermediate in the Friedel–Crafts Acetylation of Butadienetricarbonyliron: *X*-Ray Study of Tricarbonyl(1—3-η-hexen-5-one)iron Hexafluorophosphate †

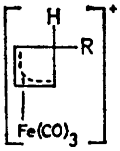
By **A. D. U. Hardy** and **G. A. Sim,*** Chemistry Department, University of Glasgow, Glasgow G12 8QQ

The molecular geometry of the title cation has been determined by *X*-ray analysis of its hexafluorophosphate salt. The tricarbonyliron group is bound to the allyl fragment and the oxygen atom of the $CH_2\cdots CH\cdots CH\cdot CH_2\cdot CO\cdot CH_3$ ligand, with Fe–C 2·141(10), 2·063(9), and 2·144(8) and Fe–O 1·999(5) Å. The Fe–CO bond *trans* to oxygen is 1·787(7) Å, whilst those *trans* to allyl are 1·840(9) and 1·828(8) Å. The mean P–F separation in the hexafluorophosphate anion is 1·578(9) Å. The complex crystallizes in the orthorhombic space group *Pbca*, with $Z = 8$ and $a = 15{\cdot}136(11)$, $b = 15{\cdot}256(8)$, $c = 12{\cdot}123(10)$ Å. *X*-Ray intensity data were collected on a diffractometer, and the atomic parameters were determined by Fourier and least-squares methods, the final *R* being 7·1% over 2365 independent reflections.

THE Friedel–Crafts acetylation of butadienetricarbonyliron in methylene chloride yields a crystalline intermediate of composition $[C_4H_6\cdot CO\cdot CH_3\cdot Fe(CO)_3]^+[AlCl_4]^-$.[2] The organometallic cation was assigned the *anti*-allyl structure (1) from ^1H n.m.r. spectra, and it



(1)



(2)

was suggested that the iron atom obtains a closed-shell configuration by intramolecular σ-donation of a pair of electrons from the acyl oxygen atom.[2] Since this is the first intermediate isolated and characterized during the electrophilic substitution of a hydrocarbon ligand π-bonded to a transition metal, and corresponds to the type of cation (2) postulated by Pettit as arising in the substitution of tricarbonylcyclobutadieneiron,[3] we undertook an *X*-ray crystallographic study of the hexafluorophosphate salt of (1) in order to define rigorously the geometry of the organometallic cation.

The crystal structure of the hexafluorophosphate salt was elucidated by Fourier and least-squares methods

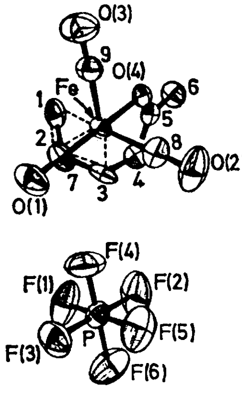


FIGURE 1 The atomic arrangement projected on to the plane of the carbonyl oxygen atoms O(1), O(2), and O(3)

in which we employed 2365 independent reflections having $I > 2{\cdot}5\sigma(I)$, and the analysis terminated at R 7·1%. Figure 1 shows the atomic arrangement in the tricarbonyl-(5-oxo-1,2,3-hexenyl)iron cation and

---

† No reprints available.

[1] Part XIII, A. D. U. Hardy and G. A. Sim, *J.C.S. Dalton*, 1972, 1900.

[2] E. O. Greaves, G. R. Knox, and P. L. Pauson, *Chem. Comm.*, 1969, 1124.

[3] R. Pettit, *Pure and Appl. Chem.*, 1968, **17**, 253.

the hexafluorophosphate anion, looking on to the plane defined by the carbonyl oxygen atoms O(1), O(2), and O(3), and Figure 2 shows a general view of the cation. The crystal structure is illustrated in Figure 3. The atomic co-ordinates and thermal parameters are listed in Tables 1 and 2, and the various interatomic distances and angles are in Tables 3—5.†

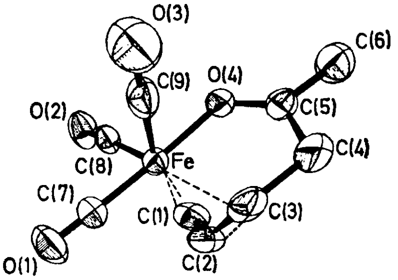


FIGURE 2 A general view of the cation, showing the co-ordination of the iron atom

TABLE 1

Atomic co-ordinates (as fractions of the cell edges) with standard deviations in parentheses. The hydrogen atoms are numbered according to the carbon atoms to which they are attached

Atom	x	y	z
Fe	0·1079(1)	0·1944(1)	0·0556(1)
P	0·3657(1)	0·0909(1)	−0·2205(2)
F(1)	0·3144(5)	0·1315(5)	−0·3218(7)
F(2)	0·4190(4)	0·0508(5)	−0·1199(5)
F(3)	0·3405(5)	−0·0040(3)	−0·2601(5)
F(4)	0·2792(5)	0·0914(6)	−0·1504(7)
F(5)	0·3919(6)	0·1872(4)	−0·1846(9)
F(6)	0·4535(4)	0·0862(5)	−0·2918(6)
O(1)	0·1114(5)	0·0173(4)	−0·0365(6)
O(2)	0·2800(5)	0·1637(5)	0·1627(8)
O(3)	−0·0243(5)	0·1309(4)	0·2166(6)
O(4)	0·1065(3)	0·3120(3)	0·1285(4)
C(1)	0·0058(7)	0·2503(7)	−0·0444(8)
C(2)	0·0820(8)	0·2343(6)	−0·1038(7)
C(3)	0·1656(7)	0·2692(5)	−0·0757(6)
C(4)	0·1809(7)	0·3608(6)	−0·0281(7)
C(5)	0·1368(5)	0·3747(4)	0·0810(6)
C(6)	0·1327(8)	0·4653(6)	0·1258(10)
C(7)	0·1099(6)	0·0867(5)	−0·0020(7)
C(8)	0·2152(6)	0·1747(5)	0·1225(7)
C(9)	0·0275(6)	0·1559(5)	0·1570(6)
H(1a)	0·0021(46)	0·3059(47)	−0·0017(59)
H(1b)	−0·0414(112)	0·2306(111)	−0·0588(128)
H(2)	0·0709(60)	0·1859(58)	−0·1506(73)
H(3)	0·2096(43)	0·2448(45)	−0·1176(53)
H(4a)	0·1529(67)	0·3845(65)	−0·0783(79)
H(4b)	0·2442(65)	0·3828(57)	−0·0025(69)
H(6a)	0·1209(54)	0·4662(55)	0·1738(66)
H(6b)	0·1653(102)	0·5076(110)	0·1372(131)
H(6c)	0·0797(151)	0·5353(172)	0·0626(186)

TABLE 2

Thermal parameters *

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Fe	41(1)	26(0)	48(1)	1(0)	3(0)	−3(0)
P	38(1)	37(1)	88(2)	−6(1)	−3(1)	6(1)
F(1)	89(4)	78(4)	225(10)	−18(3)	−84(6)	61(5)
F(2)	74(4)	97(4)	110(6)	−17(3)	−23(4)	41(4)
F(3)	90(4)	45(2)	137(6)	−5(2)	−2(4)	−16(3)
F(4)	66(4)	114(5)	214(10)	−4(4)	58(5)	−45(6)
F(5)	120(6)	58(3)	246(12)	−29(4)	−62(7)	−8(5)
F(6)	55(3)	125(5)	144(7)	−2(3)	28(4)	52(5)
O(1)	94(5)	39(3)	110(6)	−1(3)	16(4)	−23(3)
O(2)	66(4)	51(3)	191(10)	13(3)	−59(5)	−11(5)
O(3)	80(4)	50(3)	120(7)	−11(3)	40(5)	−7(4)
O(4)	42(2)	29(2)	55(3)	−2(2)	−5(2)	−4(2)
C(1)	57(4)	52(3)	90(7)	14(4)	−36(5)	−12(5)
C(2)	89(7)	46(4)	51(5)	0(4)	−15(5)	−6(4)
C(3)	79(6)	38(3)	47(5)	9(4)	27(4)	−3(3)
C(4)	61(5)	37(3)	67(6)	−5(3)	1(4)	8(4)
C(5)	37(3)	30(3)	63(5)	0(2)	−9(3)	4(3)
C(6)	68(6)	33(3)	90(8)	−5(4)	0(6)	−7(5)
C(7)	60(4)	35(3)	65(5)	1(3)	−1(4)	−5(3)
C(8)	45(4)	25(3)	98(7)	2(2)	−11(4)	2(3)
C(9)	51(4)	31(3)	69(5)	−7(3)	12(4)	−8(3)

Atom	B	Atom	B	Atom	B
H(1a)	0·1(1·2)	H(3)	0·0(1·2)	H(6a)	0·0(1·6)
H(1b)	5·3(4·7)	H(4a)	2·1(2·1)	H(6b)	7·9(4·5)
H(2)	2·1(1·7)	H(4b)	2·6(1·8)	H(6c)	17·0(8·3)

* The anisotropic temperature factors adopted for the non-hydrogen atoms are expressed in the form $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

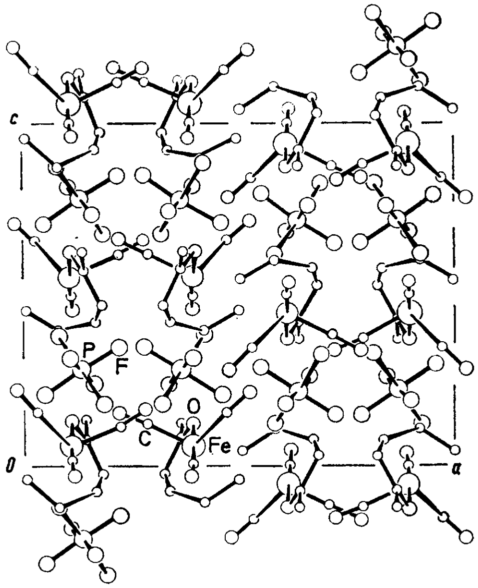


FIGURE 3 The crystal structure viewed along the b axis

Figure 2 clearly shows that the organic ligand is bound to the iron atom by the carbon atoms C(1), C(2), and C(3), but not by C(4), and by the oxygen atom O(4). The iron–carbon bonded distances [Fe–C(1) 2·141(10), Fe–C(2) 2·063(9), and Fe–C(3) 2·144(8) Å] are close to those observed in other π-allyltricarbonyliron complexes, *e.g.* 2·194(18), 2·091(16), and 2·202(17) Å in $(C_4H_6)Fe(CO)_3{\cdot}SO_2{\cdot}BF_3$,[4] and 2·200(8), 2·050(8), and 2·142(8) Å in azulenepentacarbonyldi-iron.[5] The Fe–C(terminal) and Fe–C(central) distances in tricarbonyl-1,3-dieneiron complexes, moreover, are typically 2·16

---

† Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20481 (13 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[4] M. R. Churchill and J. Wormald, *Inorg. Chem.*, 1970, **9**, 2430.

[5] M. R. Churchill, *Inorg. Chem.*, 1967, **6**, 190.

and 2·05 Å.[6] The Fe · · · C(4) distance of 2·95 Å in (1) is considerably longer than these Fe–C bonded distances. The C(1)–C(2) and C(2)–C(3) distances of 1·380(15) and 1·415(15) Å in the allyl fragment are intermediate between single- and double-bond values for carbon–carbon bonds, whilst the C(3)–C(4) distance of 1·530(12) Å is close to Sutton's value of 1·510 Å for a C(sp^2)–C(sp^3) single bond.[7] Carbon atom C(4) in the cation deviates appreciably from the plane through C(1), C(2), and C(3), the torsion angle about the C(2)–C(3) bond being

TABLE 3

Interatomic distances (Å)

(*a*) Bond lengths

Fe–O(4)	1·995(5)	O(4)–C(5)	1·207(8)
Fe–C(1)	2·141(10)	C(1)–C(2)	1·380(15)
Fe–C(2)	2·063(9)	C(2)–C(3)	1·415(15)
Fe–C(3)	2·144(8)	C(3)–C(4)	1·530(12)
Fe–C(7)	1·787(8)	C(4)–C(5)	1·496(12)
Fe–C(8)	1·840(9)	C(5)–C(6)	1·487(12)
Fe–C(9)	1·828(8)	C(1)–H(1a)	1·00(7)
P–F(1)	1·580(9)	C(1)–H(1b)	0·80(17)
P–F(2)	1·585(7)	C(2)–H(2)	0·95(9)
P–F(3)	1·572(6)	C(3)–H(3)	0·92(7)
P–F(4)	1·562(8)	C(4)–H(4a)	0·83(10)
P–F(5)	1·583(8)	C(4)–H(4b)	1·06(10)
P–F(6)	1·587(7)	C(6)–H(6a)	0·61(8)
O(1)–C(7)	1·137(10)	C(6)–H(6b)	0·82(16)
O(2)–C(8)	1·109(12)	C(6)–H(6c)	1·54(25)
O(3)–C(9)	1·131(11)		

(*b*) Non-bonded distances in the organometallic cation

C(2) · · · C(7)	2·60	C(1) · · · C(9)	2·85
O(4) · · · C(8)	2·66	C(3) · · · C(8)	2·90
O(4) · · · C(9)	2·69	Fe · · · C(4)	2·95
O(4) · · · C(3)	2·71	C(1) · · · C(7)	3·00
O(4) · · · C(1)	2·76	C(3) · · · C(7)	3·04
Fe · · · C(5)	2·80		

(*c*) Interionic contacts (⩽3·75 Å)

C(3) · · · F(1$^{\mathrm{VI}}$)	2·94	O(3) · · · C(2$^{\mathrm{VI}}$)	3·40
O(3) · · · F(5$^{\mathrm{II}}$)	3·08	O(1) · · · O(3$^{\mathrm{I}}$)	3·41
C(8) · · · F(3$^{\mathrm{IV}}$)	3·09	O(4) · · · F(6$^{\mathrm{II}}$)	3·42
O(1) · · · F(4)	3·10	O(1) · · · F(3$^{\mathrm{IV}}$)	3·44
C(7) · · · F(4)	3·13	C(7) · · · F(6$^{\mathrm{VIII}}$)	3·44
C(9) · · · F(5$^{\mathrm{II}}$)	3·17	C(4) · · · F(2$^{\mathrm{V}}$)	3·45
O(2) · · · F(1$^{\mathrm{VI}}$)	3·17	O(3) · · · C(1$^{\mathrm{VI}}$)	3·45
O(2) · · · F(3$^{\mathrm{IV}}$)	3·18	C(9) · · · C(2$^{\mathrm{VI}}$)	3·45
C(6) · · · F(1$^{\mathrm{VI}}$)	3·19	C(6) · · · F(6$^{\mathrm{II}}$)	3·47
C(4) · · · F(1$^{\mathrm{VI}}$)	3·22	O(3) · · · F(6$^{\mathrm{IV}}$)	3·48
C(2) · · · F(6$^{\mathrm{VIII}}$)	3·24	C(6) · · · F(3$^{\mathrm{VI}}$)	3·49
C(6) · · · F(2$^{\mathrm{II}}$)	3·25	O(1) · · · F(6$^{\mathrm{IV}}$)	3·50
C(7) · · · F(3$^{\mathrm{IV}}$)	3·28	C(4) · · · F(3$^{\mathrm{V}}$)	3·50
C(1) · · · F(6$^{\mathrm{VIII}}$)	3·29	C(5) · · · F(2$^{\mathrm{II}}$)	3·52
O(4) · · · F(5$^{\mathrm{II}}$)	3·32	O(4) · · · F(2$^{\mathrm{II}}$)	3·53
O(4) · · · F(1$^{\mathrm{VI}}$)	3·32	O(1) · · · O(1$^{\mathrm{I}}$)	3·53
C(6) · · · O(2$^{\mathrm{V}}$)	3·33	C(6) · · · O(3$^{\mathrm{III}}$)	3·57
C(6) · · · F(2$^{\mathrm{V}}$)	3·34	C(6) · · · F(4$^{\mathrm{VI}}$)	3·61
C(3) · · · F(4)	3·34	O(1) · · · F(1$^{\mathrm{IV}}$)	3·63
O(4) · · · C(2$^{\mathrm{VI}}$)	3·34	C(8) · · · F(4)	3·67
O(2) · · · O(3$^{\mathrm{VII}}$)	3·34	O(1) · · · C(9$^{\mathrm{I}}$)	3·68
O(1) · · · F(6$^{\mathrm{VIII}}$)	3·34	C(5) · · · F(2$^{\mathrm{V}}$)	3·72
C(8) · · · F(1$^{\mathrm{VI}}$)	3·38	C(2) · · · F(4)	3·74
O(2) · · · F(5$^{\mathrm{VI}}$)	3·39	O(1) · · · C(7$^{\mathrm{I}}$)	3·74
C(1) · · · F(5$^{\mathrm{II}}$)	3·40	Fe · · · F(3$^{\mathrm{IV}}$)	3·75
O(3) · · · F(3$^{\mathrm{IV}}$)	3·40		

The superscripts in the atom labels refer to the following transformations of the co-ordinates:

I	$-x, -y, -z$	V	$\tfrac{1}{2} - x, \tfrac{1}{2} + y, z$
II	$\tfrac{1}{2} + x, \tfrac{1}{2} - y, -z$	VI	$x, \tfrac{1}{2} - y, \tfrac{1}{2} + z$
III	$-x, \tfrac{1}{2} + y, \tfrac{1}{2} - z$	VII	$\tfrac{1}{2} + x, y, \tfrac{1}{2} - z$
IV	$\tfrac{1}{2} - x, -y, \tfrac{1}{2} + z$	VIII	$-\tfrac{1}{2} + x, y, -\tfrac{1}{2} - z$

TABLE 4

Valency angles (deg.)

O(4)–Fe–C(7)	176·7(3)	Fe–C(7)–O(1)	178·5(8)
O(4)–Fe–C(8)	87·8(3)	Fe–C(8)–O(2)	179·2(7)
O(4)–Fe–C(9)	89·1(3)	Fe–C(9)–O(3)	177·4(8)
O(4)–Fe–C(1)	83·4(3)	Fe–C(1)–C(2)	67·8(6)
O(4)–Fe–C(2)	98·5(3)	Fe–C(2)–C(1)	73·9(6)
O(4)–Fe–C(3)	81·7(3)	Fe–C(2)–C(3)	73·5(5)
C(8)–Fe–C(7)	90·4(4)	C(3)–C(2)–C(1)	123·7(8)
C(9)–Fe–C(7)	88·7(4)	Fe–C(3)–C(2)	67·3(5)
C(1)–Fe–C(7)	99·0(4)	Fe–C)3)–C(4)	105·5(5)
C(2)–Fe–C(7)	84·8(4)	C(4)–C(3)–C(2)	124·8(9)
C(3)–Fe–C(7)	101·1(3)	C(5)–C(4)–C(3)	113·2(7)
C(9)–Fe–C(8)	103·8(4)	C(4)–C(5)–O(4)	118·7(6)
C(1)–Fe–C(8)	162·1(4)	C(6)–C(5)–O(4)	123·1(7)
C(2)–Fe–C(8)	129·0(4)	C(6)–C(5)–C(4)	118·2(7)
C(3)–Fe–C(8)	93·1(4)	H(1a)–C(1)–Fe	95(4)
C(1)–Fe–C(9)	91·6(4)	H(1b)–C(1)–Fe	129(12)
C(2)–Fe–C(9)	126·8(4)	H(1a)–C(1)–C(2)	118(4)
C(3)–Fe–C(9)	160·4(4)	H(1b)–C(1)–C(2)	125(12)
C(2)–Fe–C(1)	38·3(4)	H(1b)–C(1)–H(1a)	113(13)
C(3)–Fe–C(1)	70·2(4)	H(2)–C(2)–Fe	111(5)
C(3)–Fe–C(2)	39·2(4)	H(2)–C(2)–C(1)	108(6)
F(2)–P–F(1)	178·8(4)	H(2)–C(2)–C(3)	127(6)
F(3)–P–F(1)	90·3(4)	H(3)–C(3)–Fe	119(4)
F(4)–P–F(1)	90·5(4)	H(3)–C(3)–C(2)	111(4)
F(5)–P–F(1)	88·4(5)	H(3)–C(3)–C(4)	118(4)
F(6)–P–F(1)	90·3(4)	H(4a)–C(4)–C(3)	92(7)
F(3)–P–F(2)	90·2(4)	H(4b)–C(4)–C(3)	122(5)
F(4)–P–F(2)	90·5(4)	H(4a)–C(4)–C(5)	111(7)
F(5)–P–F(2)	91·1(5)	H(4b)–C(4)–C(5)	96(5)
F(6)–P–F(2)	88·6(4)	H(4b)–C(4)–H(4a)	123(8)
F(4)–P–F(3)	88·1(4)	H(6a)–C(6)–C(5)	112(8)
F(5)–P–F(3)	178·2(5)	H(6b–C(6)–C(5)	140(11)
F(6)–P–F(3)	89·8(4)	H(6c)–C(6)–C(5)	119(9)
F(5)–P–F(4)	93·2(5)	H(6b)–C(6)–H(6a)	90(9)
F(6)–P–F(4)	177·7(5)	H(6c)–C(6)–H(6a)	108(12)
F(6)–P–F(5)	89·0(5)	H(6c)–C(6)–H(6b)	82(14)
Fe–O(4)–C(5)	119·7(5)		

TABLE 5

Torsion angles (deg.) in the cation

C(7)–Fe–O(4)–C(5)	147	O(4)–Fe–C(2)–C(3)	66
C(8)–Fe–O(4)–C(5)	92	C(7)–Fe–C(2)–C(1)	112
C(9)–Fe–O(4)–C(5)	−165	C(7)–Fe–C(2)–C(3)	−115
C(1)–Fe–O(4)–C(5)	−73	C(8)–Fe–C(2)–C(1)	−162
C(2)–Fe–O(4)–C(5)	−38	C(8)–Fe–C(2)–C(3)	−29
C(3)–Fe–O(4)–C(5)	−2	C(9)–Fe–C(2)–C(1)	27
O(4)–Fe–C(7)–O(1)	−1	C(9)–Fe–C(2)–C(3)	161
C(8)–Fe–C(7)–O(1)	54	C(1)–Fe–C(2)–C(3)	134
C(9)–Fe–C(7)–O(1)	−49	C(3)–Fe–C(2)–C(1)	−134
C(1)–Fe–C(7)–O(1)	−141	O(4)–Fe–C(3)–C(2)	−115
C(2)–Fe–C(7)–O(1)	−171	O(4)–Fe–C(3)–C(4)	7
C(3)–Fe–C(7)–O(1)	148	C(7)–Fe–C(3)–C(2)	67
O(4)–Fe–C(8)–O(2)	−34	C(7)–Fe–C(3)–C(4)	−171
C(7)–Fe–C(8)–O(2)	148	C(8)–Fe–C(3)–C(2)	158
C(9)–Fe–C(8)–O(2)	−123	C(8)–Fe–C(3)–C(4)	−80
C(1)–Fe–C(8)–O(2)	26	C(9)–Fe–C(3)–C(2)	−52
C(2)–Fe–C(8)–O(2)	65	C(9)–Fe–C(3)–C(4)	70
C(3)–Fe–C(8)–O(2)	47	C(1)–Fe–C(3)–C(2)	−29
O(4)–Fe–C(9)–O(3)	128	C(1)–Fe–C(3)–C(4)	93
C(7)–Fe–C(9)–O(3)	−54	C(2)–Fe–C(3)–C(4)	122
C(8)–Fe–C(9)–O(3)	−144	Fe–O(4)–C(5)–C(4)	−5
C(1)–Fe–C(9)–O(3)	45	Fe–O(4)–C(5)–C(6)	176
C(2)–Fe–C(9)–O(3)	28	Fe–C(1)–C(2)–C(3)	−57
C(3)–Fe–C(9)–O(3)	67	Fe–C(2)–C(3)–C(4)	−94
O(4)–Fe–C(1)–C(2)	113	C(1)–C(2)–C(3)–Fe	57
C(7)–Fe–C(1)–C(2)	−70	C(1)–C(2)–C(3)–C(4)	−37
C(8)–Fe–C(1)–C(2)	52	Fe–C(3)–C(4)–C(5)	−11
C(9)–Fe–C(1)–C(2)	−158	C(2)–C(3)–C(4)–C(5)	62
C(3)–Fe–C(1)–C(2)	29	C(3)–C(4)–C(5)–O(4)	11
C(4)–Fe–C(2)–C(1)	−68	C(3)–C(4)–C(5)–C(6)	−169

---

[6] R. P. Dodge, *J. Amer. Chem. Soc.*, 1964, **86**, 5429; B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, 1964, **37**, 2084; O. S. Mills and G. Robinson, *Acta Cryst.*, 1963, **16**, 758; A. Robson and M. R. Truter, *J. Chem. Soc.* (*A*), 1968, 794; N. A. Bailey and R. Mason, *Acta Cryst.*, 1966, **21**, 652; M. G. Waite and G. A. Sim, *J. Chem. Soc.* (*A*), 1971, 1009.

[7] *Chem. Soc. Special Publ.*, No. 18, 1965.

$-37°$; on the other hand, the four conjugated carbon atoms of a 1,3-diene complexed to a tricarbonyliron group are always closely coplanar.[6]

The Fe–O(4) bond has a length of 1·999(5) Å, in excellent agreement with the corresponding distance of 2·004(10) Å in $C_4H_6Fe(CO)_3{\cdot}SO_2{\cdot}BF_3$.[4] On the basis of Pauling's covalent radii of 0·66 Å for oxygen and 0·77 Å for carbon, these Fe–O distances are consistent with the Fe–C(alkyl) distance of *ca.* 2·11 Å in complexes of the type $(\pi\text{-}C_5H_5)Fe(CO)_2R$, where R = alkyl.[8] The C(5)—O(4) distance of 1·207(8) Å agrees very well with the mean CO distance of 1·215(5) Å reported for ketones and aldehydes,[7] and so the acyl CO bond order appears to be essentially unaffected by the formation of the Fe–O(4) bond; ν(CO), however, is at 1637 cm^{-1}, whereas normal ketone absorption is at *ca.* 1715 cm^{-1}.

Within the tricarbonyliron moiety the Fe–C(7) bond *trans* to the oxygen ligand O(4) has a length of 1·787(8) Å, whereas the Fe–C(8) and Fe–C(9) bonds *trans* to the π-allyl system have lengths of 1·840(9) and 1·828(8) Å. The contraction of the iron–carbonyl distance *trans* to O(4) is not unexpected, for whilst the back-donation of d_π electron density from the metal atom to the π-allyl system undoubtedly plays a part in the bonding scheme of the complex,[9] back-donation of charge to the oxygen atom O(4) is negligible, the Fe–O(4) distance of 1·999(5) Å being indicative of an essentially single bond. The enlargement of the C(8)–Fe–C(9) angle (103·8°) beyond the values of *ca.* 90° appropriate to C(7)–Fe–C(8) and C(7)–Fe–C(9) in the approximately octahedral environment of the iron atom is clearly a response to the angle C(1)–Fe–C(3) being constrained by the C(1)–C(2)–C(3) chain to be smaller than 90°.

The hexafluorophosphate anion approximates very closely to ideal octahedral geometry. The P–F distances lie in the range 1·562—1·587, mean 1·578 Å, and the root-mean-square deviation of the individual values from the mean is 0·009 Å. The mean of 1·578 Å is in good accord with the earlier estimate of 1·58 Å for the P–F separation in $NaPF_6$ and KPF_6.[10] The thermal parameters obtained for the fluorine atoms are normal (see Figure 1), and there is no suggestion of any disorder in the packing of the bulky anions in the crystal structure. In $[Ir(O_2)(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)]^+[PF_6]^-$ and the Rh analogue, on the other hand, the PF_6^- anions are disordered, and the P–F distance was held fixed at 1·58 Å in the *X*-ray analyses.[11]

EXPERIMENTAL

Crystal Data.—$C_9H_9F_6FePO_4$, $M = 383{\cdot}0$, Orthorhombic, $a = 15{\cdot}136(11)$, $b = 15{\cdot}256(8)$, $c = 12{\cdot}123(10)$ Å, $U = 2799$ Å^3, $D_m = 1{\cdot}80$, $Z = 8$, $D_c = 1{\cdot}82$, $F(000) = 1520$. Space group $Pbca$ (D_{2h}^{15}). Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å, $\mu(\text{Mo-}K_\alpha) = 13{\cdot}0\ cm^{-1}$.

Crystallographic Measurements.—The crystal employed in the *X*-ray measurements was coated with Araldite to prevent attack by moisture and oxygen. The final values of the cell dimensions were determined by least-squares analysis of twelve sets of θ, χ, φ setting angles measured on a Hilger and Watts four-circle diffractometer. Intensity data for the octant *hkl* with $\theta \leqslant 30°$ (Mo-K_α) were collected by the θ–2θ step scan procedure, with background counts at each end of the scan range. Two reference reflections were monitored after every 40 intensity measurements and used to ensure that all the reflections were on a common scale. The intensities were corrected for Lotentz-polarization effects, but not for absorption (the crystal was *ca.* 1·7 mm in length and 0·70 × 0·75 mm^2 in cross-section). In all, 2365 independent reflections with $I > 2{\cdot}5\sigma(I)$ were obtained.

Structure Analysis.—Initial co-ordinates for the iron atom were obtained from the three-dimensional Patterson function, and the remaining atoms (apart from hydrogen) located in two subsequent electron-density distributions. More accurate atomic co-ordinates were obtained by a series of least-squares calculations with the 'X-Ray '63' version of the full-matrix program ORFLS. Atomic scattering factors were taken from ref. 12 and dispersion corrections $\Delta f'$ and $\Delta f''$ from ref. 13. The weighting scheme adopted was $w = 1/\sigma^2(F_o)$. Refinement with isotropic thermal parameters converged at R 14·5%. The residual R was further reduced to 10·6% when anisotropic thermal parameters were assigned to the iron, phosphorus, and fluorine atoms, to 9·5% when the carbonyl oxygen atoms were similarly treated, and to 8·6% when the remaining atoms were so treated. The nine hydrogen atoms were located in a difference electron-density distribution, and when they were included with isotropic thermal parameters in subsequent least-squares calculations convergence was reached at R 7·4%.

We next investigated the effect of changing to an alternative set of weights defined by $w = (A + B|F_o| + C|F_o|^2)^{-1}$. The coefficients A, B, and C were adjusted in two cycles of calculations so that $\langle w\Delta^2\rangle$ was approximately constant when evaluated over various ranges of $|F_o|$ and with $A = 10{\cdot}69$, $B = -0{\cdot}369$, and $C = 0{\cdot}011$, refinement converged at R 7·1%. The atomic co-ordinates were only very slightly altered in this process.

Of the nine hydrogen atoms included in the structure analysis, the three of the terminal methyl group were the most poorly defined and showed the greatest departures from the mean C–H separation of 0·95 Å.

We thank the S.R.C. for an equipment grant which enabled us to acquire the diffractometer, and Eli Lilly and Company for a studentship (to A. D. U. H.). The calculations were carried out at the Atlas Computing Laboratory. The excellent crystals were supplied by Dr. G. R. Knox.

[2/1099 *Received*, 15*th May*, 1972]

---

[8] M. R. Churchill, *Perspectives in Structural Chem.*, 1970, **3**, 91.

[9] M. L. H. Green and P. L. I. Nagy, *Adv. Organometallic Chem.*, 1964, **2**, 325; M. R. Churchill and R. Mason, *ibid.*, 1967, **5**, 93.

[10] H. Bode and G. Teufer, *Z. anorg. Chem.*, 1951, **265**, 229; 1952, **268**, 20.

[11] J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1969, **91**, 6301.

[12] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[13] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.