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Structure of Tricarbonyl[2–4-η-(5-methylhepten-6-one)]iron Hexafluorophosphate

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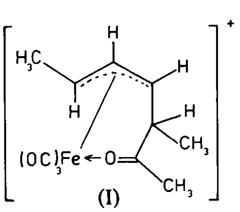
Abstract. $[Fe(C_8H_{13}O)(CO)_3]PF_6$, monoclinic, $P2_1/c$, $a = 9.363\,(6)$, $b = 12.174\,(9)$, $c = 16.547\,(10)$ Å, $\beta = 121.60\,(5)°$, $U = 1607$ Å^3, $D_m = 1.68$, $Z = 4$, $D_c = 1.694$ Mg m^{-3}, $F(000) = 824$, $\mu(\text{Mo } K\alpha) = 1.15$ mm^{-1}. $R = 0.080$ for 1538 diffractometer data. The 5-methyl group in the organometallic cation has *endo* stereochemistry. The tricarbonyliron group is bound to the allyl fragment and the O atom of the $CH_3.CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH.CH(CH_3).CO.CH_3$ ligand, with Fe—C 2.210 (12), 2.087 (13) and 2.132 (14) Å and Fe—O 1.987 (10) Å. The Fe—CO bond *trans* to O is 1.782 (18) Å, whilst the others are 1.809 (12) and 1.852 (10) Å. The PF_6^- ion is orientationally disordered.

Introduction. The cation (I) is formed as an intermediate in the Friedel–Crafts acetylation of tricarbonyl(*trans,trans*-hexa-2,4-diene)iron (Greaves, Knox, Pauson, Toma, Sim & Woodhouse, 1974). In order to establish whether acetylation had occurred by *exo* or *endo* attack, an X-ray study of the hexafluorophosphate salt of the complex was undertaken. Mo $K\alpha$ radiation was employed and X-ray intensities for reflections with $\theta < 27°$ were measured by the ω–2θ step-scan procedure on a Hilger & Watts automatic diffractometer fitted with a graphite monochromator. The 1538 independent intensity measurements that satisfied the criterion $I > 3\sigma(I)$ were used in the subsequent analysis.



(I)

The coordinates of the Fe and P atoms were deduced from a Patterson synthesis and the C and O atoms of the cation and six F atoms of the anion were located in successive electron-density distributions. Least-squares adjustment of the atomic coordinates and isotropic temperature factors converged at $R = 0.14$ and when anisotropic temperature factors were introduced R was reduced to 0.092.

At this stage, a difference synthesis showed: (*a*) four well resolved peaks and two elongated regions of electron density at bonding distances from the P atom, (*b*) four peaks, representing the non-methyl H atoms and (*c*) poorly resolved regions of electron density in the region of the methyl H atoms. The positions of the H atoms of the methyl group at C(5) were calculated on the assumption of a staggered conformation about C(5)—C(8). These H atoms were assigned an isotropic temperature factor equal to that of C(8) and included with fixed parameters during subsequent block-diagonal refinement. The H atoms on the terminal methyl groups C(1) and C(7) were ignored since the conformations around C(1)—C(2) and C(6)—C(7) were uncertain.

The peaks in the difference synthesis at bonding distances from the P atom, the diffuseness of the F atom peaks in the initial F_o maps, and the large thermal parameters of the F atoms (mean $B_{\text{iso}} = 15.4$ Å^2) suggested disorder of the PF_6^- ion. Accordingly, the residual electron density around the P atom was drawn on a stack of glass sheets and examined closely. This suggested a model for the anion consisting of three distinct orientations of the PF_6^- octahedron. Coordinates of the F atoms in the two minor orientations were calculated on the basis of ideal octahedra with P—F = 1.58 Å and from a comparison of peak heights in F_o and $(F_o - F_c)$ syntheses the population parameters of the three orientations were estimated to be 0.68, 0.16 and 0.16. The F atoms of the minor orientations were assigned $B_{\text{iso}} = 9.0$ Å^2.

In the final stages of the least-squares calculations, the C and O atoms of the cation, the Fe and P atoms, and the F atoms of the major orientation of the anion were given anisotropic temperature factors. The non-methyl H atoms were refined with isotropic temperature factors. The weighting scheme, adjusted to ensure approximate constancy of $\langle w\Delta^2 \rangle$ over various ranges of F_o and $\sin\theta$, was $w = 1/(5 + 0.07|F_o| + 0.01|F_o|^2 - 6.66 \sin\theta)$. These calculations converged at $R = 0.080$.

Scattering factors, with dispersion corrections for Fe and P, were taken from *International Tables for X-ray Crystallography* (1962). The calculations were performed with programs developed for the Glasgow

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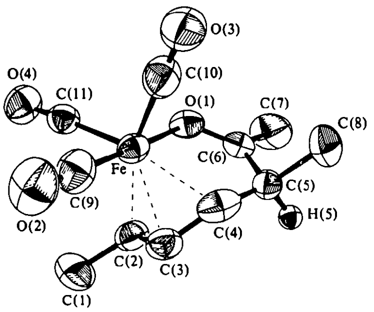

Fig. 1. View of the tricarbonyl[2–4-η-(5-methylhepten-6-one)]-iron cation, illustrating the 50% probability thermal ellipsoids.

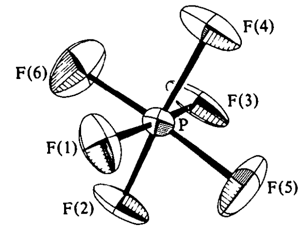

Fig. 2. View of the major orientational component of the hexafluorophosphate anion, illustrating the 20% probability thermal ellipsoids.

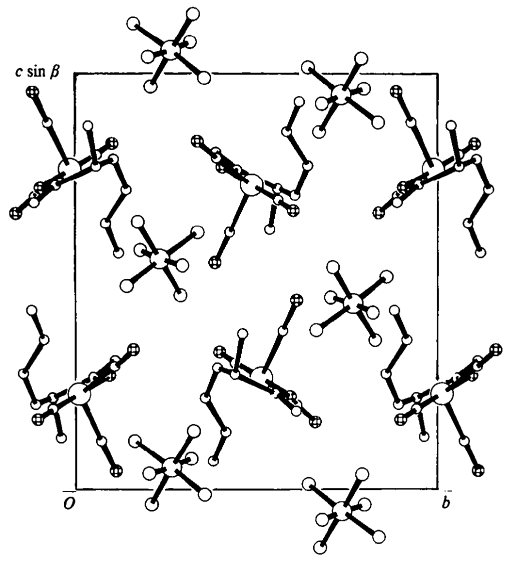

Fig. 3. Crystal structure of the complex, viewed along *a*. For clarity, only the major orientation of the anion is shown.

University KDF9 computer by D. W. J. Cruickshank, J. G. F. Smith and J. G. Sime.*

Table 1. *Atomic coordinates*

	x	*y*	*z*
Fe	0·05319 (18)	0·01305 (11)	0·23181 (10)
O(1)	–0·0767 (9)	0·0952 (5)	0·2762 (5)
O(2)	0·2515 (15)	–0·1012 (9)	0·1673 (8)
O(3)	–0·1593 (13)	0·1131 (10)	0·0434 (7)
O(4)	0·3445 (11)	0·1615 (7)	0·3354 (7)
C(1)	0·3101 (18)	–0·1203 (14)	0·4314 (12)
C(2)	0·1332 (14)	–0·0841 (9)	0·3620 (8)
C(3)	0·0303 (16)	–0·1415 (9)	0·2786 (9)
C(4)	–0·1306 (17)	–0·1081 (9)	0·2060 (9)
C(5)	–0·2569 (13)	–0·0576 (9)	0·2217 (7)
C(6)	–0·2020 (13)	0·0512 (8)	0·2699 (7)
C(7)	–0·2910 (19)	0·1088 (11)	0·3104 (11)
C(8)	–0·4252 (15)	–0·0384 (13)	0·1248 (9)
C(9)	0·1730 (17)	–0·0576 (11)	0·1927 (9)
C(10)	–0·0745 (16)	0·0751 (12)	0·1155 (9)
C(11)	0·2327 (13)	0·1087 (9)	0·2962 (7)
H(2)	0·043 (21)	–0·044 (14)	0·391 (11)
H(3)	0·091 (16)	–0·182 (11)	0·267 (9)
H(4)	–0·165 (12)	–0·111 (8)	0·159 (7)
H(5)	–0·294 (13)	–0·098 (9)	0·263 (7)
H(8*a*)	–0·405	0·009	0·085
H(8*b*)	–0·461	–0·107	0·094
H(8*c*)	–0·507	–0·007	0·135
P	0·23566 (41)	0·26390 (27)	0·05379 (19)
F(1)	0·3679 (16)	0·2032 (10)	0·0377 (11)
F(2)	0·0854 (17)	0·2092 (15)	–0·0351 (10)
F(3)	0·1100 (18)	0·3199 (19)	0·0739 (14)
F(4)	0·3863 (15)	0·3275 (14)	0·1414 (10)
F(5)	0·2338 (25)	0·3571 (16)	–0·0121 (14)
F(6)	0·2455 (29)	0·1637 (19)	0·1171 (16)
F(11)	0·399	0·250	0·050
F(12)	0·194	0·138	0·030
F(13)	0·073	0·279	0·058
F(14)	0·278	0·389	0·076
F(15)	0·122	0·292	–0·056
F(16)	0·339	0·237	0·164
F(21)	0·285	0·141	0·054
F(22)	0·052	0·239	–0·030
F(23)	0·186	0·387	0·055
F(24)	0·420	0·289	0·138
F(25)	0·287	0·293	–0·020
F(26)	0·184	0·235	0·128

Table 2. *Bond lengths* (Å)

Fe–C(2)	2·210 (12)	C(6)–O(1)	1·244 (16)
Fe–C(3)	2·087 (13)	C(9)–O(2)	1·149 (24)
Fe–C(4)	2·132 (14)	C(10)–O(3)	1·127 (15)
Fe–C(9)	1·782 (18)	C(11)–O(4)	1·102 (13)
Fe–C(10)	1·809 (12)	C(2)–H(2)	1·26 (23)
Fe–C(11)	1·852 (10)	C(3)–H(3)	0·84 (17)
Fe–O(1)	1·987 (10)	C(4)–H(4)	0·67 (11)
C(1)–C(2)	1·501 (17)	C(5)–H(5)	1·04 (14)
C(2)–C(3)	1·384 (15)	P–F(1)	1·580 (18)
C(3)–C(4)	1·404 (16)	P–F(2)	1·555 (13)
C(4)–C(5)	1·470 (22)	P–F(3)	1·539 (23)
C(5)–C(6)	1·490 (15)	P–F(4)	1·596 (13)
C(5)–C(8)	1·563 (13)	P–F(5)	1·568 (23)
C(6)–C(7)	1·488 (26)	P–F(6)	1·578 (26)

Discussion. Views of the cation and the principal orientation of the anion are given in Figs. 1 and 2. The crystal packing is illustrated in Fig. 3. The atomic

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34344 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Valency angles* (°)

C(2)–Fe–C(10)	162·2 (6)	C(3)–C(2)–H(2)	108 (6)
C(2)–Fe–C(4)	69·5 (4)	C(2)–C(3)–H(3)	108 (7)
C(4)–Fe–C(11)	160·5 (6)	C(4)–C(3)–H(3)	122 (8)
C(9)–Fe–O(1)	178·5 (6)	C(3)–C(4)–H(4)	128 (10)
C(9)–Fe–C(11)	87·6 (6)	C(5)–C(4)–H(4)	107 (10)
C(9)–Fe–C(10)	90·4 (7)	C(4)–C(5)–H(5)	120 (6)
C(10)–Fe–C(11)	104·0 (6)	C(6)–C(5)–H(5)	102 (6)
C(10)–Fe–O(1)	89·4 (6)	C(8)–C(5)–H(5)	104 (5)
C(11)–Fe–O(1)	91·0 (5)	F(1)–P–F(2)	92·4 (9)
C(1)–C(2)–C(3)	121·5 (13)	F(1)–P–F(3)	177·3 (10)
C(2)–C(3)–C(4)	125·1 (12)	F(1)–P–F(4)	89·0 (8)
C(3)–C(4)–C(5)	124·8 (13)	F(1)–P–F(5)	86·8 (11)
C(4)–C(5)–C(6)	112·5 (10)	F(1)–P–F(6)	88·4 (12)
C(4)–C(5)–C(8)	110·7 (11)	F(2)–P–F(3)	88·8 (10)
C(6)–C(5)–C(8)	107·0 (9)	F(2)–P–F(4)	176·2 (9)
C(5)–C(6)–C(7)	122·7 (12)	F(2)–P–F(5)	88·7 (9)
C(5)–C(6)–O(1)	118·2 (12)	F(2)–P–F(6)	90·3 (10)
C(7)–C(6)–O(1)	119·0 (10)	F(3)–P–F(4)	90·0 (9)
Fe–O(1)–C(6)	119·0 (7)	F(3)–P–F(5)	95·7 (13)
Fe–C(9)–O(2)	178·6 (14)	F(3)–P–F(6)	89·1 (14)
Fe–C(10)–O(3)	177·3 (15)	F(4)–P–F(5)	87·9 (9)
Fe–C(11)–O(4)	176·7 (11)	F(4)–P–F(6)	93·2 (9)
C(1)–C(2)–H(2)	121 (6)	F(5)–P–F(6)	175·1 (15)

Table 4. *Interionic contacts* (≤3·20 Å)

Because of the disorder of the PF_6^- anion, e.s.d.'s cannot be given for all the interionic contacts. Where e.s.d.'s can be calculated they are *ca* 0·02 Å.

F(25)···O(4)$^{\mathrm{I}}$	2·77	F(2)···C(9)$^{\mathrm{III}}$	3·07
F(15)···O(1)$^{\mathrm{I}}$	2·77	F(6)···C(11)	3·10
F(13)···O(3)	2·88	O(2)···O(3)$^{\mathrm{III}}$	3·12
F(16)···O(4)	2·96	F(26)···O(3)	3·13
F(26)···C(11)	2·99	F(6)···C(10)	3·17
F(11)···C(1)$^{\mathrm{II}}$	3·02	F(5)···C(11)$^{\mathrm{I}}$	3·19
F(26)···C(10)	3·03	F(21)···C(8)$^{\mathrm{IV}}$	3·19
F(2)···O(2)$^{\mathrm{III}}$	3·04	F(6)···C(9)	3·19
F(25)···C(11)$^{\mathrm{I}}$	3·05	F(5)···O(4)$^{\mathrm{I}}$	3·20
F(22)···O(2)$^{\mathrm{III}}$	3·05	F(22)···O(3)	3·20
F(26)···O(4)	3·06	F(3)···C(2)$^{\mathrm{V}}$	3·20

Symmetry code

(I)	x,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$	(IV)	$1+x$,	y,	z
(II)	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	(V)	$-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
(III)	$-x$,	$-y$,	$-z$				

coordinates, bond lengths, valency angles and interionic contacts are listed in Tables 1–4.

The analysis establishes that *endo* acylation has taken place in the Friedel–Crafts reaction. The organic ligand is bound to the Fe atom by the η^3-allyl residue, C(2)C(3)C(4), and by the acyl O(1).

The dimensions of the Fe-allyl fragment are in good agreement with those reported for tricarbonyl(1–3-η-hexen-5-one)iron hexafluorophosphate (Hardy & Sim, 1972), with the mean Fe–C(terminal) length *ca* 0·1 Å longer than the Fe–C(central) length. The mean $\mathrm{C}\overset{\cdots}{\text{—}}\mathrm{C}$ distance in these allyl residues is 1·40 Å. The terminal C atoms of the allyl fragment, C(2) and C(4), are coplanar with the carbonyl C atoms C(10) and C(11) to within ±0·01 Å and the Fe atom deviates from this plane by 0·12 Å, in the direction away from the acyl O(1). C(1) and C(5) deviate from the allyl plane by 0·14 and −0·78 Å, respectively, and the torsion angles C(1)–C(2)–C(3)–C(4) and C(2)–C(3)–C(4)–C(5) are −174 and −40°. The latter angle is close to the corresponding angle (−37°) in the tricarbonyl(1–3-η-hexen-5-one)iron cation (Hardy & Sim, 1972). The C(sp^2)–C(sp^3) single bonds in the organic ligand have lengths 1·470–1·501 Å, mean 1·487 Å, and the C(sp^3)–C(sp^3) distance is 1·563 Å.

The Fe–CO distance *trans* to O(1) is shorter than the Fe–CO distances *trans* to C(2) and C(4) of the allyl fragment. A similar result was obtained for the tricarbonyl(1–3-η-hexen-5-one)iron cation. The Fe–O(1) length, 1·987 (10) Å, may be compared with 1·999 (5) Å in the tricarbonyl(1–3-η-hexen-5-one)iron cation and 2·004 (10) Å in $C_4H_6Fe(CO)_3.SO_2.BF_3$ (Churchill & Wormald, 1970).

The orientational disorder of the PF_6^- ion is not unexpected, since similar effects have been reported in $[RuCl(NO)_2(PPh_3)_2]^+[PF_6]^-$ (Pierpont & Eisenberg, 1972), $[IrO_2(Ph_2PCH_2CH_2PPh_2)]^+[PF_6]^-$ and its Rh analogue (McGinnety, Payne & Ibers, 1969). On the other hand, the anion in tricarbonyl(1–3-η-hexen-5-one)iron hexafluorophosphate is not disordered and there the P–F distances are 1·562–1·587 Å, mean 1·578 Å. In the present case, the P–F distances in the principal orientational component of the anion are 1·539–1·596 Å, mean 1·569 Å.

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