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# {2–4:6-7-η-(8-Acetylbicyclo[3.2.1]octadienylium)}tricarbonyliron Hexafluorophosphate

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Abstract. $[(C_{10}H_{11}O)Fe(CO)_3]^+[PF_6]^-$, monoclinic, $P2_1/c$, $a = 8.052$ (4), $b = 14.419$ (4), $c = 14.980$ (4) Å, $\beta = 114.43$ (6)°, $U = 1583.5$ Å³, $Z = 4$, $D_x = 1.812$ g cm⁻³, μ(Mo $K\alpha$) = 10.6 cm⁻¹. The structure was solved by direct methods and refined to an R of 0.047 for 1207 unique diffractometer data. A bicyclo-[3.2.1]octadienylium ligand is found in contrast to the originally proposed [5.1.0] structure. The acetyl group is *endo* to the localized double bond, and the PF_6^- anion is disordered.

Introduction. Johnson, Lewis & Randall (1971) showed that tricarbonyl(cyclooctatetraene)iron (Ia) reacts with acetyl chloride under Friedel-Crafts conditions to produce the cation $[C_8H_8COCH_3Fe(CO)_3]^+$ together with a little (Ib). They proposed structure (IIb) for the cation by analogy with the protonation of (Ia) which gives (IIa) (Davison, McFarlane, Pratt & Wilkinson, 1962; Brookhart & Davis, 1971). Further chemical and spectroscopic evidence indicated the bicyclo[3.2.1] structure (III), confirmed by this analysis; this evidence and preliminary details of the crystal structure have been given by Charles, Diversi, Johnson, Karlin, Lewis, Rivera & Sheldrick (1977).

(Ia) R = H
(Ib) R = COCH₃

(IIa) R = H
(IIb) R = COCH₃

(III) R = COCH₃
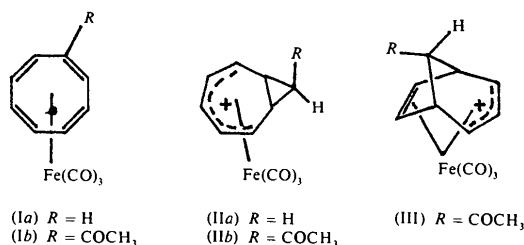
Intensities were measured with a Stoe STADI-2 two-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, and two crystals, $0.27 \times 0.27 \times 0.23$ mm and $0.19 \times 0.23 \times 0.23$ mm, mounted about [010] and [001] respectively. 3398 reflexions were measured, Lp corrections were applied but no absorption corrections were made; interlayer scale factors were derived by linear least squares from common reflexions. Equivalent reflexions were then averaged to give 1207 unique reflexions with $F > 4\sigma(F)$ based on counting statistics. Cell dimensions were obtained by a least-squares fit to 585 diffractometer ω medians for reflexions in both zero layers. The Fe and P atoms were located by multisolution $\sum_2$ sign expansion, and the remaining atoms from difference syntheses. The structure was refined by

Table 1. *Atom coordinates* $(\times 10^4)$ *and isotropic temperature factors* $(\text{Å}^2 \times 10^3)$

	x	y	z	U
Fe	3620 (1)	−189 (1)	7305 (1)	
C(1)	5767 (9)	1234 (5)	8469 (5)	
C(2)	5191 (12)	1051 (6)	7395 (6)	
C(3)	5922 (11)	289 (8)	7129 (6)	
C(4)	6550 (12)	−450 (7)	7791 (7)	
C(5)	7076 (10)	−242 (6)	8860 (6)	
C(6)	5257 (9)	−255 (6)	8922 (5)	
C(7)	4489 (10)	594 (5)	8706 (5)	
C(8)	7600 (10)	776 (5)	9072 (5)	
C(9)	8312 (9)	1004 (6)	10162 (6)	
C(10)	8764 (12)	1999 (6)	10455 (7)	
C(11)	2736 (11)	−441 (5)	6008 (6)	
C(12)	3034 (11)	−1358 (7)	7522 (5)	
C(13)	1512 (12)	388 (6)	7095 (5)	
O(9)	8460 (7)	410 (4)	10751 (4)	
O(11)	2151 (10)	−627 (4)	5204 (5)	
O(12)	2688 (9)	−2097 (4)	7629 (4)	
O(13)	197 (9)	763 (5)	6979 (4)	
P	2598 (3)	1988 (1)	4416 (2)	
F(1)	1080 (8)	1323 (4)	3751 (5)	
F(2)	4178 (8)	2662 (4)	5044 (4)	
F(3)	2163 (10)	1772 (5)	5308 (5)	
F(4)	3062 (10)	2196 (4)	3518 (4)	
F(5)	3980 (11)	1169 (4)	4735 (5)	
F(6)	1249 (11)	2824 (5)	4126 (6)	
F(1')	843 (32)	1632 (22)	4493 (31)	42 (15)
F(2')	4349 (33)	2343 (25)	4342 (33)	151 (35)
F(3')	3357 (53)	2306 (28)	5502 (11)	197 (51)
F(4')	1833 (50)	1673 (27)	3333 (11)	76 (19)
F(5')	3497 (46)	1025 (13)	4748 (28)	119 (43)
F(6')	1687 (44)	2952 (12)	4088 (26)	28 (14)

Table 2. H *atom coordinates* $(\times 10^3)$ *and isotropic temperature factors* $(\text{Å}^2 \times 10^2)$

	x	y	z	U
H(1)	562 (8)	192 (4)	860 (4)	5 (2)
H(2)	467 (8)	152 (4)	693 (4)	5 (2)
H(3)	573 (9)	18 (5)	641 (5)	7 (2)
H(4)	704 (11)	−98 (6)	764 (6)	10 (3)
H(5)	785 (8)	−71 (4)	924 (4)	4 (2)
H(6)	481 (8)	−76 (5)	919 (4)	5 (2)
H(7)	339 (10)	81 (4)	882 (4)	6 (2)
H(8)	846 (8)	97 (4)	886 (4)	3 (2)
H(101)	936 (7)	235 (5)	1002 (4)	12 (3)
H(102)	748 (5)	232 (5)	1034 (4)	15 (4)
H(103)	968 (6)	203 (5)	1122 (1)	11 (3)

Table 3. *Bond lengths* (Å)

C(2)–Fe	2·162 (11)	C(3)–Fe	2·094 (12)
C(4)–Fe	2·195 (11)	C(6)–Fe	2·230 (8)
C(7)–Fe	2·226 (9)	C(11)–Fe	1·808 (11)
C(12)–Fe	1·816 (12)	C(13)–Fe	1·797 (12)
C(1)–C(2)	1·503 (13)	C(1)–C(7)	1·530 (14)
C(1)–C(8)	1·526 (12)	C(3)–C(2)	1·380 (16)
C(4)–C(3)	1·400 (15)	C(5)–C(4)	1·508 (14)
C(6)–C(5)	1·505 (14)	C(8)–C(5)	1·525 (13)
C(7)–C(6)	1·349 (12)	C(9)–C(8)	1·526 (13)
O(9)–C(9)	1·198 (11)	C(10)–C(9)	1·501 (13)
O(11)–C(11)	1·129 (11)	O(12)–C(12)	1·129 (13)
O(13)–C(13)	1·137 (13)		

Table 4. *Bond lengths involving* H (Å)

H(1)–C(1)	1·02 (6)	H(2)–C(2)	0·94 (6)
H(3)–C(3)	1·03 (8)	H(4)–C(4)	0·93 (9)
H(5)–C(5)	0·94 (6)	H(6)–C(6)	0·97 (7)
H(7)–C(7)	1·01 (8)	H(8)–C(8)	0·92 (7)

Table 5. *Selected bond angles* (°)

C(1)–C(2)–C(3)	118·0 (8)	C(2)–Fe–C(4)	66·4 (5)
C(1)–C(7)–C(6)	108·5 (8)	C(6)–Fe–C(7)	35·2 (3)
C(1)–C(8)–C(5)	100·2 (6)	C(11)–Fe–C(12)	89·5 (4)
C(2)–C(3)–C(4)	118·3 (10)	C(11)–Fe–C(13)	89·0 (5)
C(2)–C(1)–C(7)	101·7 (7)	C(12)–Fe–C(13)	99·5 (5)
C(2)–C(1)–C(8)	110·6 (8)	C(3)–Fe–C(11)	84·6 (5)
C(3)–C(4)–C(5)	117·5 (10)	O(11)–C(11)–Fe	177·4 (8)
C(4)–C(5)–C(6)	102·1 (7)	O(12)–C(12)–Fe	177·2 (9)
C(4)–C(5)–C(8)	110·2 (8)	O(13)–C(13)–Fe	178·6 (7)
C(6)–C(5)–C(8)	101·0 (8)	C(8)–C(9)–O(9)	120·8 (8)
C(1)–C(8)–C(9)	112·6 (8)	O(9)–C(9)–C(10)	122·0 (9)
C(5)–C(8)–C(9)	112·3 (8)	C(8)–C(9)–C(10)	117·2 (8)
C(7)–C(1)–C(8)	100·4 (7)		

blocked least squares with complex neutral-atom scattering factors and the weighting scheme $w = [\sigma^2(F) + 0·005F^2]^{-1}$. It was found necessary to refine two PF_6^- groups, with site-occupation factors of k and $1 − k$ respectively, constrained to be regular octahedra with the P atom as the common centre and P–F 1·550 (10), F···F 2·192 (14) Å; k refined to 0·9. The H atoms were refined freely, except those of the methyl group, which were constrained to lie 1·08 (1) Å from C(10)

and 1·76 (1) Å from each other. Anisotropic temperature factors were employed for all atoms except for the H atoms and the F atoms of the minor PF_6^- contributor, which were given individual isotropic temperature factors. The refinement converged to $R' = \sum w^{1/2}\Delta / \sum w^{1/2}F_o = 0·046$, and $R = 0·047$. Final positional and isotropic thermal parameters are given in Tables 1 and 2, bond lengths and angles in Tables 3–5.*

Discussion. The cation geometry (Fig. 1) is similar to that found in (bicyclo[3.2.1]octadienyl)tricarbonyliron tetrafluoroborate (Margulis, Schiff & Rosenblum, 1965). The C—C lengths and H atom positions are

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33347 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
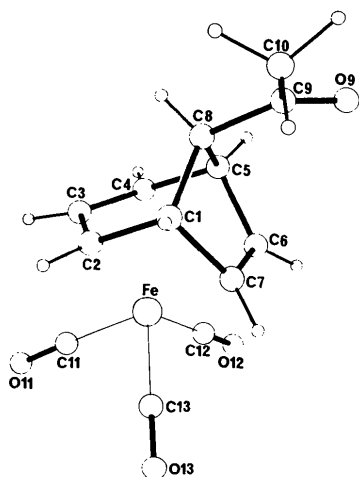
Fig. 1. The [(C₁₀H₁₁O)Fe(CO)₃]⁺ cation, showing the atom labelling.

consistent with a π-allyl interaction between Fe and C(2)—C(3)—C(4), and a π-alkene interaction between Fe and C(6)—C(7). There is no evidence to support further delocalization in the C_7 ring, as proposed by Margulis, Schiff & Rosenblum (1965). Although C(1), C(7), C(6) and C(5) are coplanar to within 0·004 Å, C(1) and C(5) lie 0·55 and 0·53 Å respectively above the plane defined by C(2), C(3) and C(4). The acetyl group is *endo* to the localized double bond [C(6)—C(7)], with a dihedral angle C(5)—C(8)—C(9)—O(9) of

2·1°. Except for the acetyl group, the cation possesses approximate mirror symmetry through C(3), C(8), Fe, C(11) and O(11). The valence angles at Fe are consistent with this mirror plane but indicate appreciable distortion from local C_{3v} symmetry for the Fe(CO)₃ group; however, there are no significant variations in Fe—C (mean 1·807) or C—O (mean 1·132 Å) lengths within this group. The Fe—C—O units are almost linear, with a mean angle of 177·7°.

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Bis(triphenylphosphine)iminium μ-Hydrido-decacarbonyltriosmium-μ-carboxylato-heptadecacarbonylhexaosmate, [(Ph₃P)₂N]⁺[HOs₃(CO)₁₀·O₂C·Os₆(CO)₁₇]⁻

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Abstract. $C_{64}H_{31}NO_{29}P_2Os_9$, monoclinic, $P2_1/c$, $a = 18\cdot75$ (1), $b = 15\cdot20$ (1), $c = 28\cdot41$ (1) Å, $\beta = 114\cdot5$ (1)°, $U = 7368$ Å³, $Z = 4$, $D_x = 2\cdot751$ g cm⁻³. The structure was refined to an R of 0·076 for 3274 unique diffractometer data. The complex anion consists of Os₃ and Os₆ units linked by a CO_2 bridge.

Introduction. The anion was prepared from Os₆(CO)₁₈ and [Os₃(CO)₁₁H]⁻ in CH₂Cl₂, and isolated as the [(Ph₃P)₂N]⁺ salt (Eady, Guy, Johnson, Lewis, Malatesta & Sheldrick, 1976). The crystal structure

determination reveals not an Os₉ cluster as intended, but Os₃ and Os₆ clusters linked by a novel CO_2 bridge.

Dark-brown crystals were obtained by slow diffusion of cyclohexane into a solution in dichloromethane. Intensities were measured with a Syntex $P2_1$ four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, and a crystal 0·28 × 0·11 × 0·09 mm. 5014 reflexions ($1 \le 2\theta \le 55°$) were measured and corrected for absorption ($\mu = 150$ cm⁻¹); the 3274 data with $F > 4\sigma(F)$ were employed for structure refinement. The nine Os atoms were found by multisolution $\sum_2$ sign