

## SHORT STRUCTURAL PAPERS

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(5-*exo*-Triphenylphosphinocyclohexa-1,3-diene)tricarbonyliron Tetrafluoroborate

BY JOHN J. GUY, BERNHARD E. REICHERT AND GEORGE M. SHELDRIK

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

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**Abstract.**  $C_{27}H_{22}BF_4FeO_3P$ ; monoclinic,  $P2_1/c$ ;  $a=9.24$  (1),  $b=18.85$  (2),  $c=16.82$  (2) Å,  $\beta=118.04$  (5)°,  $U=2585$  Å<sup>3</sup>;  $Z=4$ ,  $D_x=1.459$  g cm<sup>-3</sup>. The cation may be described as a phosphonium ion in which P is attached to one of the two adjacent saturated C atoms of the cyclohexadiene ring, the diene being bonded symmetrically to an  $Fe(CO)_3$  group. The structure was refined to  $R=0.056$  for 1644 diffractometer data.

**Introduction.** The title compound was the first example of attack of a phosphine on a cationic dienyl complex of iron tricarbonyl which resulted in addition to the ring (Evans, Howe, Johnson & Lewis, 1973). The proposed structure is confirmed by this single-crystal X-ray diffraction study.

The crystals were grown as pale-yellow diamond-shaped tablets by slow evaporation of a dichloromethane/hexane solution. Intensities were determined with an automated Syntex  $P2_1$  four-circle diffractometer, Mo  $K\alpha$  radiation and graphite monochromator. 3349 reflexions were recorded from a crystal,  $0.35 \times 0.15 \times 0.12$  mm, for  $0 < 2\theta < 42^\circ$ ; after application of  $L_p$  but not absorption corrections [ $\mu(Mo K\alpha)=6.4$  cm<sup>-1</sup>] equivalent reflexions were merged to give 2825 unique reflexions, of which 1644 with  $|F_o| > 5\sigma(F_o)$  were employed for structure refinement.

The structure was solved by multisolution  $\sum_2$  sign expansion; the first  $E$  map, based on the 549  $E$  magnitudes  $> 1.2$ , revealed all but one of the 37 non-hydrogen atoms. The structure was refined by full-matrix least squares with complex neutral atom scattering factors and weights  $w=1/[\sigma^2(F_o)+0.0001|F_o|^2]$ . Full-matrix least-squares refinement converged to  $R_w=\sum w^{1/2}|F_o-F_c|/\sum w^{1/2}|F_o|=0.048$  with a corresponding  $R$  of 0.056. In the final cycles anisotropic temperature factors were employed for Fe, P, F, O and carbonyl C atoms, isotropic temperature factors for B and the remaining C atoms, and an overall isotropic factor for H. All the H atoms were located in successive difference syntheses; in the final stages they were refined subject to the constraint  $C-H=1.08$  Å. A final difference synthesis revealed no features higher than

Table 1. Atom coordinates ( $\times 10^4$ ) and isotropic temperature factors (Å<sup>2</sup>  $\times 10^3$ )

	x	y	z	U
C(1)	8795 (9)	2239 (4)	4065 (5)	44 (2)
C(2)	10374 (9)	1947 (4)	4878 (5)	47 (2)
C(3)	9978 (10)	1660 (5)	5603 (6)	59 (2)
C(4)	8890 (11)	2028 (5)	5818 (6)	67 (3)
C(5)	7446 (10)	2280 (4)	5091 (6)	54 (2)
C(6)	7301 (9)	2132 (4)	4225 (5)	43 (2)
C(7)	9402 (9)	3666 (4)	4847 (5)	49 (2)
C(8)	8022 (10)	3890 (5)	4929 (6)	63 (2)
C(9)	8235 (11)	4184 (5)	5752 (6)	68 (3)
C(10)	9776 (13)	4235 (5)	6458 (7)	86 (3)
C(11)	11107 (12)	4027 (5)	6388 (7)	81 (3)
C(12)	10975 (10)	3746 (5)	5581 (6)	63 (2)
C(13)	7298 (9)	3508 (4)	2903 (5)	45 (2)
C(14)	6850 (10)	4222 (5)	2867 (6)	56 (2)
C(15)	5464 (11)	4466 (5)	2089 (6)	68 (3)
C(16)	4617 (10)	4023 (5)	1381 (6)	61 (2)
C(17)	5057 (10)	3325 (5)	1415 (6)	58 (2)
C(18)	6432 (9)	3057 (5)	2186 (6)	52 (2)
C(19)	10806 (9)	3229 (4)	3642 (5)	48 (2)
C(20)	11522 (10)	3887 (5)	3704 (6)	67 (2)
C(21)	12795 (11)	3949 (6)	3446 (7)	80 (3)
C(22)	13235 (11)	3369 (5)	3135 (6)	73 (3)
C(23)	12541 (10)	2729 (5)	3071 (6)	65 (3)
C(24)	11291 (9)	2948 (4)	3329 (5)	54 (2)
B(1)	5508 (18)	1205 (9)	1704 (10)	89 (4)
Fe(1)	7632 (1)	1202 (1)	4981 (1)	
P(1)	9083 (2)	3170 (1)	3875 (1)	
F(1)	4902 (7)	1625 (3)	961 (4)	
F(2)	7199 (6)	1308 (4)	2184 (4)	
F(3)	4858 (7)	1406 (4)	2265 (4)	
F(4)	5151 (9)	514 (3)	1461 (5)	
O(1)	8477 (9)	240 (4)	6514 (5)	
O(2)	4065 (8)	1000 (4)	4172 (5)	
O(3)	8537 (8)	273 (4)	3892 (5)	
C(25)	8113 (12)	615 (6)	5910 (7)	
C(26)	5453 (13)	1064 (5)	4488 (6)	
C(27)	8151 (11)	636 (5)	4306 (7)	

0.37 e Å<sup>-3</sup>. Positional and thermal parameters are given in Tables 1, 2 and 3.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31769 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Anisotropic temperature factors (Å<sup>2</sup> × 10<sup>3</sup>)

The temperature factor exponent takes the form:

$$-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^*).$$

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Fe(1)	55 (1)	57 (1)	54 (1)	5 (1)	26 (1)	-7 (1)
P(1)	36 (1)	50 (1)	49 (1)	2 (1)	21 (1)	-3 (1)
F(1)	109 (5)	107 (5)	91 (5)	7 (4)	22 (4)	-2 (4)
F(2)	93 (4)	147 (6)	85 (4)	-22 (4)	28 (3)	20 (4)
F(3)	121 (5)	183 (7)	127 (6)	-65 (5)	78 (4)	-34 (5)
F(4)	195 (7)	71 (4)	130 (6)	-26 (4)	73 (5)	-22 (4)
O(1)	108 (6)	126 (7)	109 (6)	63 (6)	60 (5)	13 (5)
O(2)	59 (4)	117 (6)	125 (6)	-15 (5)	39 (5)	-25 (5)
O(3)	96 (5)	91 (6)	106 (6)	-17 (5)	54 (5)	5 (5)
C(25)	81 (7)	85 (9)	85 (9)	18 (7)	55 (7)	5 (6)
C(26)	75 (7)	61 (7)	76 (7)	7 (6)	41 (6)	-10 (6)
C(27)	58 (6)	46 (7)	75 (8)	7 (6)	31 (6)	-3 (5)

Table 3. Hydrogen-atom coordinates (× 10<sup>4</sup>) and isotropic temperature factors (Å<sup>2</sup> × 10<sup>3</sup>)

	x	y	z	U
H(1)	8582	1946	3471	81
H(2)	11192	2382	5214	81
H(2')	10911	1517	4682	81
H(3)	10901	1308	6077	81
H(4)	8886	2152	6443	81
H(5)	6475	2527	5176	81
H(6)	6156	2249	3636	81
H(8)	6819	3788	4380	81
H(9)	7084	4312	5736	81
H(10)	9740	4407	7059	81
H(11)	12395	4041	6864	81
H(12)	11993	3610	5466	81
H(14)	7474	4551	3458	81
H(15)	5284	5020	2178	81
H(16)	3576	4219	784	81
H(17)	4635	2942	876	81
H(18)	6736	2512	2138	81
H(20)	11416	4262	4157	81
H(21)	13265	4441	3798	81
H(22)	14015	3372	2819	81
H(23)	12743	2203	2889	81
H(24)	10763	2135	3308	81

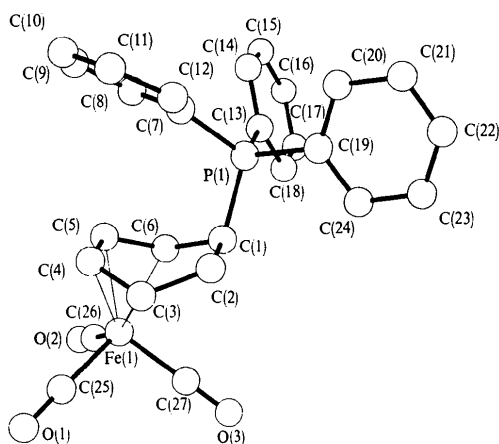


Fig. 1. The structure of the cation, showing the labelling of the atoms.

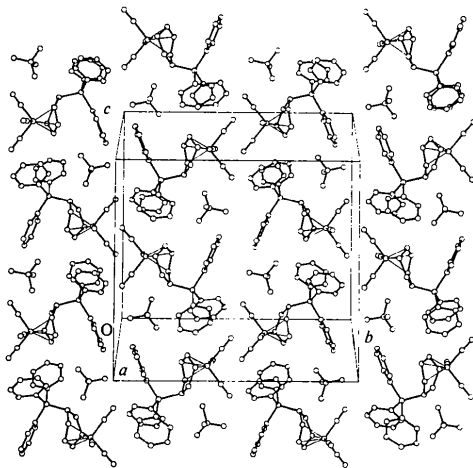


Fig. 2. Perspective view of the structure projected down an axis close to *a*.

Table 4. Bond lengths (Å)

Fe(1)-C(3)	2.10 (1)	C(12)-C(7)	1.40 (2)
Fe(1)-C(4)	2.05 (2)	C(14)-C(13)	1.40 (2)
Fe(1)-C(5)	2.05 (1)	C(15)-C(14)	1.41 (2)
Fe(1)-C(6)	2.10 (1)	C(16)-C(15)	1.36 (2)
Fe(1)-C(25)	1.79 (2)	C(17)-C(16)	1.37 (2)
Fe(1)-C(26)	1.80 (2)	C(18)-C(17)	1.41 (2)
Fe(1)-C(27)	1.78 (2)	C(18)-C(13)	1.38 (2)
O(3)-C(27)	1.15 (2)	C(20)-C(19)	1.39 (2)
O(2)-C(26)	1.14 (2)	C(21)-C(20)	1.44 (2)
O(1)-C(25)	1.15 (2)	C(22)-C(21)	1.35 (2)
C(2)-C(1)	1.56 (2)	C(23)-C(22)	1.35 (2)
C(3)-C(2)	1.53 (2)	C(24)-C(23)	1.42 (2)
C(4)-C(3)	1.40 (2)	C(24)-C(19)	1.38 (2)
C(5)-C(4)	1.40 (2)	P(1)-C(1)	1.83 (1)
C(6)-C(5)	1.43 (2)	P(1)-C(7)	1.78 (1)
C(6)-C(1)	1.54 (2)	P(1)-C(13)	1.81 (1)
C(8)-C(7)	1.41 (2)	P(1)-C(19)	1.81 (1)
C(9)-C(8)	1.42 (2)	F(1)-B(1)	1.36 (2)
C(10)-C(9)	1.36 (2)	F(2)-B(1)	1.39 (2)
C(11)-C(10)	1.35 (2)	F(3)-B(1)	1.39 (2)
C(12)-C(11)	1.41 (2)	F(4)-B(1)	1.36 (2)

**Discussion.** The structure determination confirms the attachment of P to the ring, and the expected *exo* stereochemistry. The structure of the cation is shown in Fig. 1, and the packing of the ions in Fig. 2. Bond lengths and angles are given in Tables 4 and 5; these are similar to those found in other (cyclohexa-1,3-diene)-tricarbonyliron derivatives (Churchill & Mason, 1967; Cotton, Frenz & Troup, 1973; Ireland, Brown, Stanford & McKenzie, 1974). The sets C(1), C(2), C(3), C(6) and C(3), C(4), C(5), C(6) each form good planes (within 0.009 Å); the interplanar angle of 40.0° is close to the value of 38.5° found by Cotton, Frenz &

Table 5. Bond angles (°)

C(4)—Fe(1)—C(3)	39.4 (5)	C(1)—P(1)—C(7)	108.5 (6)
C(5)—Fe(1)—C(3)	70.0 (6)	C(1)—P(1)—C(13)	110.6 (6)
C(5)—Fe(1)—C(4)	39.9 (5)	C(1)—P(1)—C(19)	108.1 (6)
C(6)—Fe(1)—C(3)	77.3 (6)	C(13)—P(1)—C(7)	109.4 (6)
C(6)—Fe(1)—C(4)	69.9 (6)	C(19)—P(1)—C(7)	112.5 (6)
C(6)—Fe(1)—C(5)	40.1 (4)	C(19)—P(1)—C(13)	107.7 (6)
C(25)—Fe(1)—C(3)	92.5 (7)	P(1)—C(1)—C(2)	109.9 (9)
C(25)—Fe(1)—C(4)	92.3 (7)	P(1)—C(1)—C(6)	111.9 (9)
C(25)—Fe(1)—C(5)	121.9 (7)	P(1)—C(7)—C(8)	118.6 (10)
C(25)—Fe(1)—C(6)	161.5 (6)	P(1)—C(7)—C(12)	121.3 (10)
C(26)—Fe(1)—C(3)	163.4 (6)	P(1)—C(13)—C(14)	120.2 (11)
C(26)—Fe(1)—C(4)	125.1 (7)	P(1)—C(13)—C(18)	118.7 (10)
C(26)—Fe(1)—C(5)	93.5 (7)	P(1)—C(19)—C(20)	118.3 (11)
C(26)—Fe(1)—C(6)	91.7 (6)	P(1)—C(19)—C(24)	120.8 (10)
C(26)—Fe(1)—C(25)	94.5 (7)	C(9)—C(8)—C(7)	119.7 (13)
C(27)—Fe(1)—C(3)	92.3 (7)	C(10)—C(9)—C(8)	119.2 (14)
C(27)—Fe(1)—C(4)	131.0 (6)	C(11)—C(10)—C(9)	121.7 (16)
C(27)—Fe(1)—C(5)	135.2 (6)	C(12)—C(11)—C(10)	121.7 (15)
C(27)—Fe(1)—C(6)	97.0 (6)	C(11)—C(12)—C(7)	118.2 (13)
C(27)—Fe(1)—C(25)	98.9 (7)	C(12)—C(7)—C(8)	119.4 (12)
C(27)—Fe(1)—C(26)	101.4 (7)	C(15)—C(14)—C(13)	118.3 (14)
Fe(1)—C(3)—C(2)	109.0 (9)	C(16)—C(15)—C(14)	120.6 (14)
Fe(1)—C(3)—C(4)	68.6 (9)	C(17)—C(16)—C(15)	121.1 (14)
Fe(1)—C(4)—C(5)	70.1 (8)	C(18)—C(17)—C(16)	120.1 (14)
Fe(1)—C(4)—C(3)	72.1 (9)	C(17)—C(18)—C(13)	118.8 (13)
Fe(1)—C(5)—C(4)	70.0 (8)	C(18)—C(13)—C(14)	121.0 (13)
Fe(1)—C(5)—C(6)	71.7 (8)	C(21)—C(20)—C(19)	118.6 (14)
Fe(1)—C(6)—C(1)	109.1 (8)	C(22)—C(21)—C(20)	119.3 (15)
Fe(1)—C(6)—C(5)	68.2 (8)	C(23)—C(22)—C(21)	122.4 (15)
Fe(1)—C(25)—O(1)	177.7 (14)	C(24)—C(23)—C(22)	119.7 (14)
Fe(1)—C(26)—O(2)	177.7 (14)	C(23)—C(24)—C(19)	119.4 (13)
Fe(1)—C(27)—O(3)	177.8 (14)	C(24)—C(19)—C(20)	120.6 (12)
C(3)—C(2)—C(1)	110.4 (10)	F(2)—B(1)—F(1)	108.5 (18)
C(4)—C(3)—C(2)	120.1 (13)	F(3)—B(1)—F(1)	110.1 (19)
C(5)—C(4)—C(3)	116.5 (14)	F(3)—B(1)—F(2)	107.0 (18)
C(6)—C(5)—C(4)	114.8 (12)	F(4)—B(1)—F(1)	110.2 (19)
C(5)—C(6)—C(1)	119.5 (11)	F(4)—B(1)—F(2)	110.7 (19)
C(6)—C(1)—C(2)	110.3 (10)	F(4)—B(1)—F(3)	110.2 (18)

Troup (1973) in [5-(tricarbonylironmethyl)-6-allyl-cyclohexa-1,3-diene]tricarbonyliron.

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