the corresponding values (2·114 Å for the former; 2·154 Å for the latter) of the edta complexes. This may result from the lowered electron density on the N atoms in the phdta complexes (Nakasuka, Kunimatsu, Matsumura & Tanaka, 1985) as well as a stereochemical requirement imposed by the planar N—C—C—N linkage in the o-phenylenediaminetetraacetate anion. Although no general rule is found for Zn—O bonds, the shortest one in the three zinc complex molecules is the Zn—O(H_2O) bond of the protonated phdta complex. The diamine-containing chelate ring is practically planar judging from the sum of the interior angles, which is nearly equal to 540° [539·9° for K_2ZnL.-$3H_2O$; 539·9 and 538·9° for $H_2ZnL(H_2O).H_2O$. This is not the case, however, for any of the glycinate rings in both phdta complexes [520·9–536·8° for K_2ZnL.-$3H_2O$; 523·8–535·4° for $H_2ZnL(H_2O).H_2O$], while one of the four rings is almost planar in the edta complexes (539·5°).

Differing from the heptacoordinate structure of hydrated Mn^{II}–phdta (Nakasuka, Azuma, Katayama, Honda, Tanaka & Tanaka, 1985) or monoaqua-manganese(II)–edta (Richards, Pedersen, Silverton & Hoard, 1964), zinc(II) and cobalt(II) complexes of phdta are hexacoordinate. These metal ions are relatively smaller than the manganese(II) ion, and the ligand anion manages to encircle the former metal ions. However, it is no longer possible for the ligand to encircle the larger manganese(II) ion completely, and a water molecule must coordinate to the central metal ion to give rise to the heptacoordinate structure for the manganese(II) complexes.

Packing diagrams are given in Fig. 2.

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Acetyldicarbonyl(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)-[o-phenylenebis(dimethylarsine)]iron(II) Tetrafluoroborate

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Abstract. [Fe(C_2H_3O)(CO)$_2$($C_6H_{11}O_3P$)($C_{10}H_{16}As_2$)]-BF_4, $M_r = 689·9$, monoclinic, $P2_1/n$, $a = 16·824$ (2), $b = 9·384$ (1), $c = 17·189$ (2) Å, $\beta = 93·50$ (3)°, $V = 2708·7$ (9) Å^3, $D_m = 1·67$ (flotation), $D_x = 1·69$ Mg m^{-3}, $Z = 4$, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 8·00$ mm^{-1}, $F(000) = 1384$, $T = 289$ K. $R = 0·087$ for 2538 observed terms. In the complex cation, the geometry about Fe is distorted octahedral with a carbonyl trans to each As atom and acetyl group trans to P. When trans to As the Fe—C bond has a mean length 1·76 (2) Å, and when trans to P it is 2·00 (2) Å. The Fe—As and Fe—P bonds have lengths 2·366 (2) (mean) and 2·217 (4) Å respectively. The BF$_4^-$ anion is disordered.

Introduction. Insertion of carbon monoxide into the Fe—C bond of methyl derivatives of iron(II) and decarbonylation of the acetyl products have led to rearranged products, and the rates of the insertion and decarbonylation reactions appear to vary with the nature and stereochemistry of the other ligands attached to iron (Jablonski, Wang & Taylor, 1985). An X-ray crystal-structure analysis of the title compound was undertaken to confirm the structure deduced from spectroscopic data (IR, H and ^{13}C NMR) and as the first of a comparative series in which the nature of the phosphorus ligand is varied.

Experimental. Synthesis was as described by Jablonski & Wang (1982). Weissenberg photographs showed that the pale-yellow plate-like crystals, elongated along **b**, were monoclinic and systematic extinctions indicated the space group $P2_1/n$. Crystal ca $0.08 \times 0.19 \times 0.32$ mm aligned on a Rigaku-AFC four-circle diffractometer; cell parameters determined by least squares from 2θ values measured for 25 strong reflections ($35 < 2\theta < 65°$) with Cu $K\alpha$ radiation (graphite-crystal monochromator). Integrated intensities by an $\omega-2\theta$ scan rate $2°$ min^{-1}, scan range $(\Delta\omega)$ $1.2° + 0.5° \tan\theta$, 10 s stationary background counts; of 4070 non-equivalent terms measured to $2\theta_{max} = 130°$ (h -19–19,

k 0–11, l 0–20), 2538 for which $|F_o| \geq 3\sigma|F_o|$ considered observed and used for structure refinement; during data-collection period three reference reflections (230, 006, $\bar{2}30$) monitored every 50 reflections showed a gradual 5% decrease in intensity and a linear scale factor was applied to the data; intensities corrected for Lorentz, polarization and absorption effects (transmission factors from 0.246 to 0.553); four large low-order terms badly affected by extinction omitted from final refinement; complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).

Structure solved by Patterson and Fourier methods, and least-squares refinement with anisotropic temperature factors given to non-H atoms of complex cation converged to $R = 0.087$, $wR = 0.085$ and $S = 2.54$; H atoms excluded; during refinement, the BF_4^- anion, which is disordered, was constrained to regular tetrahedral geometry with a B—F bond length 1.32 Å; B and F atoms given an overall isotropic temperature factor; function minimized $\sum w(|F_o| - |F_c|)^2$ with weights $(\sigma^2|F_o| + 0.0003|F_o|^2)^{-1}$; Δ/σ (mean) $= 0.002$ and Δ/σ (max.) $= 0.06$; largest peaks on final difference map of heights $+1.0$ (in vicinity of BF_4^- anion) and -1.3 e Å^{-3}. The high residual density and the poor overall agreement between the $|F_o|$ and $|F_c|$ terms, reflected in the R indices, no doubt result from the disorder in the crystal. Major calculations made with *SHELX*76 (Sheldrick, 1976).

Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors, with e.s.d.'s in parentheses*

$$B_{eq} = 8\pi^2 U_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}(Å²)
As(1)	866 (1)	2522 (2)	3043 (1)	3·6 (1)
As(2)	324 (1)	365 (1)	1653 (1)	3·6 (1)
Fe	763 (1)	2772 (2)	1677 (1)	3·5 (1)
P	−487 (2)	3528 (4)	1638 (2)	3·8 (2)
O(1)	793 (8)	2850 (13)	−6 (7)	7·0 (5)
O(2)	1341 (7)	5652 (13)	1862 (8)	6·1 (6)
O(3)	2062 (6)	900 (13)	2044 (6)	5·4 (7)
O(4)	−625 (6)	5170 (10)	1826 (6)	4·3 (5)
O(5)	−1077 (6)	2759 (10)	2186 (5)	4·3 (5)
O(6)	−928 (6)	3362 (11)	798 (5)	4·8 (5)
C(1)	773 (9)	2795 (18)	665 (10)	5·0 (8)
C(2)	1133 (10)	4538 (19)	1782 (9)	4·7 (8)
C(3)	1873 (10)	2000 (18)	1714 (9)	4·3 (7)
C(4)	2578 (11)	2782 (23)	1384 (12)	7·6 (12)
C(5)	−1489 (11)	5636 (19)	1846 (11)	6·3 (10)
C(6)	−2023 (10)	4372 (18)	1504 (12)	5·0 (9)
C(7)	−1911 (9)	3161 (18)	2109 (10)	4·5 (10)
C(8)	−1792 (10)	3870 (20)	717 (10)	5·7 (11)
C(9)	−2916 (12)	4796 (23)	1556 (15)	6·9 (11)
C(10)	−3148 (17)	5775 (38)	1030 (15)	13·1 (21)
C(11)	610 (8)	562 (15)	3282 (8)	3·3 (6)
C(12)	666 (9)	137 (18)	4105 (9)	4·3 (7)
C(13)	451 (11)	−1279 (22)	4229 (11)	6·0 (8)
C(14)	150 (12)	−2210 (19)	3618 (11)	6·1 (8)
C(15)	119 (11)	−1727 (19)	2852 (10)	5·7 (8)
C(16)	366 (8)	−319 (17)	2696 (8)	3·4 (6)
C(17)	923 (10)	−1032 (16)	1069 (10)	5·0 (7)
C(18)	−754 (8)	−143 (17)	1295 (10)	4·1 (8)
C(19)	1921 (8)	2865 (19)	3540 (9)	4·5 (8)
C(20)	177 (10)	3687 (18)	3685 (9)	5·4 (8)
B(1)†	1878	4673	5538	
F(1)†	2568	4724	5207	
F(2)†	1389	5640	5215	
F(3)†	1561	3389	5438	
F(4)†	1995	4939	6294	

† Atomic coordinates were constrained during refinement and the atoms given an overall isotropic temperature factor, $B = 16.3$ (3) Å².

Table 2. *Bond lengths* (Å) *and selected bond angles* (°), *with e.s.d.'s in parentheses*

Fe—As(1)	2·356 (2)	O(3)—C(3)	1·21 (2)
Fe—As(2)	2·376 (3)	O(4)—C(5)	1·52 (2)
Fe—P	2·217 (4)	O(5)—C(7)	1·45 (2)
Fe—C(1)	1·74 (2)	O(6)—C(8)	1·53 (2)
Fe—C(2)	1·78 (2)	C(3)-C(4)	1·53 (3)
Fe—C(3)	2·00 (2)	C(5)—C(6)	1·58 (3)
As(1)—C(11)	1·94 (1)	C(6)—C(7)	1·54 (3)
As(2)—C(16)	1·90 (1)	C(6)—C(8)	1·51 (3)
As(1)—C(19)	1·95 (1)	C(6)—C(9)	1·56 (3)
As(1)—C(20)	1·98 (2)	C(9)—C(10)	1·33 (4)
As(2)—C(17)	1·97 (2)	C(11)—C(12)	1·47 (2)
As(2)—C(18)	1·94 (1)	C(11)—C(16)	1·35 (2)
P—O(4)	1·59 (1)	C(12)—C(13)	1·40 (3)
P—O(5)	1·58 (1)	C(13)—C(14)	1·44 (3)
P—O(6)	1·59 (1)	C(14)—C(15)	1·39 (3)
O(1)—C(1)	1·16 (2)	C(15)—C(16)	1·42 (2)
O(2)—C(2)	1·11 (2)		
As(1)—Fe—As(2)	85·8 (1)	Fe—As(2)—C(18)	121·5 (5)
As(1)—Fe—P	94·2 (1)	C(11)—As(1)—C(19)	105·8 (6)
As(2)—Fe—P	90·6 (1)	C(11)—As(1)—C(20)	105·1 (6)
As(1)—Fe—C(2)	89·3 (6)	C(19)—As(1)—C(20)	102·3 (7)
As(1)—Fe—C(3)	85·4 (5)	C(16)—As(2)—C(17)	105·4 (6)
As(2)—Fe—C(1)	90·9 (6)	C(16)—As(2)—C(18)	101·3 (6)
As(2)—Fe—C(3)	86·8 (5)	C(17)—As(2)—C(18)	100·0 (7)
As(1)—Fe—C(1)	173·1 (6)	Fe—P—O(4)	116·9 (4)
As(2)—Fe—C(2)	174·7 (6)	Fe—P—O(5)	117·7 (4)
P—Fe—C(1)	91·9 (6)	Fe—P—O(6)	112·7 (4)
P—Fe—C(2)	91·7 (6)	O(4)—P—O(5)	102·5 (5)
P--Fe—C(3)	177·4 (5)	O(4)—P—O(6)	102·3 (5)
C(1)--Fe—C(2)	93·7 (8)	O(5)--P—O(6)	102·8 (5)
C(1)—Fe—C(3)	88·3 (7)	P—O(4)—C(5)	115·7 (9)
C(2)—Fe—C(3)	90·8 (7)	P—O(5)—C(7)	117·7 (9)
Fe—As(1)—C(11)	107·6 (4)	P—O(6)—C(8)	116·1 (9)
Fe—As(2)—C(16)	108·1 (4)	Fe—C(1)—O(1)	177·9 (15)
Fe—As(1)—C(19)	115·5 (5)	Fe—C(2)—O(2)	177·5 (16)
Fe—As(1)—C(20)	119·4 (5)	Fe—C(3)—O(3)	122·8 (12)
Fe—As(2)—C(17)	118·3 (5)	Fe—C(3)- C(4)	123·8 (12)

Discussion. Final atomic coordinates are given in Table 1;* Fig. 1, which contains the atom numbering, and Fig. 2 have been prepared from the output of ORTEP (Johnson, 1965). A perspective view of the complex cation is shown in Fig. 1, while bond lengths and selected angles are given in Table 2. The complex cation has a distorted octahedral coordination about Fe, and has dimensions very similar to comparable ones in cis,cis-[(diars)Fe(CO)₂(Me)(PMe₃)]BF₄ [diars = o-phenylenebis(dimethylarsine)] (Jablonski et al., 1985)— see Table 3. In this compound a significant difference between the Fe—As bond lengths is observed depending upon whether the As is trans to CO or trans to P. In the title compound, in which both As atoms are trans to CO groups, the mean length is 2·366 (3) Å, similar to the comparable value 2·362 (2) Å in the above complex. Also the Fe—P bond length would appear to be subject to a trans influence of P. In the cis,cis-[(diars)Fe(CO)₂(Me)(PMe₃)]⁺ cation with the P atom trans to As the mean value is 2·259 (4) Å, whereas in the title compound in which an acetyl group is trans the shorter value 2·217 (4) Å is observed. In both the complexes the bite angle of the bidentate ligand is 85·8 (1)°. The other principal angle distortions from regular octahedral geometry in the title compound are closure of As(1)—Fe—C(3) and As(2)—Fe—C(3) to respective values 85·4 (5) and 86·8 (5)° and opening of As(1)—Fe—P to 94·2 (1)° and C(1)—Fe—C(2) to 93·7 (8)°.

* Lists of structure amplitudes, anisotropic thermal parameters, intermolecular contacts and additional bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42768 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
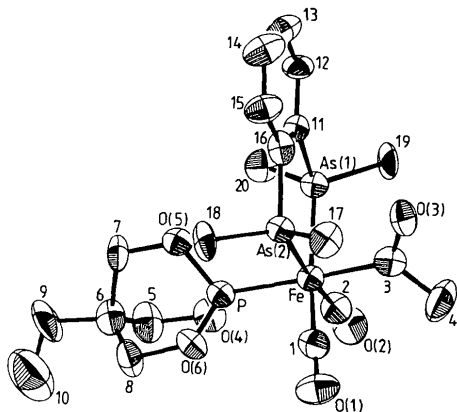
Table 3. *Comparison of bond lengths (Å) and angles (°) in the coordination sphere for the title compound and cis,cis-[(diars)Fe(CO)₂(Me)(PMe₃)]BF₄ (Jablonski et al., 1985)*

	[(diars)Fe(CO)₂(Me)(PMe₃)]⁺*	[(diars)Fe(CO)₂(MeCO)(C₆H₁₁O₃P)]⁺
Fe—As	2·360 (2), 2·364 (2)ᵃ	2·356 (2)ᵃ
	2·337 (2), 2·335 (2)ᵇ	2·376 (3)ᵃ
Fe—P	2·253 (4), 2·264 (4)ᶜ	2·217 (4)ᵈ
Fe—C(carbonyl)	1·77 (1), 1·75 (1)ᶜ	1·74 (2)ᶜ
	1·79 (1), 1·78 (1)ᶜ	1·78 (2)ᶜ
Fe—C(methyl)	2·11 (1), 2·12 (1)ᵈ	
Fe—C(acetyl)		2·00 (2)ᵇ
As—Fe—As	85·7, 85·9	85·8 (1)

(a) trans to CO; (b) trans to P; (c) trans to As; (d) trans to acetyl; (e) trans to methyl.
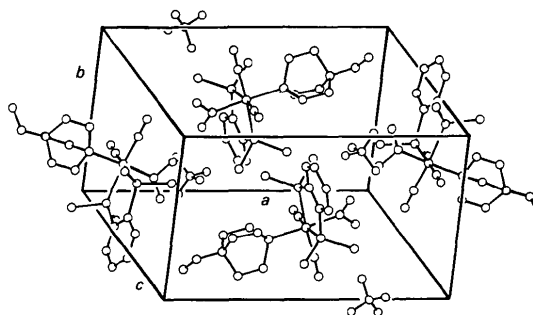
* Two cations in the asymmetric unit.

Fig. 2. The crystal packing.

Atoms C(11)–C(16) of the o-phenylenebis(arsine) moiety are coplanar within ±0·03 (2) Å with As(1) and As(2) lying −0·112 (2) and 0·027 (2) Å respectively from the plane. The mean As—C(aromatic) bond length 1·92 (1) Å is significantly shorter than the As—C(methyl) bond 1·96 (1) Å. The P—O bonds range in length between 1·584 (10) and 1·594 (10) Å with the C—O bonds in the phosphite moiety having a mean value 1·50 (2) Å. The angles subtended at the P atom associated with Fe have a mean of 115·8 (4)° compared with the mean value 102·5 (5)° for the O—P—O angles.

The crystal packing is illustrated in Fig. 2. All interionic contacts are normal.

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Fig. 1. Perspective view of the complex cation with thermal ellipsoids scaled to 50% probability. The C atoms are denoted by numerals only.