Crystal Structure of Nonacarbonyl-μ-dimethylarsino-μ-[2-(diphenylphosphino)tetrafluorocyclobut-1-enyl]-tri-iron

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The crystal structure of the title compound has been solved using *X*-ray counter data. Crystals are orthorhombic, space group $P2_12_12_1$, with $Z = 8$ in a cell of dimensions: $a = 12{\cdot}172(3)$, $b = 48{\cdot}935(8)$, and $c = 10{\cdot}233(2)$ Å; there are two molecules in the asymmetric unit which have been shown to be chemically equivalent. The structure was solved by tangent refinement procedures and refined by full-matrix least-squares methods to R 0·052 for 2175 observed reflections. The molecule is based on three $Fe(CO)_3$ groups and an Me_2As group which are linked to form a four-membered ring. The mean Fe–As is 2·387 Å. The ligand, $(Ph_2P)\cdot\overline{C{:}C\cdot CF_2\cdot C}F_2$, forms a bond with each iron atom through the phosphorus atom, Fe–P 2·48 Å, the cyclobutenyl double bond, Fe–(midpoint)C=C 1·96 Å, and a carbon atom of the cyclobutene ring, Fe–C 1·94 Å, and thus bridges the two iron–iron bonds. Every iron atom has approximate octahedral co-ordination. The two iron–iron distances in each molecule are inequivalent, 2·676 and 2·866 Å, and this appears to be a result of constraints caused by the ligand bridges. One of the methyl groups bonded to arsenic has close non-bonded intramolecular contacts with a phenyl ring.

ORGANOMETALLIC complexes of transition-metal carbonyls and ligands of type $\overline{CE^1{:}CE^2\cdot[CF_2]_n\cdot C}F_2$ ($E^1 = E^2 = Me_2As$, $n = 1$, $f_4$fars; $E^1 = E^2 = Ph_2P$, $n = 1$ $f_4$fos, $n = 2$ $f_6$fos, $n = 3$ $f_8$fos; $E^1 = Ph_2P$, $E^2 = Me_2As$, $n = 1$, $f_4$asp) have been extensively studied.[1] In the ligand, each Group V atom and the ethylene-type linkage are potential donor sites and complexes, in which one, two, and all three donor sites are utilized, have been synthesized. However, although the complexes are air-stable at room temperature, both as solids and in solution, it has been found that cleavage reactions involving the ligand can occur on mild heating under reflux. Thus when $(f_4fars)Fe_3(CO)_{10}$ is heated under reflux in cyclohexane, an Me_2As is split off and inserts between two iron atoms in the iron triangle;[1c,2] Me_2As is cleaved from the fluorocyclobutenyl in $(f_4fars)Mn_2(CO)_8$ and then inserts into the Mn–Mn bond;[3] when $(f_4fars)CO_2(CO)_6$, is heated under reflux in hexane, Me_2As is cleaved and inserts into the Co–Co bond, and two fluorocyclobutenyl moieties dimerize.[3]

When $Fe_3(CO)_{12}$ is heated under reflux with $f_4$asp in cyclohexane, a compound of empirical formula $Fe_3(CO)_9(f_4asp)$ is formed. The ^1H n.m.r. spectrum of this compound shows two upfield singlets, one at −0·10 and the other at −1·0 p.p.m.[4] The latter is consistent with an AsMe group; however, the former suggests the possible presence of an FeMe grouping. Our single-crystal *X*-ray analysis has shown that Me_2As has been cleaved from $f_4$asp and has been inserted into one of the Fe–Fe bonds in the iron triangle to give a structure which is very similar to that described in ref. 2. Moreover, the structure provides an explanation for the two different methyl-group resonances.

EXPERIMENTAL

Crystals from carbon disulphide were dark red plates of various thicknesses with the longest direction along *c*. Weissenberg photographs of nets *hk*0—4 and precession photographs of zones 0*kl* and *h*0*l*, taken with Cu-K_α radiation, indicated the crystals were orthorhombic.

Crystal Data.—$C_{27}H_{16}AsF_4Fe_3O_9P$, $M = 833{\cdot}6$, Orthorhombic, $a = 12{\cdot}172(3)$, $b = 48{\cdot}935(8)$, $c = 10{\cdot}233(2)$ Å, $U = 6094{\cdot}8$ Å^3, $D_m = 1{\cdot}75(3)$ (Bermann density balance), $Z = 8$, $D_c = 1{\cdot}82$, $F(000) = 3296$. λ(Mo-$K_{\alpha1}$) = 0·70926, λ(Mo-K_α) = 0·7107 Å, μ(Mo-K_α) = 27·1 cm^{-1}. Space group $P2_12_12_1$ from systematic absences: *h*00 when *h* is odd, 0*k*0 when *k* is odd, 00*h* when *l* is odd.

Two crystals were used, one (*ca.* 0·2 × 0·3 × 0·45 mm) was for cell dimension measurements, and the other, (0·3 × 0·3 × 0·42 mm) for data collection. In both cases, the crystal was mounted with c^* approximately along ϕ and, in the case of data collection, c^* and ϕ were *ca.* 4° from coincidence in order to minimize intrinsic multiple reflection. Cell dimensions were obtained from the least-squares analysis of 2θ values for 16 reflections ($2\theta > 28°$) which had been automatically centred on a computer-controlled, Picker four-circle diffractometer,† with Mo-$K_{\alpha1}$ radiation, and take-off angle 1·1°. Errors in the cell dimensions are those determined by the least-squares process.

Intensity data for one octant were collected by the θ—2θ scan technique by use of Mo-K_α radiation (niobium filtered) and a scintillation counter equipped with pulse-height analysis. Because of the length of the *b* axis, overlap of reflections can be a problem. To eliminate overlap, the take-off angle was kept at 1·7° and the detector was placed 28 cm from the crystal and the detector aperture was 2 mm high and 3 mm wide. Each reflection was scanned for 0·9° in 2θ (extended for spectral dispersion) at a rate of 2° min^{-1}. At each end of the scan range, a stationary background count was made for 10s. Every 50 reflections, two standard reflections were monitored and the maximum deviation of

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† Computer programs for diffractometer control and preliminary calculations were written by P. G. Lenhert, Vanderbilt University. All other programs for calculation are described in F. W. B. Einstein and R. D. G. Jones, *J. Chem. Soc.* (*A*), 1971, 3359.

[1] (*a*) W. R. Cullen, D. A. Harbourne, B. V. Liengme and J. R. Sams, *Inorg. Chem.*, 1969, **8**, 95; (*b*) *ibid.*, p. 1464; (*c*) *ibid.*, 1970, **9**, 702; (*d*) W. R. Cullen and D. A. Harbourne, *ibid.*, p. 1839; (*e*) W. R. Cullen, P. S. Dhaliwal, and C. J. Stewart, *ibid.*, 1967, **6**, 2256; (*f*) J. P. Crow and W. R. Cullen, *ibid.*, 1971, **10**, 1529; (*g*) *ibid.*, p. 2165; (*h*) W. R. Cullen and J. A. J. Thompson, *Canad. J. Chem.*, 1970, **48**, 1730; (*i*) W. R. Cullen, D. F. Dong, and J. A. J. Thompson, *ibid.*, 1969, **47**, 4671.

[2] F. W. B. Einstein, Anne-Marie Pilotti, and R. Restivo, *Inorg. Chem.*, 1971, **10**, 1947.

[3] F. W. B. Einstein, R. D. G. Jones, A. C. MacGregor, and W. R. Cullen, unpublished results.

[4] W. R. Cullen, personal communication.

any standard from the mean was 4%. In this manner, intensities for 3285 reflections with $2\theta \leq 40°$ were measured. The reflection 0,2,0 could not be determined because the beam-stop intercepts the detector.

Intensities were corrected for background (normalized to scan time), variation of the standard reflections, and the Lorentz-polarization factor. No absorption correction was applied (μR 0·41). If the nett count for a reflection was $< 2{\cdot}5\sigma$, σ(background + total count)$^{\frac{1}{2}}$, the reflection was considered unobserved. The number of observed reflections was 2175.

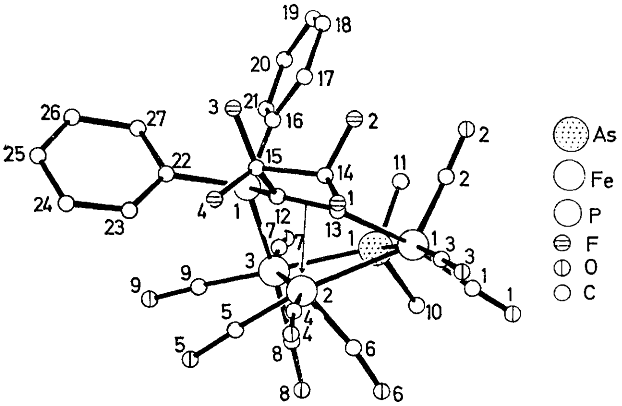
Structure Determination.—The tangent refinement procedure[5] was used to initiate the structure solution with data having $2\theta \leq 30°$. E Values were determined and 0,4,1 (3·27, 0), 3,14,6 (2·56, π), 2,33,0 (2·46,0), and 1,4,0 (3·32, $\pi/2$) were used to fix the origin and enantiomorph. Two series of tangent refinement with an additional reflection 0,8,3 in the starting set with alternate phase of 0 and π led to R_K* values of 0·24 and 0·31.

An E map [R_K 0·24, phase 3,14,6 = 0·33 π (0·49 π after final refinement)] showed positions for two arsenic atoms, six iron atoms, and two phosphorus atoms and indicated two molecular entities in the asymmetric unit. Two electron-density difference syntheses allowed location of all non-hydrogen atoms and showed the two molecules were equivalent. Using all data, refinement of the atomic parameters by full-matrix least-squares, latterly with anisotropic temperature factors for the arsenic atoms and a fixed contribution from phenyl hydrogen atoms placed at calculated positions, gave R 0·058. Each reflection was given unit weight and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Because of the limitations of the least-squares program, in each refinement cycle the parameters for all heavy and the light atoms for one molecule were varied while the contributions from the other light atoms were included as a fixed contribution. There was evidence for anisotropic motion of the iron atoms and, with this change and a weighting scheme described in ref. 6 R was 0·052 and R' was 0·063.†

At this stage it was observed that there was relatively poor structure-factor agreement, for the $0kl$ data ($|F_o| > |F_c|$) which we thought may be due to positional errors of the heavy atoms. The heavy-atoms parameters were refined with data for $30° < 2\theta \leq 40°$ and were fixed at these values while all data was used to refine the light-atom parameters. Even though there were some small shifts of the heavy atoms, the agreement did not improve.

C(1′) and O(1′) have larger temperature factors than the other carbonyl groups. Difference maps showed no unusual features in this region. However to check if this indeed was a methyl group, refinement was carried out with a methyl instead of a carbonyl group but significantly worse agreement resulted. The final weighting scheme parameters were $A = 6{\cdot}1$, $B = 40{\cdot}0$, and $C = 120{\cdot}0$ and the error-of-fit was 1·0. Except for the low angle, large intensity regions affected by $0kl$ data, wΔ^2 showed no trends with F_0 or sin $\theta\lambda^{-1}$. A final electron-density difference map had several peaks and troughs of magnitude *ca.* 0·5 e Å^{-3} associated with the heavy atoms and some carbonyl oxygen atoms.

Atomic scattering factors for the non-hydrogen atoms were obtained from ref. 7, those for hydrogen from ref. 8, and anomolous scattering corrections $\Delta f'$ and $\Delta f''$ for the arsenic and iron atoms from ref. 9.



A diagram of one molecule

Table 1 lists the final atomic parameters; the parameters for arsenic, iron, and phosphorus atoms were those obtained in the refinement with data $30° < 2\theta \leq 40°$. Interatomic distances and angles are in Table 2, the errors given being derived from co-ordinate errors only. The equations to selected planar groupings of atoms are in Table 3. The Figure shows a diagram of one molecule of the compound. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 20473 (5 pp., 1 microfiche).‡

DISCUSSION

The structure is another of the group in which the fluorocyclobutenyl ligand has had one of its potential donors cleaved, in this case Me_2As. Although it represents the first confirmed case in which $f_4$asp has undergone dissociation and shows that Me_2As is cleaved rather than Ph_2P, the structure is similar to that of {Me_2As)-$\overline{C{:}C\cdot CF_2\cdot C}F_2\cdot(Me_2As)Fe_3(CO)_9$} (I).[2]

There are two molecules in the asymmetric unit which, from inspection of the interatomic distances and angles, are chemically equivalent. Because of this, only one molecule will be described. Interatomic distances and angles in the text are the mean values over both molecules unless otherwise specifically stated. The molecules are numbered (1) and (2) and differentiated by primes in the Tables.

The observed geometry is based on three $Fe(CO)_3$ groups and an Me_2As which are linked to form a four-membered ring in which the arsenic atom lies out of the plane of the iron atoms [0·22 and 0·30 Å for each mole-

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* $R_K = [\Sigma||E_h|_o - |E_h|_c|]/\Sigma|E_h|_o$

† $R' = \{\Sigma w(||F_o| - |F_c||)^2(\Sigma w F_o^2\}^{\frac{1}{2}}$.

‡ For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[5] (*a*) J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849; (*b*) J. Karle, *ibid.*, 1968, *B*, **24**, 182.

[6] F. W. B. Einstein and R. D. G. Jones, *J. Chem. Soc.* (*A*), 1971, 3359.

[7] D. T. Cromer and D. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[9] ' International Tables for *X*-Ray Crystallography,' vol. III, 1962, Kynoch Press, Birmingham, p. 213.

TABLE 1

Positional (fractional co-ordinates) and thermal parameters (Å^2) with estimated standard deviations in parentheses; unprimed atoms belongs to molecule (1) and primed atoms to molecule (2)

Atom	x	y	z	B_{iso}
As(1)	0·6393(2)	0·2156(1)	0·3849(3)	*
Fe(1)	0·6359(3)	0·2406(1)	0·1857(4)	*
Fe(2)	0·6942(3)	0·1909(1)	0·1010(4)	*
Fe(3)	0·6672(3)	0·1676(1)	0·3557(4)	*
P(1)	1·0027(6)	0·3362(1)	0·7435(8)	2·74(1)
F(1)	1·029(1)	0·2764(3)	0·136(2)	5·2(3)
F(2)	0·894(1)	0·2701(3)	0·005(2)	5·5(4)
F(3)	0·851(1)	0·3229(3)	0·015(1)	4·8(3)
F(4)	1·005(1)	0·3308(3)	0·113(2)	5·5(3)
C(1)	0·741(2)	0·2611(5)	0·274(2)	3·5(6)
O(1)	0·812(2)	0·2747(4)	0·284(2)	5·6(4)
C(2)	0·528(3)	0·2598(7)	0·233(3)	6·6(8)
O(2)	0·453(2)	0·2739(5)	0·271(3)	8·6(7)
C(3)	0·651(2)	0·2575(4)	0·034(2)	3·0(5)
O(3)	0·656(2)	0·2722(4)	−0·053(2)	5·9(4)
C(4)	0·724(3)	0·1963(7)	−0·060(3)	6·7(8)
O(4)	0·748(2)	0·1984(5)	−0·169(2)	7·6(6)
C(5)	0·750(2)	0·1590(6)	0·085(3)	4·7(6)
O(5)	0·796(2)	0·1376(4)	0·073(2)	6·8(5)
C(6)	0·813(2)	0·2077(4)	0·147(2)	2·7(5)
O(6)	0·903(2)	0·2164(4)	0·163(2)	5·8(4)
C(7)	0·636(3)	0·1646(6)	0·519(3)	5·0(6)
O(7)	0·621(2)	0·1623(4)	0·631(2)	7·4(5)
C(8)	0·808(2)	0·1731(5)	0·371(3)	4·1(6)
O(8)	0·903(2)	0·1749(4)	0·394(2)	7·6(5)
C(9)	0·689(2)	0·1325(5)	0·332(3)	4·0(6)
O(9)	0·697(2)	0·1085(4)	0·326(2)	6·9(5)
C(10)	0·757(2)	0·2294(6)	0·500(3)	5·2(7)
C(11)	0·521(2)	0·2253(6)	0·505(3)	5·3(7)
C(12)	0·521(2)	0·1847(4)	0·115(2)	2·6(5)
C(13)	0·552(2)	0·2119(4)	0·102(2)	2·5(4)
C(14)	0·484(2)	0·2135(5)	−0·022(2)	3·5(5)
C(15)	0·458(2)	0·1847(4)	−0·016(2)	3·1(5)
C(16)	0·881(2)	0·3260(4)	0·658(2)	2·8(5)
C(17)	0·803(2)	0·3101(5)	0·712(2)	3·8(5)
C(18)	0·703(3)	0·3030(6)	0·649(3)	5·8(8)
C(19)	0·686(2)	0·3134(5)	0·523(3)	4·8(7)
C(20)	0·766(2)	0·3285(5)	0·462(3)	3·9(6)
C(21)	0·865(2)	0·3353(4)	0·530(2)	3·4(5)
C(22)	0·467(2)	0·1297(5)	0·194(2)	3·2(5)
C(23)	0·519(2)	0·1191(5)	0·089(3)	4·8(6)
C(24)	0·501(2)	0·0912(5)	0·050(3)	4·5(6)
C(25)	0·436(2)	0·0753(5)	0·116(3)	5·5(6)
C(26)	0·382(2)	0·0863(6)	0·225(3)	5·3(7)
C(27)	0·397(2)	0·1133(5)	0·265(2)	3·2(5)
As(1′)	0·9343(3)	0·0510(1)	0·9047(3)	*
Fe(1′)	0·8299(4)	0·0574(1)	0·7093(5)	*
Fe(2′)	1·0193(3)	0·0376(1)	0·6168(4)	*
Fe(3′)	1·1233(3)	0·0404(1)	0·8679(4)	*
P(1′)	1·1499(6)	0·0814(1)	0·7754(7)	2·37(1)
F(1′)	0·906(1)	0·0829(3)	0·386(2)	5·3(3)
F(2′)	0·899(1)	0·1172(3)	0·517(2)	5·8(4)
F(3′)	1·114(1)	0·1214(3)	0·508(2)	5·4(4)
F(4′)	1·128(1)	0·0830(3)	0·407(2)	5·7(3)
C(1′)	0·733(3)	0·0359(8)	0·779(4)	9·2(10)
O(1′)	0·665(2)	0·0231(5)	0·828(3)	10·6(8)
C(2′)	0·778(2)	0·0879(6)	0·760(3)	4·7(6)
O(2′)	0·743(2)	0·1096(4)	0·791(2)	7·0(5)
C(3′)	0·754(2)	0·0551(5)	0·558(3)	4·6(6)
O(3′)	0·704(2)	0·0518(4)	0·466(2)	6·4(5)
C(4′)	1·001(2)	0·0332(5)	0·448(3)	4·6(6)
O(4′)	0·984(2)	0·0260(4)	0·341(2)	6·1(5)
C(5′)	1·141(2)	0·0194(4)	0·605(2)	3·6(5)
O(5′)	1·220(2)	0·0064(4)	0·584(2)	6·5(5)
C(6′)	0·934(2)	0·0109(5)	0·655(2)	3·8(5)
O(6′)	0·886(2)	−0·0099(4)	0·669(2)	5·3(4)
C(7′)	1·148(2)	0·0477(5)	1·032(2)	4·2(5)
O(7′)	1·157(2)	0·0496(3)	1·147(2)	5·5(4)
C(8′)	1·096(2)	0·0061(5)	0·882(3)	3·9(5)
O(8′)	1·078(2)	−0·0175(4)	0·887(2)	5·6(4)
C(9′)	1·262(2)	0·0327(4)	0·840(2)	2·2(4)
O(9′)	1·354(2)	0·0265(3)	0·830(2)	5·6(4)
C(10′)	0·876(2)	0·0210(5)	1·010(3)	4·8(6)
C(11′)	0·910(2)	0·0806(5)	1·038(3)	4·9(6)
C(12′)	1·065(2)	0·0802(4)	0·636(2)	3·1(5)
C(13′)	0·952(2)	0·0748(4)	0·620(2)	3·3(5)
C(14′)	0·950(2)	0·0928(5)	0·499(3)	4·4(6)
C(15′)	1·075(2)	0·0954(5)	0·506(3)	4·1(6)
C(16′)	1·119(2)	0·1110(5)	0·863(2)	4·3(5)
C(17′)	1·048(2)	0·1321(5)	0·816(3)	4·9(6)
C(18′)	1·027(3)	0·1559(6)	0·894(3)	6·6(7)
C(19′)	1·069(3)	0·1576(6)	1·017(3)	6·7(8)
C(20′)	1·137(2)	0·1371(5)	1·066(3)	5·2(7)
C(21′)	1·157(2)	0·1143(5)	0·994(3)	4·3(6)
C(22′)	1·287(2)	0·0884(4)	0·712(2)	2·6(5)
C(23′)	1·331(2)	0·0733(5)	0·609(3)	4·4(6)
C(24′)	1·435(2)	0·0770(5)	0·567(2)	3·5(5)
C(25′)	1·501(2)	0·0967(5)	0·620(2)	3·3(5)
C(26′)	1·461(2)	0·1127(5)	0·719(3)	4·5(6)
C(27′)	1·351(2)	0·1079(5)	0·764(2)	3·7(5)
H(17)	0·819	0·303	0·799	7·5
H(18)	0·646	0·291	0·690	7·5
H(19)	0·617	0·309	0·477	7·5
H(20)	0·752	0·335	0·376	7·5
H(21)	0·927	0·346	0·487	7·5
H(23)	1·069	0·369	0·963	7·5
H(24)	1·039	0·416	1·025	7·5
H(25)	0·927	0·443	0·909	7·5
H(26)	0·834	0·426	0·724	7·5
H(27)	0·858	0·379	0·661	7·5
H(17′)	1·016	0·130	0·728	7·5
H(18′)	0·981	0·170	0·859	7·5
H(19′)	1·050	0·173	1·070	7·5
H(20′)	1·169	0·139	1·155	7·5
H(21′)	1·203	0·100	1·029	7·5
H(23′)	1·287	0·059	0·569	7·5
H(24′)	1·465	0·066	0·496	7·5
H(25′)	1·574	0·100	0·588	7·5
H(26′)	1·505	0·127	0·760	7·5
H(27′)	1·321	0·119	0·834	7·5

* Anisotropic temperature parameters in the form: $\exp-[2\pi(U_{11}a^{*2}h^2 + U_{22}b^{*}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^{*}b^{*}hk + 2U_{13}a^{*}c^{*}hl + 2U_{23}b^{*}c^{*}kl)]$ where the parameters are as follows:

Atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
As(1)	40(2)	44(1)	23(1)	−7(2)	−1(1)	1(1)
Fe(1)	35(2)	36(2)	33(2)	2(2)	−1(1)	3(2)
Fe(2)	36(2)	45(2)	25(2)	0(2)	5(2)	−1(2)
Fe(3)	35(2)	43(2)	31(2)	−1(2)	−4(2)	0(2)
As(1′)	37(2)	45(1)	39(2)	−0(2)	6(1)	−3(1)
Fe(1′)	34(2)	52(2)	46(2)	−4(2)	−5(2)	−1(2)
Fe(2′)	42(2)	39(2)	25(2)	−1(2)	−4(2)	−5(2)
Fe(3′)	43(2)	36(2)	25(2)	1(2)	−3(2)	0(2)

cule); *cf.* 0·3 Å in (I)]. In the fluorocyclobutenyl fragment, C(13), the point of cleavage of Me_2As, is σ bonded to Fe(1), P(1) is bonded to Fe(3), while the bond to Fe(2) can best be described as a π bond from the fluorocyclobutenyl double bond. Every iron atom is also bonded to three terminal carbonyl groups. If As(1) donates two electrons to the As(1)–Fe(1) bond and shares one electron with Fe(3), all iron atoms can be considered to attain a closed-shell configuration.

Each iron atom has an approximate octahedral co-ordination, the largest angular deviations involving Fe(1) and Fe(2). Two different iron–iron bond lengths are observed, Fe(1)–Fe(2) 2·676 and Fe(2)–Fe(3) 2·866 Å; *cf.* 2·667 and 2·917 Å in (I). In $(f_4fars)Fe_2(CO)_6$, where one iron atom is co-ordinated to the double bond of a fluorocyclobutenyl ring and the other is chelated by the arsenic atoms, Fe–Fe is 2·89 Å.[10] The longer bond, in

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[10] F. W. B. Einstein and J. Trotter, *J. Chem. Soc.* (*A*), **1967**, 824.

every case, occurs when the iron atoms are bridged by the Group V atom and the double bond of the cyclobutenyl ring. For the present compound and for (I), the shorter distance is bridged by the double bond and the carbon forming the Fe–C σ bond. Iron–iron bonds exhibit large variations but most lie within the range

Table 2

Molecular geometry with estimated standard deviations in parentheses

(*a*) Interatomic distances (Å) *

	Molecule (1)	Molecule (2)
As(1)–Fe(1)	2·379	2·389
As(1)–Fe(3)	2·390	2·388
Fe(1)–Fe(2)	2·679	2·673
Fe(2)–Fe(3)	2·863	2·868
Fe(3)–P(1)	2·252	2·243
As(1)–C(10)	1·98	1·96
As(1)–C(11)	1·96	2·01
Fe(1)–C(1)	1·74	1·74
Fe(1)–C(2)	1·69	1·70
Fe(1)–C(3)	1·77	1·81
Fe(2)–C(4)	1·70	1·76
Fe(2)–C(5)	1·71	1·74
Fe(2)–C(6)	1·73	1·72
Fe(3)–C(7)	1·72	1·74
Fe(3)–C(8)	1·74	1·72
Fe(3)–C(9)	1·76	1·76
Fe(1)–C(13)	1·94	1·94
Fe(2)–mid	1·96	1·96
C(1)–O(1)	1·16	1·15
C(2)–O(2)	1·20	1·19
C(3)–O(3)	1·15	1·14
C(3)–O(3)	1·15	1·14
C(4)–O(4)	1·16	1·17
C(5)–O(5)	1·19	1·17
C(6)–O(6)	1·19	1·18
C(7)–O(7)	1·16	1·18
C(8)–O(8)	1·19	1·17
C(9)–O(9)	1·18	1·16
P(1)–C(12)	1·79	1·77
P(1)–C(16)	1·79	1·74
P(1)–C(22)	1·84	1·82
C(12)–C(13)	1·39	1·41
C(12)–C(15)	1·52	1·52
C(13)–C(14)	1·44	1·53
C(14)–C(15)	1·54	1·53
C(14)–F(1)	1·39	1·36
C(14)–F(2)	1·37	1·36
C(15)–F(3)	1·36	1·36
C(15)–F(4)	1·37	1·35
C(16)–C(17)	1·35	1·43
C(16)–C(21)	1·39	1·43
C(17)–C(18)	1·42	1·44
C(18)–C(19)	1·40	1·35
C(19)–C(20)	1·37	1·39
C(20)–C(21)	1·43	1·36
C(22)–C(23)	1·35	1·39
C(22)–C(27)	1·38	1·35
C(23)–C(24)	1·44	1·34
C(24)–C(25)	1·30	1·37
C(25)–C(26)	1·40	1·37
C(26)–C(27)	1·40	1·43
C(11) · · · C(16)	3·46	3·45
C(11) · · · C(17)	3·87	3·79
C(11) · · · C(20)	4·08	3·46
C(11) · · · C(21)	3·54	3·46

Table 2 (*Continued*)

(*b*) Interatomic angles (°)

Fe(1)–As(1)–Fe(3)	113·6	114·1
Fe(1)–As(1)–C(10)	110	112
Fe(1)–As(1)–C(11)	114	113
Fe(3)–As(1)–C(10)	108	106
Fe(3)–As(1)–C(11)	115	114
C(10)–As(1)–C(11)	95	97
As(1)–Fe(1)–Fe(2)	78·8	77·9
As(1)–Fe(1)–C(1)	89	86
As(1)–Fe(1)–C(2)	93	93
As(1)–Fe(1)–C(3)	173	169
As(1)–Fe(1)–C(13)	91	93
Fe(2)–Fe(1)–C(1)	117	121
Fe(2)–Fe(1)–C(2)	144	138
Fe(2)–Fe(1)–C(3)	97	97
Fe(2)–Fe(1)–C(13)	49	48
C(1)–Fe(1)–C(2)	98	99
C(1)–Fe(1)–C(3)	88	88
C(2)–Fe(1)–C(3)	94	97
C(13)–Fe(1)–C(1)	165	169
C(13)–Fe(1)–C(2)	97	93
C(13)–Fe(1)–C(3)	90	91
Fe(1)–Fe(2)–Fe(3)	92·1	92·7
Fe(1)–Fe(2)–C(4)	103	106
Fe(1)–Fe(2)–C(5)	165	162
Fe(1)–Fe(2)–C(6)	73	71
Fe(1)–Fe(2)–mid.	64	64
Fe(3)–Fe(2)–C(4)	165	161
Fe(3)–Fe(2)–C(5)	77	73
Fe(3)–Fe(2)–C(6)	92	96
Fe(3)–Fe(2)–mid.	86	86
C(4)–Fe(2)–C(5)	88	88
C(4)–Fe(2)–C(6)	91	93
C(5)–Fe(2)–C(6)	97	98
mid.–Fe(2)–C(4)	102	100
mid.–Fe(2)–C(5)	124	125
mid.–Fe(2)–C(6)	136	135
As(1)–Fe(3)–P(1)	90·7	90·6
As(1)–Fe(3)–Fe(2)	74·9	74·1
As(1)–Fe(3)–C(7)	86	88
As(1)–Fe(3)–C(8)	89	90
As(1)–Fe(3)–C(9)	179	180
P(1)–Fe(3)–Fe(2)	74·0	74·2
P(1)–Fe(3)–C(7)	104	101
P(1)–Fe(3)–C(8)	158	160
P(1)–Fe(3)–C(9)	90	89
Fe(2)–Fe(3)–C(7)	161	162
Fe(2)–Fe(3)–C(8)	85	87
Fe(2)–Fe(3)–C(9)	104	106
C(7)–Fe(3)–C(8)	98	99
C(7)–Fe(3)–C(9)	95	92
C(8)–Fe(3)–C(9)	91	90
Fe(1)–C(1)–O(1)	178	176
Fe(1)–C(2)–O(2)	178	177
Fe(1)–C(3)–O(3)	169	175
Fe(2)–C(4)–O(4)	176	169
Fe(2)–C(5)–O(5)	176	173
Fe(2)–C(6)–O(6)	169	170
Fe(3)–C(7)–O(7)	176	172
Fe(3)–C(8)–O(8)	172	177
Fe(3)–C(9)–O(9)	174	175
Fe(3)–P(1)–C(12)	102	103
Fe(3)–P(1)–C(16)	119	120
Fe(3)–P(1)–C(22)	116	117
C(12)–P(1)–C(16)	110	108
C(12)–P(1)–C(22)	106	105
C(16)–P(1)–C(22)	103	103
P(1)–C(12)–C(13)	131	132
P(1)–C(12)–C(15)	130	130
C(12)–C(13)–Fe(1)	143	141
C(12)–C(13)–C(14)	89	90
C(14)–C(13)–Fe(1)	128	129
C(13)–C(14)–C(15)	92	90
C(12)–C(15)–C(14)	86	85

Table 2 (*Continued*)

C(13)–C(14)–F(1)	121	119
C(13)–C(14)–F(2)	111	114
C(15)–C(14)–F(1)	118	118
C(15)–C(14)–F(2)	113	112
F(1)–C(14)–F(2)	102	104
C(12)–C(15)–F(3)	118	118
C(12)–C(15)–F(4)	119	119
C(14)–C(15)–F(3)	115	115
C(14)–C(15)–F(4)	115	114
F(3)–C(15)–F(4)	105	106
P(1)–C(16)–C(17)	123	124
P(1)–C(16)–C(21)	119	120
C(17)–C(16)–C(21)	117	116
C(16)–C(17)–C(18)	124	120
C(17)–C(18)–C(19)	117	120
C(18)–C(19)–C(20)	121	121
C(19)–C(20)–C(21)	120	120
C(16)–C(21)–C(20)	120	123
P(1)–C(22)–C(23)	121	122
P(1)–C(22)–C(27)	120	121
C(23)–C(22)–C(27)	119	117
C(22)–C(23)–C(24)	121	122
C(23)–C(24)–C(15)	121	121
C(24)–C(25)–C(26)	118	119
C(25)–C(26)–C(27)	122	119
C(22)–C(27)–C(26)	119	122

* Estimated standard deviations in interatomic distances are: As–Fe 0·005, Fe–Fe 0·006, Fe–P 0·008, As–C 0·03, Fe–C 0·03 to 0·04, C–F 0·03, C–O 0·03, to 0·04, C–C 0·03 to 0·04 Å. Estimated standard deviations in interatomic angles are: Fe–As–Fe, As–Fe–Fe, Fe–Fe–Fe, As–Fe–P, Fe–Fe–P 0·2, C–As–C, Fe–As–C, Fe–Fe–C, C–Fe–C, Fe–P–C 1 C–C–F F–C–F, C–C–C 2, Fe–C–O, 2 to 3.

2·5—2·7 Å; *e.g.* $Fe_3(CO)_{12}$ 2·560—2·678,[11] and $Fe(CO)_3(PhC_2PhC_2Ph)_2Fe(CO)$ 2·494(5) Å.[12] The compounds $(C_{10}H_8)Fe_2(CO)_5$ [13] and $(C_{12}H_8)Fe_2(CO)_5$ [14] have long iron–iron distances [2·782(1) and 2·769(3) Å], which was attributed to the fact that no group such as CO or MeS bridged the iron atoms and to the constraints caused by the bridging organic ligand, which is fairly rigid. We suggest that this structure is also largely determined by the stereochemical requirements of the ligand. Further evidence in support of this conclusion is that in the $f_4$fars compounds (I) and $(f_4fars)Fe_2(CO)_6$, the long iron–iron distances of 2·917 and 2·89 Å are longer than in the present compound and are consistent with iron–arsenic and carbon–arsenic bond lengths being longer than similar bonds with phosphorus.

Table 3

Equations of selected planes in the form $AX + BY + CZ + D = 0$ where X, Y, and Z are co-ordinates in Å along axes parallel to *a*, *b*, and *c*

	A	*B*	*C*	*D*	χ^2
Plane (I): Fe(1)—(3)	−0·956	−0·204	−0·201	10·203	
Plane (II): C(16)—(21)	0·432	−0·824	−0·367	10·986	2·12
Plane (III): C(22)—(27)	−0·762	0·282	−0·583	3·698	0·09
Plane (IV): C(12)—(15)	0·825	−0·248	−0·508	−2·419	6·64
Plane (V): Fe(1′)—(3′)	0·308	0·930	−0·201	−4·267	
Plane (VI): C(16′)—(21′)	0·808	0·459	−0·370	−10·204	2·93
Plane (VII): C(22′)—(27′)	−0·342	0·663	−0·666	7·337	0·84
Plane (VIII): C(12′)—(15′)	0·165	−0·838	−0·521	4·50	16·07 *

As(1) and As(1′) lie 0·22 and 0·30 Å from planes (I) and (V) respectively. P(1) and P(1′) lie 0·81 and 0·66 Å from planes (IV) and (VIII).

* This group is not planar within commonly accepted standards. The equation represents the 'best fit' to the grouping. The deviations of individual atoms are C(12′) −0·04, C(13′) 0·04, C(14′) −0·05, and C(15′) 0·05 Å.

The phosphorus atom is not in the plane of the fluorocyclobutenyl ring to which it is bonded, a feature common to all the $f_4$fars structures in which the fluorocyclobutenyl double-bond is linked to the metal atom ($f_4$fars is used loosely here to describe structures in which no Me_2As group has been cleaved and others where it has been).[2,3,10] In all other cases involving co-ordination of $f_4$fars-type ligands, the fluorocyclobutenyl ring and the Group V donor atom(s) are coplanar.[3,6,15] Since C(12)–C(13) is 1·40 Å, the Fe(2)–mid-point of vector distance (1·96 Å) is approximately normal to the fluorocyclobutenyl ring and the deviation of the P(1)–C(12) vector, 1·78 Å, from this ring is small (*ca.* 15°), we prefer to describe Fe(2) as being π-bonded to C(12)–C(13) and not as having two iron–carbon σ bonds.

Inspection of the non-bonded intramolecular contacts in Table 2 shows that C(11) has reasonably short contacts with the phenyl group C(16) through C(21) (3·45—4·08 Å). In particular, the methyl group lies above the plane of the phenyl ring and it is known that such an orientation leads to downfield shifts in the n.m.r. signal from that observed for a free methyl group.[16] We believe that the two methyl resonances observed for this compound are a result of these contacts for one of the methyl groups.

The iron–arsenic and –phosphorus distances are

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[11] C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1969, **91**, 1351.

[12] E. F. Epstein and L. F. Dahl, *J. Amer. Chem. Soc.*, 1970, **92**, 493.

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

[14] M. R. Churchill and J. Wormald, *Inorg. Chem.*, 1970, **9**, 2239.

[15] (*a*) P. J. Roberts and J. Trotter, *J. Chem. Soc.* (*A*), 1970, 3246; (*b*) *ibid.*, 1971, 1479; (*c*) W. Harrison and J. Trotter, *ibid.*, 1971, 1607; (*d*) P. J. Roberts, B. R. Penfold, and J. Trotter, *Inorg. Chem.*, 1970, **9**, 2137; (*e*) F. W. B. Einstein and R. D. G. Jones, following paper; (*f*) F. W. B. Einstein and R. D. G. Jones, *Inorg. Chem.*, in the press; (*g*) F. W. B. Einstein and C. R. S. M. Hampton, *Canad. J. Chem.*, 1971, **49**, 1901; (*h*) J. P. Crow, W. R. Cullen, F. L. Hou, L. Y. Y. Chan, and F. W. B. Einstein, *Chem. Comm.*, 1971, 1229.

[16] E. D. Becker, 'High-Resolution N.m.r.' Academic Press, New York, 1969, p. 77.

within the range of previously reported values.[2,9,15d,e] There are no unusual features associated with the interatomic distances and angles in the fluorocyclobutenyl ring and the diphenylphosphine group or any unusual intermolecular contacts, the closest contact, O(1) · · · O(4)*, being 3·03 Å.

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* O(4) is at $\frac{1}{2} + x, \frac{1}{2} - y, -z$.