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**Crystal Structure of**  
**1-(Diphenylphosphino)-2-(dimethylarsino)tetrafluorocyclobut-1-ene- $\mu$ -**  
**(1-(diphenylphosphino)-2-(dimethylarsino)tetrafluorocyclobut-1-ene)-tetracarbonyldiiron,**  
 $[\text{Ph}_2\text{PC}=\text{C}(\text{Me}_2\text{As})\text{CF}_2\text{CF}_2]_2\text{Fe}_2(\text{CO})_4$

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The crystal structure of the title compound has been determined from three-dimensional X-ray data collected by counter methods ( $2\theta \leq 45^\circ$ ) using Mo K $\alpha$  radiation. The compound crystallizes in the monoclinic space group  $C2/c$ ; the unit cell contains eight molecules and has dimensions  $a = 36.129$  (9),  $b = 11.620$  (3),  $c = 19.174$  (5) Å, and  $\beta = 92.37$  (1) $^\circ$ ;  $d_{\text{measd}} = 1.65$  and  $d_{\text{calcd}} = 1.74$  g cm $^{-3}$  for eight molecules. The structure was determined by the symbolic addition procedure and refined by full-matrix least-squares techniques to  $R = 0.033$  and  $R_w = 0.036$  for 3458 observed reflections. The molecule contains two iron atoms, Fe(1) and Fe(2), with Fe(1)-Fe(2) = 2.869 (1) Å, which are in different environments. Fe(1) has distorted octahedral geometry, the coordination groups being two bidentate  $f_{4\text{asp}}$  ligands ( $f_{4\text{asp}} = \text{Ph}_2\text{PC}=\text{C}(\text{Me}_2\text{As})\text{CF}_2\text{CF}_2$ ) and a terminal carbonyl group while Fe(2) lies in the sixth position and is trans to P(1); Fe(1)-P(1) = 2.270 (2) Å. As(1) is trans to P(2) with Fe(1)-As(1) = 2.363 (1) Å; As(2) is trans to a carbonyl group; Fe(1)-As(2) = 2.449 (1) Å and Fe(1)-C = 1.731 (7) Å. Fe(2) is in an approximately trigonal-bipyramidal environment. Two terminal carbonyl groups and the carbon-carbon double bond of one  $f_{4\text{asp}}$  ligand form an equatorial plane while another terminal carbonyl and Fe(1) are at the apices. Hence one of the  $f_{4\text{asp}}$  ligands bridges the iron-iron bond while the other is simply chelating. Fe(2) $\rightarrow\parallel = 1.876$  (6) Å and the Fe(2)-CO average is 1.783 Å (individual esd 0.007 Å). In addition, the uncoordinated double bond, 1.326 (8) Å, is significantly different from the coordinated one, 1.476 (8) Å. An explanation is offered for the variation in bond lengths.

**Introduction**

Structural<sup>1</sup> and chemical<sup>2</sup> studies of the transition metal carbonyl complexes of the ligand  $\text{E}_1\text{C}=\text{CE}_2\text{CF}_2\text{CF}_2$  ( $\text{E}_1 = \text{E}_2 = \text{Me}_2\text{As}$ ,  $f_{4\text{fars}}$ ;  $\text{E}_1 = \text{Ph}_2\text{P}$ ,  $\text{E}_2 = \text{Me}_2\text{As}$ ,  $f_{4\text{asp}}$ ) have shown that the ligand has versatility in its coordination. *E.g.*, in  $(f_{4\text{fars}})\text{Fe}(\text{CO})_6$ ,<sup>1d</sup> the two arsenic atoms chelate to one iron atom while the perfluorocyclobutenyl double bond is linked to the other; in  $(f_{4\text{fars}})\text{Ru}_3(\text{CO})_{10}$ ,<sup>1b</sup> the ligand bridges a ruthenium-ruthenium bond by way of the arsenic atoms; in  $(f_{4\text{asp}})\text{Fe}(\text{CO})_4$ ,<sup>1f</sup> the ligand is monodentate and is bonded to the iron through the phosphorus atom.

When  $(f_{4\text{asp}})\text{Fe}_2(\text{CO})_6$  and excess  $f_{4\text{asp}}$ , in acetone, are irradiated with uv radiation for 7 days,  $(f_{4\text{asp}})_2\text{Fe}_2(\text{CO})_4$  is formed. The Mossbauer spectrum indicates that one of the ligands bridges the iron-iron linkage.<sup>3</sup> This structural analysis shows that one coordinated ligand bridges the iron-iron bond in a manner similar to that in  $(f_{4\text{fars}})\text{Fe}_2(\text{CO})_6$ <sup>1d</sup> while the other is chelated to an iron atom such that the four group Va atoms are coordinated to the same iron atom. Simple chelation by the perfluorocyclobutenyl derivatives has not been confirmed by structural studies previously. In addition, the length of the ethylene-type bond is highly significantly longer than the uncoordinated one.

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(3) W. R. Cullen, personal communication.

**Experimental Section**

Red crystals grew from acetone and were nearly equidimensional parallelepipeds. Weissenberg photographs of nets  $hk(0-2)$  and precession photographs of nets  $h0l-h2l$  and the zone  $0kl$ , taken with Cu K $\alpha$  radiation, indicated that the crystal was monoclinic. The following systematic absences were noted: for  $hkl$ ,  $h + k = \text{odd}$ ; for  $h0l$ ,  $l = \text{odd}$  ( $h = \text{odd}$ ); for  $0k0$ , ( $k = \text{odd}$ ). The space group is either  $C2/c$  or  $Cc$  ( $C2/c$  from structure analysis).

**Crystal Data.** The compound,  $\text{C}_{40}\text{H}_{32}\text{As}_2\text{F}_8\text{Fe}_2\text{O}_4\text{P}_2$ , mol wt 1051.7, crystallizes in the monoclinic space group  $C2/c$  or  $Cc$  with unit cell dimensions  $a = 36.129$  (9),  $b = 11.620$  (3),  $c = 19.174$  (5) Å,  $\beta = 92.37$  (1) $^\circ$ , and  $U = 8042.7$  Å $^3$ ;  $d_{\text{measd}} = 1.65$  (floatation in  $\text{ZnBr}_2$  solution),  $d_{\text{calcd}} = 1.74$  g cm $^{-3}$ ;  $Z = 8$ .  $F(000) = 4192$ ,  $\lambda(\text{Cu K}\alpha) 1.5418$  Å,  $\lambda(\text{Mo K}\alpha_1) 0.70926$  Å, and  $\mu(\text{Mo K}\alpha) 21.6$  cm $^{-1}$ .

A crystal was ground to an approximate sphere of diameter 0.38 mm and was used to measure the cell dimensions and the intensity data. It was mounted with a general orientation in order to minimize intrinsic multiple reflection. Cell dimensions were obtained by the least-squares analysis of the  $2\theta$  values ( $2\theta > 29^\circ$ ; the function minimized was  $\Sigma \Delta\theta^2$ ) of 12 reflections which had been accurately centered on a computer-controlled four-circle Picker diffractometer.<sup>4</sup> The radiation was Mo K $\alpha_1$ , the takeoff angle was  $1^\circ$ , and the temperature was  $22^\circ$ . The errors in the cell dimensions are those determined in the least-squares process.

Intensity data for one quadrant were collected by the  $\theta-2\theta$  scan technique using Mo K $\alpha$  radiation (niobium filter) and a scintillation counter equipped with pulse height analysis. The takeoff angle was  $2.5^\circ$ , the detector was positioned 28 cm from the crystal, and the detector aperture was 5.0 mm high and 4.0 mm wide. Each reflection was scanned in  $2\theta$  for  $1^\circ$  (extended for spectral dispersion) at a scan rate of  $2^\circ$  min $^{-1}$ . At each end of the scan range, the background scattering was counted for 10 sec. Every 75 reflections, two standard reflections were measured and the maximum deviation of any individual standard from the mean was 2.5%. In this manner, intensities for 5284 reflections, with  $2\theta \leq 45^\circ$ , were measured.

Intensities were corrected for background (normalized to the scan time) and for the Lorentz-polarization factor. No absorption correction was applied ( $\mu R = 0.41$ ) and the maximum error introduced in  $F_0$  by this neglect is  $\sim 1\%$ . If the net count for a reflection was  $< 2\sigma$ ,  $\sigma = (\text{total count and background})^{1/2}$ , the reflection was considered unobserved. The number of observed reflections was 3458.

**Structure Determination.** The structure solution was initiated

(4) Computer programs for diffractometer control and preliminary calculations were written by P. G. Lenhert, Vanderbilt University. All other programs for calculation are described in ref 1h.



Table II. Molecular Geometry with Esd's in Parentheses

(A) Interatomic Distances, Å							
Fe(1)-Fe(2)	2.869 (1)	Fe(1)-C(1)	1.731 (7)	C(9)-F(1)	1.331 (7)	C(27)-F(5)	1.365 (7)
Fe(1)-As(1)	2.363 (1)	Fe(2)-C(2)	1.778 (8)	C(9)-F(2)	1.337 (7)	C(27)-F(6)	1.371 (7)
Fe(1)-As(2)	2.449 (1)	Fe(2)-C(3)	1.786 (7)	C(10)-F(3)	1.341 (7)	C(28)-F(7)	1.366 (7)
Fe(1)-P(1)	2.270 (2)	Fe(2)-C(4)	1.787 (7)	C(10)-F(4)	1.356 (7)	C(28)-F(8)	1.370 (7)
Fe(1)-P(2)	2.239 (2)	C(1)-O(1)	1.161 (7)	C(11)-C(12)	1.375 (9)	C(29)-C(30)	1.385 (8)
Fe(2)-C(25)	2.015 (6)	C(2)-O(2)	1.149 (8)	C(11)-C(16)	1.392 (9)	C(29)-C(34)	1.395 (9)
Fe(2)-C(26)	2.023 (6)	C(3)-O(3)	1.144 (8)	C(12)-C(13)	1.395 (10)	C(30)-C(31)	1.391 (9)
Fe(2)-mid	1.879 (6)	C(4)-O(4)	1.152 (7)	C(13)-C(14)	1.359 (10)	C(31)-C(32)	1.361 (10)
As(1)-C(5)	1.937 (7)	As(2)-C(23)	1.952 (7)	C(14)-C(15)	1.335 (10)	C(32)-C(33)	1.373 (10)
As(1)-C(6)	1.943 (7)	As(2)-C(24)	1.964 (7)	C(15)-C(16)	1.400 (10)	C(33)-C(34)	1.380 (9)
As(1)-C(7)	1.935 (6)	As(2)-C(25)	1.908 (6)	C(17)-C(18)	1.391 (8)	C(35)-C(26)	1.387 (8)
P(1)-C(8)	1.832 (6)	P(2)-C(26)	1.772 (6)	C(17)-C(22)	1.397 (8)	C(35)-C(40)	1.382 (8)
P(1)-C(11)	1.832 (6)	P(2)-C(29)	1.837 (6)	C(18)-C(19)	1.386 (9)	C(36)-C(37)	1.391 (9)
P(1)-C(17)	1.821 (6)	P(2)-C(35)	1.820 (6)	C(19)-C(20)	1.376 (9)	C(37)-C(38)	1.367 (9)
C(7)-C(8)	1.326 (8)	C(25)-C(26)	1.476 (8)	C(20)-C(21)	1.367 (9)	C(38)-C(39)	1.376 (9)
C(7)-C(10)	1.506 (8)	C(25)-C(28)	1.497 (8)	C(21)-C(22)	1.390 (9)	C(39)-C(40)	1.389 (9)
C(8)-C(9)	1.524 (8)	C(26)-C(27)	1.501 (8)	As(1)···P(1)	3.264		
C(9)-C(10)	1.550 (9)	C(27)-C(28)	1.538 (9)	As(2)···P(2)	3.169		
(B) Interatomic Angles, Deg							
As(1)-Fe(1)-As(2)	98.14 (4)	Fe(1)-Fe(2)-C(2)	88.6 (2)	C(8)-C(9)-F(1)	116.8 (5)	Fe(2)-C(25)-As(2)	103.4 (3)
As(1)-Fe(1)-Fe(2)	96.44 (4)	Fe(1)-Fe(2)-C(3)	178.0 (3)	C(8)-C(9)-F(2)	117.2 (5)	Fe(2)-C(25)-C(28)	119.0 (4)
As(1)-Fe(1)-P(1)	89.55 (5)	Fe(1)-Fe(2)-C(4)	90.1 (2)	C(10)-C(9)-F(1)	115.3 (5)	Fe(2)-C(26)-P(2)	103.6 (3)
As(1)-Fe(1)-P(2)	164.63 (6)	Fe(1)-Fe(2)-C(25)	77.8 (2)	C(10)-C(9)-F(2)	114.5 (5)	Fe(2)-C(26)-C(27)	118.1 (4)
As(1)-Fe(1)-C(1)	84.9 (2)	Fe(1)-Fe(2)-C(26)	75.1 (2)	F(1)-C(9)-F(2)	106.8 (5)	C(26)-C(27)-F(5)	118.4 (5)
As(2)-Fe(1)-Fe(2)	70.25 (3)	Fe(1)-Fe(2)-mid	75.4 (2)	C(7)-C(10)-F(3)	117.5 (5)	C(26)-C(27)-F(6)	115.7 (5)
As(2)-Fe(1)-P(1)	109.07 (5)	C(2)-Fe(2)-C(3)	91.9 (3)	C(7)-C(10)-F(4)	115.6 (5)	C(28)-C(27)-F(5)	116.6 (5)
As(2)-Fe(1)-P(2)	84.93 (5)	C(2)-Fe(2)-C(4)	100.3 (3)	C(9)-C(10)-F(3)	116.5 (5)	C(28)-C(27)-F(6)	113.0 (5)
As(2)-Fe(1)-C(1)	160.1 (2)	C(2)-Fe(2)-mid	126.1 (3)	C(9)-C(10)-F(4)	115.0 (5)	F(5)-C(27)-F(6)	104.5 (5)
Fe(2)-Fe(1)-P(1)	174.00 (6)	C(3)-Fe(2)-C(4)	91.7 (3)	F(3)-C(10)-F(4)	105.9 (5)	C(25)-C(28)-F(7)	120.0 (6)
Fe(2)-Fe(1)-P(2)	70.30 (5)	C(3)-Fe(2)-mid	102.7 (3)	P(1)-C(11)-C(12)	116.6 (5)	C(25)-C(28)-F(8)	115.4 (5)
Fe(2)-Fe(1)-C(1)	89.9 (2)	C(4)-Fe(2)-mid	130.2 (3)	P(1)-C(11)-C(16)	125.8 (5)	C(27)-C(28)-F(7)	115.8 (5)
P(1)-Fe(1)-P(2)	103.74 (6)	C(25)-Fe(2)-C(26)	42.9 (2)	C(12)-C(11)-C(16)	117.5 (6)	C(27)-C(28)-F(8)	111.4 (5)
P(1)-Fe(1)-C(1)	87.3 (2)	C(2)-Fe(2)-C(25)	105.3 (2)	C(11)-C(12)-C(13)	121.7 (7)	F(7)-C(28)-F(8)	105.0 (5)
P(2)-Fe(1)-C(1)	90.6 (2)	C(4)-Fe(2)-C(26)	109.0 (2)	C(12)-C(13)-C(14)	118.6 (8)	P(2)-C(29)-C(30)	119.5 (5)
Fe(1)-As(1)-C(5)	118.8 (2)	Fe(1)-As(2)-C(23)	125.6 (2)	C(13)-C(14)-C(15)	121.8 (8)	P(2)-C(29)-C(34)	122.5 (5)
Fe(1)-As(1)-C(6)	130.7 (2)	Fe(1)-As(2)-C(24)	129.7 (2)	C(14)-C(15)-C(16)	120.0 (8)	C(30)-C(29)-C(34)	118.0 (6)
Fe(1)-As(1)-C(7)	100.1 (2)	Fe(1)-As(2)-C(25)	91.2 (2)	C(12)-C(16)-C(15)	120.2 (7)	C(29)-C(30)-C(31)	121.5 (6)
C(5)-As(1)-C(6)	102.0 (3)	C(23)-As(2)-C(24)	95.0 (3)	P(1)-C(17)-C(18)	118.3 (5)	C(30)-C(31)-C(32)	119.3 (7)
C(5)-As(1)-C(7)	100.1 (3)	C(23)-As(2)-C(25)	104.8 (3)	P(1)-C(17)-C(22)	123.9 (4)	C(31)-C(32)-C(33)	120.2 (7)
C(6)-As(1)-C(7)	98.5 (3)	C(24)-As(2)-C(25)	107.0 (3)	C(18)-C(17)-C(22)	117.5 (6)	C(32)-C(33)-C(34)	120.9 (7)
Fe(1)-P(1)-C(8)	104.8 (2)	Fe(1)-P(2)-C(26)	98.6 (2)	C(17)-C(18)-C(19)	121.3 (6)	C(29)-C(34)-C(33)	119.9 (6)
Fe(1)-P(1)-C(11)	122.1 (2)	Fe(1)-P(2)-C(29)	119.6 (2)	C(18)-C(19)-C(20)	119.5 (6)	P(2)-C(35)-C(36)	122.7 (5)
Fe(1)-P(1)-C(17)	117.4 (2)	Fe(1)-P(2)-C(35)	121.9 (2)	C(19)-C(20)-C(21)	120.9 (7)	P(2)-C(35)-C(40)	119.2 (4)
C(8)-P(1)-C(11)	98.8 (2)	C(26)-P(2)-C(29)	109.4 (3)	C(20)-C(21)-C(22)	119.5 (6)	C(36)-C(35)-C(40)	118.0 (6)
C(8)-P(1)-C(17)	102.0 (2)	C(26)-P(2)-C(35)	106.5 (3)	C(17)-C(22)-C(21)	121.3 (6)	C(35)-C(36)-C(37)	120.5 (6)
C(11)-P(1)-C(17)	107.8 (3)	C(29)-P(2)-C(35)	100.1 (3)	Fe(1)-C(1)-O(1)	177.1 (6)	C(36)-C(37)-C(38)	120.2 (6)
As(1)-C(7)-C(8)	120.6 (4)	As(2)-C(25)-C(26)	117.1 (4)	Fe(2)-C(2)-O(2)	176.7 (7)	C(37)-C(38)-C(39)	120.5 (7)
As(1)-C(7)-C(10)	144.7 (5)	As(2)-C(25)-C(28)	135.7 (4)			C(38)-C(39)-C(40)	119.0 (6)
P(1)-C(8)-C(9)	121.1 (4)	P(2)-C(26)-C(25)	117.6 (4)			C(35)-C(40)-C(39)	121.7 (6)
P(1)-C(8)-C(9)	144.8 (5)	P(2)-C(26)-C(27)	136.2 (5)			Fe(2)-C(3)-O(3)	174.5 (7)
C(8)-C(7)-C(10)	94.7 (5)	C(26)-C(25)-C(28)	91.2 (5)			Fe(2)-C(4)-O(4)	175.9 (6)
C(7)-C(8)-C(9)	93.8 (5)	C(25)-C(26)-C(17)	91.1 (5)				
C(8)-C(9)-C(10)	85.5 (5)	C(26)-C(27)-C(28)	88.7 (5)				
C(7)-C(10)-C(9)	86.0 (5)	C(25)-C(28)-C(27)	88.9 (5)				

environments. This iron-iron distance is longer than is usually found; e.g., in  $\text{Fe}_3(\text{CO})_{12}$ , the range is 2.560-2.678 Å,<sup>14</sup> and in  $\text{Fe}(\text{CO})_3(\text{PhC}_2\text{C}_6\text{H}_4\text{C}_2\text{Ph})_2\text{Fe}(\text{CO})$ , the distance is 2.494 (5) Å.<sup>15</sup> Long iron-iron bond lengths have also been observed in  $\text{C}_{10}\text{H}_8\text{Fe}_2(\text{CO})_5$ <sup>16</sup> and  $\text{C}_{12}\text{H}_8\text{Fe}_2(\text{CO})_5$ ,<sup>17</sup> the values being 2.782 (1) and 2.769 (3) Å. These latter distances were attributed to the absence of bridging groups such as CO and  $\text{CH}_3\text{S}$  and to constraints caused by the rigidity of the bridging organic ligand. It was suggested that ligand constraint was the major factor in determining the long iron-iron distance in II and similar reasoning would also explain I. We also propose that this factor is mainly responsible for the

length of the iron-iron bond in the present compound.

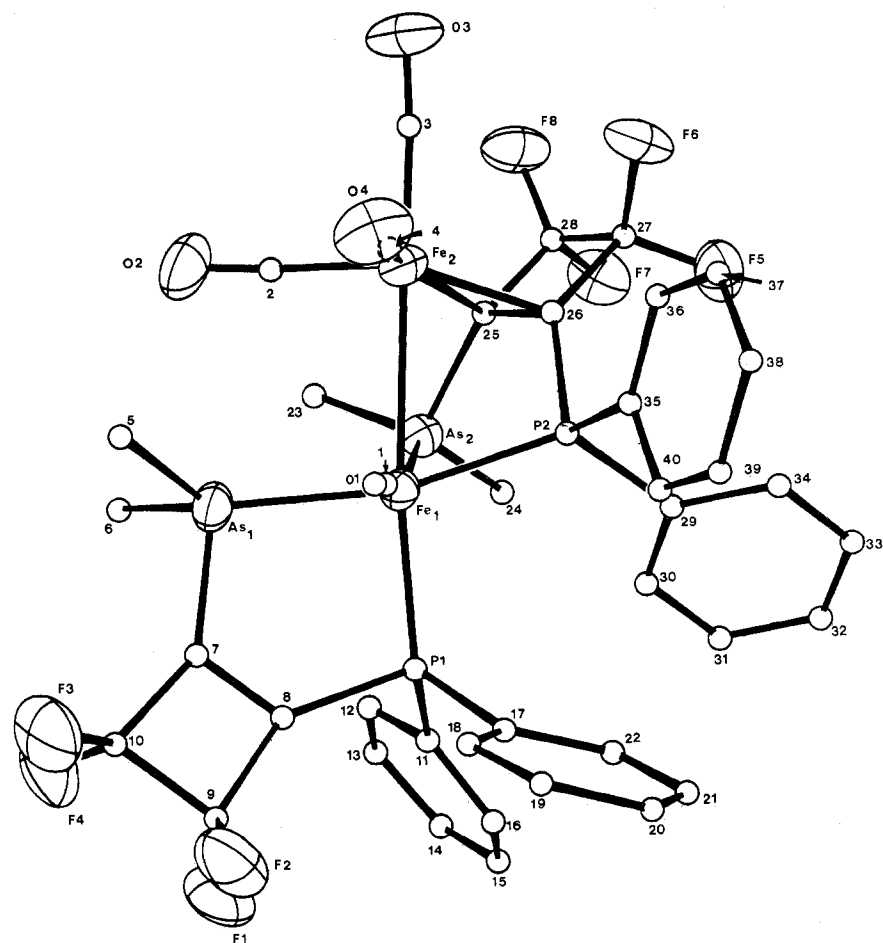
The arrangement of the group Va atoms about Fe(1) and the distance from Fe(1) to each are of interest. As(1) and P(2) are approximately trans to each other and Fe(1)-As(1) = 2.363 (1) Å and Fe(1)-P(2) = 2.239 (2) Å. These distances are significantly shorter than the other iron-arsenic and iron-phosphorus distances in this compound. As(2), which is very nearly trans to C(1), has Fe(1)-As(2) = 2.449 (1) Å, some  $5\sigma$  longer than Fe(1)-As(1). Fe(1)-C(1), 1.731 (7) Å, is also shorter ( $\sim 5\sigma$ ) than the mean of the other iron-carbonyl distances, 1.783 Å (individual esd 0.007 Å). Trans to the Fe(1)-Fe(2) link is P(1) with Fe(1)-P(1) = 2.270 (2) Å,  $12\sigma$  longer than Fe(1)-P(2). Since As(2) is competing with a carbonyl group for the same  $\pi$  molecular orbital on Fe(1) whereas As(1) is competing with P(2), one would expect the Fe(1)-As(1) bond to have more  $\pi$  character and so be shorter than Fe(1)-As(2). However, this does not explain the measured difference in the iron-phosphorus distances as

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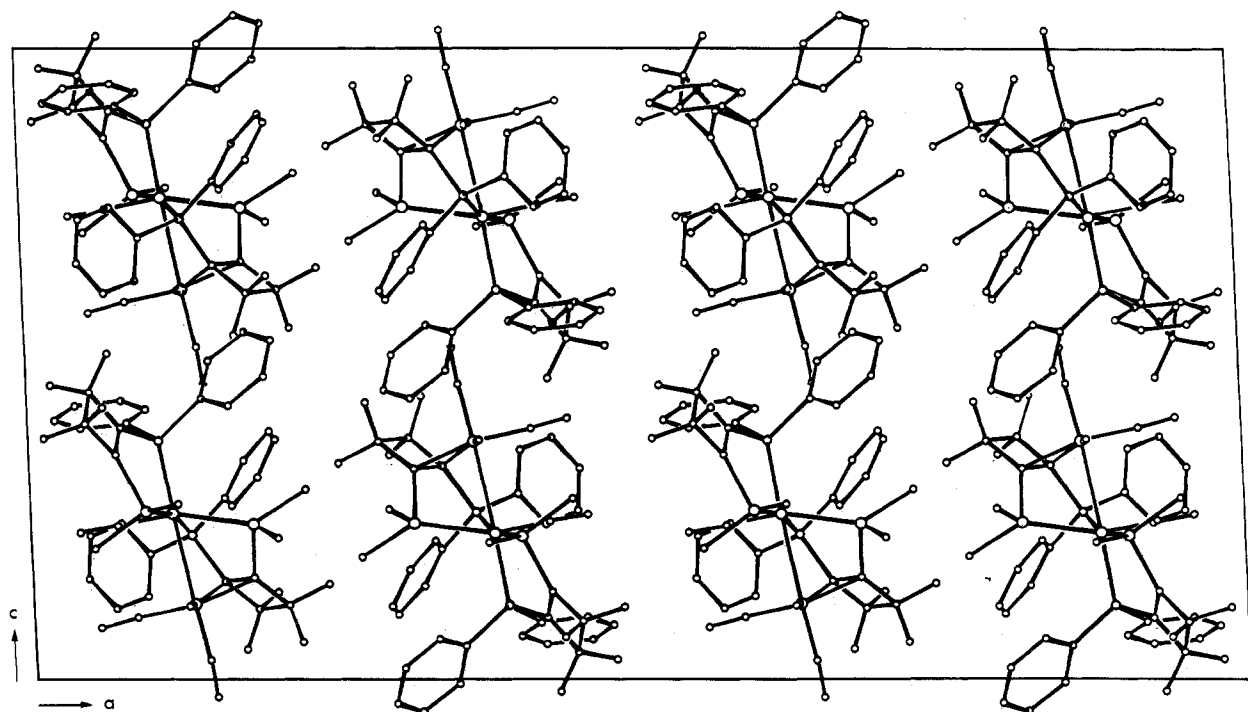
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**Figure 1.** A diagram of the molecule with the numbering system used. Carbon atoms do not have their chemical symbol attached. For atoms with anisotropic temperature factors, 50% probability thermal ellipsoids are shown.



**Figure 2.** A projection of the unit cell contents looking down the  $-b$  axis.

it could be expected that Fe(1)-P(1) would have the most  $\pi$  character. The covalent radius of each group Va atom in

the direction of the iron atom could be a factor but, since the variation in geometry about both arsenic and phosphorus

**Table III.** Equations of Planes to Selected Atomic Groupings of the Form  $AX + BY + CZ + D = 0$  Where  $X$ ,  $Y$ , and  $Z$  Are in Å and Are Parallel to  $a$ ,  $b$ , and  $c^*$

Plane No.	Atoms in plane	A	B	C	D	$\chi^2$
1	C(11)-C(16)	0.624	-0.577	-0.527	-6.121	19.9 <sup>a</sup>
2	C(17)-C(22)	0.103	-0.294	-0.950	1.330	1.5
3	C(29)-C(34)	0.831	0.223	-0.509	-9.229	3.0
4	C(35)-C(40)	-0.677	0.710	-0.196	6.766	2.4
5	C(7)-C(10)	-0.791	-0.429	-0.436	13.402	7.1 <sup>a</sup>
6	C(25)-C(28)	-0.425	0.383	-0.821	8.951	2.8
7	Fe(2), C(25), C(26)	0.379	-0.197	-0.904	2.152	
8	As(2), P(2), C(25), C(26)	-0.745	0.569	-0.349	8.968	0.1

Deviations from plane 5 (Å): As(1), -0.020 (1); P(1), 0.162 (2); Fe(1), -0.368 (1)

Deviations from plane 6 (Å): As(2), 0.965 (1); P(2), 0.905 (2); Fe(2), -1.621 (1)

Dihedral angles (deg): 6 and 7, 59.6; 6 and 8, 34.9

<sup>a</sup> The maximum deviation of any atom from plane 1 is 0.018 (7) Å and from plane 5 is 0.010 (7) Å.

atoms is small, this influence will be insignificant. One should note that the longer iron-arsenic bond and the shorter iron-phosphorus bond are in one ligand whereas the reverse situation is true for the other. In I, the iron-arsenic bonds in the  $f_4$ asp ligand are significantly different, 2.35 (1) and 2.47 (1) Å, and there was no clear explanation for this difference. Perhaps the trend is due, in part, to strain caused by the ligand "bite" on chelation; cf. ligand "bites" of 3.264 and 3.169 Å for this compound and 3.22 Å in I. When these types of ligand bridge metal-metal bonds by way of the group Va atoms, the "bite" is ~4.1 Å and the metal-group Va atom distances are equal; e.g., see ref 1g.

A distinctive feature of this compound is that one ligand molecule is coordinated by way of the four-membered carbon ring whereas the other is not. In the latter, the carbon-carbon link which joins the arsenic and phosphorus atoms is 1.326 (8) Å, a formal double bond, whereas the corresponding bond in the coordinated species is 1.476 (8) Å, a significant lengthening. Such an increase in the length of the ethylene linkage on coordination is common.<sup>1d,18,19</sup> Manojlovic-Muir, *et al.*,<sup>18</sup> suggested that the electron-withdrawing capability of the groups attached to the olefin is a decisive factor, the bond length increasing with increasing electronegativity of the attached groups.

The Dewar-Chat<sup>20</sup> model for bonding of ethylene to transition metals has two extremes—(a) a  $\pi$  bond and (b) two  $\sigma$  bonds—and it is generally accepted that the real situation is somewhere in between. It seems reasonable to assume that the favored positions of the metal atom for maxi-

imum  $\pi$  bonding would be either in the plane of the fluorocyclobutene ring or above the carbon-carbon double bond. In this compound, the plane Fe(2)-C(25)-C(26) makes an angle of 59.6° with the carbon ring while the plane As(2)-P(2)-C(25)-C(26) makes an angle of 34.9° with the same ring. In addition, the bond angles about C(25) and C(26) could be interpreted as indicating four single bonds to each atom. This evidence would seem to favor the formation of two iron-carbon  $\sigma$  bonds.

The available evidence can also be interpreted in a different way. It has been calculated for biphenyl<sup>21</sup> that, even when the phenyl rings are rotated to their minimum energy position (dihedral angle ~40°), there is still significant conjugation between the rings. Therefore, it is not unreasonable to expect that significant transfer of  $\pi$ -electron density can occur from ethylene to metal and of d electrons from metal to  $\pi^*$  orbitals of ethylene, even though the orientation of metal orbitals and ethylene orbitals is far from ideal. Because of the electron-withdrawing groups attached to C(25) and C(26), the energy of the  $\pi^*$  orbitals of the double bond will be raised. It is for this reason that it is postulated that there will be little transfer of  $\pi$ -electron density to the metal but that there is a considerable transfer of electron density from metal to  $\pi^*$  orbitals.<sup>22</sup> As a result, the ligand  $\pi^*$  orbitals will be occupied and the carbon-carbon bond will be increased.<sup>23</sup> This description is the one normally favored. Similar descriptions could be used to describe the bonding in I.

It is noteworthy that As(2)-C(25) and P(2)-C(26) are significantly shorter than the same bonds in the other  $f_4$ asp ligand. From considerations of the geometry at C(25), C(26) and C(7), C(8) alone, it is expected that the orbitals used for bonding to the group Va atoms by C(7) and C(8) would have more s-orbital character than those used by C(25) and C(26). This suggests C(7)-As(1) and C(8)-P(1) should be the shortest which is contrary to observation. Hence the shortening observed must be involved with As(2) and P(2) but the nature of the involvement is not clear.<sup>24</sup>

**Registry No.** [Ph<sub>2</sub>PC=C(Me<sub>2</sub>As)CF<sub>2</sub>CF<sub>2</sub>]<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub>, 37036-98-9.

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(24) A structure factor table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-255.

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