On the other hand, the shortening of both Ru–O bond distances relative to those in RuO_2 and the diamagnetism of ruthenium red clearly indicate metal–metal interaction requiring either a molecular orbital or a superexchange interpretation.

Optical spectra of solutions of the ethylenediamine compound of interest here closely resemble corresponding spectra of solutions of ruthenium red and can be interpreted on the basis of a molecular orbital scheme.[20] Fully occupied bonding molecular orbitals involve d_{xz}, d_{yz} orbitals of the terminal ruthenium atoms and p_x, p_y orbitals of the bridging oxygens. Antibonding orbitals principally composed of d_{xz}, d_{yz} orbitals of Ru(1) remain unoccupied.

Shielding of s electrons by different configurations of d electrons largely accounts for isomer shifts observed in Mössbauer spectroscopy of ruthenium compounds.[21] The molecular orbital scheme corresponds to a lower d-electron density on the central ruthenium atom than on the terminal ones and is consistent with the Mössbauer spectrum of ruthenium red.[19] This molecular orbital model is consistent with the low magnetic moment of ruthenium red and the observed 45° angle of twist between central and terminal ruthenium atoms: it is more difficult to accommodate this angle in a model in which low magnetic moment results from superexchange between metal atoms in localized (III, IV, III) oxidation states.

To translate the molecular orbital model to the vocabulary of localized oxidation states, the assignment (II, VI, II) should be considered. In view of the sensitivity of isomer shifts to covalency variations, this seems to be a possible assignment and it is one which more easily accommodates the 45° angle of twist reported here.

Acknowledgments.—We are grateful to Professor Mary L. Good for providing unpublished data and to the Air Force Office of Scientific Research for Grant 71-20-03.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
SIMON FRASER UNIVERSITY, BURNABY 2, BRITISH COLUMBIA, CANADA

A Novel Iron Carbonyl Complex Containing Arsenic.

The Crystal Structure of $(As(CH_3)_2)C{=}CCF_2CF_2\{(As(CH_3)_2)Fe_3(CO)_9\}$

BY F. W. B. EINSTEIN,* ANNE-MARIE PILOTTI, AND ROD RESTIVO

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The crystal structure of ffars$Fe_3(CO)_9$ where the ligand ffars is $(As(CH_3)_2)C{=}C(As(CH_3)_2)CF_2CF_2$ has been determined from three-dimensional X-ray data collected by scintillation counter methods. The structure has been refined by full-matrix least-squares techniques (iron and arsenic atoms with anisotropic thermal parameters) to a conventional R factor of 5.9% for the 1364 observed reflections. The compound crystallizes in the monoclinic space group $P2_1/n$ with four formula units in a cell of dimensions a = 13.803 (3), b = 19.001 (4), c = 9.482 (2) Å, and β = 82.77 (2)°. The compound may be viewed as formed by skeletal rearrangement of an $Fe_3(CO)_{12}$ molecule and coordination of an ffars ligand which has undergone cleavage of an $As(CH_3)_2$ group. The resulting structure may be described in terms of three $Fe(CO)_3$ groups and an $As(CH_3)_2$ group being linked together at the corners of a tetrahedrally distorted square-planar arrangement. The rearranged ligand, $(As(CH_3)_2)C{=}CCF_2CF_2$, is bonded to the first iron atom by an arsenic linkage, to the second iron atom by a π bond from the cyclobutene ring, and to the third iron atom by a σ bond from the cyclobutene ring. The long iron–iron bond of 2.917 (5) Å involves the iron atom bonded to the two arsenic atoms while the shorter contact 2.667 (5) Å involves one Fe–As bond.

Substitution reactions of polynuclear iron carbonyl complexes with phosphine derivatives which result in displacement of terminal carbonyl groups are relatively common. For example, the crystal structure determination of the compound $(P(C_6H_5)_3)Fe_3(CO)_{11}$[1] has revealed two different molecules in the asymmetric unit. In one molecule, the $P(C_6H_5)_3$ group has replaced a terminal carbonyl group from the unique iron atom of the parent compound $Fe_3(CO)_{12}$,[2] and, in the other, a terminal carbonyl group from one of the two equivalent iron atoms has been replaced. The compounds $Fe_3(CO)_{11}P(OCH_3)_3$, $Fe_3(CO)_{10}\{P(OCH_3)_3\}_2$, and $Fe_3(CO)_9\{P(OCH_3)_3\}_3$[3] have been reported to retain the iron triangle and bridging carbonyl groups of $Fe_3(CO)_{12}$. An X-ray crystal structure study of $\{(\pi\text{-}C_5H_5)_2Fe_2(CO)_3\}_2$DPPA[4,5] [DPPA = bis(diphenylphosphino)acetylene] showed that DPPA reacted with the parent compound $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ by substitution of a terminal carbonyl group, leaving the bridging-carbonyl groups intact.

Replacement of both terminal and bridging car-

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[5] A. J. Carty, A. Efraty, T. W. Ng, and T. Birchall, *Inorg. Chem.*, **9**, 1263 (1970).

TABLE I

Final Positional and Thermal Parameters for $(As(CH_3)_2)\overline{C{=}CCF_2C}F_2\{(As(CH_3)_2)Fe_3(CO)_9\}$

Atom	x	y	z	B, Å^2
Fe(1)	0.1882 (2)	0.2435 (2)	0.2433 (3)	
Fe(2)	0.2933 (2)	0.1126 (2)	0.1712 (4)	
Fe(3)	0.2987 (2)	0.0914 (2)	0.4484 (4)	
As(4)	0.1955 (2)	0.1909 (1)	0.4685 (3)	
As(5)	0.0776 (2)	0.1584 (1)	0.1901 (3)	
F(6)	0.0277 (11)	−0.0207 (7)	0.2176 (15)	4.4 (3)
F(7)	0.1511 (11)	−0.0230 (8)	0.0533 (16)	5.0 (4)
F(8)	0.1371 (10)	−0.0533 (7)	0.4133 (15)	4.6 (3)
F(9)	0.2636 (11)	−0.0658 (8)	0.2559 (17)	5.3 (4)
C(10)	0.1221 (18)	−0.0018 (13)	0.1911 (26)	3.2 (5)
C(11)	0.1857 (18)	−0.0244 (13)	0.2977 (27)	3.4 (6)
C(12)	0.2108 (16)	0.0548 (11)	0.3241 (23)	2.1 (5)
C(13)	0.1428 (15)	0.0748 (11)	0.2283 (23)	2.1 (5)
C(14)	0.2976 (19)	0.2846 (13)	0.2704 (26)	3.5 (6)
O(15)	0.3692 (13)	0.3130 (9)	0.2922 (18)	4.3 (4)
C(16)	0.1914 (18)	0.2835 (13)	0.0733 (28)	3.6 (6)
O(17)	0.1910 (14)	0.3107 (10)	−0.0373 (22)	5.8 (5)
C(18)	0.1025 (16)	0.3051 (12)	0.3245 (24)	2.6 (5)
O(19)	0.0468 (14)	0.3441 (10)	0.3850 (20)	5.3 (4)
C(20)	0.4000 (19)	0.1473 (13)	0.2079 (26)	3.7 (6)
O(21)	0.4796 (13)	0.1732 (9)	0.2189 (18)	4.7 (4)
C(22)	0.2948 (18)	0.1548 (13)	0.0071 (28)	3.6 (6)
C(23)	0.3034 (14)	0.1756 (10)	−0.1121 (22)	5.7 (5)
C(24)	0.3492 (22)	0.0413 (16)	0.0846 (32)	5.5 (7)
O(25)	0.3913 (15)	−0.0047 (11)	0.0135 (22)	6.4 (5)
C(26)	0.3843 (19)	0.1421 (14)	0.5237 (28)	4.2 (6)
O(27)	0.4436 (14)	0.1772 (10)	0.5684 (19)	5.1 (4)
C(28)	0.2445 (22)	0.0571 (16)	0.6034 (33)	5.6 (7)
O(29)	0.2024 (16)	0.0342 (11)	0.7152 (24)	6.8 (5)
C(30)	0.3800 (21)	0.0197 (16)	0.4194 (30)	5.1 (7)
O(31)	0.4343 (17)	−0.0283 (12)	0.3972 (24)	7.5 (6)
C(32)	0.0538 (18)	0.1482 (13)	−0.0007 (27)	3.8 (6)
C(33)	−0.0550 (18)	0.1530 (13)	0.2858 (27)	4.1 (6)
C(34)	0.0683 (16)	0.1641 (12)	0.5810 (24)	3.8 (5)
C(35)	0.2281 (19)	0.2659 (14)	0.6010 (28)	4.4 (6)

Anisotropic Thermal Parameters[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	0.0034 (2)	0.0012 (1)	0.0070 (5)	0.0000 (1)	−0.0003 (3)	0.0003 (2)
Fe(2)	0.0032 (2)	0.0015 (1)	0.0091 (5)	0.0002 (1)	−0.0001 (3)	−0.0000 (2)
Fe(3)	0.0040 (2)	0.0017 (1)	0.0096 (5)	−0.0000 (1)	−0.0017 (3)	0.0004 (2)
As(4)	0.0036 (2)	0.0017 (1)	0.0069 (3)	0.0000 (1)	−0.0006 (2)	0.0001 (2)
As(5)	0.0028 (2)	0.0015 (1)	0.0091 (4)	0.0001 (1)	−0.0013 (2)	0.0001 (1)

[a] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

bonyl groups in polynuclear iron carbonyl compounds by fluoroalicyclic-bridged ditertiary arsine and phosphine derivatives has resulted in isolation of several interesting substituted iron complexes.[6] The reaction of the fluorocarbon-bridged ligand, ffars,[7] with the compound $Fe_3(CO)_{12}$ resulted in the product ffars$Fe_2(CO)_6$.[8] Its structure, confirmed by an X-ray crystal study,[9] contains a diiron fragment lacking the bridging carbonyl groups of the parent compound.

This paper reports, in detail, the crystal structure of the compound ffars$Fe_3(CO)_9$,[6] the product of the reaction between ffars and $Fe_3(CO)_{12}$. An earlier communication[10] described our preliminary findings.

Experimental Section

A sample of the compound ffars$Fe_3(CO)_9$, whose preparation has been described elsewhere,[6] was kindly supplied by Dr. W. R. Cullen.

Weissenberg photographs of the zones *hk*0–*hk*5 inclusive using Cr Kα radiation, together with Mo Kα precession photographs of the zones 0*kl* and *h*0*l*, showed absences for *h*0*l* with $h + l = 2n + 1$ and 0*k*0 with $k = 2n + 1$. This combined with the Laue group (2/*m*) indicated unambiguously the space group $P2_1/n$.

Crystal Data.—$(As(CH_3)_2)\overline{C{=}CCF_2C}F_2\{(As(CH_3)_2)Fe_3(CO)_9\}$, formula weight 737.6, is monoclinic, space group $P2_1/n$. The dimensions of the unit cell are a = 13.803 (3), b = 19.001 (4), c = 9.482 (2) Å, β = 82.77 (2)° (λ 0.70926 Å for Mo Kα_1 radiation); V = 2467 Å^3, d_m = 2.03 (4) g cm^{-3} (Berman density balance determination[11]), Z = 4, d_x = 1.99 g cm^{-3}, $F(000)$ = 2951, μ(Mo Kα) = 46.75 cm^{-1}, and μR(Mo Kα) = 0.47.

All data were collected from an approximately cube-shaped crystal of 0.20-mm edge mounted with its c axis parallel to Φ. Cell dimensions were determined by a least-squares fit of 20 general high-angle reflections whose 2θ values were accurately determined on a Picker four-circle diffractometer (at 22°).

Reflection intensities for the unique set of data were manually measured with zirconium-filtered Mo Kα radiation by use of a scintillation detector with pulse-height analysis. Measurements were made with a 1.3° takeoff angle using a symmetrical θ–2θ scan of 1.5° width (carried out at a rate of 4°/min). The detector was positioned 23 cm from the crystal and the symmetrically variable aperture device was arranged so that the detector aperture was 4.0 mm high and 4.0 mm wide.

Background was estimated in five different directions in reciprocal space, and a curve as a function of θ only satisfactorily de-

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[6] W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **9**, 702 (1970).

[7] W. R. Cullen, P. S. Dhaliwal, and C. J. Stewart, *ibid.*, **6**, 2256 (1967).

[8] W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *ibid.*, **8**, 95 (1969).

[9] F. W. B. Einstein, W. R. Cullen, and J. Trotter, *J. Amer. Chem. Soc.*, **88**, 5670 (1966); F. W. B. Einstein and J. Trotter, *J. Chem. Soc. A*, 824 (1967).

[10] F. W. B. Einstein and A.-M. Svensson, *J. Amer. Chem. Soc.*, **91**, 3663 (1969).

[11] M. Berman, *Amer. Mineral.*, **24**, 434 (1939).

scribed the results obtained. Accordingly, each reflection which did not count 2.0 times the estimated background was coded as unobserved and assigned a value of half the local background intensity. Of the 2265 intensities recorded in the range $0° < 2\theta < 40°$, 1364 were regarded as observed. Three standard reflections were measured every 100 reflections and retained a constancy within 1% over the entire data collection. Lorentz and polarization factors were applied. Since the maximum difference in the transmission coefficients between extreme cases is of the order of 3%, no absorption correction was applied to the data.

Structure Determination

The density and space group requirements could only be met by having four formula units per unit cell, each asymmetric unit consisting of one formula unit. From the unsharpened three-dimensional Patterson function, it was possible to assign positions for the three independent iron atoms and two arsenic atoms. Block-diagonal least-squares refinement of these atomic positions and of individual isotropic temperature factors was carried out, assuming initial values for the temperature factors of 3.0 Å^2. A value of 0.27 was obtained for the conventional R_1 factor (defined as $\Sigma|F_o| - |F_c|/\Sigma|F_o|$). The remaining atomic positions for the molecules were located from an electron density Fourier difference map computed at this stage. After two cycles of full-matrix least-squares refinement, in which all positional and isotropic thermal parameters were varied, the R_1 value converged to 0.089. A Fourier difference map indicated that the iron and arsenic atoms were moving anisotropically. The R_1 and R_2 (defined as $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{1/2}$) values for the 1364 observed reflections after two cycles of least-squares refinement allowing anisotropic thermal parameters for these atoms were, respectively, 0.059 and 0.072. The parameter shifts were less than 0.1 standard deviation in the final cycle. All reflections received a constant weight ($W = 0.016$) such that the standard deviation of an observation of unit weight was 1.05. Throughout the refinement, the structure factor agreement was examined as a function of both $|F_o|$ and $\sin\theta$. At no time were significant trends in $\Sigma w(|F_o| - |F_c|)^2$ formed. A final difference map showed no peaks larger than 0.34 e$^-$/Å^3.

Scattering factors[12] used were those calculated on the SCF model. Full allowance was made for anomalous scattering[13] by the iron and arsenic atoms. The final atomic positions and their standard deviations are given in Table I. Calculations were carried out using the following computer programs: FORDAP, crystallographic Fourier summation with optional peak searching, by A. Zalkin; BUCILS, crystallographic structure factor[14] and full-matrix least squares, from the University of Canterbury.

Discussion

The molecular configuration and the packing of the molecules in the unit cell are shown in Figures 1 and 2. The structure obtained is novel in that the ligand ffars had undergone cleavage. It has been suggested by Cullen and coworkers[6] that the compound ffarsFe$_3$(CO)$_{10}$,[6,15] where the ligand is attached symmetrically

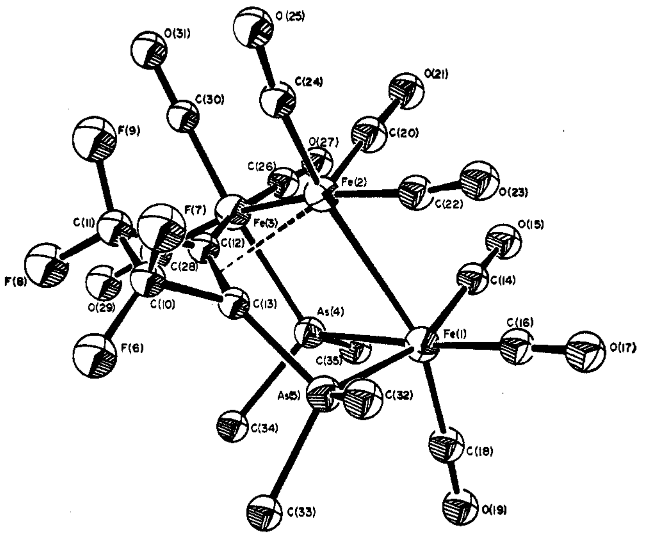

Figure 1.—The molecular structure of $(\mathrm{As(CH_3)_2})\overline{\mathrm{C{=}CCF_2CF_2}}$-$\{(\mathrm{As(CH_3)_2})\mathrm{Fe_3(CO)_9}\}$. The isotropic thermal parameters of the light atoms have all been set equal to 3.0 Å^2. For other atoms 50% probability ellipsoids are shown.

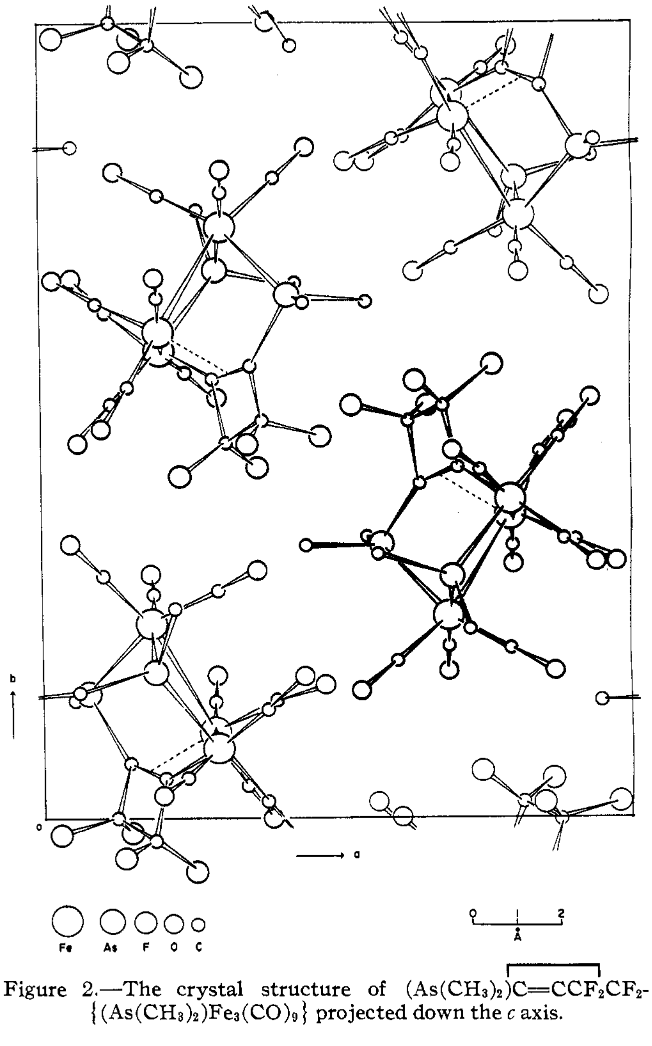

Figure 2.—The crystal structure of $(\mathrm{As(CH_3)_2})\overline{\mathrm{C{=}CCF_2CF_2}}$-$\{(\mathrm{As(CH_3)_2})\mathrm{Fe_3(CO)_9}\}$ projected down the *c* axis.

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[12] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

[13] D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

[14] A listing of observed and calculated structure factors (with F_c given the sign of the real component) will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

[15] W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *J. Amer. Chem. Soc.*, **90**, 3293 (1968).

TABLE II

BOND DISTANCES AND ANGLES WITH STANDARD DEVIATIONS

A. Intramolecular Distances, Å

Fe–Fe Distances	
Fe(1)–Fe(2)	2.917 (5)
Fe(2)–Fe(3)	2.667 (5)

Fe–As Distances	
Fe(1)–As(4)	2.371 (4)
Fe(1)–As(5)	2.322 (4)
Fe(3)–As(4)	2.360 (4)

Fe–C(carbonyl)	
Fe(1)–C(14)	1.75 (3)
Fe(1)–C(16)	1.78 (3)
Fe(1)–C(18)	1.77 (2)
Fe(2)–C(20)	1.69 (3)
Fe(2)–C(22)	1.75 (3)
Fe(2)–C(24)	1.72 (3)
Fe(3)–C(26)	1.75 (3)
Fe(3)–C(28)	1.69 (3)
Fe(3)–C(30)	1.77 (3)

Fe–C(fluorocarbon)	
Fe(2)–C(12)	2.05 (2)
Fe(2)–C(13)	2.20 (2)
Fe(2)–MDPT (midpoint of C(12)–C(13)	2.00 (2)

As–C(methyl)	
As(4)–C(34)	2.00 (2)
As(4)–C(35)	1.99 (3)
As(5)–C(32)	1.88 (2)
As(5)–C(33)	1.94 (3)

As–C(fluorocarbon)	
As(5)–C(13)	1.88 (2)

C–O(carbonyl)	
C(14)–O(15)	1.17 (3)
C(16)–O(17)	1.17 (3)
C(18)–O(19)	1.17 (3)
C(20)–O(21)	1.22 (3)
C(22)–O(23)	1.19 (3)
C(24)–O(25)	1.21 (3)
C(26)–O(27)	1.18 (3)
C(28)–O(29)	1.22 (3)
C(30)–O(31)	1.18 (3)

C=C(fluorocarbon)	
C(12)–C(13)	1.44 (3)

C–C(fluorocarbon)	
C(10)–C(11)	1.48 (3)
C(10)–C(13)	1.53 (3)
C(11)–C(12)	1.57 (3)

B. Intermolecular Contacts Less Than 3.4 Å

F(6)–O(29), I[a]	3.17	O(15)–C(34), IV	3.22
F(7)–O(29), II	3.38	O(19)–O(25), V	3.18
F(8)–O(15), III	3.21	O(19)–O(21), VI	3.20
F(9)–C(14), III	2.99	O(19)–C(23), VI	3.38
F(9)–O(15), III	3.01	C(23)–O(27), II	3.38
F(9)–C(18), III	3.11	O(25)–O(25), VII	2.99
F(9)–O(19), III	3.27	O(27)–O(31), VIII	3.33
F(9)–C(16), III	3.39	O(31)–O(31), VIII	3.02
C(11)–O(15), III	3.31	O(31)–C(30), VIII	3.28

C. Bond Angles, Deg

Angles Centered on Fe(1)	
Fe(2)–Fe(1)–As(4)	77.0 (1)
Fe(2)–Fe(1)–As(5)	71.2 (1)
Fe(2)–Fe(1)–C(14)	90.1 (8)
Fe(2)–Fe(1)–C(16)	101.4 (8)
As(4)–Fe(1)–As(5)	90.4 (1)
As(4)–Fe(1)–C(14)	85.5 (8)
As(4)–Fe(1)–C(18)	89.4 (7)
As(5)–Fe(1)–C(16)	92.4 (8)
As(5)–Fe(1)–C(18)	97.6 (7)
C(14)–Fe(1)–C(16)	92.9 (11)
C(14)–Fe(1)–C(18)	100.5 (11)
C(16)–Fe(1)–C(18)	92.9 (11)
Fe(2)–Fe(1)–C(18)	162.1 (7)
As(4)–Fe(1)–C(16)	176.2 (10)
As(5)–Fe(1)–C(14)	161.3 (8)

Angles Centered on Fe(2)	
Fe(1)–Fe(2)–C(12)	94.3 (6)
Fe(1)–Fe(2)–C(13)	78.1 (6)
Fe(3)–Fe(2)–C(12)	45.8 (6)
Fe(3)–Fe(2)–C(13)	81.4 (6)
Fe(1)–Fe(2)–Fe(3)	88.4 (1)
Fe(1)–Fe(2)–C(20)	92.3 (9)
Fe(1)–Fe(2)–C(22)	76.5 (8)
Fe(1)–Fe(2)–MDPT	85.7 (6)
Fe(3)–Fe(2)–C(20)	73.9 (9)
Fe(3)–Fe(2)–C(24)	106.6 (10)
Fe(3)–Fe(2)–MDPT	64.0 (6)
C(20)–Fe(2)–C(22)	95.2 (12)
C(20)–Fe(2)–C(24)	93.2 (13)
C(22)–Fe(2)–C(24)	89.0 (13)
C(22)–Fe(2)–MDPT	124.8 (10)
C(24)–Fe(2)–MDPT	99.5 (12)
Fe(1)–Fe(2)–C(24)	164.9 (10)
Fe(3)–Fe(2)–C(22)	161.2 (8)
C(12)–Fe(2)–C(26)	164.0 (11)
C(20)–Fe(2)–MDPT	137.9 (10)

Angles Centered on As(4)	
Fe(1)–As(4)–Fe(3)	111.0 (2)
Fe(1)–As(4)–C(34)	116.9 (7)
Fe(1)–As(4)–C(35)	107.8 (8)
Fe(3)–As(4)–C(34)	108.6 (7)
Fe(3)–As(4)–C(35)	116.3 (8)
C(34)–As(4)–C(35)	95.6 (10)

Angles Centered on As(5)	
Fe(1)–As(5)–C(13)	101.7 (7)
Fe(1)–As(5)–C(32)	118.6 (8)
Fe(1)–As(5)–C(33)	122.9 (8)
C(13)–As(5)–C(32)	104.0 (10)
C(13)–As(5)–C(33)	108.1 (10)
C(32)–As(5)–C(33)	100.1 (11)

Angles for Fluorocarbon Ring	
C(11)–C(10)–C(13)	88.5 (17)
C(10)–C(11)–C(12)	89.6 (18)
C(11)–C(12)–C(13)	88.7 (16)
C(10)–C(13)–C(12)	92.9 (17)
F(6)–C(10)–F(7)	105.0 (18)
F(8)–C(11)–F(9)	107.6 (20)

Angles for Fe–C–O	
Fe(1)–C(14)–O(15)	178.0 (23)
Fe(1)–C(16)–O(17)	178.2 (26)
Fe(1)–C(18)–O(19)	176.3 (21)
Fe(2)–C(20)–O(21)	173.0 (22)
Fe(2)–C(22)–O(23)	170.7 (23)
Fe(2)–C(24)–O(25)	174.0 (27)
Fe(3)–C(26)–O(27)	177.0 (25)
Fe(3)–C(28)–O(29)	177.4 (28)
Fe(3)–C(30)–O(31)	178.7 (31)

Angles Centered on Fe(3)			
Fe(2)–Fe(3)–As(4)	82.4 (1)	C(12)–Fe(3)–C(28)	98.5 (12)
Fe(2)–Fe(3)–C(12)	49.7 (7)	C(12)–De(3)–C(30)	93.6 (11)
Fe(2)–Fe(3)–C(26)	115.1 (9)	C(26)–Fe(3)–C(28)	96.1 (13)
Fe(2)–Fe(3)–C(30)	93.4 (9)	C(26)–Fe(3)–C(30)	92.3 (12)
As(4)–Fe(3)–C(12)	85.3 (6)	C(28)–Fe(3)–C(30)	92.3 (14)
As(4)–Fe(3)–C(26)	87.6 (9)	Fe(2)–Fe(3)–C(28)	148.1 (10)
As(4)–Fe(3)–C(28)	92.4 (10)	As(4)–Fe(3)–C(30)	175.2 (10)
		C(12)–Fe(3)–C(26)	164.0 (11)

[a] Key: I, $-X, -Y, 1 - Z$; II, $X, Y, Z - 1$; III, $1/2 - X, Y - 1/2, 1/2 - Z$; IV, $1/2 + X, 1/2 - Y, Z - 1/2$; V, $1/2 - X, 1/2 + Y, 1/2 - Z$; VI, $X - 1/2, 1/2 - Y, 1/2 + Z$; VII, $1 - X, -Y, -Z$; VIII, $1 - X, -Y, 1 - Z$.

to the two equivalent iron atoms and replaces two terminal carbonyl groups, is an intermediate in the formation of $(As(CH_3)_2)\overline{C{=}CCF_2C}F_2\{(As(CH_3)_2)Fe_3(CO)_9\}$. This product lacks the bridging carbonyl groups of the parent compound $Fe_3(CO)_{12}$ and may be viewed as derived from ffars$Fe_2(CO)_6$[9] by insertion of an $Fe(CO)_3$ group into one of the arsenic–ring carbon bonds.

TABLE III

EQUATIONS OF PLANES WITH DISTANCES OF ATOMS FROM THESE PLANES[a]

		Max dev	Dev of As(4) and As(5)
(1)	Plane formed by Fe (1), Fe (2) and Fe(3) $0.8683X + 0.4926Y - 0.0587Z - 4.6522 = 0$		−0.30, −2.12 Å
(2)	Mean plane of fluorocarbon ring $0.6765X - 0.0134Y - 0.7363Z + 0.0554 = 0$	0.028 Å	−1.03, −0.42 Å

[a] The orthogonal system of axes has X along the a axis, Y in the a,b plane and Z along the c^* axis. Unit weights were used for all atoms forming the plane.

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDE OF VIBRATION (Å) ALONG THE AXES OF THE THERMAL ELLIPSOIDS

Atom	Principal axis	Axis 2	Axis 3
Fe(1)	0.145 (7)	0.174 (6)	0.186 (6)
Fe(2)	0.159 (6)	0.175 (6)	0.205 (5)
Fe(3)	0.170 (6)	0.185 (6)	0.216 (6)
As(4)	0.171 (5)	0.179 (5)	0.185 (4)
As(5)	0.156 (5)	0.169 (5)	0.204 (4)

The bond distances and angles in Table II indicate that the molecular structure may be described as formed by the linkage of three dissimilar iron atoms and an arsenic atom at the corners of a distorted square-planar arrangement. The plane through the three iron atoms is given in Table III. The atom As(4) is significantly displaced from this plane (0.30 Å).

No corrections for thermal motion were applied to the Fe–Fe and Fe–As bond distances. The only appropriate correction for libration would have been to consider the heavy atoms as comprising a rigid body. As can be seen from Table IV, these atoms have only a small amount of anisotropic motion so that any correction for thermal motion would be negligible.

TABLE V

COMPARISON OF IRON–IRON AND IRON–ARSENIC BOND DISTANCES (Å) IN VARIOUS IRON COMPLEXES

Compound	Fe–Fe	Fe–As	Ref
$(As(CH_3)_2)C{=}CCF_2CF_2\{(As(CH_3)_2)Fe_3(CO)_9\}$	2.917 (5), 2.667 (5)	2.371 (4), 2.322 (4), 2.360 (4)	*a*
$(As(CH_3)_2)C{=}C(As(CH_3)_2)CF_2CF_2\{Fe(CO)_3\}_2$	2.89 (1)	2.47 (1), 2.35 (1)	*b*
$\{Fe(CO)_3\}_2(AsCH_3)_4$	2.680 (7)	2.336 (7), 2.311 (7)	*c*
$Fe_3(CO)_{12}$	2.668 (7), 2.678 (5), 2.560 (6)		*d*
$\{(\pi\text{-}C_5H_5)_2Fe_2(CO)_3\}_2((C_6H_5)_2PCCP(C_6H_5)_2)$	2.54		*e*

[a] Present work. [b] Reference 9. [c] B. M. Gatehouse, *Chem. Commun.*, 948 (1969). [d] Reference 2. [e] Reference 4.

Fe(1) is octahedrally coordinated to three carbonyl groups and the two dimethylarsenic groups, with the sixth position filled by an iron–iron bond. Arsenic atoms As(4) and As(5) make angles of 77.0 (1) and 71.2 (1)°, respectively, with the vector joining the iron atoms. The remaining angles about the Fe(1) atom average 93.3 (11)° which is consistent with octahedral geometry. Fe(2) has a pseudooctahedral configuration involving bonding to three carbonyl groups, the fluorocyclobutene π system, and two iron atoms. Using the vector from the iron atom to the midpoint of the C(12) and C(13) atoms, the angles around Fe(2) average to 83.3 (12)°. Fe(3) also has a distorted octahedral environment composed of three carbonyl groups, a dimethylarsenic group, a σ bond from the fluorocarbon ring, and an iron–iron bond.

The iron–iron bonds are quite different in length. The long Fe–Fe bond of 2.917 (5) Å involves the iron atom linked to the two arsenic atoms. This value might be compared to the Fe–Fe length of 2.89 (1) Å found in $ffarsFe_2(CO)_6$[9] which also was considered short enough to indicate some degree of bonding. The shorter Fe–Fe bond of 2.667 (5) Å involves coordination to a single arsenic atom and is similar to the distance of 2.680 (1) Å in $\{Fe(CO)_3\}_2(AsCH_3)_4$ (Table V). These distances are comparable to those found for nonbridged Fe–Fe bonds[9] in $Fe_3(CO)_{12}$ (2.69 and 2.68 Å);[2] however, even shorter bridged Fe–Fe bonds have been found for $\{(\pi\text{-}C_5H_5)_2Fe_2(CO)_3\}_2$-DPPA, 2.54 Å (Table V).

The Fe–Fe bond may be considered in valence bond terms as involving overlap of two d^2sp^3 orbitals so that each iron atom attains a "noble gas" configuration. An equally valid description may also be a delocalized system consisting of an electron from each iron atom, the two fluorocyclobutene π electrons, and empty 4d orbitals on the arsenic atoms.

The Fe–As bond lengths averaging to 2.35 Å are internally consistent and are similar to other Fe–As distances quoted in Table V.

There is no crystallographic or molecular symmetry imposed on the molecule. The fluorocyclobutene ring is planar with a maximum deviation of 0.028 Å. However, the arsenic atoms are asymmetrically displaced from the plane (Table III). The skeletal geometry of the molecule is similar to that of $ffarsFe_2(CO)_6$.[9] The mean Fe–CO length of 1.74 Å and the mean C–O 1.19 Å are similar to the corresponding bonds (1.74 and 1.23 Å) found for $ffarsFe_2(CO)_6$. The Fe(2)–C(12) and Fe(2)–C(13) distances average 2.14 Å which is considerably longer than the value of 2.04 Å in $ffarsFe_2(CO)_6$. Since the C(12)–Fe(2)–C(13) angle is only 39°, it is best to describe this system in terms of π bonding. The distance from Fe(2) to the midpoint of C(12)–C(13) is 2.00 (2) Å while the corresponding value in $ffarsFe_2(CO)_6$, where π bonding has also been invoked, is 1.90 Å. The mean As–CH_3 length is 1.95 Å and the arsenic–ring carbon distance is 1.88 (2) Å which might be compared to values of 1.95 and 1.91 Å, respectively, in $ffarsFe_2(CO)_6$. The C—C distance of 1.53 Å and the C=C length of 1.44 (3) Å may be compared to 1.54 and 1.51 Å in $ffarsFe_2(CO)_6$; all these values are consistent with a slightly weaker π bond in $(As(CH_3)_2)C{=}CCF_2CF_2\{(As(CH_3)_2)Fe_3(CO)_9\}$.

All the intermolecular contacts in Table II correspond to van der Waals interactions; most of the shorter contacts involve F · · · O or O · · · O contacts.

The formation of the compound $(As(CH_3)_2)C{=}CCF_2CF_2\{(As(CH_3)_2)Fe_3(CO)_9\}$ has involved the breakage of a nominally strong As—C bond[16] and resulted in formation of Fe—As and Fe—C σ bonds. As noted by Cullen and coworkers,[6] such fragmentations are more common than had previously been expected. The compound formerly thought to be $\{(diars)_3Ni\}\{ClO_4\}_2$ was shown to have rearranged and is $\{(diars)(triars)Ni\}(ClO_4)_2$[17] [diars = *o*-phenylenebis(dimethylarsine), triars = bis(*o*-dimethylarsinophenyl)methylarsine]. Cullen and coworkers have also reported the apparent rearrangement of diars during its reaction with iron carbonyls.[18]

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(16) Compare to a slightly longer As–C bond length of 1.96 (5) Å in tri(*p*-tolyl)arsenic: J. Trotter, *Can. J. Chem.*, **41**, 14 (1963).

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