X-Ray Structure Determination of a New Metal Cluster Complex: Di-μ_3-arsino-tris(tricarbonyliron)(3*Fe*–*Fe*)

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Arsenic trifluoride and iron pentacarbonyl react at 120 °C to give dark violet crystals of $As_2[Fe(CO)_3]_3$ with orthorhombic symmetry, space group *Bmmb*, cell dimensions a_0 = 10·82(2), b_0 = 10·96(2), and c_0 = 13·29(2) Å, and Z = 4.

The structure was solved from photographic data by three-dimensional Patterson and Fourier methods and refined by least squares methods to *R* 0·107 for 630 independent reflections. The structure is disordered with one molecule randomly distributed in two orientations which are related by a crystallographic two-fold rotation axis. The idealized molecular symmetry is 3/*m* (C_{3h}). The molecule is characterized by an equilateral triangle of iron atoms, mean Fe–Fe 2·62(1) Å. The two arsenic atoms lie above and below the iron triangle, and are related by a mirror plane containing the iron atoms. Both arsenic atoms are bonded equally to the iron triangle, mean As–Fe 2·35 Å. Other mean bond lengths: Fe–C 1·80, C–O 1·12 Å.

THE ability of trifluorophosphine to function as a π-acceptor in transition-metal complexes has been well documented,[1] but the analogous trifluoroarsine complexes have only been isolated.[2] This fact can be explained by the added reactivity of the As–F over the P–F bond, resulting in oxidative addition and preventing isolation of complexes where AsF_3 acts in a donor–acceptor capacity. The only AsF_3 complex so far reported is $(\pi\text{-}C_5H_5)Mn(CO)_2(AsF_3)$, formed[2] by substitution of C_7H_{12} from $(\pi\text{-}C_5H_5)Mn(CO)_2(C_7H_{12})$ under mild conditions. The reactivity of complexed AsF_3 was demonstrated by the easy alcoholysis to give $(\pi\text{-}C_5H_5)Mn(CO)_2AsF_2(OEt)$.

The title compound is a member of a growing class of Group VB-metal cluster complexes, including $As_2[Co(CO)_3]_2$[3] and $As_3Co(CO)_3$,[4] both of which are derived from As_4 by successive substitution of arsenic by isoelectronic $Co(CO)_3$ moieties. More recently, a triply-bridging Group VB complex, $Sb_4[Co(CO)_3]_4$ has been isolated.[5] The present work illustrates that arsenic, like antimony, can function as a triply-bridging species. The methylimino-complex $(MeN)_2Fe_3(CO)_9$[6] is not isostructural with $As_2[Fe(CO)_3]_3$, since the methylimino-group functions as a four-electron source, forcing one Fe–Fe non-bonded separation. In $As_2[Fe(CO)_3]_3$ arsenic acts as a three-electron donor; this requires three Fe–Fe bonds, as shown by the *X*-ray structure determination, to satisfy the EAN rule.

EXPERIMENTAL

Preparation. Trifluoroarsine (0·151 mol, 8 ml), iron carbonyl (0·151 mol, 20 ml), and benzene (10 ml) were placed in a 75 ml stainless steel bomb and heated for 20 h at 125 ± 5 °C. After the carbon monoxide was vented, benzene, unreacted AsF_3, and $Fe(CO)_5$ were pumped out of the bomb under high vacuum. The black amorphous residue remaining in the bomb was leached with light petroleum (50 ml). The wine coloured solution was then passed through a short fluorisil column to remove ionic material, evaporated to 3 ml, and allowed to crystallize at −10 °C. The well formed violet-black crystals (*ca.* 60 mg) could be sublimed (0·05 Torr, 105 °C), but decompose >150°. Found: C, 19·1; As, 26·4; Fe, 29·2. $C_9As_2Fe_3O_9$ requires C, 19·0; As, 26·3; Fe, 29·4%.

Mass Spectrum.—The mass spectrum was obtained at an ionizing voltage of 70 eV on a Hitachi–Perkin-Elmer RMU 6 D, by utilizing the solid inlet system. Successive loss of nine CO groups (*m*/*e* 28) resulted in the base peak (*I* 100) at *m*/*e* 318 (corresponding to $As_2Fe_3^+$), followed by fragmentation of this cluster to form $As_2Fe_2^+$ (*I* 84), As_2Fe^+ (*I* 23) and $AsFe_2^+$ (*I* 21).

I.r. Spectrum.—A methylcyclohexane solution of $As_2[Fe(CO)_3]_3$ has three bands in the carbonyl stretch region at 2035·2s, 2004·9m, and 1994·3w cm^{-1}.

Crystal Data.—$C_9O_9As_2Fe_3$, M = 569·5, Orthorhombic, a = 10·82(2), b = 10·96(2), c = 13·29(2), U = 1576·0 Å^3, D_m = 2·33, Z = 4, D_c = 2·40, $F(000)$ = 1080. Mo-K_α radiation, λ = 0·7107 Å, μ = 72 cm^{-1}. Space group $Bm2_1b$ (equivalent to $Cmc2_1$, No. 36), *B2mb* (equivalent to *Ama*2, No. 40), or *Bmmb* (equivalent to *Cmcm*, No. 63). The correct space group proved to be *Bmmb* which has the equivalent positions (x, y, z), $(x, -y, -z)$, $(x, \frac{1}{2}-y, z)$, $(x, \frac{1}{2}+y, -z)$, $(-x, -y, -z)$, $(-x, y, z)$, $(-x, \frac{1}{2}+y, -z)$, $(-x, \frac{1}{2}-y, z)$. The crystal outlined the form $\{111\}$.

Intensity Data.—Cell dimensions were measured from Weissenberg photographs. Equi-inclination Weissenberg photographs of the 0—10*hkl* levels of a single crystal (0·2 × 0·2 × 0·3 mm) were recorded by the triple-film pack technique. The intensities of 630 independent reflections were estimated visually by comparison with a calibrated scale. After the Lorentz and polarization factors had been applied, the reflections were initially scaled by time exposure. Near the end of the refinement a rescale factor for each layer was calculated by a least-squares fit. No absorption corrections were made.

Structure Determination.—An outstanding feature of the 0*kl* precession photograph is the pseudo-trigonal (or hexagonal) pattern consisting of six intense reflections (024, $02\bar{4}$, $0\bar{4}0$, 040, $0\bar{2}\bar{4}$, and $0\bar{2}4$). If the structure contained a triangle of iron atoms, this pseudo-trigonal pattern suggests that the triangle is perpendicular to the *a* axis. A series of Patterson sections parallel to (100) were computed.

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[4] A. S. Foust, M. S. Foster, L. F. Dahl, *J. Amer. Chem. Soc.*, 1969, **91**, 5631.

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From an interpretation of the As · · · As vectors, the arsenic atoms in one molecule were located at (0·166, 0·25, 0·25) and (−0·166, 0·25, 0·25). An unsuccessful attempt was made to locate the positions of all Fe · · · As or Fe · · · Fe vector peaks. The arsenic atoms alone were then used to determine the phase angles for the first electron-density map in space group $Bm2_1b$. The positions of the arsenic atoms generate centres of symmetry and mirror planes (at $Y = \frac{1}{4}, \frac{3}{4}$ and $Z = \frac{1}{4}, \frac{3}{4}$) in addition to the symmetry elements of space group $Bm2_1b$. Aside from the arsenic peaks, the strongest electron density peaks on this map occurred on the mirror plane at $X = 0$; this indicated that the iron atoms are in this plane. Since the expected Fe–Fe bond distance was *ca.* 2·6 Å, the arrangement of peaks could only be interpreted in terms of a molecule with three iron atoms at the apices of an equilateral triangle. This agrees with the pseudo-trigonal pattern occurring on the $0kl$ level.

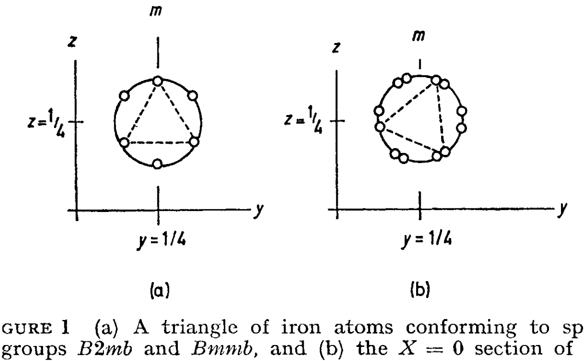

FIGURE 1 (a) A triangle of iron atoms conforming to space groups *B2mb* and *Bmmb*, and (b) the $X = 0$ section of the Fourier synthesis with only the arsenic atoms used as a phasing model

For a single molecule to conform to the symmetry requirements of space group *B2mb* or *Bmmb*, one iron atom must be on the mirror plane at $Y = \frac{1}{4}$ and the other two must be related by this mirror plane. The false symmetry elements present in the first electron-density map would generate peaks additional to those of this triangle of iron atoms [Figure 1(a)]. Two of these six peaks must occur at $Y = \frac{1}{4}$. The strong peaks which were actually observed on the mirror plane at $X = 0$ on this first electron density map are shown in Figure 1(b). None of these strong peaks occurred on the mirror plane at $Y = \frac{1}{4}$. Therefore, a single molecule of $As_2[Fe(CO)_3]_3$ could be interpreted from this map as conforming to only space group $Bm2_1b$. From an examination of the positions of these peaks and from the expected Fe–Fe distances, only one choice existed for the positions of the iron atoms.

A second electron-density map was calculated with the phase angles based on both the arsenic atoms and these iron atoms. The map which was obtained showed an unsymmetrical distribution of electron density about the iron atoms. The peak shape suggested an overlap of each iron peak with another strong peak, *i.e.* there appeared to be a statistical distribution of two iron atom triangles. Aside from this, an attempt to locate the carbonyl groups was made. Three terminal carbonyl groups are expected for each iron atom in the molecule. For the carbonyl groups to conform to space group $Bm2_1b$, one carbonyl bonded to each iron must be in the mirror plane at $X = 0$. The remaining two carbonyl groups of each iron atom must be related by this mirror plane. A consideration of intermolecular steric requirements and peak positions on the second electron-density map led to only one set of carbonyl groups. Least-squares refinement of all atoms in the space group $Bm2_1b$ resulted in R 0·242.

As indicated earlier, the crystals are pseudo-tetragonal in shape, and appear to have a centre of symmetry. *Bmmb* is the only possible centrosymmetric space group. The electron-density map phased only on arsenic atoms indicated that the molecule did not conform to this space group, nor to the non-centrosymmetric *B2mb*. As a result, the non-centrosymmetric space group $Bm2_1b$ was initially, and unsuccessfully, used. In order to assess the indicated possibility of the statistical occurrence of two different orientations of the iron triangle, a third electron-density map was computed in the centrosymmetric space group *Bmmb* with phase angles determined by the arsenic and iron atoms. The atomic positions corresponding to each orientation were assigned an occupancy of one-half, and the two orientations were related by the two-fold axis at $X = 0$, $Y = \frac{1}{4}$ or by the mirror plane at $Y = \frac{1}{4}$. This arrangement of atoms and half-atoms is consistent with the strong peaks on the mirror plane at $X = 0$ for the initial electron-density map [Figure 1(b)]. The third electron-density map revealed the positions of the carbonyl groups. The two iron triangle orientations result in only small changes in the two corresponding carbonyl groups (Figure 2). Least-squares refinement indicated that some carbon and oxygen atoms were best considered as coincident in the two sets of carbonyl groups, *e.g.* C(5) and O(2) in Figure 2. Refinement of the atomic positions and anisotropic thermal parameters produced R 0·107. The final atomic parameters are given in Table 1. Unit weights were employed for all reflections until the last cycle of refinement where $w = \dfrac{1}{(1 + 0{\cdot}169|F_o|)^2}$

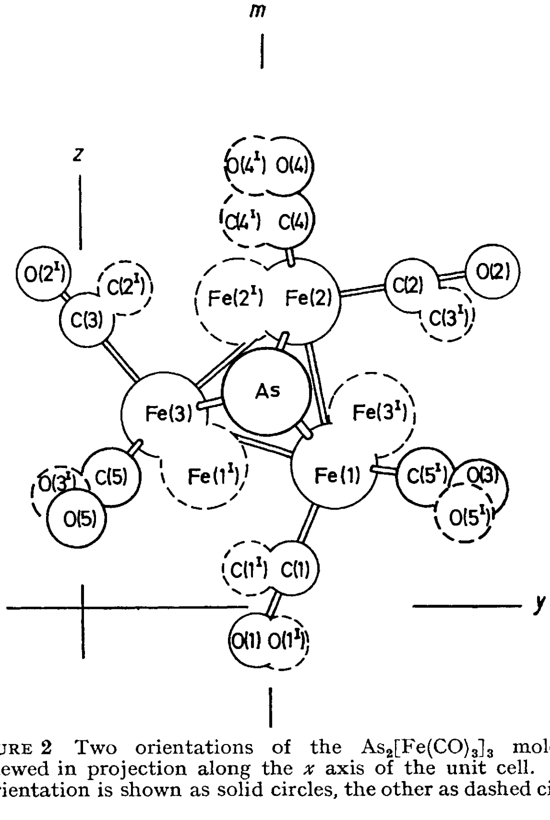

FIGURE 2 Two orientations of the $As_2[Fe(CO)_3]_3$ molecule viewed in projection along the x axis of the unit cell. One orientation is shown as solid circles, the other as dashed circles

TABLE 1

Fractional co-ordinates and thermal parameters with estimated standard deviations in parentheses

Atom	X	Y	Z
As	0·1659(2)	0·25	0·2451(1)
Fe(1) *	0	0·3394(4)	0·1608(3)
Fe(2) *	0	0·2869(4)	0·3536(3)
Fe(3) *	0	0·1116(4)	0·2186(4)
O(1) *	0	0·2349(98)	−0·0401(20)
O(2) *	0	0·5494(18)	0·3868(15)
O(3) *	0·1907(37)	0·5314(19)	0·1341(19)
O(4) *	0·1946(22)	0·2686(21)	0·5058(14)
O(5) *	0·1992(24)	−0·0057(18)	0·1027(14)
C(1) *	0	0·2783(21)	0·1445(29)
C(2) *	0	0·4437(24)	0·3715(25)
C(3) *	0	0·0092(40)	0·3334(27)
C(4) *	0·1212(29)	0·2712(14)	0·4474(23)
C(5)	0·1187(18)	0·0398(16)	0·1464(11)

* These atoms have an occupation factor of 0·5.

Anisotropic thermal parameters $(\text{Å}^2 \times 10^3)$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As	10	50	37	0	0	0
Fe(1)	16	33	30	0	0	0
Fe(2)	12	42	32	−6	0	0
Fe(3)	15	35	38	−9	0	0
O(1)	164	75	29	33	0	0
O(2)	151	61	65	−43	0	0
O(3)	181	37	69	−42	98	−54
O(4)	30	44	65	−23	−25	12
O(5)	48	50	29	23	23	19
C(1)	108	0	41	11	0	0
C(2)	56	16	37	6	0	0
C(3)	23	56	36	−5	0	0
C(4)	37	0	75	3	20	3
C(5)	49	69	47	−25	0	16

TABLE 2

(*a*) Bond distances (Å) with estimated standard deviations in parentheses

As–Fe(1)	2·331(3)	Fe(1)–Fe(2)	2·626(6)
As–Fe(2)	2·338(3)	Fe(1)–Fe(3)	2·612(7)
As–Fe(3)	2·376(3)	Fe(2)–Fe(3)	2·630(7)
Mean As–Fe	2·348(2)	Mean Fe–Fe	2·623(4)
Fe(1)–C(1)	1·69(4)	C(1)–O(1)	1·22(6)
Fe(1)–C(5$^{\mathrm{I}}$)	1·85(2)	C(2)–O(2)	1·18(3)
Fe(2)–C(2)	1·73(3)	C(3)–O(2$^{\mathrm{I}}$)	0·96(4)
Fe(2)–C(4)	1·82(3)	C(4)–O(4)	1·11(4)
Fe(3)–C(3)	1·89(4)	C(5)–O(5)	1·16(3)
Fe(3)–C(5)	1·79(2)	C(5$^{\mathrm{I}}$)–O(3)	1·12(4)
Mean Fe–C	1·80(1)	Mean C–O	1·12(2)

(*b*) Bond angles (deg.) with estimated standard deviations in parentheses

Fe(1)–As–Fe(2)	68·4(1)	Fe(1)–Fe(2)–Fe(3)	59·6(1)
Fe(1)–As–Fe(3)	67·4(1)	Fe(1)–Fe(3)–Fe(2)	60·1(1)
Fe(2)–As–Fe(3)	67·8(1)	Fe(2)–Fe(1)–Fe(3)	60·3(1)
Mean Fe–As–Fe	67·9(1)	Mean Fe–Fe–Fe	60·0(1)
C(1)–Fe–C(5$^{\mathrm{I}}$)	100·8(10)	Fe–C(1)–O(1)	179·6(36)
C(5-)–Fe(1)–C(5$^{\mathrm{III}}$)	87·6(8)	Fe(1)–C(5$^{\mathrm{I}}$)–O(3)	177·4(21)
C(2)–Fe(2)–C(4)	90·0(12)	Fe(2)–C(2)–O(2)	177·9(22)
C(4)–Fe(2)–C(4$^{\mathrm{III}}$)	92·4(12)	Fe(2)–C(4)–O(4)	176·0(25)
C(3)–Fe(3)–C(5)	99·9(12)	Fe(3)–C(3)–O(2$^{\mathrm{I}}$)	174·2(31)
C(5)–Fe(3)–C(5$^{\mathrm{II}}$)	91·9(8)	Fe(3)–C(5)–O(5)	177·1(18)
Mean C–Fe–C	94·8(4)	Mean Fe–C–O	177·0(11)

(*c*) Interatomic contacts (Å)

O(4) ··· O(5$^{\mathrm{IV}}$)	3·09(3)	O(4) ··· O(3$^{\mathrm{VI}}$)	3·13(3)
O(4) ··· O(5$^{\mathrm{V}}$)	3·12(3)		

Roman numerals as superscripts refer to atoms in the following equivalent positions relative to the reference molecule:

I $x, \frac{1}{2} - y, z$	IV $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
II $-x, y, z$	V $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$
III $-x, \frac{1}{2} - y, z$	VI $\frac{1}{2} - x, 1 - y, \frac{1}{2} - z$

was used. The 024 and 040 reflections were affected by extinction and were thus removed. In the final cycle, the maximum and mean positional parameters shifted by $<0{\cdot}3$ and $<0{\cdot}1\sigma$. A difference-Fourier synthesis, carried out for the last cycle of refinement, showed nothing significant. Computations were carried out on an IBM 360 65 computer using the N.R.C. Crystallographic Programs of Dr. F. R. Ahmed. A full-matrix conversion of the least-squares program was employed for refinement.*

RESULTS AND DISCUSSION

This crystal structure analysis reveals the presence of two orientations (each with one-half occupancy) of a molecule of $As_2[Fe(CO)_3]_3$ distributed equally and randomly throughout the crystal. A projection of the two orientations of the molecule viewed along the x axis of the unit cell is shown in Figure 2. The complete molecule is generated by reflection of the atoms listed in Table 1 through the mirror plane at $X = 0$. The second orientation of the molecule is generated by rotation about the two-fold axis at $X = 0$, $Y = \frac{1}{4}$ (or by a reflection through the mirror plane at $Y = \frac{1}{4}$).

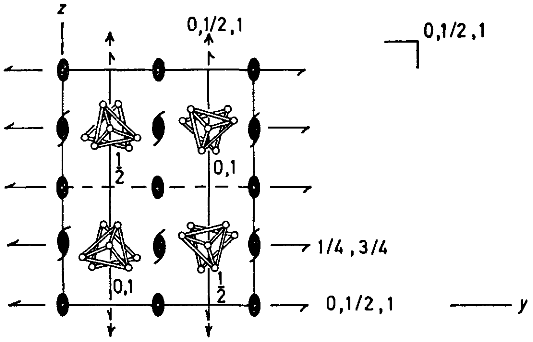

FIGURE 3 Projection along the x axis of the unit cell with only the arsenic and iron atoms of the two orientations shown

The presence of two molecular orientations can be illustrated by an examination of the outer portion, namely the oxygen atoms. The nine oxygen atoms are nearly coincident in both orientations (see Figure 2). The placing of one molecule in either orientation in the unit cell makes little difference sterically to the placing of the next molecule, resulting in random packing.

The statistically disordered crystal structure of $As_2[Fe(CO)_3]_3$ is similar in some respects to that of $Fe_3(CO)_{12}$,[7] where the random distribution of molecules in the unit cell is related by a crystallographic centre of symmetry. The smallest intermolecular separation in $As_2[Fe(CO)_3]_3$ is 3·1 Å; that in $Fe_3(CO)_{12}$ is 3·0 Å (both between oxygen atoms).

Figure 3 shows a projection of the unit cell along the x axis, illustrating the placement of As and Fe atoms in

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* Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20549 (4 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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

the two orientations. Figures 2 and 4 illustrate that the idealized molecular symmetry is $3/m$ (C_{3h}).

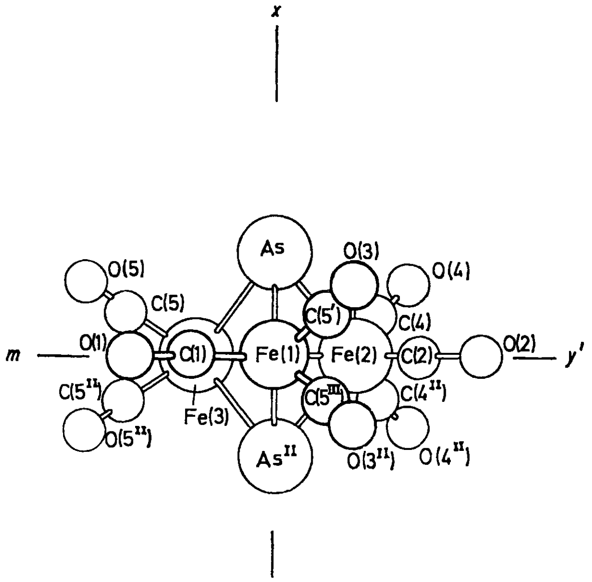

FIGURE 4 Projection of the molecule along the line in common with the $X = 0$ plane and As, Fe(1), and As^{II}

The mean Fe–Fe distance remains relatively constant within a series of tri-iron clusters: 2·62 in $As_2[Fe(CO)_3]_3$, 2·63 in $Fe_3(CO)_{12}$,[7] and 2·62 Å in $HFe_3(CO)_{11}^-$.[8] The insensitivity of intermetallic separations to the nature of the binding ligands has been rationalized in terms of a qualitative molecular orbital treatment.[9] If it is considered that each arsenic atom possesses a non-bonded electron-pair directed outward along the three-fold axis of the cluster, then 6 of the 30 tri-iron valence electrons will be used to form six As–Fe σ bonds. Dahl *et al.*[9] have shown that the remaining 24 tri-iron valence electrons can be accommodated in bonding MO's delocalized about the cluster. The presence of exactly 24 valence electrons, rather than the nature of the substituent ligands, will be the factor determining the strength of metal–metal bonding within the cluster. All the aforementioned tri-iron clusters possess this 24 electron structure, and hence are expected to have similar intermetallic bond lengths.

Three crystallographically different As–Fe bond lengths were determined in the crystal structure of $AsMe_2\cdot\overline{C{:}C\cdot CF_2\cdot C}F_2\cdot[AsMe_2Fe_3(CO)_9]$,[10] ranging from 2·32—2·37 Å, but their mean, 2·35 Å, is identical with that found in the present work.

The present work allows some speculation to be made on the structure of $As_2Fe(CO)_{11}$, a brown crystalline paramagnetic material prepared[11] from the reaction of $AsCl_3$ with $Fe(CO)_4^{2-}$. $As_2Fe_3(CO)_{11}$ is likely to be related to $As_2[Fe(CO)_3]_3$ by the insertion of two carbonyl groups in either terminal or bridging positions in the $As_2[Fe(CO)_3]_3$ cluster (the i.r. spectrum of $As_2Fe_3(CO)_{11}$ has not been reported).

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