The Crystal Structure of $[Fe(CO)_3]_2(AsCH_3)_4$; a Compound with a Noncyclic Tetramethyltetra-arsine Ligand

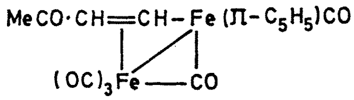
By B. M. GATEHOUSE†

(*Crystallography Lab., University of Pittsburgh, Pittsburgh, Pennsylvania* 15213)

Summary The determination of the crystal structure of $[Fe(CO)_3]_2(AsCH_3)_4$ has confirmed the noncyclic nature of the ligand in this molecule.

CYCLIC polyphosphines have been reported[1] to react with chromium, molybdenum, and tungsten hexacarbonyls, or related substituted carbonyls,[2] to give complexes in which the phosphine ring is still intact, as shown by mass spectral[1] and *X*-ray[3] structural studies. Both cyclic penta-phosphines[1] and -arsines,[4] however, react with $Fe(CO)_5$ to give compounds of empirical formula $[Fe(CO)_3]_2[P(\text{or As})R]_4$, the mass spectra of which do not show individual $[P(\text{or As})R]^+_4$ species.

TABLE

Compound	Fe–Fe	Fe–As	As–As	As–C	Fe–C	C–O	Ref.
$(AsCH_3)_5$			2·428	1·95			5
$(AsC_6H_5)_6$			2·456	1·97			6
$(As_6)_\infty$			2·51				6
As_4			2·44				6
$MeC{=}CMe{\cdot}H_2Fe_2(CO)_8$	2·49				2·13 1·95 1·78	1·14	7
$Me_2AsC{=}C(AsMe_2)CF_2{\cdot}CF_2[Fe(CO)_3]_2$ ..	2·88	2·47 2·35		1·95	1·74	1·23	8
	2·556				1·79	1·16	9
$[Fe(CO)_3]_2(AsCH_3)_4$	2·680	2·336 2·311	2·453 $\begin{bmatrix}1\text{–}2\\3\text{–}4\end{bmatrix}$ [a] 2·391 (2–3) 2·888 (1–4)	1·97	1·76	1·13	This work

All distances in Å.
[a] See Figure.

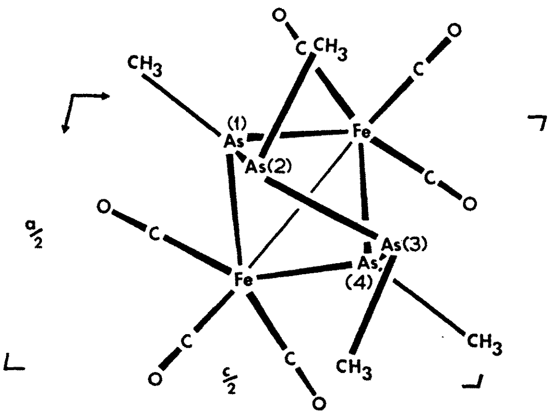


FIGURE. *The* $[Fe(CO)_3]_2(AsCH_3)_4$ *molecule viewed down the* b *axis.*

The structure of $[Fe(CO)_3]_2(AsCH_3)_4$ has been determined, establishing the presence of two arsenido-bridges in the molecule and confirming the absence of a cyclic arsine ligand.

$[Fe(CO)_3]_2(AsCH_3)_4$ crystallises‡ in the space group $P2_1/c$, with a unit cell, $a = 8{\cdot}03$, $b = 17{\cdot}62$, $c = 13{\cdot}71$ Å and $\beta = 101{\cdot}0°$; $D_m = 2{\cdot}21$, for $Z = 4$, $D_c = 2{\cdot}23$ g. cm.$^{-3}$. A total of 1048 independent reflections obtained with a Weissenberg camera and Cu-K_α radiation, were used in the structural determination. The initial parameters for the Fe and As atoms were obtained by direct methods of phase determination, and the remaining atoms, with the exception of hydrogen, were located by the usual three-dimensional Fourier methods. Full-matrix least-squares refinement of the structure with individual isotropic temperature factors has reduced the reliability index to a present value of 0·090.

The structure is shown in the Figure (010 projection) and consists of three different levels of heavy atoms. The lowest contains the two Fe atoms, the next As(1) and As(4) and the uppermost As(2) and As(3). The mean distances in the molecule are set out in the Table together with other compounds having cyclic arsenic systems or iron–iron interactions for comparison.

It is clear that in the compound reported here we have (i) a non-cyclic tetramethyltetra-arsine ligand, the nearest approach of As(1) to As(4) being 2·888 Å, and (ii) iron–iron

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† On study leave from Monash University, Clayton, Vic. 3168, Australia.

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interaction, the bond length of 2·680 Å being consistent with previously reported distances, and supporting the observation that this compound is diamagnetic.[10] The Fe–C–O groups are all very nearly linear, the Fe–C and C–O bond lengths being similar to those previously reported for a variety of compounds. The e.s.ds at present are ±0·007 Å for heavy-atom distances, ±0·04 Å for Fe–C and As–C, and ±0·05 Å for the C–O bond lengths. It is interesting to note the two apparently significantly different Fe–As distances, and the two As–As bonded distances.

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