X-Ray Determination of the Structure of $Fe(CO)_4(AsC_6F_5)_2$, a Complex containing "Decafluoro-arsenobenzene"

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Summary Tetrakispentafluorophenylcyclotetra-arsine reacts with $Fe(CO)_5$ giving $Fe(CO)_4(AsC_6F_5)_2$, in which the molecule $(AsC_6F_5)_2$ contains an As–As linkage and is bonded by each As atom to Fe; $(PC_6F_5)_4$, however, yields $Fe_3(CO)_9(PC_6F_5)_2$ and traces of $[Fe(CO)_3]_2(PC_6F_5)_4$ under similar conditions.

There have been no previous reports of stable P or As compounds $[RP(As)]_2$ analogous to azo-derivatives.[1] Reactions likely to produce such compounds give cyclic derivatives containing 4-, 5-, or 6-membered P or As rings. We have now prepared $Fe(CO)_4(AsC_6F_5)_2$ in which the molecule $(AsC_6F_5)_2$ contains an As–As bond and is further stabilized by bonding of each As atom to Fe. The parent arsine may be considered to be "decafluoro-arsenobenzene," an analogue of azobenzene.

Tetrakis(pentafluorophenyl)cyclotetra-arsine[2] reacts with pentacarbonyliron in benzene (120°; 15 h or u.v. irradiation; *ca.* 60°; 4 h) to form $Fe(CO)_4(AsC_6F_5)_2$ (yellow plates from acetone, m.p. 149—150°). The mass spectrum of the compound shows a parent ion at *m/e* 652; ions corresponding to $Fe(CO)_2(AsC_6F_5)_2^+$ (*m/e* 596), $Fe(CO)(AsC_6F_5)_2^+$ (568), $Fe(AsC_6F_5)_2^+$ (540), and $FeAs_2^+$ (206) can also be distinguished. The ^{19}F n.m.r. spectrum shows *ortho-*, *meta-*, and *para*-resonances centred at 117·9, 159·2 and 150·7 p.p.m., respectively, ($CFCl_3$ external ref.). CO stretching frequencies occur in the i.r. spectrum at 2098(s), 2050(s), and 2030(vs) cm^{-1} ($CHCl_3$).

$Fe(CO)_4(AsC_6F_5)_2$ crystallises in the space group $C2/c$; $a = 23{\cdot}27$, $b = 7{\cdot}79$, $c = 11{\cdot}58$ Å; $\beta = 111{\cdot}5°$; $Z = 4$, $D_c = 2{\cdot}22$ g cm^{-3}, D_m 2·17—2·28 g cm^{-3} (the exact density was difficult to determine). The structure analysis was based on 725 visually estimated, independent reflections obtained with a Weissenberg camera using Fe-K_α radiation. The structure was solved by three dimensional Patterson and Fourier methods and refined by least-squares analysis to $R = 0{\cdot}13$. The isotropic thermal parameters of all the pentafluorophenyl atoms are high (average B is 6·6 Å^2 for carbon and 10·5 Å^2 for fluorine), but are apparently typical for compounds containing the C_6F_5 group.[3,4] The structure (Figure) consists of a distorted octahedral arrangement of ligands about the central iron atom. The molecule possesses C_2 symmetry with the iron atom sited on the two-fold axis. Bond distances and angles for the co-ordinating atoms are given in the Table. The As–As distance of 2·388(7) Å is significantly shorter than the As–As distances in the cyclic arsines $(AsMe)_5$[5] [2·428(8) Å] and $(AsPh)_6$[6] [2·456(5) Å] but is considerably longer than the As–As "double bond" of 2·273(3) Å found in $As_2Co_2(CO)_5PPh_3$.[7]

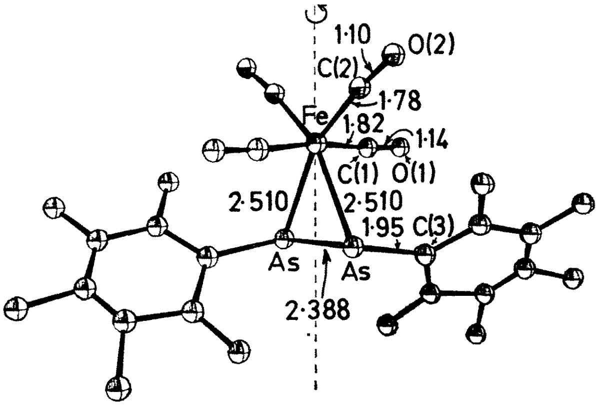


FIGURE. *Molecular structure of* $Fe(CO)_4(AsC_6F_5)_2$. *The position of the two-fold axis is shown by a broken line, and bond lengths are in* Å.

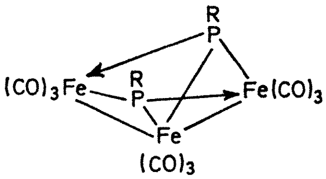
TABLE

Intramolecular bond distances (Å) *and angles* (°) *of* $Fe(CO)_4(AsC_6F_5)_2$

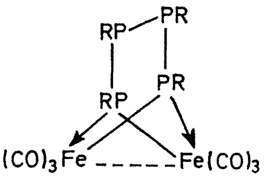
Fe–As ..	2·510(9)	As(1)–Fe–As(2)	56·8(0·3)
Fe–C(1) ..	1·82(4)	Fe–As(1)–As(2)	61·6(0·1)
Fe–C(2) ..	1·78(4)	Fe–As–C(3)	101·7(1·1)
C(1)–O(1)	1·14(4)	Fe–C(1)–O(1)	173·7(0·6)
C(2)–O(2)	1·10(4)	Fe–C(2)–O(2)	173·5(0·7)
As–As ..	2·388(7)		
As–C(3) ..	1·95(3)		

The arsenic–pentafluorophenyl bond length is 1·95(3) Å. The eleven atoms of the pentafluorophenyl group are planar within experimental error. Mean distances within this ligand are; C–C, 1·34(5) Å, C–F, 1·39(5) Å. Angles within the ring vary from 111·9 to 125.9°, average value 119·9°.

In contrast to the arsine reaction, $(PC_6F_5)_4$[8] reacts with $Fe(CO)_5$ (160°; 24 h) to yield $Fe_3(CO)_9(PC_6F_5)_2$ and traces of $Fe_2(CO)_6(PC_6F_5)_4$. The compounds were characterized by their mass spectra: $Fe_3(CO)_9(PC_6F_5)_2$; parent ion at *m/e* 816 which decomposes by loss of 9 CO groups to $Fe_3(PC_6F_5)_2^+$; $Fe_2(CO)_6(PC_6F_5)_4$; parent ion at *m/e* 1072 which decomposes by loss of 6 CO groups to form $Fe_2(PC_6F_5)_4^+$. The i.r. spectra (chloroform) of these compounds contain no peaks in the bridging carbonyl stretching region [$Fe_3(CO)_9(PC_6F_5)_2$ 2060(s), 2040(s), and 2020br (m) cm^{-1}; $Fe_2(CO)_6(PC_6F_5)_4$ 2075(s), 2045(s), 2015(s), and 2010(sh) cm^{-1}]. Consideration of possible structures and application of the EAN rule appears to rule out the existence of a "phosphorobenzene" analogue in $Fe_3(CO)_9(PC_6F_5)_2$ and (A) is suggested as a plausible structure.



(A)



(B)

$Fe_2(CO)_6(PC_6F_5)_4$ appears to be a similar compound to those previously obtained with other cyclic phosphines[9] and with $(AsMe)_5$[10] and hence to contain a bridging chain of P atoms (B).

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