Metal–Metal Bonding in Co-ordination Complexes. Part XII.[1] Crystal Structure of Tetracarbonyl(triphenylstibine)iron

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The title compound crystallizes in the triclinic space group $P\bar{1}$, with Z = 2 in a unit cell with a = 10·557(1), b = 10·043(1), c = 11·230(1) Å, α = 114·22(1), β = 91·95(1), γ = 92·25(1)°. The structure was solved by the heavy-atom method, from 3217 independent reflections measured by counter diffractometry. Refinement by least-squares methods gave R 0·024.

To a good approximation the molecule has C_3 symmetry with the Ph_3Sb ligand occupying an axial position in the trigonal-bipyramidal co-ordination sphere of the iron atom; Sb–Fe 2·472(1) Å. Mean Fe–C(eq) is 1·787(5), Fe–C(ax) 1·765(5) Å, indicating a slight *trans*-effect. The equatorial angles at Fe are 117·7, 118·7, and 123·4(2)° and the mean Sb–Fe–C(eq) angle is 88·3(1)°. Antimony is tetrahedrally co-ordinated, mean Sb–C 2·125(3) Å. Mean Fe–Sb–C and C–Sb–C angles are 116·4(1) and 101·8(2)°, indicating an enhanced *s* character in the Sb–Fe relative to the Sb–C bonds.

As a continuation of our studies of mixed-metal bonding[2] we have determined the structure of $Ph_3SbFe(CO)_4$ in order to obtain an accurate measure of the Sb–Fe bond distance, and by examination of the pattern of valence angles at the antimony atom to evaluate the character of the metal–metal bond.

EXPERIMENTAL

Crystals of the compound are air-stable yellow prisms.

Crystal Data.—$C_{22}H_{15}FeO_4Sb$, M = 521, Triclinic, a = 10·557(1), b = 10·043(1), c = 11·230(1) Å, α = 114·22(1), β = 91·95(1), γ = 92·25(1)°, U = 1083 Å^3, D_m = 1·60 (pycnometer, ZnI_2), Z = 2, D_c = 1·596(5), $F(000)$ = 512. Space group $P\bar{1}$, no molecular symmetry implied. Mo-K_α radiation, λ = 0·71069 Å; μ(Mo-K_α) 20 cm^{-1}.

Unit-cell parameters were obtained by a least-squares fit to the observed diffractometer values of $\pm 2\theta$ for 24 strong general reflections.

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Intensity Measurements.—These were made, by diffractometry, from a crystal of dimensions $0{\cdot}5 \times 0{\cdot}5 \times 0{\cdot}25$ mm using techniques previously described in detail.[3] Monochromatic Mo-K_α radiation was used to survey some 6100 reciprocal lattice points in the range $2\theta \leqslant 60°$, and scattered intensity significantly above background was measured at 5198 locations. To yield an adequate ratio of observations to parameters, but also to provide a manageable set of observations, the 3217 reflections with $|F_0| > 10{\cdot}5$ on an absolute scale were used in the actual structure determination and refinement. Absorption corrections were applied to the intensity measurements and the stability of the experimental conditions allowed use of a single scale factor.

Structure Determination and Refinement.—The structure was solved in a routine manner by application of the heavy-atom method (R 0·18).

Refinement of the atomic parameters was carried out by use of the block-diagonal least-squares approximation. With isotropic thermal parameters assumed, convergence was reached with R 0·067, and with anisotropic thermal parameters at R 0·037. Fourteen of the 15 hydrogen atoms in the molecule were clearly visible in a three-dimensional difference electron-density map calculated at this stage. All hydrogen atoms were included in the refinement with fixed parameters, assuming C–H 1·08 Å, and with the isotropic thermal parameter of the carbon atom to which each is attached. At convergence R was 0·024, R' 0·032, for the 3217 reflections used. The ratio of observations to parameters was 13 : 1, and the maximum shift in any parameter in the last cycle of refinement was $< 0{\cdot}15\sigma$.[4] The maximum residual electron density was 0·4 eÅ^{-3} at a structurally non-significant site.

Atomic scattering factors for the neutral atoms were taken from ref. 5, with corrections for both real and imaginary components of the anomalous dispersion for antimony and iron taken from ref. 6. The weighting scheme used included allowance for effects of both statistical and non-statistical types.[7] All calculations were carried out on an XDS Sigma 2 computer, also used to control the diffractometer, with programs written in this laboratory.

Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21117 (10 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Atomic parameters are in Table 1, and bond lengths and angles in Table 2. Figure 1 shows a view of the molecular structure, and Figure 2 a projection of the structure viewed down the Sb–Fe bond axis. Selected intra- and inter-molecular contacts are listed in Table 3.

The molecule has effective, but not exact, C_3 symmetry. The iron atom has trigonal-bipyramidal co-ordination with the triphenylstibine ligand in an axial position. The structure thus matches that found for $(Me_3Sb)Fe(CO)_4$ and $(Me_3As)Fe(CO)_4$ where the three-fold symmetry is crystallographically exact.[8] The Sb–Fe bond distance [2·472(1) Å] is comparable to that [2·49(2) Å] reported for the trimethyl analogue and is between that (2·54 Å) for $\{[Fe(C_5H_5)(CO)_2]_3SbCl\}^+$ (ref. 9) and for $\{[Fe(C_5H_5)(CO)_2]_2SbCl_2\}^+$ (2·44 Å).[10]

The co-ordination of the antimony atom is tetrahedral, but with distortions of a type found for Sn–Fe complexes.[2] The three Fe–Sb–C angles agree closely, mean 116·4°; correspondingly, the C–Sb–C angles do not differ significantly from the mean value of 101·8°. The same effect is noted in the trimethyl analogue[8] with Fe–Sb–C 113(3) and C–Sb–C 106(1)°. Related patterns of valence angles are also present in the two cations of refs. 9 and 10. We interpret these values as indicating that the Sb–Fe bond has enhanced *s* character relative to the Sb–C bonds which are of predominantly *p* character, and characterize the Sb–Fe bond as a two-electron σ bond.

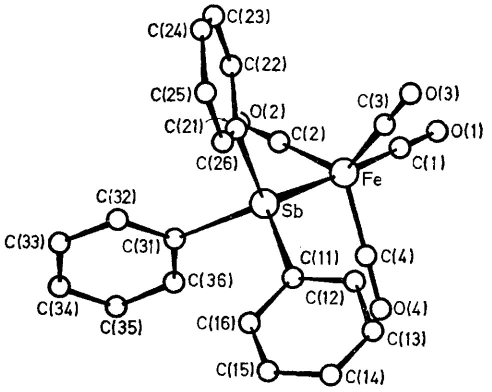

FIGURE 1 View of the molecular structure showing the numbering scheme adopted. Hydrogen atoms are numbered according to the carbon atom to which they are attached

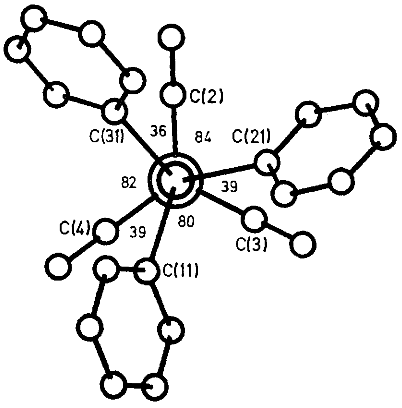

FIGURE 2 Projection of the molecular structure viewed down the Sb–Fe axis and showing the torsion angles (°) between the Sb–C and Fe–C bonds

The extensive discussion in the literature on the relative importance of directional σ bond effects *vs.* d_π–d_π bonding in Sn–Fe systems has been summarized by

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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TABLE 1

Positional parameters (fractional co-ordinates × 10^4, for hydrogen × 10^3), and anisotropic thermal parameters * (× 10^4), with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	7874·5(3)	8636·8(3)	1891·8(3)	73·8(2)	95·9(2)	82·0(2)	0·8(2)	5·4(2)	43·2(2)
Fe	6420·4(5)	7676·9(6)	3071·2(5)	81·3(5)	115·3(7)	85·1(5)	−3·8(5)	9·0(4)	46·8(5)
O(1)	4664(4)	6501(5)	4380(4)	199(6)	253(7)	190(5)	−39(5)	60(4)	107(5)
O(2)	4833(4)	10130(4)	3412(4)	134(4)	188(6)	226(6)	69(4)	31(4)	74(5)
O(3)	6209(4)	4871(4)	769(4)	178(5)	138(4)	153(4)	−14(4)	16(4)	11(4)
O(4)	8464(4)	8152(5)	5052(4)	166(5)	346(9)	142(4)	−39(5)	−53(4)	134(5)
C(1)	5346(5)	6968(5)	3866(5)	127(5)	163(7)	123(5)	−22(5)	15(4)	65(5)
C(2)	5448(4)	9170(5)	3273(5)	97(4)	155(6)	126(5)	8(4)	20(4)	58(5)
C(3)	6290(4)	5975(5)	1662(4)	102(4)	135(6)	122(5)	−10(4)	11(4)	57(4)
C(4)	7672(4)	7979(5)	4275(4)	119(5)	185(7)	101(4)	−13(5)	6(4)	76(5)
C(11)	9789(4)	8047(4)	1855(4)	96(4)	106(4)	90(4)	5(3)	1(3)	37(3)
C(12)	10059(5)	6678(5)	1735(7)	134(6)	129(6)	274(10)	24(5)	19(6)	98(7)
C(13)	11324(6)	6306(7)	1690(8)	164(8)	173(8)	305(13)	66(7)	20(8)	96(9)
C(14)	12270(5)	7285(7)	1798(6)	102(5)	248(10)	180(8)	42(6)	1(5)	41(7)
C(15)	12005(5)	8653(7)	1906(7)	84(5)	224(10)	272(11)	−3(5)	−22(6)	100(8)
C(16)	10766(4)	9035(5)	1945(6)	93(4)	140(6)	214(8)	−1(4)	−4(5)	74(6)
C(21)	7395(4)	7993(4)	−126(4)	101(4)	117(5)	90(4)	−15(3)	−10(3)	54(4)
C(22)	6129(5)	7805(7)	−563(5)	111(5)	291(11)	140(6)	−33(6)	−19(4)	116(7)
C(23)	5823(6)	7355(8)	−1894(6)	155(7)	348(14)	173(8)	−66(8)	−74(6)	151(9)
C(24)	6740(7)	7092(7)	−2763(5)	246(10)	230(10)	112(6)	−74(8)	−38(6)	93(6)
C(25)	7988(6)	7286(6)	−2332(5)	203(8)	174(7)	96(5)	−9(6)	15(5)	60(5)
C(26)	8317(5)	7730(5)	−1016(4)	141(5)	134(6)	90(4)	−3(4)	3(4)	51(4)
C(31)	8110(4)	10951(4)	2583(4)	89(4)	91(4)	134(5)	−1(3)	8(3)	46(4)
C(32)	8129(5)	11603(5)	1713(6)	138(6)	128(6)	186(7)	22(4)	17(5)	97(5)
C(33)	8278(6)	13120(6)	2200(8)	193(8)	135(7)	303(12)	21(6)	28(8)	132(8)
C(34)	8425(7)	13946(6)	3528(8)	198(9)	96(6)	334(14)	19(6)	50(9)	50(7)
C(35)	8416(7)	13289(6)	4385(7)	235(10)	117(7)	222(10)	1(6)	30(8)	14(6)
C(36)	8254(6)	11781(5)	3918(5)	178(7)	125(6)	132(6)	−13(5)	15(5)	29(5)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
H(12)	928	587	165	H(25)	873	708	−303
H(13)	1154	521	159	H(26)	931	788	−66
H(14)	1326	698	176	H(32)	801	1094	65
H(15)	1276	946	200	H(33)	829	1364	150
H(16)	1054	1013	206	H(34)	854	1514	390
H(22)	538	800	12	H(35)	851	1395	546
H(23)	481	721	−222	H(36)	824	1126	461
H(24)	648	675	−379				

* In the form: $-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$.

Toan and Dahl[9] who conclude from a comparison of Sn–Fe and Sb–Fe bond distances in electronically equivalent systems that the latter effect is of minor importance. We have earlier argued[2] in favour of the predominance of the σ directional effect on the basis of an apparent freedom of rotation about the Sn–Fe bond in complexes of type $(X_3Sn)Fe(C_5H_5)(CO)_2$ and because of similarities in the pattern of valence angles at tin in Ph_2Cl_2Sn and $[Fe(C_5H_5)(CO)_2]_2SnCl_2$.[11] Dahl[9] and

TABLE 2

Principal interatomic distances and angles *

(*a*) Bond lengths (Å)

Sb–Fe	2·472(1)	Fe–C(3)	1·787(4)
Sb–C(11)	2·125(3)	Fe–C(4)	1·782(4)
Sb–C(21)	2·122(3)	C(1)–O(1)	1·138(6)
Sb–C(31)	2·128(3)	C(2)–O(2)	1·144(5)
Fe–C(1)	1·765(4)	C(3)–O(3)	1·147(5)
Fe–C(2)	1·792(4)	C(4)–O(4)	1·143(6)

(*b*) Bond angles (°)

Fe–Sb–C(11)	116·4(1)	C(11)–Sb–C(21)	101·7(2)
Fe–Sb–C(21)	116·0(1)	C(11)–Sb–C(31)	101·6(2)
Fe–Sb–C(31)	116·8(1)	C(21)–Sb–C(31)	102·0(2)
Sb–Fe–C(1)	178·1(4)	C(1)–Fe–C(2)	91·9(2)
Sb–Fe–C(2)	87·6(2)	C(1)–Fe–C(3)	90·3(2)
Sb–Fe–C(3)	88·5(2)	C(1)–Fe–C(4)	93·0(2)
Sb–Fe–C(4)	88·9(2)	C(2)–Fe–C(3)	123·4(2)
Fe–C(1)–O(1)	179(1)	C(2)–Fe–C(4)	117·7(2)
Fe–C(2)–O(2)	179(1)	C(3)–Fe–C(4)	118·7(2)
Fe–C(3)–O(3)	178·9(7)		
Fe–C(4)–O(4)	178·7(7)		

* Estimated standard deviations, in parentheses, include the effects of possible cell-parameter errors and correlations between the parameters of an individual atom. No account has been taken of possible correlations between the parameters of different atoms.

TABLE 3

Selected shorter intra- and inter-molecular contacts (Å)

(*a*) Intramolecular contacts

C(11) · · · H(26)	2·79	C(4) · · · H(36)	3·19
C(21) · · · H(32)	2·77	Sb · · · H(12)	3·11
C(31) · · · H(16)	2·74	Sb · · · H(16)	3·11
C(1) · · · C(2)	2·56	Sb · · · H(22)	3·12
C(1) · · · C(3)	2·52	Sb · · · H(26)	3·11
C(1) · · · C(4)	2·57	Sb · · · H(32)	3·16
C(2) · · · H(22)	3·23	Sb · · · H(36)	3·10
C(3) · · · H(12)	3·16		

(*b*) Intermolecular contacts

C(4) · · · $H(34^{III})$	2·90	O(2) · · · $H(15^{IV})$	2·56
C(25) · · · $H(16^{I})$	2·87	H(12) · · · $H(33^{III})$	2·38
C(26) · · · $H(13^{II})$	2·77		

Roman numeral superscripts denote the following equivalent positions, relative to the reference molecule at *x*, *y*, *z*:

I $2 - x, 2 - y, \bar{z}$

II $2 - x, 1 - y, \bar{z}$

III $x, y - 1, z$

IV $x - 1, y, z$

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[11] P. T. Greene and R. F. Bryan, *J. Chem. Soc.* (*A*), 1971, 2549; J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, 1967, **6**, 968.

Struchkov[12] incline to the view that these valence-angle patterns are at least partially dictated by steric considerations but we have suggested that they are a direct consequence of bonding effects.[11] Because of the different stereochemistry of the iron atom in this complex, no direct comparison can usefully be made between the present bond distance and those observed in the cations. Further studies are necessary on analogous complexes with different substituents attached to antimony in order to examine the effects of substituent variation on the Sb–Fe bond.

The three Sb–C bond lengths agree closely with the mean value of 2·125(3) Å. This distance is longer, but in view of the low accuracy of the analysis of $(Me_3Sb)Fe(CO)_4$ not significantly longer, than the Sb–C distance [2·02(5) Å] for the trimethyl complex. No other determinations of tetrahedral Sb–C bond distances are known to us, but the tetrahedral radius for antimony of 1·40 Å suggested by these values * seems reasonable.

At the iron atom the equatorial C–Fe–C angles follow a familiar pattern with one angle significantly greater than and two significantly less than 120°.[13] No bond-length variation in Fe–C is associated with this distortion. In $(HPh_2P)Fe(CO)_4$ an identical distortion was attributed[14] to angular widening caused by repulsion between an *ortho*-hydrogen and two of the equatorial carbonyl groups. The shortest C · · · H distance noted there was 2·9 Å while in this structure the shortest comparable distance is C(3) · · · H(12) 3·16 Å. However, short intermolecular contacts in the present structure involve both C(4) · · · H(34) (2·90 Å) and O(2) · · · H(15) (2·56 Å) and these probably play a role in dictating the pattern of equatorial angles. Likewise, although explanations involving π bonding[15] and valence-shell electron-pair repulsions[16] have been advanced to account for such distortions, the observation that the equatorial angles in $(Me_3Sb)Fe(CO)_4$ are crystallographically equivalent suggests that steric effects predominate in the present case.

There is an apparent *trans*-effect with the axial Fe–C bond significantly shorter than the equatorial Fe–C. The shortening, *ca.* 0·027 Å, is comparable to that reported[17] in an electron-diffraction study of $Fe(CO)_5$ although no such effect was observed[18] in an *X*-ray study of the same compound. Other complexes $LFe(CO)_4$ are known both with[19] and without[20] observable *trans*-effects depending on the nature of the ligand L. Arguments involving the relative importance of ligand–ligand repulsions and *d* electron–ligand repulsions have been advanced to account for the *trans*-effect in five-co-ordinate metal complexes.[21] Frenz and Ibers[13] have reviewed the available evidence from diffraction studies on trigonal-bipyramidal complexes with five identical ligands. From their data it seems that the two opposing forces are closely balanced in $Fe(CO)_5$, and the same seems to be true in the present compound.

As was found in the trimethyl analogue, and as is common in other carbonyl complexes,[22] the carbonyl groups in the equatorial plane are not coplanar with the metal atom. The displacements of these atoms from a plane perpendicular to the Sb–Fe bond axis and passing through the iron atom range from 0·03 to 0·12 Å, being in each case toward the antimony atom. Again, such displacements have been attributed to repulsions between equatorial and axial ligands[8] but the observation that one of the two independent $Mn(CO)_5^-$ anions in the crystal of tris-(1,10-phenanthroline)nickel(II) pentacarbonylmanganate shows such behaviour while the other does not suggests that intermolecular steric effects may be as important in determining the final configuration.[13] Coplanarity of the equatorial carbonyl groups and the iron atom has also been noted[14] in the closely related $(HPh_2P)Fe(CO)_4$ structure. In the present compound the carbonyl carbon atom C(4), which is least displaced from the plane, is not involved in the shortest intramolecular C · · · H contact but is involved in the shortest axial-equatorial C · · · C contact.

The molecule adopts a close to staggered configuration about the Sb–Fe bond (Figure 2), similar to that found in the trimethyl analogue[8] and in $(HPh_2P)Fe(CO)_4$.[14] The dihedral angles made by the phenyl rings, one with another, are 84·8, 87·9, and 88·4°, close to the preferred arrangement in MPh_3 systems. The combination of these dihedral angles and the particular form of staggered configuration observed seems dictated by the limiting contacts between one set of *ortho*-hydrogen atoms and the equatorial carbon atoms, the energy lost by not adopting a fully staggered arrangement being compensated by the optimal arrangement of the phenyl rings.

The thermal parameters of the atoms are in the normal range for complexes of this type and follow physically reasonable patterns. The atomic amplitudes of vibration are greater the greater the distance of an atom from the molecular centre of gravity.

Contacts between molecules in the crystal are of normal van der Waals type.

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* The radius of a carbon atom *exo* to a phenyl ring is assumed to be 0·725 Å.

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