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Preliminary communication

SYNTHESIS AND X-RAY STRUCTURE OF [(TRICARBONYL-TRIPHENYLSTIBINEPHENYLIRON)DIPHENYLSTIBINE]TETRACARBONYLIRON, $Ph_3Sb\cdot(CO)_3PhFe\cdot Ph_2Sb\cdot Fe(CO)_4$

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Summary

Irradiation of a hexane solution of triphenylstibine and $Fe_3(CO)_{12}$ yields $Ph_3Sb\cdot(CO)_3PhFe\cdot Ph_2Sb\cdot Fe(CO)_4$ as the major product; an X-ray structural examination reveals a chain of iron and antimony atoms.

When deoxygenated hexane solutions of triphenylstibine and $Fe_3(CO)_{12}$ are irradiated at $\lambda > 600$ nm, three products are formed. In addition to the expected $Ph_3SbFe(CO)_4$ and $(Ph_3Sb)_2Fe(CO)_3$, [(tricarbonyl-triphenylstibine-phenyliron)diphenylstibine]tetracarbonyliron, $Ph_3Sb\cdot(CO)_3$-$PhFe\cdot Ph_2SbFe(CO)_4$ is produced as the major product (40%).

The title compound crystallises in deep-red rectangular plates, m.p. 125—126°C***. The crystals are monoclinic, space group $P2_1/c$ with $a = 17.95$, $b = 10.76$, $c = 23.98$ Å, $\beta = 116.6°$ and $Z = 4$. Intensities were measured with a Stoe two-circle computer-controlled diffractometer within the range $0.1 < \sin\theta/\lambda < 0.59$. The structure was solved by Paterson and Fourier methods and refined by least-squares calculations to R 4.4% for 4,219 observed reflections $[I > 3\sigma(I)]$.

A feature of this molecule is the chain of four metal atoms, Sb—Fe—Sb—Fe. Also noteworthy is the presence of both a penta- and a hexacoordinate iron atom, the latter containing an iron—carbon σ bond. The environment of both antimony atoms is distorted tetrahedral; that around Sb(1) shows the carbon—antimony—carbon bond angles compressed (C—Sb(1)—C = 99.5, 101 and 103°) as in trimethylstibinetetracarbonyliron [1] and triphenylstibinedicarbonylnitrosylcobalt [2]. The distortion around Sb(2) is less so, only the C—Sb(2)—C bond-

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***Infra-red, ultra-violet and mass spectral data fully compatible with the observed structure have been obtained and will be described elsewhere.

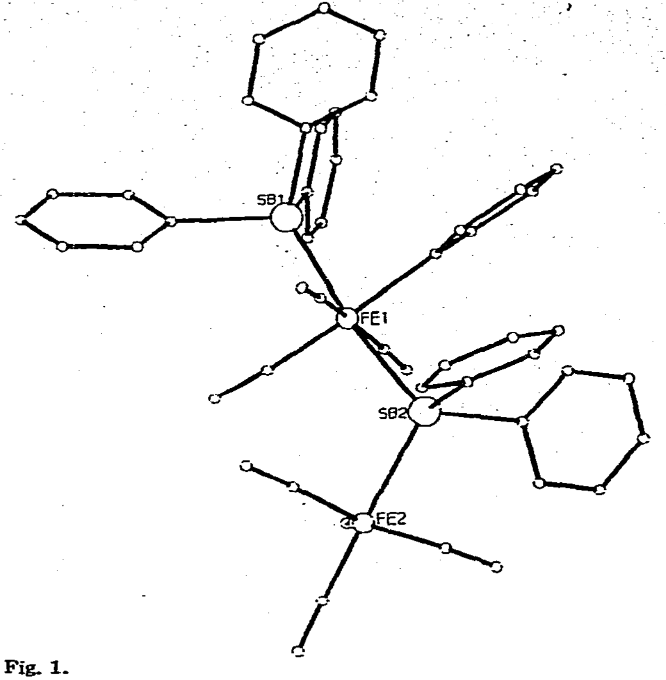

Fig. 1.

angle is substantially less than tetrahedral, 102.5° and only the Fe(1)—Sb(2)—Fe(2) bond angle is substantially greater than tetrahedral, 117°.

The environment around Fe(1) is distorted octahedral, the angles made by the iron atom and diametrically opposed atoms being 171, 172 and 174°. Of the twelve near right-angles, the largest deviation from ideality is 9°. The environment around Fe(2) shows only small deviations from ideal trigonal-bipyramidal. The angle Sb(2)—Fe(2)—CO(axial) is 179°, the angles (C—Fe(2)—C) between the equatorial carbonyl groups are 118, 118.5 and 123°, and the angles Sb(2)—Fe(2)—CO(equatorial) are 86, 87 and 90°. These values are similar to those found for diphenylphosphinetetracarbonyliron [3] and trimethylstibinetetracarbonyliron [1].

The mean bond lengths between the carbonyl carbons and Fe(1) are slightly longer (1.80 Å) than those involving Fe(2) at 1.78 Å. The axial and equatorial carbonyl bond-lengths are all in the range 1.13—1.15 Å. These values are similar to those in diphenylphosphinetetracarbonyliron [3]. The bond lengths between Sb(1) and Fe(1), and between Sb(2) and Fe(2) are similar (2.515 and 2.525 Å), that between Fe(1) and Sb(2) is rather longer (2.606 Å) as might be expected for a formal σ bond. We shall comment on the significance of these findings for the nature of the iron—antimony bonding in our full paper.

It is noteworthy that when triphenylphosphine and triphenylarsine are irradiated under the same conditions with $Fe_3(CO)_{12}$, only the binuclear $Ph_3XFe(CO)_4$ and the trinuclear $(Ph_3X)_2Fe(CO)_3$ [X = P or As] are formed [4]. The mode of formation of the title compound must involve either the insertion of an iron atom into a carbon—antimony bond or the migration of a phenyl group from antimony to an iron atom that is already bonded to the antimony. In either event the mechanism involves certain unique features and is under active investigation.

In the reactions between ruthenium [5] and osmium [6] dodecacarbonyls and triphenylphosphine insertion of the metal into the carbon—hydrogen bond of the benzene ring is a typical process; insertion of the metal into the carbon—phosphorus bond, so that the mono-substituted benzene ring is retained is not observed. The present example of iron inserting into a carbon—antimony bond appears to be the first of its kind.

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