Journal of Organometallic Chemistry, 165 (1979) C47—C48

Preliminary communication

A NEW FLUORINE BRIDGED ORGANOANTIMONY(V) MIXED HALIDE; THE CRYSTAL STRUCTURE OF $Ph_4Sb_2Br_5F$

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(Received November 16th, 1978)

Summary

Reaction between diphenylantimony(III) fluoride and bromine at —90°C in dichloromethane leads to formation of a new organoantimony(V) mixed halide, $Ph_4Sb_2Br_5F$. A crystal structure determination shows that the compound consists of Ph_2SbBr_2F and Ph_2SbBr_3 molecules linked by a strong fluorine bridge. Coordination polyhedra about the antimony atoms are distorted but are close to trigonal bipyramidal and octahedral respectively.

Although Ph_2SbCl_3 is a dimer with a double chlorine bridge [1], structures of the corresponding bromide and the mixed bromide-chlorides, Ph_2SbBr_2Cl and $Ph_2SbBrCl_2$ [2], are based on trigonal bipyramidal geometry. Substantial distortion occurs in the latter as a result of intermolecular interactions between antimony and an axial halogen atom. The structures of fluorine containing analogues are of interest in view of the pronounced tendency of fluorine to form strong intermolecular Sb—F—Sb bridges and to promote the formation of tetramers [3]. Preparation of the compound Ph_2SbBr_2F was therefore attempted.

Equimolecular quantities of diphenylantimony(III) fluoride and bromine reacted in dichloromethane at —90°C giving a crystalline material melting at 156°C with the empirical formula $Ph_2SbBr_{2.5}F_{0.5}$. In view of this unexpected result, a crystal structure determination was carried out. Crystals of the compound are orthorhombic with *a* 14.57(1), *b* 14.81(1), and *c* 12.88(1) Å, space group *Pnma*, and intensity data were measured for 1654 independent reflexions. The asymmetric unit consists of two independent antimony atoms which together with the bromine and fluorine atoms lie on a mirror plane. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares to *R* 5.1% with anisotropic thermal parameters.

Figure 1 shows the dimeric structure of the compound, which should be formulated as $Ph_2SbBr_2F \cdot Ph_2SbBr_3$. Coordination about Sb(1) is close to

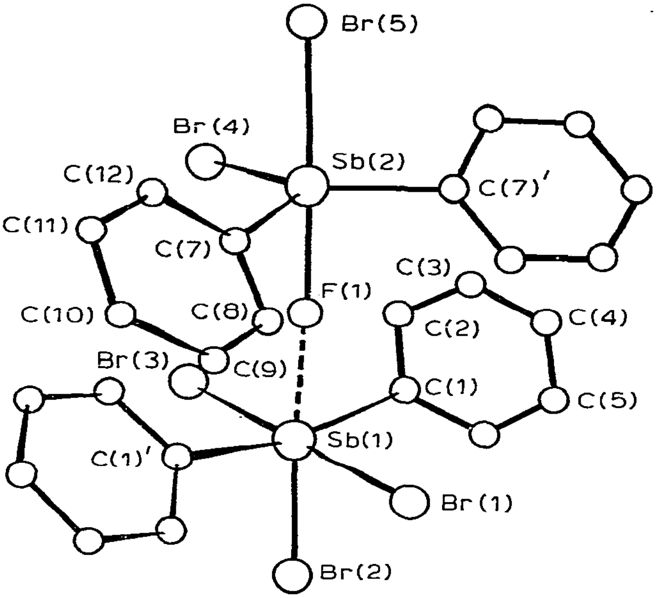

Fig.1. Structure of $Ph_2SbBr_2F \cdot Ph_2SbBr_3$ showing the atom numbering scheme.

octahedral while there is trigonal bipyramidal coordination about Sb(2). A strong, almost linear, fluorine bridge links the two heavy atoms (Sb(2)—F(1) 2.077 and Sb(1)$\cdots$F(1) 2.343 Å). Antimony—bromine distances vary between 2.449 and 2.626 Å with the equatorially bonded Sb(1)—Br(4) distance being the shortest. The angles at Sb(1) between Br(1), Br(2), and Br(3) are close to those expected for octahedral coordination but the angle between the symmetry related phenyl groups, C(1)—Sb(1)—C(1)′, is 160.3°. At Sb(2), the corresponding angle, C(7)—Sb(1)—C(7)′ is 131.2°, greater than that expected for trigonal bipyramidal geometry, and is associated with weak intermolecular contacts between Sb(2) and Br(3).

The unexpected formation of this new mixed halide is unlikely to result from the displacement of fluorine by bromine during the oxidation process. A more plausible mechanism is based on a halogen redistribution reaction in the, perhaps initially formed, Ph_2SbBr_2F; further investigations are concentrating on the search for species containing two or more fluorine atoms per antimony.

References

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