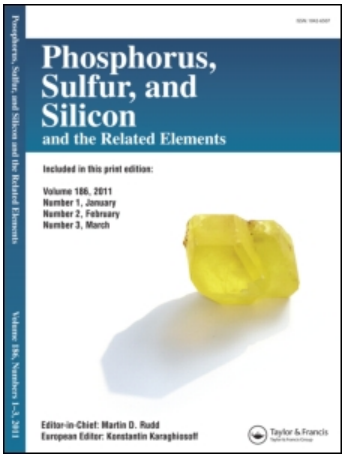

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Multiply Bridged Diantimony Compounds

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MULTIPLY BRIDGED DIANTIMONY COMPOUNDS

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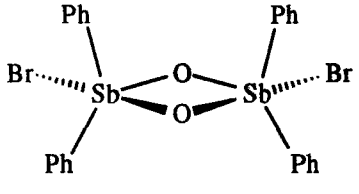
Abstract Metathesis reactions between compounds containing either double, $(Ph_2SbBrO)_2$, or single, $(Ph_3SbBr)_2O$, Sb-O-Sb bridges and arsinates, phosphinates, phosphates and carboxylates have been used in attempts to form products containing, respectively, quadruple and triple bridges. Although triply bridged systems are obtained from $(Ph_3SbBr)_2O$ and both the arsenic and phosphorus based ligands, only the former react with $(Ph_2SbBrO)_2$ to produce products with four bridges between the antimony atoms. Ligand bite is considered to be an important parameter in stabilising such products.

INTRODUCTION

Oxidation of Ph_2SbX, where X = Br, Cl or Ph, etc., leads to dimeric antimony(V) oxides, $(Ph_2SbXO)_2$, containing a four-membered Sb_2O_2 ring[1,2]. Metathesis between the bromide $(Ph_2SbBrO)_2$ (1) and two mols of tetrabutylammonium molybdate leads to a quadruply bridged product[3], originally prepared by an alternative route from triphenylantimony di-iodide [4], in which two further bridging groups have been added.



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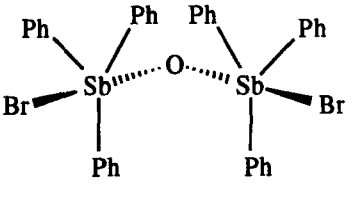

(2)

Multiply bridged systems of this kind are not widely encountered and we have extended this type of reaction to determine if any specific ligand parameters influence their formation. Singly oxygen bridged diantimony compounds, $(Ph_3SbX)_2O$, for X = Br (2), etc., are also known and these are suitable precursors for products with potentially a triple bridge between two antimony atoms. Two compounds of this type, $[F_3Sb(O_2CCF_3)]_2O$ [5] and $[Cl_3Sb(O_2PMe_2)]_2O$ [6] have been prepared previously.

REACTIONS OF $(Ph_2SbBrO)_2$

Among ligands known to have a high bridging tendency are those containing dithiophosphorus groups, but with antimony(V) reagents ligand oxidation usually takes place unless the antimony carries methyl substituents. Thus, reactions of $(Ph_2SbBrO)_2$ with two mols of either sodium dimethyldithiophosphinate or its diphenyl analogue in dichloromethane lead to the reduced product, $Ph_2Sb(S_2PR_2)$, for R = Me or Ph, in which the ligand both bridges and chelates to give dimeric units in the solid state. Clearly such redox processes should be hindered with less readily oxidised ligands and we have chosen to investigate reactions with diorgano-arsinates, -phosphinates, phosphates and carboxylates.

Reactions proceeded smoothly with both sodium dimethyl- and diphenyl-arsinates leading to neutral compounds with the stoichiometry $[Ph_2Sb(O_2AsR_2)O]_2$. This unit represented the highest mass peak in the FAB mass spectra and ir spectroscopy pointed to retention of the Sb_2O_2 ring. Crystallographic quality crystals could be obtained for the dimethylarsinate and the result of an X-ray structure determination is given in Figure 1. Although there were difficulties in crystallising the phenyl analogue, our data point to it having the same quadruply bridged structure. Each antimony atom now shows six-fold octahedral geometry, which is distorted primarily due to constraints associated with the four-membered ring [mean O-Sb-O 79.5°]. The lack of strain in incorporating the arsinate bridges is shown by a trans O-Sb-O angle of 174.3° and Sb-O-As angles of 119.0 and 119.5°. Replacement of only one bromine atom in $(Ph_2SbBrO)_2$ should be possible to give a triply bridged intermediate compound and this is being investigated.

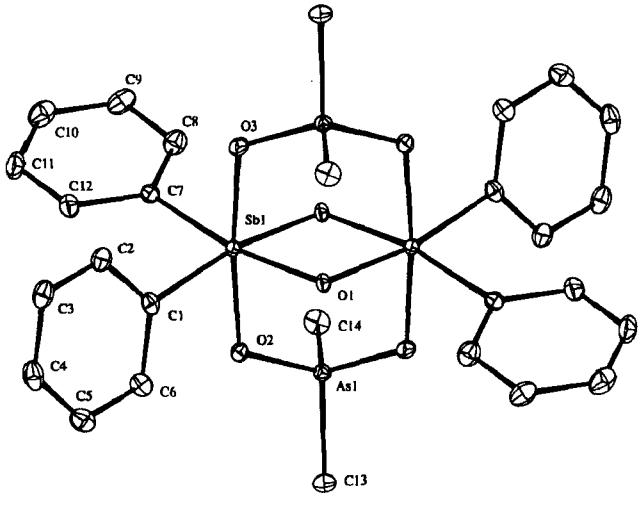

FIGURE 1 The structure of $[Ph_2Sb(O_2AsMe_2)O]_2$

Corresponding reactions with both sodium acetate and sodium trimethylacetate lead to precipitation of sodium bromide and isolation of carboxylates, but the product from the former reaction was not the expected analogue of the above dimethyl-arsinate but was

identical with a compound, $[(Ph_2Sb)_4O_2(OH)_2(OAc)_2 .HOAc)]$, previously obtained as the final hydrolysis product of $Ph_2Sb(OAc)_3$ [7] (see Figure 2). The compound is based on two four-membered $Sb_2O(OH)$ groups interlinked by single oxygen bridges to give an $Sb_4O_4(OH)_2$ cage-type structure. Isolation of this compound highlights a number of problems in this system as, although reactions were carried out in dried solvents using Schlenk techniques, water clearly reacts forcing loss of one of the acetate groups of the expected product, $[Ph_2Sb(OAc)O]_2$. One of the ring oxygen atoms is protonated and a molecule of acetic acid is hydrogen bonded across the 'cage'. A more curious observation was that an ostensibly duplicate reaction gave as the product, $[(Ph_2Sb)_4O_2(OH)(OEt)(OAc)_2]$, (see Figure 3) in which one of the OH groups has been replaced by an ethoxy group, probably from reaction with adventitious ethanol. Clearly then, although both acetate and arsinate are ligands can bridge between pairs antimony atoms, there are distinct difficulties in stabilising a compound with two oxygen and two acetate bridges.

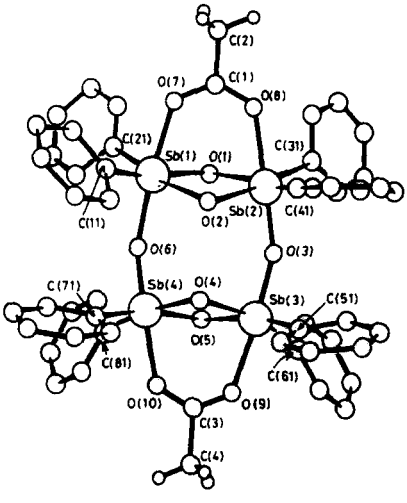

FIGURE 2 Structure of the acetate product.

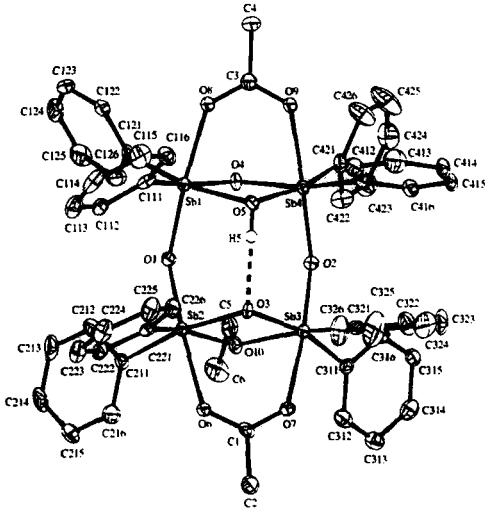

FIGURE 3 Structure of the ethoxy analogue.

One possible reason for this difference in behaviour is the smaller bite of the acetate ligand in comparison with that of the arsinates, which could easily lead to strain within a quadruply bridged structure. To test this, we have used ligands, such as dimethyl- and diphenyl-phosphinate and diphenyl-phosphate, with an intermediate bite. In each case, however, reaction was slow in refluxing dichloromethane, giving low yields of crystalline products and undefined byproducts. Replacing the solvent by refluxing toluene improved the yield of crystalline material, but there were still obvious byproducts and it was immediately obvious from ir and ^1H nmr spectroscopy that the products contained neither the Sb_2O_2 ring nor were there two phenyl groups attached to antimony.

X-ray crystallography of the dimethylphosphinate product (see Figure 4) confirmed these observations and revealed a triply bridged rearrangement product based on a $Ph_3SbOSbPh_3$ skeleton.

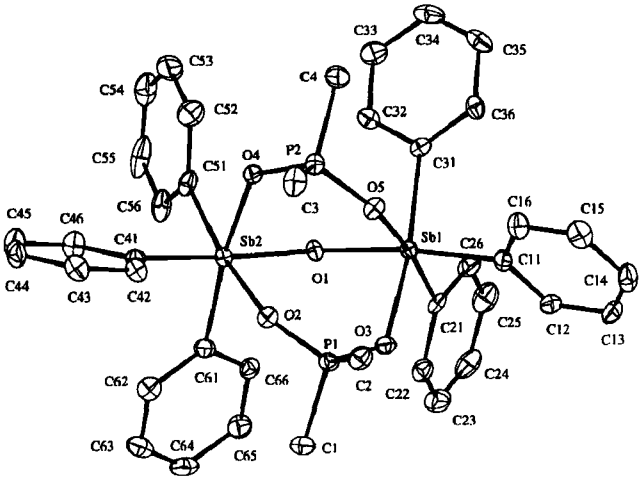

FIGURE 4 Structure of $[Ph_3Sb(O_2PMe_2)]_2O$.

REACTIONS OF $(Ph_3SbBr)_2O$

Using this compound as starting material, it was possible to replace the two bromine atoms with bridging dimethylphosphinate groups to give, in almost quantitative yield, a product identical with that from the phenyl group rearrangement reaction above (see Figure 4). As perhaps expected, dimethyl- and diphenyl-arsinates also reacted smoothly to give related triply bridged compounds, $[Ph_3Sb(O_2AsR_2)]_2O$; the former isostructural with the dimethylphosphinate product.

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