

S0277-5387(96)00162-3

# REDUCTION OF ANTIMONY(V) BY DITHIOPHOSPHINATES AND THE CRYSTAL STRUCTURE OF DIMERIC DIPHENYLANTIMONY(III) DIMETHYLDITHIOPHOSPHINATE

## MARTIN N. GIBBONS and D. BRYAN SOWERBY\*

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K.

and

#### CHRISTIAN SILVESTRU and IONEL HAIDUC

Department of Chemistry, Babes-Bolyai University, R-3400 Cluj-Napoca, Romania

(Received 14 March 1996; accepted 3 April 1996)

**Abstract**—Reactions between three diorganodithiophosphinates and diphenylantimony(V) bromide oxide  $(SbPh_2OBr)_2$ , led to antimony reduction while dithiophosphinate oxidation followed a complex path varying in detail with the nature of the organic groups on dithiophosphinate. Antimony(III) dithiophosphinates,  $SbPh_2(S_2PR_2)$  where R = Me, Et and Ph, have been isolated and characterised and an X-ray structure determination for the methyl derivative shows weakly associated dimers in the solid state, intermediate between those in  $(SbPh_2S_2PPh_2)_2$  and  $[Sb(4-MeC_6H_4)_2S_2PEt]_2$ . Copyright © 1996 Elsevier Science Ltd

Simple replacement of the halogen atoms occurs when trimethylantimony(V) dibromide reacts with dithiophosphorus based ligands and SbMe<sub>3</sub>  $(S_2PMe_2)_2$ , for example, can be isolated.<sup>1</sup> With phenyl substituted antimony(V) starting materials, on the other hand, there is a redox reaction and antimony reduction products such as  $SbPh_2(S_2PR_2)$  are obtained. In some cases, an antimony(III) halide was also isolated, together with the expected ligand oxidation product  $(R_2PS_2)_2$ . Oxygen based ligands are less susceptible to this redox process and we have recently shown that the bromine atoms in diphenylantimony(V) bromide oxide (SbPh<sub>2</sub>OBr)<sub>2</sub> 1, can be replaced by dimethylarsinate groups to give  $[SbPh_2O(O_2AsMe_2)]_2$  in which the antimony atoms are linked by four bridging groups.<sup>2</sup> This work returns to the problems of the redox process and reports the results of attempts to replace the bromine atoms in 1 with the dithiophosphinates

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 $Na(S_2PR_2) \cdot 2H_2O$  where R = Me or Et and  $Na(S_2PPh_2)$ .

## **RESULTS AND DISCUSSION**

Redox reactions are observed in the reactions of  $(SbPh_2OBr)_2$  and dithiophosphinates but they appear to be more complex than those with simple phenyl substituted antimony(V) halides; the reactions monitored by NMR spectroscopy in CDCl<sub>3</sub> vary in detail with the nature of the substituent at phosphorus.

The major soluble antimony(III) product from a reaction between  $(SbPh_2OBr)_2$  and two mols of  $Na(S_2PMe_2) \cdot 2H_2O$  in CDCl<sub>3</sub> in an NMR tube is  $SbPh_2(S_2PMe_2)$ , formed within 30 min of mixing the reactants, and identified by its characteristic <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra. The aromatic region of the <sup>13</sup>C spectrum contains further signals and these are probably associated with SbPh<sub>2</sub>Br. This monobromide has been identified together with SbPh<sub>2</sub> (S<sub>2</sub>COEt) as the antimony reduction product in a

<sup>\*</sup> Author to whom correspondence should be addressed.







similar reaction between 1 with potassium ethylxanthate.<sup>3</sup> Rather surprisingly there was no NMR evidence for the expected disulfane oxidation product  $(Me_2PS_2)_2$ , but elemental sulfur was isolated during attempts to obtain X-ray quality crystals of the antimony(III) product. A second possible antimony(III) reduction and desulfurised product is SbPh<sub>2</sub>(O<sub>2</sub>PMe<sub>2</sub>), but this was not isolated as a pure compound. Like SbPh<sub>2</sub>(O<sub>2</sub>PPh<sub>2</sub>),<sup>4</sup> a polymeric structure is expected and the compound would pre-

cipitate from CDCl<sub>3</sub> solution with the NaBr byproduct; no NMR signal would therefore be observed. This information allows the following equation to be written for the reaction with hydrated sodium dimethyldithiophosphinate:

$$(SbPh_2OBr)_2 + 2Na(S_2PMe_2) \cdot 2H_2O$$
  

$$\rightarrow SbPh_2(S_2PMe_2) + SbPh_2(O_2PMe_2)$$
  

$$+ 2NaBr + 2S + 4H_2O$$

Related reactions with  $Na(S_2PEt_2) \cdot 2H_2O$  and anhydrous  $NH_4(S_2PPh_2)$  were also followed by NMR spectroscopy. With the former there was again no evidence for the expected oxidation product,  $(Et_2PS_2)_2$ , and the only NMR signals, which again appeared within 30 min of mixing the reagents, were assigned to  $SbPh_2(S_2PEt_2)$ ; this reaction is therefore considered to follow a similar path to that in the equation above. The corresponding reaction with diphenyldithiophosphinate, on the other hand, appeared to follow a different course. In the first instance the amount of insoluble material was greater than in the two cases above and after 30 min there were <sup>31</sup>P NMR signals for both the expected antimony reduction product, SbPh<sub>2</sub>(S<sub>2</sub>PPh<sub>2</sub>) (<sup>31</sup>P  $\delta$  61.2 ppm) and the disulfane,  $(Ph_2PS_2)_2$  (<sup>31</sup>P  $\delta$  70.3 ppm), in contrast to the situation with the alkyldithiophosphinates. There was no<sup>31</sup>P signal that could be assigned to other possible antimony(III) species, i.e.  $SbPh_2(SOPPh_2)$  ( $\delta$  51.7) or Sb(S<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub> ( $\delta$  56.5), but after long standing there was a weak signal at 22.3 ppm, possibly due to SbPh<sub>2</sub>(O<sub>2</sub>PPh<sub>2</sub>).

Both SbPh<sub>2</sub>(S<sub>2</sub>PR<sub>2</sub>), for R = Me or Ph, have been isolated previously from reactions between diphenylantimony acetate and the appropriate sodium dithiophosphinate<sup>5</sup> and can be recrystallised from chloroform. The <sup>31</sup>P NMR spectrum of the dimethyldithiophosphinate showed the expected binomial septet at 56.5 ppm (referenced to H<sub>3</sub>PO<sub>4</sub>, <sup>2</sup>J<sub>P-H</sub> 12.9 Hz) and assignment of the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the diphenyldithiophosphinate has been possible *via* a two dimensional <sup>13</sup>C <sup>1</sup>H COSY investigation.

The FAB mass spectrum of diphenylantimony(III) dimethyldithiophosphinate contained an intense parent ion (m/z 400), intensity 71%) and peaks for the two primary fragmentation products arising from loss of, respectively, a phenyl group (m/z 323, 100%) and an S<sub>2</sub>PMe<sub>2</sub> ligand group  $(m/z \ 275, \ 72\%)$ . Rather surprisingly the spectrum also showed an intense peak (m/z 675, 33%)assigned to an ion arising from loss of  $S_2PMe_2$  from an  $[SbPh_2(S_2PMe_2)]_2$  dimer. The diphenyl-dithiophosphinate spectrum similarly showed both a parent ion (m/z 524, 22%) and the equivalent primary fragmentation processes, i.e. loss of either phenyl (m/z 447, 80%) or S<sub>2</sub>PPh<sub>2</sub> (m/z 275, 33%) but there was no evidence for a dimer in this case. Loose dimers are, however, known to be present in the solid state structure of this compound<sup>5</sup> and it was therefore of interest to determine the structure of the methyl analogue.

An X-ray structure determination confirmed the stoichiometry of the compound showing that it crystallised as loose centrosymmetric dimers, similar to those in the phenyl compound. In each case the dithiophosphinate ligand both bridges and chelates and although bridging is somewhat stronger in the methyl case (see below), the observation of dimeric fragments in the mass spectrum is probably better ascribed to its higher volatility than to any increased strength of bridging. A diagram showing the structure is in Fig. 1 and important distances and angles are collected in Table 1.

The antimony-sulfur distances [2.493(1) and 3.450(1) (bridge), 3.779(1) Å (chelate)] point to effectively unidentate behaviour of the dithiophosphinate ligand (*cf* 4.2 Å for the sum of the van der Waals radii) and this is reinforced by phosphorus-sulfur distances of 1.964(1) and 2.072(1) Å, close to the values, *ca* 1.95 and 2.00 Å, respectively, expected for double and single bonds<sup>6</sup> [*cf* PPh<sub>2</sub>(S)SH<sup>7</sup> P=S, 1.954(1); P-S, 2.077(1) Å]. If this view is taken, coordination at antimony in the monomeric unit is trigonal pyramidal with angles at antimony ranging between 92.5(1)

Table 1. Important distances (Å) and angles (°)

| Sb(1) - S(1)            | 2 493(1)  |
|-------------------------|-----------|
| Sb(1) - S(2)            | 3.779(1)  |
| Sb(1) - S(2')           | 3.450(1)  |
| Sb(1) - C(1)            | 2.158(3)  |
| Sb(1) - C(7)            | 2 155(3)  |
| P(1) - S(1)             | 2.072(1)  |
| P(1) - S(2)             | 1.964(1)  |
| P(1) - C(13)            | 1.794(5)  |
| P(1) - C(14)            | 1.800(4)  |
|                         |           |
| S(1)—Sb(1)—S(2)         | 62.52(3)  |
| S(1) - Sb(1) - S(2')    | 173.83(3) |
| S(1) - Sb(1) - C(1)     | 94.2(1)   |
| S(1) - Sb(1) - C(7)     | 92.5(1)   |
| S(2)— $Sb(1)$ — $S(2')$ | 121.45(2) |
| S(2)— $Sb(1)$ — $C(1)$  | 86.1(1)   |
| S(2) - Sb(1) - C(7)     | 155.0(1)  |
| S(2') - Sb(1) - C(1)    | 90.9(1)   |
| S(2')— $Sb(1)$ — $C(7)$ | 83.5(1)   |
| C(1) - Sb(1) - C(7)     | 96.1(1)   |
| S(1) - P(1) - S(2)      | 116.67(6) |
| S(1) - P(1) - C(13)     | 102.4(2)  |
| S(2) - P(1) - C(13)     | 112.9(2)  |
| S(1) - P(1) - C(14)     | 108.3(2)  |
| S(2) - P(1) - C(14)     | 110.7(2)  |
| C(13) - P(1) - C(14)    | 105.0(3)  |
| Sb(1) - S(1) - P(1)     | 98.96(5)  |
| Sb(1) - C(1) - C(2)     | 121.5(3)  |
| Sb(1)-C(1)-C(6)         | 120.2(3)  |
| Sb(1)-C(7)-C(8)         | 118.1(3)  |
| Sb(1) - C(7) - C(12)    | 122.5(3)  |

Atoms carrying a prime are related by the symmetry operation 1-x, 1-y, -z.



Fig. 1. Structure of Ph<sub>2</sub>SbS<sub>2</sub>PMe<sub>2</sub> showing the atom numbering scheme.

and 96.1(1)°. Geometry at phosphorus is distorted tetrahedral with angles falling between 116.67(6) for S(1)—P(1)—S(2) and 102.4(2) for S(1)—P(1)—C(13). The Sb—C and P—C bond lengths are normal.

The longer intra- and particularly inter-molecular Sb  $\cdots$  S contacts, however, cannot be ignored. The latter lead to dimerisation and the formation of an eight membered Sb<sub>2</sub>S<sub>4</sub>P<sub>2</sub> ring while the former give added transannular contacts. In this respect the overall structure is similar to that of the phenyl substituted analogue.<sup>5</sup>

Structures observed for complexes containing organophosphorus ligands are often intimately dependent on details of their constitution and "remote" changes, for example in the peripheral phosphorus substituents, sometimes lead to dramatic overall structure changes. One example is the change from pentagonal pyramidal geometry at antimony in  $Sb(S_2PPh_2)_3^8$  to distorted octahedral geometry in the ethyl analogue;<sup>9</sup> there are similarly substantial changes in lead(II) dithiophosphinate structures depending on whether the substituents are methyl,<sup>10</sup> ethyl<sup>11</sup> or phenyl.<sup>12</sup> In the present case, the effect of changing the phosphorus substituent is more subtle. In SbPh<sub>2</sub>(S<sub>2</sub>PPh<sub>2</sub>),<sup>5</sup> for example, ligand bridging and chelating strengths are comparable developing the dimeric tricyclic system 3. In the related ethyl derivative, Sb(4-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(S<sub>2</sub>PEt<sub>2</sub>),<sup>13</sup> a similar dimer 4 is formed giving the eight membered Sb<sub>2</sub>S<sub>4</sub>P<sub>2</sub> ring but here chelation is much weaker and transannular Sb...S contacts are at the limit of the sum of the van der Waals radii. The present compound represents an intermediate position where, although the bridging ability of the ligand is more highly developed, the weak chelation cannot be ignored.

# **EXPERIMENTAL**

Diphenylantimony bromide oxide was prepared by oxidising diphenylantimony bromide with *t*-butyl hydroperoxide as described previously.<sup>14</sup> NMR spectra were recorded using either a Bruker WM250 or a Varian Gemini 300 spectrometer and FAB mass spectra with an MS902.

### Preparation of SbPh<sub>2</sub>(S<sub>2</sub>PMe<sub>2</sub>)

 $Na(S_2PMe_2) \cdot 2H_2O(0.46 \text{ g}, 2.5 \text{ mmol})$  was added to a solution of diphenylantimony bromide oxide

(0.93 g, 1.25 mmol) in benzene  $(25 \text{ cm}^3)$  and the mixture stirred under reflux for 2 h. The resulting yellowish reaction mixture was filtered to remove insolubles and the clear filtrate evaporated to dryness in a vacuum when white and yellow crystal deposited from an oily residue. Treatment with acetone allowed isolation of the yellow product, shown to be elemental sulfur (Found: C, 0.5; H, 0.0%). The acetone solution containing the soluble white product was evaporated to dryness and the residue crystallised from chloroform, m.p. 114°C Found: C, 41.0; H, 3.9. Calc. for C<sub>14</sub>H<sub>16</sub>PS<sub>2</sub>Sb: C, 41.9; H, 4.0%. NMR <sup>1</sup>H, 250 MHz, CDCl<sub>3</sub>, RT,  $\delta$  2.08, (d, 6H, P—Me,  ${}^{2}J_{HP}$  12.9 Hz); 7.39 (m, 6H, Sb—Ph meta + para); 7.69 (dd, 4H, Sb—Ph ortho,  ${}^{3}J_{HH}$  7.2,  ${}^{4}J_{\rm HH}$  2.1 Hz).  ${}^{13}{\rm C}\{{}^{1}{\rm H}\}$ , 69 MHz, CDCl<sub>3</sub>, RT, 29.6 (d, P—C,  ${}^{1}J_{CP}$  56.4 Hz); 129.0 (Sb—Ph meta); 129.4 (Sb--Ph para); 135.9 (Sb--Ph ortho); 140.7 (Sb--Ph ipso). <sup>31</sup>P 121.4 MHz, CDCl<sub>3</sub>, RT, 56.5 (septet,  ${}^{2}J_{PH}$  12.9 Hz).

Reaction between  $(SbPh_2OBr)_2$  and  $Na(S_2PEt_2) \cdot 2H_2O$ 

The reaction between Na(S<sub>2</sub>PEt<sub>2</sub>) · 2H<sub>2</sub>O (0.028 g, 0.13 mmol) and (SbPh<sub>2</sub>OBr)<sub>2</sub> (0.05 g, 0.067 mmol) in CDCl<sub>3</sub> (2 cm<sup>3</sup>) was carried out directly in an NMR tube and the spectra were recorded after 30 min. The resulting compounds were not isolated. NMR <sup>1</sup>H, 300 MHz, CDCl<sub>3</sub>, RT,  $\delta$  1.26 (dt, 6H, P—CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>HP</sub> 21.6, <sup>3</sup>J<sub>HH</sub> 7.4 Hz); 2.12 (dq, 4H, P—CH<sub>2</sub>CH<sub>3</sub>, <sup>2</sup>J<sub>HP</sub> 10.7, <sup>3</sup>J<sub>HH</sub> 7.4 Hz); 7.40 (m, 6H, Sb—Ph *meta*+*para*); 7.69 (dd, 4H, Sb—Ph *ortho*, <sup>3</sup>J<sub>HH</sub> 7.1, <sup>4</sup>J<sub>HH</sub> 1.9 Hz). <sup>13</sup>C{<sup>1</sup>H}, 75.4 MHz, CDCl<sub>3</sub>, 7.38 (d, P—CH<sub>2</sub>CH<sub>3</sub>, <sup>2</sup>J<sub>CP</sub> 4.8 Hz); 31.93 (d, P—CH<sub>2</sub>CH<sub>3</sub>, <sup>1</sup>J<sub>CP</sub> 52.0 Hz); 129.1 (Sb—Ph, *meta*); 129.5 (Sb—Ph, *para*); 136.0 (Sb—Ph, *ortho*); 141.8 (Sb—Ph, *ipso*). <sup>31</sup>P{<sup>1</sup>H}, 121.4 MHz, CDCl<sub>3</sub>, 77.9.

### Preparation of SbPh<sub>2</sub>(S<sub>2</sub>PPh<sub>2</sub>)

This was prepared similarly from Na(S<sub>2</sub>PPh<sub>2</sub>) (0.46 g, 1.33 mmol) and diphenylantimony bromide oxide (0.50 g, 0.66 mmol) in benzene. The product was crystallised from acetonitrile, m.p. 142–4°C (140–2°C<sup>5</sup>). Found: C, 54.4; H, 3.9. Calc. for C<sub>24</sub>H<sub>20</sub>PS<sub>2</sub>Sb: C, 54.9; H, 3.8%. NMR (CDCl<sub>3</sub>) <sup>1</sup>H, 250 MHz,  $\delta$  7.35 (m, 6H, Sb—Ph *meta+para*); 7.44 (m, 6H, P—Ph *meta+para*); 7.63 (dd, 4H, Sb—Ph *ortho*, <sup>3</sup>J<sub>PH</sub> 15.6, <sup>3</sup>J<sub>HH</sub> 8.2, <sup>4</sup>J<sub>HH</sub> 3.0 Hz). <sup>13</sup>C{<sup>1</sup>H} 69 MHz,  $\delta$  128.4, (d, P—Ph *meta*, <sup>3</sup>J<sub>PC</sub> 13.4 Hz); 129.1, (Sb—Ph *meta*); 129.5, (Sb—Ph *para*); 131.2, (d, P—Ph *ortho* <sup>2</sup>J<sub>CP</sub> 11.7 Hz); 131.5 (P—Ph *para*) 136.1 (Sb—Ph *ortho*); 137.0 (d, P—Ph *ipso*)  ${}^{1}J_{CP}$  84.7 Hz); 141.3 (Sb—Ph *ipso*).  ${}^{31}P{{}^{1}H}$ , 121.4 MHz,  $\delta$  61.4.

## Crystal structure determination for SbPh<sub>2</sub>(S<sub>2</sub>PMe<sub>2</sub>)

Crystals suitable for X-ray diffraction were obtained by vapour diffusion of hexane into a chloroform solution of the compound.

Crystal data.  $C_{14}H_{16}PS_2Sb$ , M = 401.1, triclinic, space group P-1, a = 9.389(3), b = 10.032(3), c = 10.177(3) Å,  $\alpha = 104.27(1)$ ,  $\beta = 116.67(2)$ ,  $\gamma = 94.93(2)^{\circ}; V = 808.5 \text{ Å}^3, Z = 2, D_c = 1.65 \text{ g}$  $cm^{-3}$ , F(000) = 396,  $\mu = 20.4 cm^{-1}$ , Mo- $K_x$  radiation,  $\lambda = 0.710$  69 Å, crystal size =  $0.5 \times 0.3 \times 0.3$ mm<sup>3</sup>. Data were collected on a Hilger and Watts four circle diffractometer for 4276 reflections of which 2717 with  $I > 3\sigma(I)$  were considered observed. The data were corrected for Lorentz and polarisation effects and for absorption (DIFABS);<sup>15</sup> scattering factors, including anomalous dispersion contributions were those for neutral atoms.<sup>16</sup> The structure was solved by Patterson and difference Fourier methods and refined by full matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms (CRYS-TALS).<sup>17</sup> Hydrogens were placed at their calculated positions (d(C-H) 1.0 Å) and refined riding on their respective carbon atoms with a fixed U[iso] of 0.1 Å<sup>2</sup>. Final convergence (163 least squares parameters) occurred at R = 0.039 ( $R_w = 0.044$ ) after application of a five coefficient Chebyshev weighting scheme and correction for extinction. Tables of atomic coordinates, the remaining bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates and structure factors have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgement—We thank the British Council for support via the ROMLISS program.

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