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Oxygen bridged hexa(organo)di-antimony compounds: Hydrolysis by traces of moisture and crystal structures of $[SbR_3Br]_2O$, where R = *p*- or *o*-tolyl

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Abstract

^1H and ^{13}C NMR spectroscopy of four compounds of the type $[SbR_3X]_2O$, where X = Br and R = Ph, *p*-tolyl and *o*-tolyl or X = Cl and R = Me, have been interpreted as showing that unless stringent precautions are taken to exclude moisture there is cleavage of the oxygen bridge to give solutions which contain both the hydroxo species, $SbR_3(OH)X$, and the original bridged compound. This is in agreement with earlier results from IR spectra of compounds of this type in the presence of water. Rigorous exclusion of moisture leads to NMR spectra of only the unhydrolysed compound and this is the only product isolated when NMR solutions showing the presence of both compounds are crystallised. On the other hand, a stable hydroxobromide, $Sb(mesityl)_3Br(OH)$, has been isolated from hydrolysis of $Sb(mesityl)_3Br_2$. Crystal structures are reported for the *o*- and *p*-tolyl isomers of $[Sb(tolyl)_3Br]_2O$; the latter has crystallographically imposed $\bar{3}$ symmetry with a linear Sb–O–Sb bridge but the two independent molecules of the o-tolyl derivative have bridge angles of 161.0(2) and 171.5(2)°, respectively. © 1997 Elsevier Science S.A.

1. Introduction

In contrast to the well known triorganoarsenic hydroxohalides, e.g., $AsR_3(OH)X$ where X = Cl or Br [1], there is some ambiguity concerning the existence of related antimony compounds [2–7]. Indeed, no authentic $SbR_3(OH)X$ compound appears to have been isolated in the solid state unless sterically demanding R groups are present. In contrast, there is evidence for $SbMe_3(OH)Cl$ from infrared spectra of solutions of $[SbMe_3Cl]_2O$ in dichloromethane saturated with water but on crystallisation only the condensation product $[SbMe_3Cl]_2O$ was recovered and, furthermore, this was the only product isolated in a reaction between $SbMe_3Cl_2$ and one mol of NaOH [8]. Similar IR solution studies on $[SbEt_3Br]_2O$, $[SbPr^i_3Cl]_2O$ and $[SbPh_3(OAc)]_2O$, amongst others, also showed bands due to $SbR_3(OH)X$ species, but again crystallisation gave only the original oxygen bridged compounds [9].

Compounds formulated as $SbR_3(OH)Cl$, where for example R = *m*-MeC_6H_4 [4], have been mentioned earlier, but in view of later work they are most probably $[SbR_3Cl]_2O$ species. Genuine hydroxo compounds, $Sb(cyclo\text{-}C_6H_{11})_3(OH)X$, for X = Cl, Br, OAc and NO_3, have now been prepared [9], but stringent precautions are necessary to prevent dehydration to the corresponding anhydride.

The only crystallographically established organo-antimony hydroxo species contain bulky groups and include $Sb(2,6\text{-}Me_2C_6H_3)_3(OH)I$, formed by partial hydrolysis of $Sb(2,6\text{-}Me_2C_6H_3)_3I_2$ in aqueous methanol [10], and compounds with the general formula $Sb(mesityl)_3(OH)(O_2CR)$, where R = H, Me, $CHCl_2$, CH_2F, CF_3 and $C_{10}H_{15}$ [11,12], prepared by addition of the appropriate carboxylic acid to $Sb(mesityl)_3(OH)_2$. Although the hydroxo-iodide contains a tetrahedral $[SbR_3(OH)]^+$ cation with iodide hydrogen bonded to the hydroxo hydrogen, X-ray structures for the trimesityl compounds with R = $C_{10}H_{15}$ and $CHCl_2$ are trigonal bipyramidal with hydroxo and carboxylato oxygens in axial positions. It is worth noting here that while oxidation of trimesitylantimony gives a stable dihydroxide [13], tertiary stibines with less demanding organic groups, e.g., phenyl, give either cyclic dimers $[SbPh_3O]_2$ [14] if moisture is excluded or polymers in the presence of water.

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Oxo-bridged $[SbR_3X]_2O$ compounds, on the other hand, are well known and a number, including $[SbR_3X]_2O$, where R = Me and X = Cl or N_3 [15], and R = Ph and X = Cl [16], Br [17] or I [18] have been structurally characterised. The methyl compounds have crystallographically imposed $\bar{3}$ symmetry, implying a linear Sb–O–Sb system, but residual electron density about the bridging oxygen and chloride/azide positions suggests disorder and an actual bridge angle closer to 130°. Sb–O–Sb angles in the phenyl compounds, however, vary between ca. 130 and 180°.

This paper describes an NMR investigation into the solution behaviour of four compounds of the type $[SbR_3X]_2O$ and the preparation and crystal structures of two tolyl substituted compounds.

2. Results and discussion

2.1. Preparation of compounds

Reactions of SbR_3Br_2, where R = Ph, p-MeC_6H_4 and o-MeC_6H_4 with one mol of NaOH led to good yields of the oxygen bridged compounds $[SbR_3Br]_2O$, where R = Ph **1**, *p*-tolyl **2** and *o*-tolyl **3**. The phenyl derivative is already known [2,6] and although the *p*-tolyl analogue has been mentioned [9], no data are available for the compound. The methyl analogue, $[SbMe_3Cl]_2O$ **4**, was prepared from stoichiometric quantities of $SbMe_3(OH)_2$ and $SbMe_3Cl_2$ as described previously [5]. In contrast to the course of the phenyl and tolyl reactions above, treatment of Sb(mesityl)$_3$Br$_2$ with one mol of NaOH in methanol gave a hydroxohalide, Sb(mesityl)$_3$Br(OH) **5**, which was fully characterised spectroscopically. This reaction is similar to that followed by the hydrolysis of $Sb(2,6\text{-}Me_2C_6H_3)_3I_2$ [10] and isolation of stable hydroxo-halides in these cases is presumably a consequence of steric crowding by the 2,6-methyl groups.

2.2. Infrared spectra

All three aryl compounds had complex IR spectra but bands between 750 and 780 cm^{-1} can be assigned to antisymmetric Sb–O–Sb stretching; specific values are 766, 774 for **1**, 768 for **2** and 753, 760 cm^{-1} for **3**. A similar band at 777 cm^{-1} was also found for $[SbMe_3Cl]_2O$. Only the antisymmetric mode is considered here, as according to Wing and Callahan [19], the corresponding symmetric Sb–O–Sb mode will occur below 400 cm^{-1}, the limit of the available spectrometer.

There have been a number of attempts, e.g., [20], to correlate IR band positions in $[SbPh_3X]_2O$ compounds with crystallographically determined Sb–O–Sb angles but there are doubts about the validity. This is reinforced by observations on the two tolyl compounds considered here where the Sb–O band positions differ little even though (see later) the Sb–O–Sb bond angles in **2** and **3** are significantly different, i.e., 180 and 166° (mean), respectively. Further, the band in **2** with an angle of 180° occurs at the same energy as that in $[SbPh_3Cl]_2O$, which has an angle of only 139.0° [16]. It is clear then that factors other than the simple bond angle, and probably associated with the nature of the substituents, are also important.

Identification of **5** as the bromidehydroxide, Sb(mesityl)$_3$Br(OH), follows from its IR spectrum. There are no bands associated with Sb–O–Sb stretching but bands, not found in the spectrum of the corresponding dibromide, appear at 3501 and 542 cm^{-1}. The former, assigned to the O–H stretch, is broad implying some hydrogen bonding and contrasts with the sharp 3650 cm^{-1} band in Sb(mesityl)$_3$(OH)$_2$ where the O–H group, from X-ray crystallography, does not participate in hydrogen bonding. The 542 cm^{-1} band is assigned to Sb–O stretching.

2.3. NMR spectra

Complex ^1H NMR spectra were obtained when solutions of $[SbPh_3Br]_2O$ **1**, $[Sb(p\text{-}MeC_6H_4)_3Br]_2O$ **2** and $[Sb(o\text{-}MeC_6H_4)_3Br]_2O$ **3** were examined in $CDCl_3$ without precautions against atmospheric moisture. For **1**, signals in the range 7.29 to 8.26 ppm could be divided into distinct sets, pointing to the presence of two species in solution. The major species **A** showed a triplet (7.29 ppm, *m*-Ph), triplet (7.44 ppm, *p*-Ph), doublet (7.60 ppm, *o*-Ph) coupling pattern for the phenyl protons, while the minor species **B** gave multiplets at 7.57 (*m*- and *p*-Ph) and 8.26 ppm (*o*-Ph). The presence of two species was confirmed by $^{13}C\{^1H\}$ spectroscopy with signals for **A** at 129.1, 130.8, 133.3 and 141.9 ppm for the *meta*, *para*, *ortho* and *ipso* carbons, respectively, and corresponding signals for **B** at 129.5, 131.8 and 134.1 ppm for the *meta*, *para* and *ortho* carbons; the *ipso* carbon signal was not observed. Interestingly, crystallisation of the NMR sample gave quantitative recovery of **1** and this was also the case with NMR samples of the other compounds investigated.

The observation of two distinct species in solution could point to the presence of isomeric forms or products arising from hydrolysis by adventitious water. To determine if the latter was a possibility, spectra were remeasured under strictly anhydrous conditions. $CDCl_3$ was purified by trap-to-trap distillation over CaH_2 and the solution was prepared in a nitrogen filled glovebox and sealed in the NMR tube with a teflon tap. ^1H and ^{13}C spectra recorded under these conditions clearly showed signals associated with the species previously designated as **A**, with no evidence for any signals due to **B**. Species **A** is therefore considered to be the unchanged oxygen bridged compound and, as crystallisation from the mixed component NMR sample gives only this compound, species **B** is identified as the hydroxo-species $SbPh_3Br(OH)$. As with most five coordinate antimony(V) species, this is considered to be trigonal bipyramidal with bromine and hydroxo groups in axial positions. Clearly, **1** is highly susceptible to hydrolysis by traces of moisture in solution but, equally clearly, the resulting bromidehydroxide is unstable in the solid state and cannot be isolated. These observations are in good agreement with those from the earlier IR investigation [9].

The NMR behaviour of solutions of $[Sb(p\text{-}MeC_6H_4)_3Br]_2O$ **2** was similar. Under strictly anhydrous conditions, there were signals for a single species **A** with ^1H resonances at 2.40 (s, Me, 7.08 (d, *m*-Ar) and 7.51 (d, *o*-Ar) ppm for the chemically equivalent *p*-tolyl groups. ^{13}C resonances for this species were at 21.4, 129.6, 133.4 and 141.0 ppm for the methyl, *meta*, *ortho* and *ipso* carbons, respectively. Due to low solubility, a signal for the *para* carbon was not observed. New ^1H signals at 2.42 (s, Me), 7.35 (d, *m*-Ar) and 8.13 (d, *o*-Ar) ppm appeared on exposure of the sample to atmospheric moisture and again these are assigned to a hydrolysis product, $Sb(p\text{-}MeC_6H_4)_3Br(OH)$, **B**. Signals for **B** are, in fact, close to those for $Sb(p\text{-}MeC_6H_4)_3Br_2$ [2.45 (s, Me), 7.37 (d, *m*-Ar) and 8.07(d, *o*-Ar) ppm], adding support to identification of **B** as the monoantimony species, $Sb(p\text{-}MeC_6H_4)_3Br(OH)$. Additional ^{13}C resonances for **B** appeared at 21.4, 130.1, 134.0 for the methyl, *meta* and *ortho* carbons, respectively.

The ^1H spectrum of the *o*-tolyl analogue $[Sb(o\text{-}MeC_6H_4)_3Br]_2O$ **3** in $CDCl_3$ under anhydrous conditions was not as readily assignable. At room temperature, there was a broad featureless absorption at 2.31 ppm, a further broad peak at 6.88 ppm and a resolved multiplet at 7.31 ppm. The signals at 2.31 and 6.88 ppm can most probably be assigned to resonances of the *o*-methyl and the *o*-aryl protons, respectively, of the tolyl groups in the oxygen bridged compound **A** with peak broadness a function of restricted rotation of the *o*-tolyl groups. There is support for steric congestion at antimony in this compound from the crystal structure (see below) and from the greatly increased complexity in both the methyl and aryl regions of the NMR spectrum on cooling the solution to 218 K. Exposure of the solution to atmospheric moisture again gave new signals [at 2.67, 7.40 (m, *m*- and *p*-Ar) and 7.95 (d, *o*-Ar) ppm], associated with a second species **B** and by analogy with the phenyl and *p*-tolyl cases above, these are assigned to the hydrolysis product, $Sb(o\text{-}MeC_6H_4)_3Br(OH)$. Again, these signals are close to those for the related, $Sb(o\text{-}MeC_6H_4)_3Br_2$.

Previously reported ^1H NMR spectra for $[SbMe_3Cl]_2O$ **4** in $CDCl_3$ [7] showed methyl proton resonances at 1.95, 2.03 and 2.35 ppm and similar spectra were observed here when moisture was not excluded. Under strictly anhydrous conditions, however, a single sharp resonance occurred at 1.96 ppm, the position within accepted error of the major species in the previous spectrum, and hydrolysis therefore occurs in these solutions to give two, apparently different, products. As with the aryl analogues, hydrolysis is clearly reversible as crystallisation of the NMR sample led to quantitative recovery of the original compound. By analogy with suggestions above, one of the hydrolysis products is most likely to be $SbMe_3Cl(OH)$ but it is difficult to identify the second, although it may be a dimer, $[(SbMe_3Cl)_2(\mu\text{-}OH)_2]$, as has been suggested in other systems [19]. Fully hydrolysed species, such as $SbMe_3(OH)_2$ or $[SbMe_3(OH)]_2O$, are also possibilities, but if **4** is the only product isolated on crystallisation of the NMR sample, more complex hydrolysis processes must be involved.

These data illustrate the ready equilibrium between $[SbR_3X]_2O$ and $SbR_3X(OH)$; in the solid state, except when R is large, the oxo-bridged form is clearly preferred while in solution even traces of moisture give the preferred $SbR_3X(OH)$ configuration.

Unlike the compounds above, $Sb(Me_3C_6H_2)_3Br(OH)$ **5** is a stable hydroxohalide with no apparent tendency to dehydrate to an oxo bridged solid. Under these circumstances, it is not surprising that identical, single species spectra were obtained in $CDCl_3$ solution, irrespective of the presence or absence of moisture. Proton signals at 2.32 (*p*-Me), 2.52 (*o*-Me) and 7.01 (*m*-Ar) ppm are similar to those in related mono-antimony compounds such as $Sb(Me_3C_6H_2)_3Br_2$ and the $Sb(Me_3C_6H_2)_3(OH)(O_2CR)$ group of compounds. $^{13}C\{^1H\}$ spectra showed resonances at 21.0 (*p*-Me), 24.6 (*o*-Me), 131.0 (*m*-Ar), 136.5 (*p*-Ar), 142.5 (*o*-Ar) and 142.8 (*ipso*-Ar) ppm. These data do not allow an unambiguous distinction to be made between an ionic structure, as in $[Sb(2,6\text{-}Me_2C_6H_3)_3Sb(OH)]^+I^-$ [10], or the covalent alternative, $Sb(Me_3C_6H_2)_3(OH)(O_2CR)$, as in the related carboxylates. However, the presence of a degree of hydrogen bonding observed in the solid-state IR spectrum tends to suggest an ionic structure for the solid.

2.4. Mass spectrometry

FAB mass spectra of $[SbPh_3Br]_2O$ **1** and the two tolyl analogues **2** and **3** showed no evidence for the parent ion and in each case the highest mass fragments were assigned to bromine loss from the parent. No further diantimony species of major significance were found and the remaining fragments were monoantimony species such as $SbAr_3Br^+$ and $SbAr_2^+$. There was also no parent ion in the FAB spectrum of $Sb(2,4,6\text{-}Me_3C_6H_2)_3SbBr(OH)$ but from the relative intensities (65:3) of the $Sb(2,4,6\text{-}Me_3C_6H_2)_3Sb(OH)^+$ and

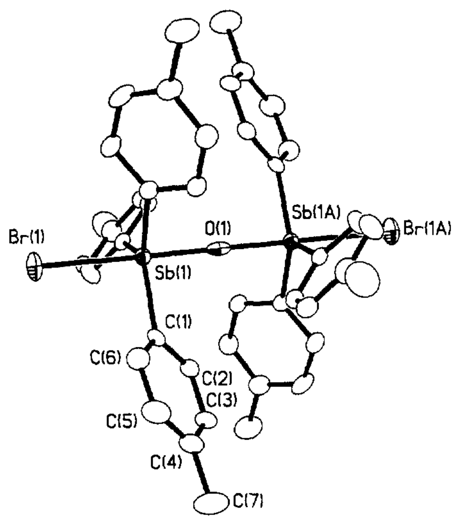

Fig. 1. Structure of $[Sb(p\text{-tolyl})_3Br]_2O$ **2**, showing the atom numbering scheme.

$Sb(2,4,6\text{-}Me_3C_6H_2)_3SbBr^+$ peaks, bromine loss is far more probable than OH loss. Subsequent fragmentation is by loss of the OH group and complete mesityl units.

2.5. X-ray crystallography

Structures have been determined for the two tolyl substituted compounds **2** and **3**, the latter as a hemi-hexane solvate, on crystals obtained by slow diffusion of hexane into concentrated chloroform solutions of the compounds. Crystals for $Sb(2,4,6\text{-}Me_3C_6H_2)_3Br(OH)$ **5** were unsuitable for crystallography.

The molecular structure of $[Sb(p\text{-}MeC_6H_4)_3Br]_2O$ **2** is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. The compound crystallises in the trigonal space group $R\bar{3}$ with the asymmetric unit comprising one sixth of the molecule. Coordination about antimony is, therefore, trigonal bipyramidal with *p*-tolyl groups in equatorial positions and bromine and the bridging oxygen in axial sites. Necessarily the Sb–O–Sb and Br–Sb–O angles are 180° and the C–Sb–C angles are equal at 119.99(1)°. Unlike the situation in $[SbMe_3Cl]_2O$ and related compounds [15], which also have crystallographically imposed $\bar{3}$ symmetry, there is no disorder about the three fold axis. The tolyl *ipso* carbon atoms are bent slightly towards bromine giving C(1)–Sb(1)–Br(1) angles of 89.45(8)° and the *p*-tolyl groups necessarily have a propeller arrangement.

Table 1
Selected bond distances (Å) and angles (°) for $[Sb(p\text{-tolyl})_3Br]_2O$ **2**

Sb(1)–Br(1)	2.7203(7)
Sb(1)–O(1)	1.9535(4)
Sb(1)–C(1)	2.117(3)
Sb(1)–O(1)–Sb(1A)	180.0
O(1)–Sb(1)–Br(1)	180.0
O(1)–Sb(1)–C(1)	90.55(7)
C(1)–Sb(1)–C(1A)	119.99(1)
C(1)–Sb(1)–Br(1)	89.44(8)

The Sb–Br separation [2.7203(7) Å] is comparable to that in $[SbPh_3Br]_2O$ [mean 2.710 Å] [17], but is significantly longer than those in other Sb(V)–Br compounds, e.g., 2.632 Å in $SbPh_3Br_2$ [21] and 2.554/2.589 Å in $[SbPh_2BrO]_2$ [22] and is probably associated with a degree of ionic character.

Opening of the Sb–O–Sb angle from 109.5° could be associated with delocalisation of oxygen lone pairs into empty antimony *d*-orbitals with maximum bond strength expected at 180°, leading to a correlation between Sb–O–Sb angles and Sb–O bond lengths. This has not been convincingly substantiated and, if the Sb–O–Sb angle were the only determining factor, Sb–O bonds in the present compound [1.964(4) Å] would be the shortest. This is not the case and shorter bonds [1.92 and 1.95 Å] are found in, for example, $[SbPh_3(NO_3)]_2O$, where the

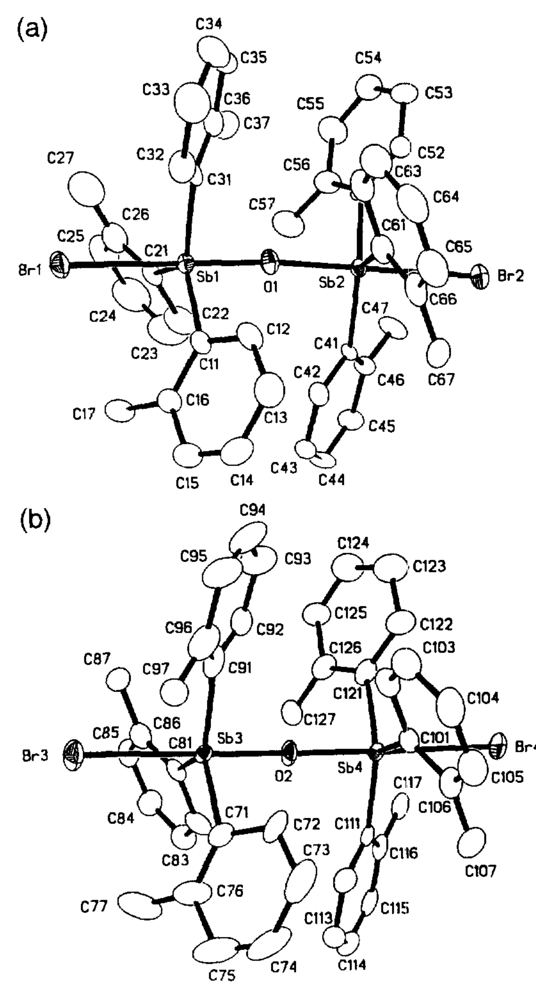

Fig. 2. Structures of (a) molecule A and (b) molecule B of $[Sb(o\text{-tolyl})_3Br]_2O$ **3**, showing the atom numbering scheme.

Table 2
Selected bond distances (Å) and angles (°) for $[Sb(o\text{-tolyl})_3Br]_2O$ **3**

Sb(1)–Br(1)	2.750(2)	Sb(3)–Br(3)	2.739(2)
Sb(1)–O(1)	1.964(4)	Sb(3)–O(2)	1.947(4)
Sb(1)–C(11)	2.113(5)	Sb(3)–C(71)	2.110(4)
Sb(1)–C(21)	2.139(4)	Sb(3)–C(81)	2.162(3)
Sb(1)–C(31)	2.111(4)	Sb(3)–C(91)	2.141(5)
Sb(2)–Br(2)	2.731(2)	Sb(4)–Br(4)	2.762(2)
Sb(2)–O(1)	1.962(4)	Sb(4)–O(2)	1.964(4)
Sb(2)–C(41)	2.112(4)	Sb(4)–C(101)	2.109(3)
Sb(2)–C(51)	2.125(5)	Sb(2)–C(111)	2.121(5)
Sb(2)–C(61)	2.133(4)	Sb(2)–C(121)	2.149(5)
Sb(1)–O(1)–Sb(2)	161.0(2)	O(2)–Sb(3)–Br(3)	176.6(1)
Sb(3)–O(2)–Sb(4)	171.5(2)	O(2)–Sb(3)–C(71)	91.4(2)
O(1)–Sb(1)–Br(1)	179.2(1)	O(2)–Sb(3)–C(81)	88.6(2)
O(1)–Sb(1)–C(11)	95.1(2)	O(2)–Sb(3)–C(91)	91.4(2)
O(1)–Sb(1)–C(21)	90.4(1)	Br(3)–Sb(3)–C(71)	91.0(1)
O(1)–Sb(1)–C(31)	93.1(2)	Br(3)–Sb(3)–C(81)	88.1(1)
Br(1)–Sb(1)–C(11)	85.3(1)	Br(3)–Sb(3)–C(91)	89.7(1)
Br(1)–Sb(1)–C(21)	90.1(1)	C(71)–Sb(3)–C(81)	117.4(2)
Br(1)–Sb(1)–C(31)	86.1(1)	C(71)–Sb(3)–C(91)	117.3(2)
C(11)–Sb(1)–C(21)	120.9(2)	C(91)–Sb(3)–C(81)	125.3(2)
C(11)–Sb(1)–C(31)	116.9(1)	O(2)–Sb(4)–Br(4)	177.7(1)
C(21)–Sb(1)–C(31)	121.6(2)	O(2)–Sb(4)–C(101)	92.8(2)
O(1)–Sb(2)–Br(2)	177.5(1)	O(2)–Sb(4)–C(111)	90.6(2)
O(1)–Sb(2)–C(41)	90.9(2)	O(2)–Sb(4)–C(121)	92.4(2)
O(1)–Sb(2)–C(51)	92.3(2)	Br(4)–Sb(4)–C(101)	85.9(1)
O(1)–Sb(2)–C(61)	94.2(2)	Br(4)–Sb(4)–C(111)	91.7(1)
Br(2)–Sb(2)–C(41)	88.7(1)	Br(4)–Sb(4)–C(121)	86.6(1)
Br(2)–Sb(2)–C(51)	85.9(1)	C(101)–Sb(4)–C(111)	120.9(2)
Br(2)–Sb(2)–C(61)	88.1(1)	C(101)–Sb(4)–C(121)	116.9(1)
C(41)–Sb(2)–C(51)	124.8(1)	C(111)–Sb(4)–C(121)	124.0(2)
C(41)–Sb(2)–C(61)	123.8(2)		
C(51)–Sb(2)–C(61)	110.9(2)		

Sb–O–Sb angle is 141.6° [23]. However, bridge bonds are substantially shorter than terminal Sb–O bonds in compounds such as $Sb(2,4,6\text{-}Me_3C_6H_2)_3(OH)_2$ [2.027 Å] [13].

The structure of $[Sb(o\text{-}MeC_6H_4)_3Br]_2O$ **3** is shown in Fig. 2 with selected bond lengths and angles in Table 2. Here the asymmetric unit comprises two complete formula units [molecule A, Sb(1) and Sb(2), molecule B, Sb(3) and Sb(4)], which show some structural differences, together with a molecule of solvent hexane. Each antimony is in trigonal bipyramidal coordination but distortions here are more severe than in the *p*-isomer. For example, Sb–C bond lengths vary between 2.109(3) and 2.149(5) Å [mean 2.127 Å], Sb–Br distances between 2.731(2) and 2.762(2) Å [mean 2.746 Å] and Sb–O distances between 1.947(4) and 1.964(4) Å [mean 1.959 Å]. Angles at antimony between bromine and carbon range between 88.1 and 88.7° while the spread of angles between the equatorial carbon atoms is from 110.9 to 124.0°. Each antimony atom is displaced by a small amount (0.02–0.10 Å) from the plane through the attached equatorial carbon atoms towards the bridging oxygen atom (see Table 3).

Table 3
Deviations (Å) of selected atoms from the best plane through the appropriate ipso carbon atoms in $[Sb(o\text{-tolyl})_3Br]_2O$ **3**

Molecule A				
Plane	C(11) C(21) C(31)		C(41) C(51) C(61)	
	Sb(1)	−0.104	Sb(2)	−0.089
	Br(1)	2.642	Br(2)	2.646
	O(1)	−2.066	O(1)	−2.049
	C(17)	1.271	C(47)	1.360
	C(27)	1.385	C(57)	−1.341
	C(37)	−1.316	C(67)	1.223
Molecule B				
Plane	C(71) C(81) C(91)		C(101) C(111) C(121)	
	Sb(3)	−0.016	Sb(4)	−0.070
	Br(3)	2.722	Br(4)	2.686
	O(2)	−1.962	O(2)	−2.033
	C(77)	1.360	C(107)	1.173
	C(87)	1.128	C(117)	1.384
	C(97)	1.331	C(127)	−1.258

The two independent molecules differ substantially in both the angle at the bridging oxygen atom [161.0(2)° for molecule A and 171.5(2)° for molecule B] and in the orientation of the tolyl groups at antimony. The latter can be seen from (a) the relative signs of the O–Sb–C(n1)–C(n6) torsion angles in Table 4 and (b) the deviations of the methyl carbon atoms from the mean

Table 4
Selected torsion angles for $[Sb(o\text{-tolyl})_3Br]_2O$ **3**

Atoms	Torsion angle (°)
O(1)–Sb(1)–C(11)–C(16)	−116.1(3)
O(1)–Sb(1)–C(21)–C(26)	−120.5(4)
O(1)–Sb(1)–C(31)–C(36)	53.0(4)
O(1)–Sb(2)–C(41)–C(46)	119.6(3)
O(1)–Sb(2)–C(51)–C(56)	−52.9(4)
O(1)–Sb(2)–C(61)–C(66)	119.4(4)
O(2)–Sb(3)–C(71)–C(76)	−117.0(3)
O(2)–Sb(3)–C(81)–C(86)	−120.1(4)
O(2)–Sb(3)–C(91)–C(96)	−121.8(4)
O(2)–Sb(4)–C(101)–C(106)	118.4(4)
O(2)–Sb(4)–C(111)–C(116)	123.2(3)
O(2)–Sb(4)–C(121)–C(126)	−53.3(3)

plane through the associated *ipso* carbons. Tolyl groups at both Sb(1) and Sb(2) in molecule A show non-propeller arrangements, while in molecule B the situation is more complex with a propeller arrangement at Sb(3) and a non-propeller arrangement at Sb(4). Only at Sb(3) do all methyl groups lie on the same side of the mean plane through the *ipso* carbons (orientated towards bromine) while at the other three antimony atoms only two methyls are orientated towards bromine. This ligand arrangement is probably associated with the presence of the ortho methyl groups, which lead to steric crowding.

3. Experimental details

3.1. Preparation of $SbAr_3$ and $SbAr_3Br_2$, where Ar = o-tolyl, p-tolyl and mesityl

The triaryl antimony compounds were prepared conventionally under Schlenk conditions from the appropriate aryl bromide, lithium slivers and antimony trichloride in ether solution and recrystallised from alcohol. Addition of the stoichiometric amount of bromine in dichloromethane at 0°C then gave the corresponding dibromides, which were recrystallised from chloroform/hexane mixtures. All products were characterised by melting point and elemental analysis, together with IR, ^{1}H NMR and mass spectrometry.

3.2. Preparation of the hydrolysis products, $(SbAr_3Br)_2O$

3.2.1. Preparation of $(SbPh_3Br)_2O$ (1)

Sodium hydroxide (0.29 g, 7.25 mmol) in the minimum of water was added to a stirred suspension of triphenylantimony dibromide (3.50 g, 6.8 mmol) in methanol (150 ml) and the resulting mixture refluxed for 18 h. The solution was allowed to cool to room temperature before water (100 ml) was added. The precipitate which formed was filtered off, dried in a vacuum and recrystallised from ethanol. Yield 2.43 g (81%). M.p. 247–250°C (248–250°C [24]). ^{1}H NMR ($CDCl_3$, 250 MHz, RT): Anhydrous conditions (species **A**): δ 7.29 (12H, t, $^3J_{HH}$ = 7.5 Hz, *m*-Ph), 7.44 (6H, t, $^3J_{HH}$ = 7.5 Hz, *p*-Ph), 7.60 (12H, d, $^3J_{HH}$ = 7.5 Hz, *o*-Ph). Moist solvent (species **B**): 7.57 (9H, m, *m*- and *p*-Ph), 8.26 (6H, m, *o*-P) in addition to the signals listed above for **A**. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 69 MHz, RT): Anhydrous conditions (**A**): δ 129.1 (*m*-Ph), 130.8 (*p*-Ph), 133.3 (*o*-Ph), 141.9 (*ipso*-Ph). Moist solvent (**B**): 129.5 (*m*-Ph), 131.8 (*p*-Ph), 134.1 (*o*-Ph) in addition to the signals listed above for **A**. IR (nujol mull, CsI): 1434s, 1330w, 1304w, 1181w, 1158w, 1063m, 1019m, 996m, 774vs, 766vs, 689s, 457s, 448s. Mass spectrum (FAB), *m/z* (rel. int. (%)): 801 ($M-Br^+$, 3), 433 ($SbPh_3Br^+$, 50) 275 ($SbPh_2^+$ 10), 154 (Ph_2^+70), 77 (Ph^+ 17). Analysis: Found: C, 49.1; H, 3.4. $C_{36}H_{30}Br_2OSb_2$ calc.: C, 49.0; H, 3.4%.

3.2.2. Preparation of $[Sb(p\text{-}MeC_6H_4)_3Br]_2O$ (2)

A mixture of sodium hydroxide (0.21 g, 5.2 mmol), tri(*p*-tolyl)antimony dibromide (2.81 g, 5.1 mmol) and methanol (100 ml) was refluxed with stirring for 24 h. Approximately half the solvent was then removed in vacuum and crude product precipitated by addition of water (50 ml). The product was filtered off and recrystallised from chloroform. Yield 1.86 g (76%). M.p. 276–282°C. ^{1}H NMR ($CDCl_3$, 250 MHz, RT): Anhydrous conditions (species **A**): δ 2.40 (18H, s, *Me*-Ar), 7.08 (12H, d, $^3J_{HH}$ = 8 Hz, *m*-Ar), 7.51 (12H, d, $^3J_{HH}$ = 8Hz, *o*-Ar). Moist solvent (species **B**): 2.42 (9H, s, Me-Ar), 7.35 (6H, d, $^3J_{HH}$ = 8Hz, *m*-Ar), 8.13 (6H, d, $^3J_{HH}$ = 8Hz, *o*-Ar) in addition to the signals listed above for **A**. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 69 MHz, RT): Anhydrous conditions (**A**): δ 21.4 (Me-Ar), 129.6 (*m*-Ar), 133.4 (*o*-Ar), 141.0 (*ipso*-Ar). Moist solvent (**B**): 21.4 (Me-Ar), 130.1 (*m*-Ar), 134.0 (*o*-Ar) in addition to the signals listed above for **A**. IR (nujol mull, CsI): 1311m, 1210m, 1188m, 1065m, 1014m, 848w, 804vs, 787w, 768s, 699w, 484s. Mass spectrum (FAB), *m/z* (rel. int. (%)): 885 ($M-Br^+$, 2), 715 ($M-2Br-MeC_6H_4^+$ 1). Analysis: Found: C, 52.2; H, 4.4. $C_{42}H_{42}Br_2OSb_2$ calc.: C, 52.2; H, 4.4%.

3.2.3. Preparation of $[Sb(o\text{-}MeC_6H_4)_3Br]_2O$ (3)

The method was similar to that described above using sodium hydroxide (0.08 g, 1.9 mmol), tris(o-tolyl)antimony dibromide (1.03 g, 1.9 mmol) and methanol (60 ml). The crude product was recrystallised from chloroform/hexane. Yield 0.68 g (74%). M.p. 250–258°C. ^{1}H NMR (250 MHz, $CDCl_3$, RT): Anhydrous conditions (species **A**): 2.31 (18H, s, very broad, Me-Ar); 6.88 (6H, s, very broad, *o*-Ar); 7.31 (18H, m, *m*- and *p*-Ar). Moist solvent (species **B**): (2.67 (9H, s, Me-Ar); 7.40 (9H, m, *m*- and *p*-Ar); 7.95 (3H, d, $^3J_{HH}$ = 8Hz, *o*-Ar) together with the signals listed above for **A**. IR (nujol mull, CsI): 1278m, 1205m, 1163w, 1121m, 908m, 799m, 760vs br, 752vs br, 731s, 699m, 485w, 437s. Mass spectrum (FAB) m/z (rel. int. (%)): 885 (M^+–Br, < 1), 715 M–2Br–$MeC_6H_4^+$, < 1), 475 ($(o\text{-}MeC_6H_4)_3SbBr^+$, 61), 303 ($(o\text{-}MeC_6H_4)_2Sb^+$, 18), 91 $MeC_6H_4^+$, 93). Analysis: Found: C, 52.1; H, 4.4. $C_{42}H_{42}Br_2OSb_2$ calc.: C, 52.2; H, 4.4%.

3.2.4. Preparation of $(SbMe_3Cl)_2O$ 4

This compound was obtained from $SbMe_3(OH)_2$ and $SbMe_3Cl_2$ as described previously [5].

Trimethylantimony dichloride (4.80 g, 20 mmol) was dissolved in boiling water (250 ml) and the resulting solution passed through an anion exchange resin in the hydroxide form (70 g, Amberlite IRA-400(OH)). A further portion of water (300 ml) was passed through the resin to ensure complete elution of the product. Water was carefully evaporated under reduced pressure from the combined eluant and the resulting solid after drying in vacuum was crystallised from acetone, as a mono-hydrate. Yield 3.98 g (98%). ^{1}H NMR (250 MHz, D_2O, RT) 1.48 (9H, s, Me-Sb). Mass spectrum (EI, m/z (rel. int.(%)): 351 ($Me_6Sb_2OH^+$, 100), 321 ($Me_4Sb_2OH^+$, 80), 291($Me_2Sb_2OH^+$, 29), 185 ($Me_2Sb(OH)_2^+$, 15), 183 (Me_3SbOH^+, 8), 168 (Me_2SbOH^+, 21) 151 (Me_2Sb^+, 89). Analysis: Found: C, 16.7; H, 6.2. $C_3H_{11}O_2Sb$ calc.: C, 17.9; H, 5.5; $C_3H_{11}O_2Sb \cdot H_2O$ calc.: C, 16.5; H, 6.0%.

A solution of trimethylantimony dichloride (4.87 g, 20. 5mmol) in water (200 ml) was added to a stirred solution of trimethylantimony dihydroxide (4.11 g, 20.5 mmol) in water (100 ml) and the resulting solution stirred for 1 h. The solvent was then removed under reduced pressure and the crude product recrystallised from ethanol. Yield 3.61 g (88%). ^{1}H NMR (250 MHz, D_2O, RT) 1.83 (s, Me-Sb), (250 MHz, $CDCl_3$, RT): Anhydrous conditions: 1.96 (18H, s, Me-Sb). Moist solvent 1.96 (s, Me-Sb), 2.04 (s, Me-Sb), 2.35 (s, Me-Sb). Analysis: Found: C, 17.1; H, 4.5. $C_6H_{18}Cl_2OSb_2$ calc.: C, 17.1; H, 4.3%.

3.2.5. Preparation of $Sb(2,4,6\text{-}Me_3C_6H_2)_3Br(OH)$ 5

A solution of sodium hydroxide (0.06 g, 1.4 mmol) in the minimum of water was added to a stirred suspension of trimesitylantimony dibromide (0.82 g, 1.3 mmol) and methanol (50 ml), leading to the rapid formation of a clear solution. The solution was refluxed for 20 h, after which the volatiles were removed in vacuum. The resulting solid was dissolved in dichloromethane (50 ml) and after filtration the solvent was evaporated to yield crude product. Recrystallisation from chloroform/hexane gave crystals of the title compound. Yield 0.61 g (82%). M.p. 188–191°C. ^{1}H NMR (250 MHz, $CDCl_3$, RT) (2.32 (9H, s, p-Me), 2.52 (18H, s, o-Me), 7.01 (6H, s, m-Ar). $^{13}C\{^1H\}$ NMR (69 MHz,

Table 5
Crystallographic data

Compound	2	3
Chemical formula	$C_{42}H_{42}Br_2OSb_2$	$C_{45}H_{49}Br_2OSb_2$
Formula weight	966.08	1009.16
Crystal size/mm	0.36×0.32×0.28	0.31×0.27×0.21
Crystal system	Trigonal	Triclinic
Space group	$R\bar{3}$	$P\bar{1}$
a/Å	13.1564(14)	12.100(8)
b/Å	13.1564(14)	19.622(12)
c/Å	19.506(12)	19.623(9)
α/°	90	112.17(4)
β/°	90	94.68(5)
γ/°	120	107.44(5)
Volume/Å^3	2923.9(6)	4015(4)
Z	3	4
D_c/g cm^{-3}	1.646	1.669
Radiation (/Å)	Mo-K_α (0.71069)	Mo-K_α (0.71069)
μ/cm^{-1}	34.66	33.69
F(000)	1422	1996
θ limits/°	2–25	2–23
Index ranges (for unique data)	$-14 < h < 12$ $-11 < k < 14$ $-21 < l < 21$	$-13 < h < 12$ $-21 < k < 19$ $0 < l < 21$
Temperature/K	150	150
Total data collected	3461	10452
Unique data	1033	
R(int)	0.0936	
Absorption correction	None	Numerical
min		0.666
max		0.721
Structure solution	Patterson (SHELXS-86)	Direct methods (SHELXS-86)
Refinement	Full matrix-LS on F^2	Full matrix-LS on F^2
Data/variables	1022/74	10409/910
Goodness of Fit (S)	1.073	1.065
Final diff. map (e Å^{-3})	+1.35, −0.72	+1.32, −1.24
R observed data [$I > 2\sigma(I)$]	0.0308	0.0602
R_w all data	0.0747	0.1565

Table 6
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) with estimated standard deviations in parentheses for $((p\text{-}MeC_6H_4)_3SbBr]_2O$

Atom	x	y	z	U(eq)
Br(1)	6667	3333	5937(1)	39(1)
Sb(1)	6667	3333	7332(1)	18(1)
O(1)	6667	3333	8333	22(1)
C(1)	6175(3)	4639(3)	7321(1)	20(1)
C(2)	5324(3)	4536(3)	7785(2)	22(1)
C(3)	5095(3)	5450(3)	7859(2)	26(1)
C(4)	5726(3)	6491(3)	7495(2)	31(1)
C(5)	6571(3)	6570(3)	7033(2)	36(1)
C(6)	6784(3)	5654(3)	6937(2)	30(1)
C(7)	5483(4)	7491(4)	7589(2)	53(1)

Table 7
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) with estimated standard deviations in parentheses for $((o\text{-MeC}_6H_4)_3SbBr]_2O.0.5C_6H_{14}$

Atom	x	y	z	U(eq)
Sb(1)	−268(1)	−2708(1)	6516(1)	27(1)
Br(1)	1445(1)	−3042(1)	5750(1)	52(1)
O(1)	−1477(3)	−2467(2)	7077(2)	38(1)
Sb(2)	−2313(1)	−1872(1)	7738(1)	25(1)
Br(2)	−3556(1)	−1104(1)	8642(1)	56(1)
O(2)	5870(3)	2350(2)	7964(2)	41(1)
Sb(3)	4483(1)	2121(1)	7223(1)	25(1)
Br(3)	2472(1)	1835(1)	6249(1)	55(1)
Sb(4)	7352(1)	2494(1)	8584(1)	24(1)
Br(4)	9409(1)	2632(1)	9434(1)	42(1)
C(11)	156(2)	−1703(2)	6283(2)	38(2)
C(12)	570(2)	−986(2)	6922(3)	42(2)
C(13)	811(3)	−287(3)	6856(3)	52(2)
C(14)	638(5)	−304(3)	6149(3)	57(2)
C(15)	229(5)	−1002(3)	5512(3)	50(2)
C(16)	−20(4)	−1720(3)	5565(3)	36(2)
C(17)	−453(5)	−2448(4)	4850(3)	60(3)
C(21)	−1562(3)	−3810(2)	5728(1)	44(2)
C(22)	−2568(3)	−3718(3)	5404(1)	73(2)
C(23)	−3520(4)	4354(3)	4923(2)	112(3)
C(24)	−3446(6)	−5075(3)	4772(4)	116(3)
C(25)	−2524(6)	−5223(3)	5045(3)	85(3)
C(26)	−1537(5)	−4558(3)	5564(3)	70(3)
C(27)	−559(6)	−4683(5)	5872(4)	105(5)
C(31)	827(2)	−2618(2)	7464(2)	43(2)
C(32)	1978(3)	−2061(2)	7691(2)	64(2)
C(33)	2732(4)	−1913(3)	8344(3)	109(3)
C(34)	2286(6)	−2335(4)	8746(3)	119(3)
C(35)	1179(6)	−2882(3)	8545(3)	96(3)
C(36)	407(5)	−3038(3)	7882(3)	62(2)
C(37)	−758(6)	−3630(4)	7713(5)	79(3)
C(41)	−3355(3)	−1902(1)	6802(2)	27(2)
C(42)	−2691(3)	−1584(1)	6372(2)	37(2)
C(43)	−3242(4)	−1607(2)	5723(3)	40(2)
C(44)	−4454(4)	−1944(3)	5496(3)	44(2)
C(45)	−5126(4)	−2265(3)	5907(3)	48(2)
C(46)	−4597(4)	−2245(3)	6579(3)	40(2)
C(47)	−5378(5)	−2615(3)	6990(3)	56(3)
C(51)	−2818(2)	−2702(2)	8209(2)	33(2)
C(52)	−2414(2)	−2366(2)	8999(2)	41(2)
C(53)	−2586(3)	−2823(3)	9387(3)	56(2)
C(54)	−3178(5)	−3630(3)	8979(3)	63(2)
C(55)	−3576(6)	−3962(3)	8220(3)	71(3)
C(56)	−3396(5)	−3506(3)	7810(3)	51(2)
C(57)	−3828(6)	−3895(4)	6982(4)	70(3)
C(61)	−727(3)	−911(3)	8427(1)	42(2)
C(62)	51(3)	−1138(3)	8809(1)	54(2)
C(63)	1088(4)	−583(3)	9286(2)	70(2)
C(64)	1336(5)	188(3)	9380(3)	81(3)
C(65)	617(5)	426(3)	9020(3)	69(3)
C(66)	−455(5)	−141(3)	8529(3)	58(2)
C(67)	−1216(6)	129(4)	8155(3)	64(3)
C(71)	5564(3)	2596(3)	6602(2)	42(2)
C(72)	6423(3)	2237(3)	6397(2)	57(2)
C(73)	7275(4)	2548(3)	6069(2)	85(2)
C(74)	7273(5)	3193(3)	5948(3)	96(2)
C(75)	6469(5)	3552(3)	6145(3)	91(2)
C(76)	5576(5)	3236(3)	6478(3)	66(2)
C(77)	4758(6)	3640(4)	6651(4)	83(3)
C(81)	3932(3)	2919(2)	8108(2)	39(2)
C(82)	4759(3)	3705(2)	8412(2)	49(2)
C(83)	4509(4)	4283(2)	8962(2)	57(2)
C(84)	3471(5)	4079(3)	9191(3)	58(2)
C(85)	2656(5)	3329(3)	8912(3)	53(2)
C(86)	2891(4)	2732(3)	8343(3)	50(2)
C(87)	2066(6)	1938(3)	8058(4)	62(3)
C(91)	3986(2)	882(3)	6907(3)	61(2)
C(92)	3975(2)	733(3)	7585(3)	68(2)
C(93)	3804(3)	−12(3)	7485(3)	99(3)
C(94)	3639(5)	−574(3)	6758(3)	89(3)
C(95)	3644(5)	−474(3)	6118(4)	90(3)
C(96)	3845(5)	324(3)	6216(3)	80(2)
C(97)	3880(7)	587(6)	5639(5)	49(4)
C(97′)	3807(7)	243(10)	5478(6)	121(8)
C(101)	7830(3)	1757(2)	7652(2)	34(2)
C(102)	7015(3)	980(2)	7320(2)	49(2)
C(103)	7204(4)	426(2)	6707(2)	57(2)
C(104)	8198(5)	648(3)	6431(3)	67(2)
C(105)	9014(5)	1392(3)	6740(3)	62(2)
C(106)	8833(4)	1970(3)	7369(3)	52(2)
C(107)	9677(6)	2766(4)	7682(4)	62(3)
C(111)	7944(2)	3728(2)	8911(3)	35(2)
C(112)	7944(2)	3926(2)	8297(3)	50(2)
C(113)	8262(3)	4692(3)	8406(3)	60(2)
C(114)	8591(5)	5262(3)	9149(3)	61(2)
C(115)	8605(4)	5097(3)	9756(3)	53(2)
C(116)	8275(4)	4303(3)	9651(3)	46(2)
C(117)	8257(5)	4129(4)	10307(3)	51(3)
C(121)	6414(3)	1920(3)	9217(2)	41(2)
C(122)	6605(3)	1217(3)	9147(2)	55(2)
C(123)	5925(4)	749(3)	9437(2)	80(2)
C(124)	5072(5)	983(3)	9780(3)	77(2)
C(125)	4872(5)	1652(3)	9872(3)	57(2)
C(126)	5553(5)	2139(3)	9579(3)	52(2)
C(127)	5321(6)	2839(3)	9673(4)	56(3)
C(6S)	9613(11)	5667(6)	3191(6)	115(5)

$CDCl_3$, RT) 21.0 (*p*-Me), 24.6 (*o*-Me), 131.0 (*m*-Ar), 136.5 (*p*-Ar), 142.5 (*o*-Ar), 142.8 (*ipso*-Ar). IR (nujol mull, CsI): 3501m, br, 1596m, 1563m, 1403w, 1291m, 1264m, 1027m, 1008w, 850s, 734s, 700w, 570m, 542s. Mass spectrum (FAB, m/z (rel. int. (%)): 559 ($M\text{–}OH^+$ 3), 495 ($M\text{–}Br^+$, 65) 478 ($(Me_3C_6H_2)_3Sb^+$, 4), 376 ($(Me_3C_6H_2)_2SbOH^+$, 3), 257 ($(Me_3C_6H_2)SbOH^+$, 7), 119 $Me_3C_6H_2^+$, 38). Analysis: Found: C, 55.0; H, 5.7. $C_{27}H_{34}BrOSb$ calc.: C, 56.3; H, 5.9%.

3.3. Structure determinations

Crystals of **2** and **3** suitable for X-ray crystallography were obtained by slow diffusion of hexane into concentrated chloroform solutions of the compounds. For **2**, slightly more than one hemisphere of data was collected on a Delft Instruments FAST TV area detector diffractometer, equipped with a rotating anode FR591 generator, while for **3**, the data were collected using a Stoe-Stadi-4 diffractometer. The data were corrected for Lorentz and polarisation and for **3** an absorption correction was applied. Crystal data and details of the structure determinations [25,26] are summarised in Table 5. Hydrogen atoms in **2** were placed in calculated positions [d(C–H), 0.95 Å (aromatic), 0.98 Å (methyl)] with fixed isotropic thermal parameters [$U_{iso}(H) = xU_{eq}(C)$, where $x = 1.2$ for aryl and 1.5 for methyl hydrogens] and refined riding on their respective carbon atoms.

One of the methyl groups in **3** was disordered [C(97) and C(97')] and the tolyl groups were restrained to planarity with equivalent methyl groups. Hydrogen atoms were treated as described above, except that the methyl hydrogens were located from a difference synthesis. The disordered solvent molecule was modelled using three fully occupied and three partially occupied carbon atoms. Atomic coordinates for compounds 2 + 3 are listed in Tables 6 and 7, respectively. Full details of the thermal parameters, hydrogen atom coordinates and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

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References

[1] G. Ferguson, E.W. Macauley, J. Chem. Soc., Chem. Commun. (1968) 1288.
[2] G. Wittig, K. Clauss, Ann. Chem. 577 (1952) 26.
[3] G.T. Morgan, F.M.G. Micklethwait, G.S. Witby, J. Chem. Soc. 97 (1910) 34.
[4] F. Challenger, F. Pritchard, J.R.A. Jinks, J. Chem. Soc. 125 (1924) 864.
[5] G.G. Long, G.O. Doak, L.D. Freedman, J. Am. Chem. Soc. 86 (1964) 209.
[6] G.O. Doak, G.G. Long, L.D. Freedman, J. Organomet. Chem. 4 (1965) 82.
[7] R.L. McKinney, H.H. Sisler, Inorg. Chem. 6 (1967) 1178.
[8] M. Shindo, R. Okawara, J. Organomet. Chem. 5 (1966) 537.
[9] Y. Kawasaki, Y. Yamamoto, M. Wada, Bull. Chem. Soc. Jpn. 56 (1983) 145.
[10] G. Ferguson, G.S. Harris, A. Khan, Acta Crystallogr. C 43 (1987) 2078.
[11] T. Westhoff, F. Huber, H. Preut, J. Organomet. Chem. 348 (1988) 185.
[12] H. Preut, T. Westhoff, F. Huber, Acta Crystallogr. C 45 (1989) 49.
[13] T. Westhoff, F. Huber, R. Ruther, H. Preut, J. Organomet. Chem. 352 (1988) 107.
[14] J. Bordner, G.O. Doak, T.S. Everett, J. Am. Chem. Soc. 108 (1986) 4206.
[15] G. Ferguson, F.C. Marchand, D.R. Ridley, Acta Crystallogr. B 31 (1975) 1260.
[16] E.R.T. Tiekink, J. Organomet. Chem. 333 (1987) 199.
[17] A. Ouchi, S. Sato, Bull. Chem. Soc. Jpn. 61 (1988) 1806.
[18] M.J. Taylor, L.J. Baker, C.E.F. Rickard, P.W.J. Surman, J. Organomet. Chem. 498 (1995) C14.
[19] R.M. Wing, K.P. Callahan, Inorg. Chem. 8 (1969) 871.
[20] R. Ruther, F. Huber, H. Preut, J. Organomet. Chem. 342 (1988) 185.
[21] M.J. Begley, D.B. Sowerby, Acta Crystallogr. C49 (1993) 1044.
[22] I.G. Southerington, G.E. Forster, M.J. Begley, D.B. Sowerby, J. Chem. Soc., Dalton Trans. (1995) 1995.
[23] I.G. Southerington, Ph.D. Thesis, University of Nottingham, 1991.
[24] G. Ferguson, C. Glidewell, I. Gosney, D. Lloyd, S. Metcalfe, J. Chem. Soc., Perkin 2 (1988) 1829.
[25] SHELXS-86, G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467.
[26] SHELXL-93. G.M. Sheldrick, Institut für Anorganische Chemie, Universität Göttingen, 1993.