Multiply bridged organodiantimony(v) compounds; crystal structures of [(SbR$_2$)$_2$(μ-O)$_2$(μ-O$_2$AsMe$_2$)$_2$] (R = Ph or p-tolyl) and [(SbR$_3$)$_2$(μ-O)(μ-O$_2$MR′$_2$)$_2$] (R = Ph, M = P, R′ = Me; R = Ph, M = As, R′ = Me or Ph; R = p-tolyl, M = P, R′ = Me)

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A number of quadruply and triply bridged organodiantimony(v) compounds have been synthesized by reactions of [(SbR$_2$BrO)$_2$] (R = Ph or p-tolyl) and [(SbR$_3$X)$_2$O] (R = Ph or p-tolyl, X = Br or Cl) with Na(O$_2$AsMe$_2$), Na(O$_2$AsPh$_2$) or Na(O$_2$AsMe$_2$). The compounds have been characterised by a range of spectroscopic methods and crystal structures are reported for two quadruply bridged, [(SbPh$_2$)$_2$(μ-O)$_2$(μ-O$_2$AsMe$_2$)$_2$] and [{Sb(p-MeC$_6$H$_4$)$_2$}$_2$(μ-O)$_2$(μ-O$_2$AsMe$_2$)$_2$], and four triply bridged compounds, [(SbPh$_3$)$_2$(μ-O)(μ-O$_2$PMe$_2$)$_2$], [(SbPh$_3$)$_2$(μ-O)(μ-O$_2$AsMe$_2$)$_2$], [(SbPh$_3$)$_2$(μ-O)(μ-O$_2$AsPh$_2$)$_2$] and [{Sb(p-MeC$_6$H$_4$)$_3$}$_2$(μ-O)(μ-O$_2$PMe$_2$)$_2$]. Related trimethylantimony(v) compounds, *i.e.* [{SbMe$_3$(O$_2$PMe$_2$)}$_2$O] and [{SbMe$_3$(O$_2$AsPh$_2$)}$_2$O], which are highly moisture sensitive, have also been obtained.

Until recently there were very few diantimony compounds known in which the atoms are spanned by either three or four bridging groups and when this work was started only two compounds containing quadruple bridges had been characterised. The first was the zwitterionic [(SbPh$_2$)$_2$(μ-O)$_2$(μ-O$_2$SbPh$_2$)$_2$],[1] obtained as a by-product in the oxidation of triphenylantimony while the second was an anionic species, [(SbPh$_2$)$_2$(μ-O)$_2$(μ-MoO$_4$)$_2$]$^{2-}$, containing two oxo and two molybdate bridges.[2,3] More recently two further species, [(SbPh$_2$)$_2$(μ-O)$_2$(μ-O$_2$PR$_2$)$_2$] where R = cyclohexyl or cyclooctyl, have been synthesized.[4]

There is a more extensive series of triply bridged compounds, synthesized by Schmidt and others, which contain in addition to dioxo chelating ligands both oxo and either hydroxo or alkoxo bridges. The general formula is [(SbCl$_3$)$_2$(μ-O)(μ-OR)(μ-X)] with, for example, R = H, X = O$_2$CMe,[5] O$_2$CCl$_3$,[6] HSO$_4$[7] or ClO$_4$;[8] R = Me, X = SO$_4$Me,[9] SO$_2$Me,[10] SO$_3$Me[10] or O$_2$PMe(OMe);[11] and R = Et, X = O$_2$PEt(OEt)[11] or O$_2$PMe(OMe).[11] Bridging in the tetranuclear compound, [Sb$_4$Ph$_8$-O$_6$(MeCO$_2$H)$_3$],[12] is similar with pairs of antimony atoms spanned by hydroxo, oxo and acetate bridges. Pairs of antimony atoms can also be bridged by either three halogens or two halogens and one oxygen, as in [NMe$_4$]$_3$[(SbCl$_3$)$_2$(μ-Br)$_3$][13] and [Hpy]$_2$[(SbCl$_2$)$_2$(μ-O)(μ-X)$_2$], where py = pyridine and X = Br or Cl,[14] respectively.

One triply bridged compound, [(SbCl$_3$)$_2$(μ-O)(μ-O$_2$PMe$_2$)$_2$], with an oxo and two dimethylphosphinate bridges has previously been synthesized[15] and, while this work was in progress, two further compounds of this type [(SbPh$_2$Cl)$_2$(μ-O)(μ-O$_2$PR$_2$)$_2$],[16] where R = cyclo-hexyl or -octyl, were isolated. Crystal structures for both [(SbCl$_3$)$_2$(μ-O)(μ-O$_2$PMe$_2$)$_2$] and [(SbPh$_2$Cl)$_2$(μ-O){μ-O$_2$P(C$_6$H$_{11}$)$_2$}$_2$] show octahedral co-ordination at antimony with bidentate phosphinate groups; the geometry is similar in the related carboxylate-bridged compound [(SbF$_3$)$_2$(μ-O)(μ-O$_2$CCF$_3$)$_2$].[17]

Phosphinates and arsinates can, however, behave as either unidentate or chelating ligands and the work described in this paper was carried out to define further the conditions under which the groups might bridge between pairs of antimony atoms already linked by either one or two oxygen atoms. The starting materials were the singly bridged dihalides [(SbR$_3$X)$_2$O], where X = Br or Cl and R = phenyl, p-tolyl or methyl, and the double bridged analogues [(SbR$_2$BrO)$_2$] where R = phenyl or p-tolyl. Related dithiophosphinates are also
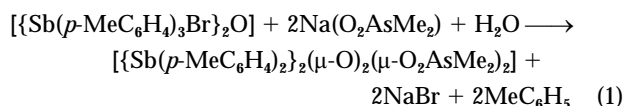
potentially good bridging ligands but complex redox reactions occur with these antimony(v) compounds and reduction products such as [SbPh$_2$(S$_2$PR$_2$)] can be isolated.[18]

Discussion

Quadruply bridged compounds

Preparation. Quadruply bridged diantimony compounds [(SbPh$_2$)$_2$(μ-O)$_2$(μ-O$_2$AsR$_2$)$_2$], where R = Me **1** or Ph **2**, have been prepared by treating [(SbPh$_2$BrO)$_2$], which contains a four-membered Sb$_2$O$_2$ ring, with 2 mol of either Na(O$_2$AsMe$_2$) or Na(O$_2$AsPh$_2$) in dichloromethane. They are high-melting stable compounds, which crystallise as chloroform solvates. An attempt to introduce a single arsinate bridge by treating [(SbPh$_2$BrO)$_2$] with 1 mol of Na(O$_2$AsMe$_2$) gave a complex reaction mixture and only a small amount of unidentified crystalline material was isolated. Similar reactions with related phosphinates, Na(O$_2$PMe$_2$) and Na(O$_2$PPh$_2$), however, failed to give the expected quadruply bridged analogues, and with dimethylphosphinate a triply bridged compound, [(SbPh$_3$)$_2$(μ-O)(μ-O$_2$PMe$_2$)$_2$] **3**, was obtained. This can only arise by an extensive rearrangement, involving loss of an oxo bridge and gain of one phenyl group per antimony, and currently no realistic mechanism can be advanced.

Unexpectedly, a third quadruply bridged compound, [{Sb(p-MeC$_6$H$_4$)$_2$}$_2$(μ-O)$_2$(μ-O$_2$AsMe$_2$)$_2$] **4**, was obtained in low yield by treating [{Sb(p-MeC$_6$H$_4$)$_3$Br}$_2$O] with 2 mol of Na(O$_2$AsMe$_2$) in dichloromethane. In this case, rearrangement with gain of an oxo bridge and loss of a p-tolyl group from each antimony may result from hydrolysis and elimination of toluene as shown in equation (1).

$$[\{Sb(p\text{-}MeC_6H_4)_3Br\}_2O] + 2Na(O_2AsMe_2) + H_2O \longrightarrow$$
$$[\{Sb(p\text{-}MeC_6H_4)_2\}_2(\mu\text{-}O)_2(\mu\text{-}O_2AsMe_2)_2] +$$
$$2NaBr + 2MeC_6H_5 \quad (1)$$

Spectroscopy. All three quadruply bridged compounds **1**, **2** and **4** give complex infrared spectra with many bands associated with aryl groups,[19] but an intense broad band centred at *ca.* 800 cm^{-1} can be assigned to AsO$_2$ stretching. The fact that the antisymmetric and symmetric modes are not resolved is taken to point to symmetrical bonding. Rather surprisingly, it is not
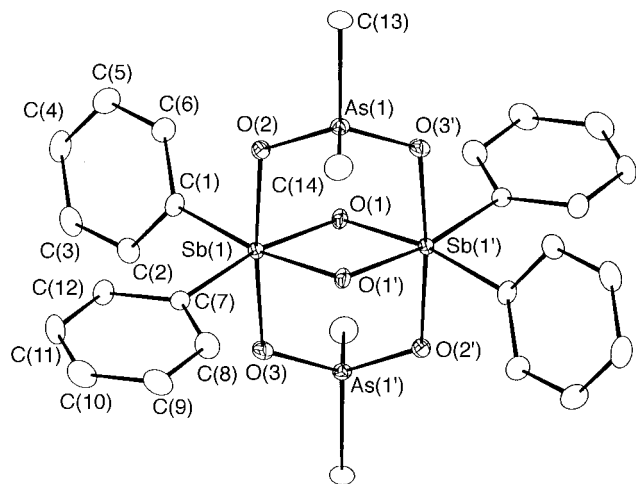
Fig. 1 Molecular structure and atom numbering scheme for [(SbPh$_2$)$_2$-(μ-O)$_2$(μ-O$_2$AsMe$_2$)$_2$]·2CHCl$_3$ **1**

Fig. 2 Molecular structure and atom numbering scheme for [{Sb(p-MeC$_6$H$_4$)$_2$}$_2$(μ-O)$_2$(μ-O$_2$AsMe$_2$)$_2$] **4**

Table 1 Selected bond distances (Å) and angles (°) for [(SbPh$_2$)$_2$(μ-O)$_2$(μ-O$_2$AsMe$_2$)$_2$]·2CHCl$_3$ **1**, with estimated standard deviations (e.s.d.s) in parentheses *

Sb(1)−O(1)	1.995(3)	Sb(1)−C(7)	2.156(4)
Sb(1)−O(1′)	2.004(3)	As(1)−O(2)	1.709(3)
Sb(1)−O(2)	2.101(3)	As(1)−O(3′)	1.711(3)
Sb(1)−O(3)	2.083(3)	As(1)−C(13)	1.909(4)
Sb(1)−C(1)	2.157(4)	As(1)−C(14)	1.911(4)
O(1)−Sb(1)−O(1′)	79.5(1)	O(3)−Sb(1)−C(7)	89.6(1)
O(1)−Sb(1)−O(2)	89.9(1)	C(1)−Sb(1)−C(7)	97.4(1)
O(1′)−Sb(1)−O(2)	85.5(1)	O(2)−Sb(1)−O(3)	174.3(1)
O(1)−Sb(1)−O(3)	85.3(1)	O(1′)−Sb(1)−C(1)	170.0(1)
O(1′)−Sb(1)−O(3)	90.7(1)	O(1)−Sb(1)−C(7)	169.3(1)
O(1)−Sb(1)−C(1)	92.5(1)	O(2)−As(1)−O(3′)	114.0(1)
O(2)−Sb(1)−C(1)	88.6(1)	C(13)−As(1)−C(14)	110.0(2)
O(3)−Sb(1)−C(1)	94.6(1)	Sb(1)−O(1)−Sb(1′)	100.5(1)
O(1′)−Sb(1)−C(7)	91.1(1)	Sb(1)−O(2)−As(1)	119.0(1)
O(2)−Sb(1)−C(7)	94.7(1)	Sb(1)−O(3)−As(1′)	119.5(1)

* Atoms carrying a prime are related by the symmetry operation $1 − x$, $1 − y$, $2 − z$.

Table 2 Selected bond distances (Å) and angles (°) for [{Sb(p-MeC$_6$H$_4$)$_2$}$_2$(μ-O)$_2$(μ-O$_2$AsMe$_2$)$_2$] **4**, with e.s.d.s in parentheses *

Sb(1)−O(3)	2.007(3)	Sb(1)−C(8)	2.161(4)
Sb(1)−O(3A)	2.007(3)	As(1)−O(1A)	1.701(3)
Sb(1)−O(2)	2.087(3)	As(1)−O(2)	1.703(3)
Sb(1)−O(1)	2.084(3)	As(1)−C(15)	1.904(4)
Sb(1)−C(1)	2.148(4)	As(1)−C(16)	1.903(4)
Sb(1)−O(1)−As(1A)	119.5(1)	O(1)−Sb(1)−C(1)	93.2(1)
O(3)−Sb(1)−O(3A)	79.0(1)	C(1)−Sb(1)−C(8)	99.0(2)
O(3)−Sb(1)−O(2)	85.4(1)	O(1)−Sb(1)−O(2)	173.0(1)
O(3A)−Sb(1)−O(2)	89.4(1)	O(3A)−Sb(1)−C(8)	167.2(1)
O(3)−Sb(1)−O(1)	89.9(1)	O(3)−Sb(1)−C(1)	171.0(1)
O(3A)−Sb(1)−O(1)	84.6(1)	O(1A)−As(1)−O(2)	113.4(1)
O(3)−Sb(1)−C(8)	89.3(1)	C(15)−As(1)−C(16)	110.4(2)
O(2)−Sb(1)−C(8)	95.1(1)	Sb(1)−O(3)−Sb(1A)	101.0(1)
O(1)−Sb(1)−C(8)	90.1(2)	Sb(1)−O(2)−As(1)	119.0(1)
O(3A)−Sb(1)−C(1)	92.9(1)	Sb(1)−O(1)−As(1A)	119.5(1)
O(2)−Sb(1)−C(1)	90.6(1)		

* Atoms designated A are related by the symmetry operation $−x$, $1 − y$, $−z$.

Table 3 Comparison of Sb$_2$O$_2$ mean ring parameters

Compound	Sb−O/Å	O−Sb−O/°	Sb−O−Sb/°	Ref.
1	2.000	79.5	100.5	This work
4	2.007	79.0	101.0	This work
[{SbPh$_2$(MoO$_4$)O}$_2$]$^{2−}$	2.019	77.1	103.0	2
[{SbPh$_2$O(O$_2$SbPh$_2$)}$_2$]	2.089	72.7	107.3	1
[(SbPh$_3$O)$_2$]	2.002	77.5	102.5	1
[(SbPh$_2$BrO)$_2$]	1.986	78.6	101.5	21

possible to assign any bands to the Sb$_2$O$_2$ ring modes, which occur for the starting material between 495 and 670 cm^{-1}.[20]

There were no unexpected features in the ^{1}H NMR spectra for the three compounds but [(SbPh$_2$)$_2$(μ-O)$_2$(μ-O$_2$AsPh$_2$)$_2$] **2** showed a broad unresolved multiplet at δ 7.30–7.80. All three compounds show parent ions in their FAB mass spectra, although for **2** the highest mass ion is attributed to [M + 2H]$^+$. Subsequent fragmentation, as expected, involves loss of both aryl and arsinate groups and there are a number of prominent monoantimony species, including [SbPh$_2$(O$_2$AsMe$_2$)]$^+$ for **1**, [SbPh$_2$(O$_2$AsPh$_2$) + H]$^+$ for **2** and the rearrangement ion [Sb-(p-MeC$_6$H$_4$)$_3$(O$_2$AsMe$_2$)]$^+$ is the base peak for **4**.

Structures. Single-crystal structures have been determined for [(SbPh$_2$)$_2$(μ-O)$_2$(μ-O$_2$AsMe$_2$)$_2$] **1**, as a bis(chloroform) solvate, and [{Sb(p-MeC$_6$H$_4$)$_2$}$_2$(μ-O)$_2$(μ-O$_2$AsMe$_2$)$_2$] **4**. The molecular structure of **1**, which has crystallographic C_i symmetry, is shown in Fig. 1 and selected bond distances and angles are listed in Table 1. The determination confirms the presence of a quadruply bridged structure with octahedrally co-ordinated antimony atoms. The Sb−O distances in the four-membered ring [1.995(3) and 2.004(3) Å] are effectively equal, in contrast to those in the starting material, which are either 'short' (1.936, 1.918 Å) or 'long' (2.061, 2.030 Å) depending on their position in the trigonal-bipyramidal co-ordination about antimony.[20]

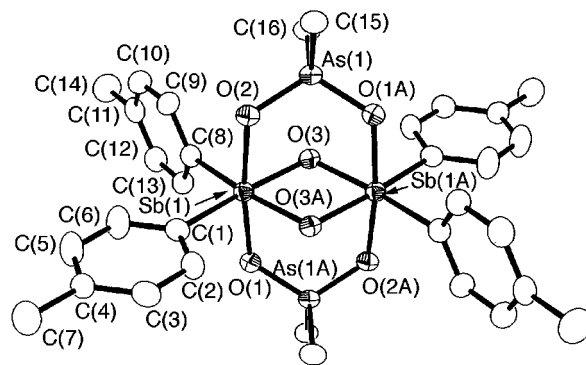Co-ordination of the dimethylarsinate groups, which consti-

tute the other two bridging groups, is highly symmetrical with identical As−O bond lengths, i.e. As(1)−O(2) 1.709(3) Å and As(1)−O(3′) 1.711(3) Å, implying complete delocalisation of the π component of the As−O system. The arsenic atom is basically tetrahedral although the O(2)−As(1)−O(3′) angle is opened to 114.0(1)°. This together with angles of ca. 119.5° at O(2) and O(3) probably represents the extent of the flexibility in this part of the system towards matching ligand bite with Sb · · · Sb separation.

Co-ordination about antimony is distorted octahedral with the O(1)−Sb(1)−O(1′) angle associated with the four-membered ring constrained to 79.5(1)°. An important point is that the *trans* angle involving the bridging groups [O(2)−Sb(1)−O(3) 174.3(1)°] is close to 180° implying that incorporation of the bridging arsinate groups imposes no great strain. This structure is clearly very similar to that of [(SbPh$_2$)$_2$(μ-O)$_2$(μ-MoO$_4$)$_2$]$^{2−}$,[2] where the significantly longer Mo−O separations (mean 1.83 Å; *cf.* As−O, mean 1.71 Å) imply a larger bite and even less strain.

Compound **4**, [{Sb(p-MeC$_6$H$_4$)$_2$}$_2$(μ-O)$_2$(μ-O$_2$AsMe$_2$)$_2$] (see Fig. 2 and Table 2) has a closely related structure with again

crystallographically imposed C_i symmetry, symmetrically co-ordinated dimethylarsinate groups [As(1)–O1(A) and As(1)–O(2) 1.701(3) and 1.703(3) Å, respectively] and similar geometries about antimony and arsenic. An interesting feature in both compounds is the relative orientations of the aryl groups. The C(1)–C(6) group is almost coplanar with the Sb_2O_2 plane (4.0° between best-fit planes) while the C(8) to C(14) group is almost perpendicular (94.5°).

Table 3 summarises data for compounds containing Sb_2O_2 rings, showing there is little variation in either Sb–O distances (*ca.* 2.00 Å) or angles (*ca.* 78°) in **1** and **4** compared with those in related compounds. The only noticeable difference is with the zwitterionic [{$SbPh_2O(O_2SbPh_2)$}$_2$] where bridging oxo groups are involved in additional bonding to the antimony centres of the bridging diphenylstibinate moieties. With the exception of [($SbPh_2BrO$)$_2$], the rings are centrosymmetric and the compounds have near D_{2h} local symmetry.

Triply bridged compounds

Preparations. Triply bridged compounds, [($SbPh_3$)$_2$(μ-O)(μ-O_2MR_2)$_2$] (M = P, R = Me **3**; M = As, R = Me **5** or Ph **6**), were prepared in good yield as stable crystalline solids by reactions of [($SbPh_3Br$)$_2O$], with 2 mol of the appropriate Na(O_2MR_2) but only unidentified products were obtained in the reaction with Na(O_2PPh_2). Reaction between [{Sb(p-MeC$_6$H$_4$)$_3$Br}$_2$O] and 2 mol of Na(O_2PMe_2) gave the expected bridged compound, [{Sb(p-MeC$_6$H$_4$)$_3$}$_2$(μ-O)(μ-O_2PMe_2)$_2$] **7**, in good yield, but surprisingly the *o*-tolyl analogue could not be obtained from [{Sb(o-MeC$_6$H$_4$)$_3$Br}$_2$O] and 2 mol of Na(O_2PMe_2). An attempt to form an unsymmetrically substituted compound, [($SbPh_3$)$_2$(μ-O)(μ-O_2AsMe_2)Br], from ($SbPh_3Br$)$_2$O and 1 mol of Na(O_2AsMe_2) gave only mixtures of **5** and unchanged ($SbPh_3Br$)$_2$O.

Related trimethylantimony(v) compounds, [($SbMe_3$)$_2$(μ-O)(μ-O_2PMe_2)$_2$] **8** and [($SbMe_3$)$_2$(μ-O)(μ-O_2AsPh_2)$_2$] **9**, were prepared in good yield from [($SbMe_3Cl$)$_2O$] and 2 mol of either Na(O_2PMe_2) or Na(O_2AsPh_2), but they are highly moisture sensitive and handling, even with stringent Schlenk and glove-box techniques, was extremely difficult. Conventional micro-analysis and IR spectroscopy were not possible but satisfactory ^{1}H and ^{13}C-{^{1}H} NMR spectra were obtained and these compounds are considered to have the same triply bridged structures as those described above.

It was noted above that reaction of [{Sb(p-MeC$_6$H$_4$)$_3$Br}$_2$O] with 2 mol of Na(O_2AsMe_2) gave, instead of the expected triply bridged product, a quadruply bridged rearrangement compound **4**, formed presumably because of its greater stability. This is all the more surprising as the related phenylated starting material, [($SbPh_3Br$)$_2$O], reacts with Na(O_2AsMe_2) to give [($SbPh_3$)$_2$(μ-O)(μ-O_2AsMe_2)$_2$] **5** in good yield. Detailed examination of the latter reaction by ^{1}H NMR spectroscopy, however, does show evidence for formation of **1**, the analogous rearrangement product, but here rearrangement is of minor importance.

Spectroscopy. The IR spectrum of [($SbPh_3$)$_2$(μ-O)(μ-O_2PMe_2)$_2$] **3** contains a strong, broad band at 1112 cm^{-1}, assigned to the ν_{asym}(PO_2) mode, and a doublet at 1046 and 1032 cm^{-1}, probably the in- and out-of-phase components of ν_{sym}(PO_2). For related tin dimethylphosphinates,[21] bands between 1200 and 1000 cm^{-1} are associated with either chelating or bridging ligands, supporting triply bridged structures here. Bands for [{Sb(p-MeC$_6$H$_4$)$_3$}$_2$(μ-O)(μ-O_2PMe_2)$_2$] **7** are at similar positions, with ν_{asym}(PO_2) assigned to peaks at 1120 and 1111 cm^{-1} and ν_{sym}(PO_2) at 1048 and 1033 cm^{-1}.

Spectra of the arsinates, [($SbPh_3$)$_2$(μ-O)(μ-O_2AsMe_2)$_2$] **5** and [($SbPh_3$)$_2$(μ-O)(μ-O_2AsPh_2)$_2$] **6**, contain intense broad bands at 852 and 831 cm^{-1}, respectively, consistent with the presence of bridging (O_2AsR_2) groups; these are at significantly higher

energy than corresponding bands (*ca.* 800 cm^{-1}) for related quadruply bridged compounds. The IR spectra for [($SbMe_3$)$_2$(μ-O)(μ-O_2PMe_2)$_2$] **8** and [($SbMe_3$)$_2$(μ-O)(μ-O_2AsPh_2)$_2$] **9** may be unreliable, as hydrolysis appears to take place, but for **8** the broad bands at 1172 and 1020 cm^{-1} may be assigned tentatively to P–O stretches of bidentate O_2PMe_2 groups, while the broad 795 cm^{-1} band for **9** can probably be assigned to the related As–O stretches.

Proton NMR spectra for the arylantimony compounds point to complex solution behaviour and it is clear that, unless stringent precautions to exclude moisture are taken, there is either complete or partial hydrolysis to hydroxo-species, such as $SbR_3(O_2MR'_2)(OH)$. Using CDCl$_3$ as received and with no precautions against moisture during solution preparation, *i.e.* 'moist' CDCl$_3$, the spectrum of [($SbPh_3$)$_2$(μ-O)(μ-O_2PMe_2)$_2$] **3** can be assigned to a single species with the expected 3:1 ratio of phenyl and dimethylphosphinate groups. Following related studies on [($SbPh_3X$)$_2$O] solutions, where X = Br or Cl,[22] this is assigned to the hydroxo-species [$SbPh_3(O_2PMe_2)(OH)$] formed as a result of hydrolysis by adventitious water. As with the halide systems, recrystallisation of the NMR sample gave quantitative recovery of **3** and no evidence for the hydroxo-species in the solid.

Under strictly anhydrous conditions, *i.e.* with dried CDCl$_3$, a sealed NMR tube and manipulations carried out in a nitrogen-filled glove-box, there were signals for two species, neither of which was the hydrolysis product, and the oxo bridge is presumed to be intact in each. The O_2PMe_2 group of the first species **A** showed a doublet at δ 0.72 [^2J(HP) = 14 Hz] and two triplets and a doublet [^3J(HH) = 7 Hz] in the phenyl region. For the second species **B** the O_2PMe_2 signal collapsed to a broad featureless signal with two second-order multiplets, centred at δ 7.38 and 7.68, in the phenyl region. The **A**:**B** ratio was *ca.* 2:3. It is difficult to assign structures to these species with any certainty but it is likely that one has the solid-state structure with bridging dimethylphosphinate groups (see later), while in the second the dimethylphosphinate groups could, perhaps, be chelating or even unidentate.

The *p*-tolyl derivative **7** behaved similarly with a single hydrolysed species in 'moist' CDCl$_3$ and two species with chemical shifts closely related to those discussed above in anhydrous solutions. Species **A** is dominant with an **A**:**B** ratio of *ca.* 5:1. Exposure of the anhydrous sample to moisture led to a spectrum showing signals for all three species. Two species were also present for [($SbPh_3$)$_2$(μ-O)(μ-O_2AsMe_2)$_2$] **5** in dry CDCl$_3$ and, although both dimethylarsinate signals (δ 0.71 and 1.89) were broad and featureless, the phenyl region clearly showed two distinct sets of signals. The first was a triplet, triplet, doublet pattern at δ 7.17, 7.27 (masked by a multiplet from a second species) and 7.61 for the *meta*, *para* and *ortho* protons, respectively, while the second showed multiplets at δ 7.27 and 7.71. The ratio of the two species was *ca.* 2:1.

In contrast, solution spectra for [($SbMe_3$)$_2$(μ-O)(μ-O_2PMe_2)$_2$] **8** and [($SbMe_3$)$_2$(μ-O)(μ-O_2AsPh_2)$_2$] **9** were more straightforward and only one species was observed in each case. The SbMe$_3$ signals were at higher field (δ 1.66) compared with those for related compounds, *e.g.* δ 1.96 for [($SbMe_3Cl$)$_2$O] and 2.07 for [{$SbMe_3[S_2P(OMe)_2]$}$_2$O].[23] The ^{13}C shifts for the methyl groups at antimony were similar, δ 16.3 and 16.8 respectively, again to higher field than those for [{$SbMe_3[S_2P(OMe)_2]$}$_2$O] (δ 18.6).

The FAB mass spectra of the triply bridged triarylantimony compounds, in contrast to those of the quadruply bridged compounds, do not show the parent ion. The spectra of [($SbPh_3$)$_2$(μ-O)(μ-O_2PMe_2)$_2$] **3**, [($SbPh_3$)$_2$(μ-O)(μ-O_2AsMe_2)$_2$] **5** and [{Sb(p-MeC$_6$H$_4$)$_3$}$_2$(μ-O)(μ-O_2PMe_2)$_2$] **7** all show peaks resulting from loss of one ligand and are assigned to the appropriate [(SbR_3)$_2$(μ-O)(μ-O_2MMe_2)]$^+$ (R = aryl) ions. Major species in all the spectra are monometallic [$SbR_3(O_2MMe_2)$]$^+$ and simple arylantimony ions.
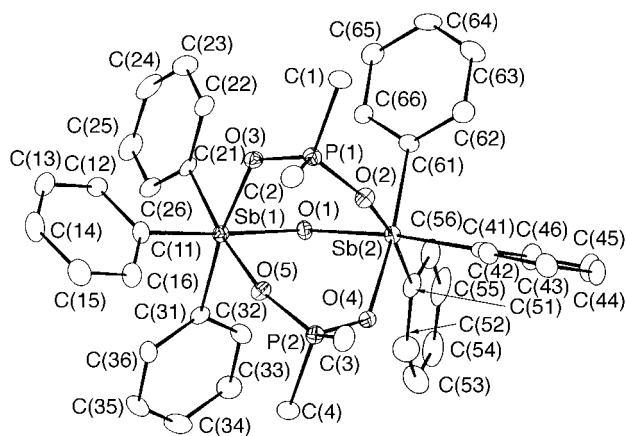
Fig. 3 Molecular structure and atom numbering scheme for [(SbPh₃)₂(μ-O)(μ-O₂PMe₂)₂]·0.5C₆H₁₄ **3**, structures for compounds **5** and **7** are similar

Structures. Single-crystal structure determinations were carried out for four of these triply bridged compounds, three of which (**3**, **4** and **7**) were hemihexane solvates, while the fourth (**6**) was a chloroform solvate. The overall structures of all four compounds, [(SbPh₃)₂(μ-O)(μ-O₂PMe₂)₂]·0.5C₆H₁₄ **3**, [(SbPh₃)₂-(μ-O)(μ-O₂AsMe₂)₂]·0.5C₆H₁₄ **5**, [(SbPh₃)₂(μ-O)(μ-O₂AsPh₂)₂]·CHCl₃ **6** and [{Sb(p-MeC₆H₄)₃}₂(μ-O)(μ-O₂PMe₂)₂]·0.5C₆H₁₄ **7**, are very similar; **3** and **5** are isostructural. A diagram showing the structure of **3**, with the skeletal numbering scheme, which is appropriate for all four compounds, is shown in Fig. 3. Selected bond distances and angles for compounds **3**, **4** and **7** are listed in Table 4 while those for **6** with diphenylarsinate bridges are in Table 5.

The structure determinations confirm that all four compounds are triply bridged diantimony species with one oxygen and two phosphinate or arsinate bridges and the structures are comparable with those of [(SbCl₃)₂(μ-O)(μ-O₂PMe₂)₂][15] and [(SbPh₂Cl)₂(μ-O){μ-O₂P(C₆H₁₁)₂}₂].[16] Antimony atoms are in distorted octahedral co-ordination to three oxygen and three carbon atoms in the *fac* isomeric form. The Sb–O–Sb bridge bonds are equal in **3** and **5** while in **6** and **7** the differences (*ca.* 0.02 Å) are on the limit of significance. As shown in Table 6, mean bridging distances in the present compounds are longer than those in the three compounds previously investigated, which have either chlorine or fluorine substituents on antimony, and the expected increased Lewis acidity would probably account for the bond shortening. The Sb–O–Sb angles in three of the compounds reported here are comparable with that in [(SbPh₂Cl)₂(μ-O){μ-O₂P(C₆H₁₁)₂}₂][16] but again there are consequences if antimony carries three electronegative substituents when the angle closes substantially. The bridge angle in **6**, on the other hand, is increased to 151.7° and is probably a consequence of the change from methyl substituents at arsenic in **5** to phenyl groups in **6**. We have previously commented[18] on the fact that, in a series of compounds, substantial structural changes sometimes result from substituent changes at a 'remote' atom and this seems to be another such example.

There is extensive delocalisation of the π component of the co-ordinated diorgano-phosphinate or -arsinate groups, giving almost symmetrical bridges. An interesting feature in the structures of compounds **5** and **6** is the shortness of the As–O bonds (mean 1.681 and 1.686 Å, respectively) compared with those in the quadruply bridged compounds **1** (mean 1.710 Å) and **4** (mean 1.702 Å) discussed above. This was to some extent expected as the As–O stretching vibrations in the IR spectra of **5** and **6** were at higher energy.

Owing to bridging, the tetrahedral geometry at phosphorus or arsenic is distorted with O–M–O angles increased to *ca.* 115° in the methyl-substituted products and to *ca.* 119° in the diphe-

nylarsinate **6**. The Sb–O–M angles are also increased and are larger in the phosphinates (mean 131.0°), as a consequence of the shorter P–O bond length, than in the corresponding arsinates (mean 127.6°). For comparison, these angles in the quadruply bridged arsinates (**1** and **2**) are further reduced to a mean of 119.2° presumably as the double oxygen bridge reduces the Sb···Sb separation.

It was not possible to assign unequivocally similar triply bridged structures to the trimethylantimony compounds, **8** and **9**, although such structures are likely. Decreased antimony

Table 4 Selected bond distances (Å) and angles (°) for [(SbPh₃)₂(μ-O)(μ-O₂MMe₂)₂]·0.5C₆H₁₄ where M = P **3** or As **5** and for [{Sb(p-MeC₆H₄)₃}₂(μ-O)(μ-O₂MMe₂)₂]·0.5C₆H₁₄ where M = P **7**, with e.s.d.s in parentheses

	3	**5**	**7**
Sb(1)–O(1)	1.958(3)	1.963(4)	1.972(5)
Sb(1)–O(3)	2.153(3)	2.122(4)	2.139(5)
Sb(1)–O(5)	2.171(3)	2.137(4)	2.170(5)
Sb(1)–C(11)	2.164(5)	2.177(6)	2.158(8)
Sb(1)–C(21)	2.152(5)	2.164(6)	2.163(8)
Sb(1)–C(31)	2.155(5)	2.164(6)	2.159(5)
Sb(2)–O(1)	1.952(3)	1.963(4)	1.954(5)
Sb(2)–O(2)	2.194(3)	2.154(4)	2.215(5)
Sb(2)–O(4)	2.154(3)	2.100(4)	2.213(5)
Sb(2)–C(41)	2.153(5)	2.173(7)	2.144(7)
Sb(2)–C(51)	2.163(5)	2.167(6)	2.144(7)
Sb(2)–C(61)	2.151(5)	2.154(7)	2.156(5)
M(1)–O(2)	1.519(4)	1.671(5)	1.521(5)
M(1)–O(3)	1.528(4)	1.685(5)	1.533(5)
M(1)–C(1)	1.798(5)	1.913(7)	1.783(8)
M(1)–C(2)	1.789(6)	1.911(7)	1.800(8)
M(2)–O(4)	1.514(4)	1.680(4)	1.524(5)
M(2)–O(5)	1.525(4)	1.687(5)	1.526(5)
M(2)–C(3)	1.787(6)	1.904(7)	1.788(8)
M(2)–C(4)	1.795(6)	1.916(7)	1.792(8)
O(1)–Sb(1)–O(3)	83.8(1)	85.2(2)	84.3(2)
O(1)–Sb(1)–O(5)	85.8(1)	87.7(2)	85.8(2)
O(3)–Sb(1)–O(5)	83.7(1)	83.1(2)	82.4(2)
O(3)–Sb(1)–C(11)	83.7(2)	85.3(2)	85.5(2)
O(5)–Sb(1)–C(11)	83.7(2)	83.4(2)	83.5(2)
O(1)–Sb(1)–C(21)	91.5(2)	90.8(2)	91.9(2)
O(3)–Sb(1)–C(21)	88.9(2)	88.4(2)	88.4(3)
C(11)–Sb(1)–C(21)	97.4(2)	96.7(2)	97.2(3)
O(1)–Sb(1)–C(31)	91.5(2)	91.2(2)	92.4(2)
O(5)–Sb(1)–C(31)	88.5(2)	90.6(2)	89.3(2)
C(11)–Sb(1)–C(31)	99.6(2)	97.4(2)	96.3(3)
C(21)–Sb(1)–C(31)	98.7(2)	97.8(2)	99.8(3)
O(1)–Sb(1)–C(11)	164.5(2)	167.7(2)	166.1(2)
O(5)–Sb(1)–C(21)	172.4(2)	171.5(2)	170.8(2)
O(3)–Sb(1)–C(31)	171.2(2)	172.8(2)	171.3(2)
O(1)–Sb(2)–O(2)	84.9(1)	85.4(2)	84.6(2)
O(1)–Sb(2)–O(4)	84.3(1)	86.0(2)	82.2(2)
O(2)–Sb(2)–O(4)	82.0(1)	82.7(2)	85.8(2)
O(2)–Sb(2)–C(41)	84.1(2)	84.6(2)	81.6(2)
O(4)–Sb(2)–C(41)	84.0(2)	85.0(2)	82.4(2)
O(1)–Sb(2)–C(51)	91.8(2)	92.8(2)	94.8(3)
O(4)–Sb(2)–C(51)	88.4(2)	88.7(2)	87.4(3)
C(41)–Sb(2)–C(51)	97.3(2)	95.9(3)	97.2(3)
O(1)–Sb(2)–C(61)	91.8(2)	91.1(2)	94.1(3)
O(2)–Sb(2)–C(61)	89.7(2)	90.5(2)	89.0(2)
C(41)–Sb(2)–C(61)	98.4(2)	96.7(3)	100.0(3)
C(51)–Sb(2)–C(61)	99.7(2)	98.0(3)	97.8(3)
O(1)–Sb(2)–C(41)	165.0(2)	167.3(2)	160.0(2)
O(2)–Sb(2)–C(51)	170.2(2)	171.4(2)	173.2(2)
O(4)–Sb(2)–C(61)	171.2(2)	172.8(2)	174.0(2)
O(2)–M(1)–O(3)	115.5(2)	115.6(2)	115.1(3)
C(1)–M(1)–C(2)	107.7(3)	110.0(3)	107.1(4)
O(4)–M(2)–O(5)	115.0(2)	113.9(2)	114.8(3)
C(3)–M(2)–C(4)	106.7(3)	108.3(4)	106.4(4)
Sb(1)–O(1)–Sb(2)	144.2(2)	145.5(2)	143.6(3)
Sb(2)–O(2)–M(1)	133.6(2)	130.2(2)	134.1(3)
Sb(1)–O(3)–M(1)	128.4(2)	123.6(2)	129.2(3)
Sb(2)–O(4)–M(2)	130.6(2)	126.2(2)	125.8(3)
Sb(1)–O(5)–M(2)	133.5(2)	129.6(2)	133.1(3)

Table 5 Selected bond distances (Å) and angles (°) for [(SbPh₃)₂(μ-O)(μ-O₂AsPh₂)₂]·CHCl₃ **6**, with e.s.d.s in parentheses

Sb(1)–O(1)	1.967(5)	Sb(2)–C(51)	2.166(7)
Sb(1)–O(3)	2.148(5)	Sb(2)–C(61)	2.148(7)
Sb(1)–O(5)	2.152(5)	As(1)–O(2)	1.699(5)
Sb(1)–C(11)	2.135(7)	As(1)–O(3)	1.680(4)
Sb(1)–C(21)	2.156(7)	As(1)–C(71)	1.926(7)
Sb(1)–C(31)	2.158(7)	As(1)–C(81)	1.921(7)
Sb(2)–O(1)	1.947(4)	As(2)–O(4)	1.686(5)
Sb(2)–O(2)	2.169(4)	As(2)–O(5)	1.677(5)
Sb(2)–O(4)	2.141(5)	As(2)–C(91)	1.919(7)
Sb(2)–C(41)	2.167(7)	As(2)–C(101)	1.923(7)
O(1)–Sb(1)–O(3)	86.6(2)	O(1)–Sb(2)–C(51)	91.9(2)
O(1)–Sb(1)–O(5)	86.4(2)	O(4)–Sb(2)–C(51)	90.4(2)
O(3)–Sb(1)–O(5)	80.2(2)	C(41)–Sb(2)–C(51)	97.4(3)
O(3)–Sb(1)–C(11)	86.3(2)	O(1)–Sb(2)–C(61)	92.6(2)
O(5)–Sb(1)–C(11)	83.4(2)	O(2)–Sb(2)–C(61)	86.7(2)
O(1)–Sb(1)–C(21)	90.9(2)	C(41)–Sb(2)–C(61)	95.7(3)
O(3)–Sb(1)–C(21)	89.5(2)	C(51)–Sb(2)–C(61)	100.1(3)
C(11)–Sb(1)–C(21)	98.1(3)	O(1)–Sb(2)–C(41)	166.2(3)
O(1)–Sb(1)–C(31)	87.7(2)	O(2)–Sb(2)–C(51)	173.1(2)
O(5)–Sb(1)–C(31)	89.7(2)	O(4)–Sb(2)–C(61)	169.4(2)
C(11)–Sb(1)–C(31)	97.7(3)	O(2)–As(1)–O(3)	118.8(2)
C(21)–Sb(1)–C(31)	100.4(3)	C(71)–As(1)–C(81)	109.3(3)
O(1)–Sb(1)–C(11)	168.4(2)	O(4)–As(2)–O(5)	118.6(2)
O(5)–Sb(1)–C(21)	169.4(2)	C(91)–As(2)–C(101)	106.8(3)
O(3)–Sb(1)–C(31)	168.7(2)	Sb(1)–O(1)–Sb(2)	151.7(3)
O(1)–Sb(2)–O(2)	86.3(2)	Sb(2)–O(2)–As(1)	125.9(2)
O(1)–Sb(2)–O(4)	85.9(2)	Sb(1)–O(3)–As(1)	129.1(3)
O(2)–Sb(2)–O(4)	82.8(2)	Sb(2)–O(4)–As(2)	128.6(2)
O(2)–Sb(2)–C(41)	83.3(2)	Sb(1)–O(5)–As(2)	127.4(2)
O(4)–Sb(2)–C(41)	83.9(2)		

Table 6 Comparison of Sb–O mean bridge parameters

Compound	Sb–O/Å	Sb–O–Sb/°	Ref.
3	1.955	144.2	This work
5	1.963	145.5	This work
6	1.957	151.7	This work
7	1.963	143.6	This work
[{SbCl₃(O₂PMe₂)}₂O]	1.942	136.0	15
[{SbPh₂Cl[O₂P(C₆H₁₁)₂]}₂O]	1.937	144.7	16
[{SbF₃(O₂CCF₃)}₂O]	1.893	131.1	17

Lewis acidity as a consequence of the electron-donating methyl groups could, however, influence ligand secondary bonding leading to changes in co-ordination mode.

Experimental

Diphenylantimony bromide oxide was prepared by oxidising diphenylantimony(III) bromide with *tert*-butyl hydroperoxide [20] and μ-oxo-bis[bromotriphenylantimony(v)], μ-oxo-bis[chloro-triphenylantimony(v)] and μ-oxo-bis[bromotris(*p*-tolyl)-antimony(v)] by partial hydrolysis of the appropriate triaryl-antimony(v) dihalide.[24] μ-Oxo-bis[chlorotrimethylantimony(v)] was obtained by treating trimethylantimony dichloride with the corresponding dihydroxide.[25] Dimethylphosphinic acid was obtained by the method of Reinhardt *et al.*[26] and the sodium salts Na(O₂AsMe₂), Na(O₂AsPh₂), Na(O₂PMe₂) and Na-(O₂PPh₂) by treating stoichiometric amounts of the corresponding acid with sodium ethoxide in ethanol.

Preparations

[(SbPh₂)₂(μ-O)₂(μ-O₂AsMe₂)₂] 1. A solution of diphenylanti-mony bromide oxide (4.00 g, 5.4 mmol) in dichloromethane (50 cm³) was added to a stirring suspension of sodium dimethyl-arsinate (1.90 g, 11.9 mmol) and dichloromethane (10 cm³) and the mixture refluxed for 24 h. After filtration and removal of the solvent, the remaining solid was recrystallised from chloroform

overlayered with twice the volume of hexane to give the product as colourless crystals. Yield 3.98 g (86%), m.p. 324–327 °C (Found: C, 39.4; H, 3.8. Calc. for C₂₈H₃₂As₂O₆Sb₂: C, 39.2; H, 3.8%); δ_H[250 MHz, CDCl₃, room temperature (r.t.)] 2.00 (12 H, s, AsMe), 7.33 [12 H, m, *m*- and *p*-H of Ph] and 7.83 (8 H, m, *o*-H of Ph); ṽ_max/cm⁻¹ (Nujol) 1430s, 1072m, 817vs (sh), 796vs, 738s, 696s, 652m, 608m, 518s, 487s and 466m; FAB mass spectrum *m/z* 858 (100, *M*⁺), 721 (30, [*M* − O₂AsMe₂]⁺), 704 (28, [*M* − 2Ph]⁺), 567 (43, [*M* − 2Ph − O₂AsMe₂]⁺), 413 {26%, [(SbO)₂O₂AsMe₂]⁺}.

[(SbPh₂)₂(μ-O)₂(μ-O₂AsPh₂)₂] 2. This was prepared in a simi-lar manner from [(SbPh₂BrO)₂] (3.2 g, 4 mmol) and sodium diphenylarsinate (2.60 g, 9.2 mmol) in dichloromethane (10 cm³) after refluxing for 40 h. A small amount of product was obtained after repeated crystallisations from chloroform–hexane. Yield 0.14 g (3%), m.p. 260–266 °C (Found: C, 51.2; H, 3.4. Calc. for C₄₈H₄₀As₂O₆Sb₂: C, 52.1; H, 3.6%); δ_H(250 MHz, CDCl₃, r.t.) 7.30–7.80 (40 H, br m, AsPh and SbPh); ṽ_max/cm⁻¹ (Nujol) 1087w, 823vs (sh), 812vs, 735s, 691s, 490m and 457m; FAB mass spectrum *m/z* 1108 (73, [*M* + 2H]⁺), 953 (16, [*M* − 2Ph + H]⁺), 845 (38, [*M* − O₂AsPh₂]⁺), 691 {100, [(SbPh₂O)₂O₂As]⁺}, 537 (75, [SbPh₂O₂AsPh₂]⁺) and 459 (36%, [SbPhO₂AsPh₂]⁺).

[(SbPh₃)₂(μ-O)(μ-O₂PMe₂)₂] 3. (*a*) *From* [(SbPh₃Br)₂O]. A solution of μ-oxo-bis[bromotriphenylantimony(v)] (0.53 g, 0.60 mmol) in dichloromethane (20 cm³) was added to a stirring suspension of sodium dimethylphosphinate (0.16 g, 1.34 mmol) and dichloromethane (10 cm³) and the mixture refluxed for 24 h. After filtration and removal of the solvent, the product was obtained by overlayering a chloroform solution with twice the volume of hexane. Yield 0.48 g (88%), m.p. 188–192 °C (Found: C, 53.1; H, 5.1. Calc. for C₄₀H₄₂O₅P₂Sb₂: C, 52.9; H, 4.7%); δ_H(250 MHz, CDCl₃, r.t.) moist solvent, 1.00 [6 H, d, ²*J*(HP) 14, PMe], 7.57 (9 H, m, *m*- and *p*-H of Ph) and 8.21 (6 H, m, *o*-H of Ph); anhydrous solvent, species **A**, 0.72 [12 H, d, ²*J*(HP) 14, MeP], 7.16 [12 H, t, ³*J*(HH) 7, *m*-H of Ph], 7.45 [6 H, t, ³*J*(HH) 7, *p*-H of Ph] and 7.56 [12 H, d, ³*J*(HH) 7 Hz, *o*-H of Ph]; species **B**, 1.03 (12 H, br, PMe), 7.38 (18 H, m, *m*- and *p*-H of Ph) and 7.68 (12 H, m, *o*-H of Ph); ṽ_max/cm⁻¹ 1430m, 1301m, 1112vs, 1062m, 1046vs, 1032vs, 998w, 871m, 863m, 749s, 735s, 693s, 659w, 512w, 487w, 464m and 437w; FAB mass spectrum *m/z* 831 (4, [*M* − Ph]⁺), 815 (9, [*M* − O₂PMe₂]⁺), 661 {5, [(SbPh₂)₂O(O₂PMe₂)]⁺} and 445 {100%, [SbPh₃(O₂PMe₂)]⁺}.

(*b*) *From* [(SbPh₂BrO)₂]. A mixture of [(SbPh₂BrO)₂] (0.53 g, 0.7 mmol), sodium dimethylphosphinate (0.17 g, 1.4 mmol) and toluene (30 cm³) was stirred at reflux for 24 h. The mixture was filtered and the solvent removed in a vacuum to give a residue which was recrystallised from chloroform–hexane mix-ture. Yield 77 mg (12%).

[{Sb(*p*-MeC₆H₄)₂}₂(μ-O)₂(μ-O₂AsMe₂)₂] 4. A mixture of μ-oxo-bis[bromotris(*p*-tolyl)antimony(v)] (0.42 g, 0.43 mmol), sodium dimethylarsinate (0.17 g, 1.06 mmol) and dichloro-methane (20 cm³) was stirred under reflux for 16 h. After filtration of the precipitated sodium bromide and evaporation of the solvent, the remaining white solid was recrystallised from a chloroform–hexane mixture to give the required product. Yield 0.10 g (26%), m.p. 313–320 °C (Found: C, 41.7; H, 4.45. Calc. for C₃₂H₄₀As₂O₆Sb₂: C, 42.05; H, 4.4. Calc. for C₄₆H₅₄As₂O₅Sb₂: C, 51.1; H, 5.0%); δ_H(250 MHz, CDCl₃, r.t.) 1.96 (12 H, s, AsMe), 2.32 (12 H, s, MeC₆H₄), 7.15 [8 H, d, ³*J*(HH) 8, *m*-H of aryl] and 7.73 [8 H, d, ³*J*(HH) 8 Hz, *o*-H of aryl]; ṽ_max/cm⁻¹ 1492m, 1307w, 1270w, 1183m, 1070m, 1018w, 901m, 869m, 824vs (sh), 805vs, 793s (sh), 722w, 652m, 609m, 578m, 516s, 488s and 430w; FAB mass spectrum *m/z* 915 (24, [*M* + H]⁺), 577 {13, [Sb(*p*-MeC₆H₄)₂(O₂AsMe₂)₂]⁺}, 531 {100, [Sb(*p*-MeC₆H₄)₃(O₂AsMe₂)]⁺} and 349 {12%, [Sb(*p*-MeC₆H₄)-(O₂AsMe₂)]⁺}.

Table 7 Crystallographic data[a] for quadruply bridged compounds **1** and **4**

	1	**4**
Chemical formula	$C_{30}H_{34}As_2Cl_6O_6Sb_2$	$C_{32}H_{40}As_2O_6Sb_2$
M	1096.61	913.98
Crystal size/mm	$0.30 \times 0.25 \times 0.15$	$0.35 \times 0.24 \times 0.06$
Space group	$P2_1/a$	$P2_1/c$
a/Å	13.830(3)	13.3821(13)
b/Å	10.2590(3)	11.4790(10)
c/Å	14.5744(12)	11.2265(10)
β/°	113.13(2)	99.411(5)
U/Å^3	1901.5(7)	1701.3(3)
D_c/g cm^{-3}	1.915	1.784
μ/cm^{-1}	36.09	35.58
$F(000)$	1064	896
Index ranges (for unique data)	$-16 < h < 14, 0 < k < 12, 0 < l < 17$	$-10 < h < 16, -12 < k < 13, -11 < l < 13$
Total data collected	8051	7176
Unique data	2932	2960
R_{int}	0.0766	0.0502
Observed data $[I > 3\sigma(I)]$	2172	
Absorption correction	DIFABS[b]	Gaussian
minimum	0.961	0.394
maximum	1.044	0.810
Structure solution	Direct (SIR 92)	Direct (SHELXS 86)
Refinement	Full-matrix least squares on F	Full-matrix least squares on F^2
Data, variables	2172, 209	2933, 195
Goodness of fit (S)	1.309	1.065
Final difference map features/e Å^{-3}	$+1.18, -0.70$	$+0.604, -1.120$
R	0.0276	
R'	0.0306	
R observed data $[I > 2\sigma(I)]$ (all data)		0.0315 (0.0355)
R' observed data (all data)		0.0794 (0.0873)

[a] Details in common: monoclinic; $Z = 2$; Mo-Kα radiation (λ 0.710 69 Å); θ limits 3–25°; 150 K. [b] Ref. 27.

Table 8 Crystallographic data* for triply bridged compounds **3** and **5–7**

	3	**5**	**6**	**7**
Chemical formula	$C_{43}H_{49}O_5P_2Sb_2$	$C_{43}H_{49}As_2O_5Sb_2$	$C_{61}H_{51}As_2Cl_3O_5Sb_2$	$C_{49}H_{61}O_5P_2Sb_2$
M	951.30	1039.16	1363.77	1035.47
Crystal size/mm	$0.20 \times 0.18 \times 0.14$	$0.32 \times 0.20 \times 0.16$	$0.15 \times 0.10 \times 0.10$	$0.24 \times 0.22 \times 0.18$
Space group	$C2/c$	$C2/c$	$P2_1/a$	$P2_1/n$
a/Å	26.704(3)	27.176(3)	11.804(12)	12.038(12)
b/Å	16.879(3)	16.826(2)	40.910(4)	17.127(13)
c/Å	22.1874(12)	22.637(3)	12.738(4)	23.35(2)
β/°	125.35(1)	126.887(8)	115.71(4)	90.27(3)
U/Å^3	8157.0(6)	8278.7(2)	5542.2(6)	4814.6(3)
Z	8	8	4	4
D_c/g cm^{-3}	1.549	1.667	1.635	1.429
μ/cm^{-1}	14.52	29.34	23.57	12.36
$F(000)$	3832	4120	2704	2108
θ Limits/°	3–25	2–25	3–25	3–25
Index ranges (for unique data)	$-29 < h < 23,$ $0 < k < 18, 0 < l < 25$	$-29 < h < 30,$ $0 < k < 18, 0 < l < 24$	$-13 < h < 11,$ $0 < k < 45, 0 < l < 14$	$-13 < h < 13,$ $0 < k < 19, 0 < l < 26$
T/K	120	150	120	150
Total data collected	17 558	17 594	21 169	23 252
Unique data	6171	6406	7933	7414
R_{int}	0.0481	0.0913	0.1616	0.0937
Observed data $[I > 3\sigma(I)]$	4315		6128	4900
Absorption correction	DIFABS	None	DIFABS	DIFABS
minimum	0.855		0.773	0.849
maximum	1.160		1.115	1.118
Structure solution	Direct (SIR 92)	Direct (SHELXS 86)	Direct (SIR 92)	Direct (SIR 92)
Data, variables	4315, 455	6406, 467	6128, 658	4900, 517
Goodness of fit (S)	1.080	0.935	1.073	1.134
Final difference map features/e Å^{-3}	$+1.10, -0.73$	$+1.736, -0.643$	$+2.09, -2.05$	$+0.74, -0.49$
R	0.0344		0.0702	0.0367
R'	0.0698		0.0942	0.0912
R observed data $[I > 2\sigma(I)]$ (all data)		0.0422 (0.0633)		
R' observed data (all data)		0.0940 (0.1247)		

* Details in common: monoclinic; Mo-Kα radiation (λ 0.710 69 Å); full-matrix least-squares refinement on F^2.

[(SbPh$_3$)$_2$(μ-O)(μ-O$_2$AsMe$_2$)$_2$] 5. A mixture of μ-oxo-bis[bromotriphenylantimony(v)] (0.74 g, 0.84 mmol), sodium dimethylarsinate (0.36 g, 2.3 mmol) and dichloromethane (35 cm^3) was stirred at reflux for 20 h. After filtration and removal of the solvent in a vacuum, the product was obtained by diffusion of hexane vapour into a concentrated chloroform solution. Yield 0.62 g (74%), m.p. 241–245 °C (Found: C, 47.85; H, 4.3. Calc. for $C_{40}H_{42}As_2O_5Sb_2$: C, 48.2; H, 4.25%); δ_H(250 MHz,

CDCl$_3$, r.t.) 0.71 (br s, AsMe), 1.89 (br s, AsMe) (integrals unreliable due to peak broadness); phenyl region, species **A**, 7.17 [12 H, t, ^3J(HH) 7, *m*-H of Ph], 7.27 [6 H (masked), t, *p*-H of Ph] and 7.61 [12 H, d, ^3J(HH) 7 Hz, *o*-H of Ph]; species **B**, 7.27 (18 H, m, *m*- and *p*-H of Ph) and 7.71 (12 H, m, *o*-H of Ph); $\tilde{\nu}_{max}$/cm^{-1} 1429s, 1265m, 1185m, 1069s, 1023w, 852vs (br), 738vs, 698vs, 657m, 641m, 465s and 421m; FAB mass spectrum *m/z* 996 (0.4, *M*$^+$), 859 (6, [*M* − O$_2$AsMe$_2$]$^+$), 489 {61, [SbPh$_3$(O$_2$AsMe$_2$)]$^+$}, 335 {28, [SbPh(O$_2$AsMe$_2$)]$^+$} and 275 (39%, SbPh$_2$$^+$).

[(SbPh$_3$)$_2$(μ-O)(μ-O$_2$AsPh$_2$)$_2$] 6. A mixture of μ-oxo-bis[bromotriphenylantimony(v)] (0.60 g, 0.68 mmol), sodium diphenylarsinate (0.49 g, 1.7 mmol) and dichloromethane (35 cm^3) was stirred at reflux for 24 h. After filtration and removal of the solvent, the residue was purified by diffusion of hexane into a concentrated chloroform solution. Yield 0.63 g (74%), m.p. 244–247 °C (Found: C, 53.1; H, 3.7. Calc. for C$_{60}$H$_{50}$As$_2$O$_5$Sb$_2$: C, 57.9; H, 4.05. Calc. for C$_{60}$H$_{50}$As$_2$O$_5$Sb$_2$·CHCl$_3$: C, 53.7; H, 3.8%); δ$_H$(250 MHz, CDCl$_3$, r.t.) 6.97 (m), 7.08 (m), 7.33 (m), 7.43 (m), 7.58 [d, ^3J(HH) 7 Hz] and 8.04 (m); $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 1440s, 1430s, 1306m, 1183m, 1090s, 1069s, 1023m, 999m, 831vs (br), 735vs, 692vs, 658m, 609w, 536m, 464s and 410m.

[{Sb(*p*-MeC$_6$H$_4$)$_3$}$_2$(μ-O)(μ-O$_2$PMe$_2$)$_2$] 7. A solution of μ-oxo-bis[bromotris(*p*-tolyl)antimony(v)] (0.59 g, 0.61 mmol) in dichloromethane (20 cm^3) was added to a suspension of sodium dimethylphosphinate (0.15 g, 1.3 mmol) in dichloromethane (10 cm^3) which was stirred at room temperature for 18 h. After filtration and removal of the solvent in a vacuum, the remaining white solid was purified by overlayering a chloroform solution with three times the volume of hexane. Yield 0.35 g (58%) (Found: C, 55.2; H, 5.4. Calc. for C$_{46}$H$_{54}$O$_5$P$_2$Sb$_2$: C, 55.7; H, 5.5%); δ$_H$(250 MHz, CDCl$_3$, r.t.) moist solvent, 0.97 [6 H, d, ^2J(HP) 14, PMe], 2.40 (9 H, s, MeC$_6$H$_4$), 7.51 [6 H, d, ^3J(HH) 8, *m*-H of aryl] and 8.12 [6 H, d, ^3J(HH) 8, *o*-H of aryl]; anhydrous solvent, species **A**, 0.70 [12 H, d, ^2J(HP) 14, PMe], 2.38 (18 H, s, MeC$_6$H$_4$), 7.10 [12 H, d, ^3J(HH) 8, *m*-H of aryl] and 7.55 [12 H, d, ^3J(HH) 8, *o*-H of aryl]; species **B**, 1.05 (12 H, br, PMe), 2.39 (18 H, s, MeC$_6$H$_4$), 7.25 [12 H, d, ^3J(HH) 8, *m*-H of aryl] and 7.61 [12 H, d, ^3J(HH) 8 Hz, *o*-H of aryl]; $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 1298m, 1187m, 1120s, 1111vs, 1048vs, 1033vs, 863s, 801s, 732s, 705w, 576w and 487s; FAB mass spectrum *m/z* 962 (4, [*M* − 2Me]$^+$), 899 (0.4, [M − O$_2$PMe$_2$]$^+$) and 487 {100%, [Sb(*p*-MeC$_6$H$_4$)$_3$(O$_2$PMe$_2$)]$^+$}.

[(SbMe$_3$)$_2$(μ-O)(μ-O$_2$PMe$_2$)$_2$] 8. A solution of μ-oxo-bis[chlorotrimethylantimony(v)] (0.84 g, 2 mmol) in dichloromethane (20 cm^3) was added to a suspension of sodium dimethylphosphinate (0.46 g, 4.4 mmol) also in dichloromethane (20 cm^3) at 0 °C under an atmosphere of argon and the mixture stirred at room temperature for 6 h. The mixture was filtered and the clear filtrate concentrated to *ca.* 5 cm^3. Over-layering with hexane (15 cm^3) gave extremely moisture-sensitive crystals of the required compound, which were isolated by decantation and dried in a vacuum. Yield 0.90 g (84%). Owing to the extreme air sensitivity of this compound, satisfactory microanalytical results could not be obtained. δ$_H$(250 MHz, CDCl$_3$, r.t., Teflon-sealed tube under N$_2$) 1.13 [12 H, d, ^2J(HP) 14, PMe] and 1.66 (18 H, s, SbMe); δ$_C$(69 MHz, CDCl$_3$, r.t.) 16.3 (s, SbMe) and 18.8 [d, ^1J(CP) 104 Hz, PMe]; $\tilde{\nu}_{max}$/cm^{-1} 1421s, 1286s, 1262w, 1221s, 1172vs (br), 1020vs (br), 851vs (br), 753vs (br), 692s, 578s, 531m, 512w, 482vs and 420vs (possible decomposition in Nujol).

[(SbMe$_3$)$_2$(μ-O)(μ-O$_2$AsPh$_2$)$_2$] 9. A mixture of μ-oxo-bis[chlorotrimethylantimony(v)] (0.39 g, 0.93 mmol), sodium diphenylarsinate (0.28 g, 1.0 mmol) and dichloromethane (35 cm^3) at 0 °C was treated as described above to yield moisture-

sensitive crystals of the required compound, shown by ^{1}H NMR spectroscopy to be a dichloromethane solvate. Again satisfactory microanalytical results could be obtained. Yield 0.60 g (75%). δ$_H$(250 MHz, CDCl$_3$, r.t., Teflon-sealed tube under N$_2$) 1.66 (18 H, s, MeSb), 5.27 (2 H, s, CH$_2$Cl$_2$), 7.41 (12 H, m, *m*- and *p*-H of Ph) and 7.70 (8 H, m, *o*-H of Ph); δ$_C$(69 MHz, CDCl$_3$, r.t.) 16.8 (SbMe), 128.7 (*m*-C of Ph), 130.4 (*p*-C of Ph), 131.2 (*o*-C of Ph) and 138.2 (*ipso*-C of Ph); $\tilde{\nu}_{max}$/cm^{-1} 1307m, 1216w, 1180w, 1157w, 1088s, 1066m, 1025m, 998m, 896s, 795vs (br), 740vs (br), 720vs (br), 692vs (br), 574s, 526w, 481s and 462s (possible decomposition in Nujol).

Crystallography

Crystallographic quality single crystals for all compounds were obtained by slow diffusion of hexane vapour into concentrated chloroform solutions of the compounds.

Crystallographic data are summarised in Table 7 for the quadruply bridged compounds and in Table 8 for the triply bridged species. The tables also contain details of the method of solution and the refinement conditions. Approximately one hemisphere of data was collected at low temperature using either a Delft Instruments FAST TV area-detector diffractometer, equipped with rotating-anode FR591 generator (for **1**, **3** and **5**–**7**) or a Siemens SMART area-detector diffractometer (for **4**). The data were corrected for Lorentz-polarisation effects, merged and systematically absent reflections removed. An absorption correction was usually applied (see Tables 7 and 8). Structures were solved by direct methods (SIR 92[28] or SHELXS 86[29]) and refined by full-matrix least squares (SHELXL 93[30] or CRYSTALS[31]); hydrogen atoms were placed at their calculated positions and refined riding on their respective carbon atoms. A standard weighting scheme was applied and corrections were made for extinction where appropriate.

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