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FULL PAPER

Synthesis and properties of antimony(III) and bismuth(III) halide complexes of diphosphines and diarsines. Crystal structures of $[Bi_2I_6\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$, $[Sb_2Br_6\{o\text{-}C_6H_4(PPh_2)_2\}_2]$, $[Sb_2Cl_6\{o\text{-}C_6H_4(AsMe_2)_2\}]$, and $[BiCl_3\{o\text{-}C_6H_4(P(O)Ph_2)_2\}(thf)]$

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Received 20th December 2000, Accepted 13th February 2001
First published as an Advance Article on the web 8th March 2001

The reaction of SbX_3 or BiX_3 (X = Cl, Br or I) with the diarsines $o\text{-}C_6H_4(AsMe_2)_2$ or $Ph_2AsCH_2CH_2AsPh_2$, the triarsine $MeC(CH_2AsMe_2)_3$, or the diphosphines $o\text{-}C_6H_4(PMe_2)_2$ or $o\text{-}C_6H_4(PPh_2)_2$ (L), yield complexes of 1 : 1 stoichiometry MX_3L irrespective of the reactant ratios used. X-Ray structures of $[Bi_2I_6\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ and $[Sb_2Br_6\{o\text{-}C_6H_4(PPh_2)_2\}_2]$ reveal distorted octahedral Bi or Sb coordination spheres, linked *via* asymmetric halide-bridges. Bond lengths suggest a bonding model based upon primary bonding in pyramidal MX_3 groups with weaker secondary interactions to the diphosphine or diarsine and the longer distance bridging halide. $[Sb_2Cl_6\{o\text{-}C_6H_4(AsMe_2)_2\}]$ is obtained by partial decomposition of $[Sb_2Cl_6\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ in hot ethanol and contains $Sb\{o\text{-}C_6H_4(AsMe_2)_2\}Cl_2$ and $SbCl_4$ units linked *via* asymmetric chlorine bridges into puckered chains, which associate further through long Sb···Cl contacts to produce a polymeric sheet structure. The mononuclear species $[BiCl_3\{o\text{-}C_6H_4(P(O)Ph_2)_2\}(thf)]$ obtained from $BiCl_3$ and $o\text{-}C_6H_4(P(O)Ph_2)_2$ in thf is a distorted octahedron with a $BiCl_3O_3$ donor set.

Introduction

We have recently reported a range of bismuth(III) and antimony(III) complexes with di- or tri- thio- or seleno-ethers and thio- or seleno-ether macrocycles,[1–4] which display a very diverse range of structures, from simple monomers, through halide-bridged dimers, to infinite chains or sheets. The chemistry of bismuth(III) and antimony(III) halides with monodentate phosphines and diphosphinoalkanes has been investigated by Norman and co-workers[5–8] and others.[9] There are also early reports[10] of 1 : 1 complexes of both elements with $o\text{-}C_6H_4(AsMe_2)_2$ suggested to be trigonal bipyramidal monomers. Examples of (O-donor) diarsine dioxide and diphosphine dioxide complexes obtained by adventitious oxidation of the corresponding diphosphine or diarsine species have been structurally characterised.[11] Here we report studies of complexes of both elements with bi- and tri-dentate arsines, specifically $o\text{-}C_6H_4(AsMe_2)_2$, $Ph_2AsCH_2CH_2AsPh_2$ and $MeC(CH_2AsMe_2)_3$. We also investigated complexes with $o\text{-}C_6H_4(PPh_2)_2$ and $o\text{-}C_6H_4(PMe_2)_2$ which (along with $o\text{-}C_6H_4(AsMe_2)_2$) usually behave as strongly bound chelates to d-block elements, the rigid aromatic backbone resisting dissociation (the "*o*-phenylene backbone" effect)[12] which we anticipated might lead to increased solution stability or higher ligand : Sb/Bi ratios compared with compounds formed by the flexible aliphatic backboned ligands.

Results and discussion

Synthesis and properties

The reactions of anhydrous MX_3 (M = Sb or Bi; X = Cl, Br or I) with the ligands $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(PPh_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, $Ph_2AsCH_2CH_2AsPh_2$ and $MeC(CH_2AsMe_2)_3$ were carried out under dinitrogen in dry MeCN or CH_2Cl_2. Occasionally thf or anhydrous EtOH were used as solvent (see the Experimental section), the products being independent of the solvent used. All the complexes isolated were of 1 : 1 MX_3 : ligand stoichiometry. Using excess $o\text{-}C_6H_4(PMe_2)_2$ or $o\text{-}C_6H_4(AsMe_2)_2$ failed to produce 1 : 2 complexes, although since the complexes are labile in solution (below), the products isolated may be determined by solubility factors. Unexpectedly, crystals with a 2 : 1 $SbCl_3$: $o\text{-}C_6H_4(AsMe_2)_2$ stoichiometry were obtained by slow evaporation from a hot ethanol solution of $[SbCl_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$. The solid complexes are stable in air for a short time, although they deteriorate over longer periods. In solution the complexes are prone to oxidation at the P or As as noted for other examples,[11] and *in situ* ^{31}P NMR studies of the diphosphine complexes of both elements show that in addition to resonances attributable to phosphine oxide impurities, a number of other resonances are present to higher frequency, which are probably due to halogenated phosphines (R_3PX^+) which are known to be decomposition products in tin(IV) systems.[13]

The complexes are poorly soluble in chlorocarbons, MeCN or $MeNO_2$ and the ^1H NMR spectra, where obtainable, were uninformative with chemical shifts little different to the "free" ligands, indicative of solution lability. Attempts to record $^{31}P\{^1H\}$ NMR spectra of $[MX_3\{o\text{-}C_6H_4(PMe_2)_2\}]$ in CH_2Cl_2 over the temperature range 200–300 K failed due to low solubility. The antimony complexes were slightly more soluble in $MeNO_2$ (mp 244 K) but at 300 K these solutions showed only weak signals due to oxidised ligands; however at 250 K, $[M'X_3\{o\text{-}C_6H_4(PMe_2)_2\}]$ ($M'X_3 = SbCl_3$ or $SbBr_3$) exhibited sharp singlets at δ +4 and −6.5 respectively, attributable to the complexes. Addition of $o\text{-}C_6H_4(PMe_2)_2$ to these solutions resulted in broad averaged resonances consistent with fast intermolecular exchange. The other complexes were insufficiently soluble for low temperature NMR studies. The IR spectra of the complexes were useful to establish the absence of phosphine oxide or arsine oxide groups, and the chloro complexes typically showed M–Cl modes in the range 200–280 cm^{-1}, but were of little use to establish the structures present. The intense colours of the bismuth complexes arise from broad and ill-defined charge transfer bands and do not contain useful information.[2,3]

DOI: 10.1039/b010179f

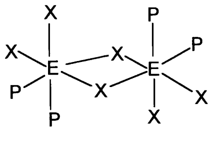
Table 1 Selected bond lengths (Å) and angles (°) for $[\mathrm{Bi_2I_6}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2]$

Bi(1)–I(1)	2.992(2)	Bi(1)–I(3)	3.032(1)
Bi(1)–I(2)	3.117(2)	Bi(1)–As(1)	2.801(2)
Bi(1)–I(2*)	3.328(1)	Bi(1)–As(2)	2.974(2)
I(1)–Bi(1)–I(2)	164.24(4)	I(2)–Bi(1)–As(2)	81.79(5)
I(1)–Bi(1)–I(2*)	93.52(4)	I(2*)–Bi(1)–As(1)	164.83(4)
I(1)–Bi(1)–I(3)	101.97(4)	I(2*)–Bi(1)–I(3)	111.39(4)
I(1)–Bi(1)–As(1)	84.60(4)	I(2*)–Bi(1)–As(2)	90.39(4)
I(1)–Bi(1)–As(2)	82.95(4)	I(3)–Bi(1)–As(1)	83.68(4)
I(2)–Bi(1)–I(2*)	90.50(3)	I(3)–Bi(1)–As(2)	157.09(5)
I(2)–Bi(1)–I(3)	90.69(5)	As(1)–Bi(1)–As(2)	74.45(5)
I(2)–Bi(1)–As(1)	87.54(4)	Bi(1)–I(1)–Bi(1*)	89.50(3)

The complex $[\mathrm{BiCl_3}\{o\text{-}\mathrm{C_6H_4(P(O)Ph_2)_2}\}(\mathrm{thf})]$ containing the diphosphine dioxide $o\text{-}\mathrm{C_6H_4(P(O)Ph_2)_2}$ was initially obtained serendipitously during attempts to grow crystals from $[\mathrm{BiCl_3}\{o\text{-}\mathrm{C_6H_4(PPh_2)_2}\}]$ in thf–hexane, and bulk samples were made by reaction of $\mathrm{BiCl_3}$ and $o\text{-}\mathrm{C_6H_4(P(O)Ph_2)_2}$ in thf–MeCN. The reaction of $\mathrm{BiBr_3}$ with $o\text{-}\mathrm{C_6H_4(P(O)Ph_2)_2}$ in thf–MeCN gave the thf-free $[\mathrm{BiBr_3}\{o\text{-}\mathrm{C_6H_4(P(O)Ph_2)_2}\}]$, the absence of thf being confirmed by analysis and the ^{1}H NMR spectrum. The diphosphine dioxide complexes show very strong ν(PO) modes at *ca.* 1150 cm^{-1}, lowered from 1200 cm^{-1} in the "free" ligand.[13] In marked contrast to the diphosphine complexes, the diphosphine dioxide complexes gave sharp $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR resonances in $\mathrm{CH_2Cl_2}$ solution at ambient temperatures, with chemical shifts only slightly to high frequency of the resonance for $o\text{-}\mathrm{C_6H_4(P(O)Ph_2)_2}$ itself, (δ +33.6), as found in other complexes of this ligand.[13]

X-Ray structures

Since the spectroscopic data on these complexes are relatively uninformative, identifying the structural units present required X-ray studies. Two examples of the 1 : 1 complexes $[\mathrm{BiI_3}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}]$ and $[\mathrm{SbBr_3}\{o\text{-}\mathrm{C_6H_4(PPh_2)_2}\}]$ were structurally characterised, and found to be dimeric with the isomer (A) structure previously observed[7] for $[\mathrm{E_2Br_6(Me_2PCH_2CH_2PMe_2)_2}]$ (E = Sb or Bi). In the red $[\mathrm{Bi_2I_6}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2]$ (Fig. 1, Table 1), which is the first structurally characterised bismuth–arsine, the bismuth coordination geometry is a distorted octahedron composed of the chelating diarsine [Bi–As = 2.801(2), 2.974(2) Å], two terminal Bi–I's [2.992(2), 3.032(2) Å], and with an asymmetric (μ-I)$_2$ bridge [Bi–I 3.117(2), 3.328(2) Å]. The *d*(Bi–I) are similar to those reported in $[\mathrm{Bi_2I_8(Me_2S)_2}]^{2-}$,[14] $[\mathrm{BiI_3}\{\mathrm{MeC(CH_2SeMe)_3}\}]$,[2] $[\mathrm{BiI_4(PMe_2Ph)_2}]^-$,[6] and $\mathrm{BiI_3}$.[15] The Bi–As bond lengths are the first examples reported, and appear long (*e.g.* they are similar in length to the Bi–I involving the larger iodine atom) and are probably best viewed as secondary interactions, with the As lone pairs donating into the Bi–I σ* orbitals.[5–8,16]



Isomer A

The structure of $[\mathrm{Sb_2Br_6}\{o\text{-}\mathrm{C_6H_4(PPh_2)_2}\}_2]$ also reveals (Fig. 2) the isomer (A) geometry, although the crystal quality was rather poor † and hence the data refinement was not as good as normal, precluding detailed comparisons of bond length and angles. Comparison of the Sb–Br distances in this complex [2.540(9), 2.657(9), 2.679(8), 3.51(1) Å] with those in $[\mathrm{Sb_2Br_6}\{\mathrm{Me_2PCH_2CH_2PMe_2}\}_2]$[7] [2.695(1), 2.828(1), 3.003(1), 3.595(1) Å] reveal a similar spread of values. However in the present complex the Sb–P distances [2.91(2), 3.01(2) Å] are much longer than those involving $\mathrm{Me_2PCH_2CH_2PMe_2}$[7] [2.575(2), 2.659(3) Å], indicating that the alkyl-substituted ligand interacts much more strongly.

Table 2 Selected bond lengths (Å) and angles (°) for $[\mathrm{Sb_2Cl_6}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}]$

Sb(1)–As(1)	2.663(1)	Sb(2)–Cl(3)	2.618(2)
Sb(1)–As(2)	2.664(1)	Sb(2)–Cl(4)	2.352(3)
Sb(1)–Cl(1)	2.573(2)	Sb(2)–Cl(5)	2.366(3)
Sb(1)–Cl(2)	2.580(2)	Sb(2)–Cl(6)	2.603(3)
Sb(1)–Cl(3)	3.141(2)	Sb(2)–Cl(1*)	3.267(3)
Sb(1*)–Cl(6*)	3.020(3)		
As(1)–Sb(1)–As(2)	81.23(3)	Cl(3)–Sb(1)–Cl(6*)	130.77(8)
As(1)–Sb(1)–Cl(1)	80.69(7)	Cl(3)–Sb(2)–Cl(4)	89.27(9)
As(1)–Sb(1)–Cl(2)	82.45(6)	Cl(3)–Sb(2)–Cl(5)	87.83(9)
As(1)–Sb(1)–Cl(3)	72.06(6)	Cl(3)–Sb(2)–Cl(6*)	177.20(9)
As(1)–Sb(1)–Cl(6*)	156.49(6)	Cl(3)–Sb(2)–Cl(1*)	81.22(7)
As(2)–Sb(1)–Cl(1)	82.51(6)		
As(2)–Sb(1)–Cl(2)	84.07(7)	Cl(4)–Sb(2)–Cl(5)	94.1(1)
As(2)–Sb(1)–Cl(3)	153.21(6)	Cl(4)–Sb(2)–Cl(6)	88.4(1)
As(2)–Sb(1)–Cl(6*)	75.65(6)	Cl(4)–Sb(2)–Cl(1*)	83.57(9)
Cl(1)–Sb(1)–Cl(2)	159.84(9)	Cl(5)–Sb(2)–Cl(6)	90.8(1)
Cl(1)–Sb(1)–Cl(3)	91.08(7)	Cl(5)–Sb(2)–Cl(1*)	168.81(9)
Cl(1)–Sb(1)–Cl(6*)	92.04(9)	Cl(6)–Sb(2)–Cl(1*)	100.02(9)
Cl(2)–Sb(1)–Cl(3)	94.17(7)	Sb(1)–Cl(1)–Sb(2*)	156.5(1)
Cl(2)–Sb(1)–Cl(6*)	99.14(9)	Sb(2)–Cl(6)–Sb(1*)	172.5(1)

Table 3 Selected bond lengths (Å) and angles (°) for $[\mathrm{BiCl_3(thf)}\{o\text{-}\mathrm{C_6H_4(P(O)Ph_2)_2}\}]$

Bi(1)–Cl(1)	2.518(2)	Bi(1)–O(1)	2.470(5)
Bi(1)–Cl(2)	2.576(2)	Bi(1)–O(2)	2.444(5)
Bi(1)–Cl(3)	2.593(2)	Bi(1)–O(3)	2.709(6)
Cl(1)–Bi(1)–Cl(2)	89.11(8)	Cl(2)–Bi(1)–O(3)	79.5(1)
Cl(1)–Bi(1)–Cl(3)	96.19(7)	Cl(3)–Bi(1)–O(1)	161.5(1)
Cl(1)–Bi(1)–O(1)	92.9(1)	Cl(3)–Bi(1)–O(2)	89.7(1)
Cl(1)–Bi(1)–O(2)	83.0(1)	Cl(3)–Bi(1)–O(3)	86.4(1)
Cl(1)–Bi(1)–O(3)	168.6(1)	O(1)–Bi(1)–O(2)	75.4(2)
Cl(2)–Bi(1)–Cl(3)	99.26(8)	O(1)–Bi(1)–O(3)	87.9(2)
Cl(2)–Bi(1)–O(1)	97.0(1)	O(2)–Bi(1)–O(3)	108.2(2)
Cl(2)–Bi(1)–O(2)	168.7(1)		

Attempts to obtain X-ray quality crystals of one $[\mathrm{SbX_3}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}]$ example were unsuccessful, the crystals obtained were either too thin in one dimension or twinned. However as described above, during crystal growth attempts from hot ethanol, colourless blocks of $[\mathrm{Sb_2Cl_6}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}]$ were formed. The structure of this compound is rather unusual (Figs. 3 and 4, Table 2), consisting of zig-zag chains weakly cross-linked into a 2D sheet motif. A very distorted six-coordinate geometry about one antimony is composed of a chelating diarsine [Sb–As = 2.663(1), 2.664(1) Å] and four chlorines [2.573(2), 2.580(2), 3.020(3), 3.141(2) Å], whilst the second antimony has four short Sb–Cl bonds [2.352(3), 2.366(3), 2.603(3), 2.618(2) Å] and one much longer Sb–Cl interaction [3.267(3) Å] positioned approximately at five of the vertices of an octahedron.

The structure of $[\mathrm{BiCl_3}\{o\text{-}\mathrm{C_6H_4(P(O)Ph_2)_2}\}(\mathrm{thf})]$ (Fig. 5, Table 3) shows a distorted octahedron about bismuth with the two Bi–Cl bonds *trans* to the O(P) bonds [2.576(2), 2.593(2) Å] markedly longer than that *trans* to thf [2.518(2) Å]. Conversely the Bi–O(P) bonds [2.470(5), 2.444(5) Å] are much shorter than Bi–O(thf) [2.709(6) Å]. The latter is also rather longer than those in $[\mathrm{BiBr_3(thf)_3}]$ [2.600(8)–2.683(7) Å].[17] Given the very weak Bi–thf interaction here, it is likely that in the thf-free bromide, dimerisation *via* Br bridging replaces the thf.

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† $[\mathrm{Sb_2Br_6}\{o\text{-}\mathrm{C_6H_4(PPh_2)_2}\}_2]$: $M = 807.9$, triclinic, $P\bar{1}$ (no. 2), a 11.025(5), b 13.726(5), c 10.797(4) Å, α 92.83(4), β 106.39(3), γ 107.59(3)°, V 1478(1) Å^3, Z 2, μ(Mo-Kα) 51.3 cm^{-1}, no. of reflections 5503, no. of refl. [$I \geq 2\sigma(I)$] 5205, $R = 0.108$, $wR = 0.121$.

Conclusions

The reactions of SbX_3 or BiX_3 with the diarsine and diphosphine ligands produce 1 : 1 adducts, which are probably all dimeric with the isomer (A) geometry established for two examples. The failure even of the rigid *o*-phenylene backboned ligands to form 2 : 1 ligand : metal complexes, is probably due to the fact that the primary interactions in these systems are in the pyramidal MX_3 units with the remaining sites on the distorted octahedron filled by weaker (secondary) bonding to the neutral ligands and the longer distance bridging X-group. From this viewpoint changes in the phosphine or arsine ligand structure or properties has much less effect on the complexes, compared with the more familiar cases of strong interaction with d-block metals. Thus far phosphorus or arsenic ligands have shown far fewer structural motifs than observed with thio- or seleno-ethers. This may partly reflect the fact that for the former, almost all examples have two-carbon backbones which lead to the favoured 5-membered chelate ring formation, rather than bridging behaviour, although since the Sb/Bi–P/As are weak secondary interactions this is unlikely to be strongly favoured. More probable is the fact that the Group 16 donor ligands having two lone pairs, greater flexibility and lower steric demands, are able to link pyramidal MX_3 or dimer M_2X_6 units into a variety of polymeric motifs, in some cases using both lone pairs on each Group 16 atom.[2–4]

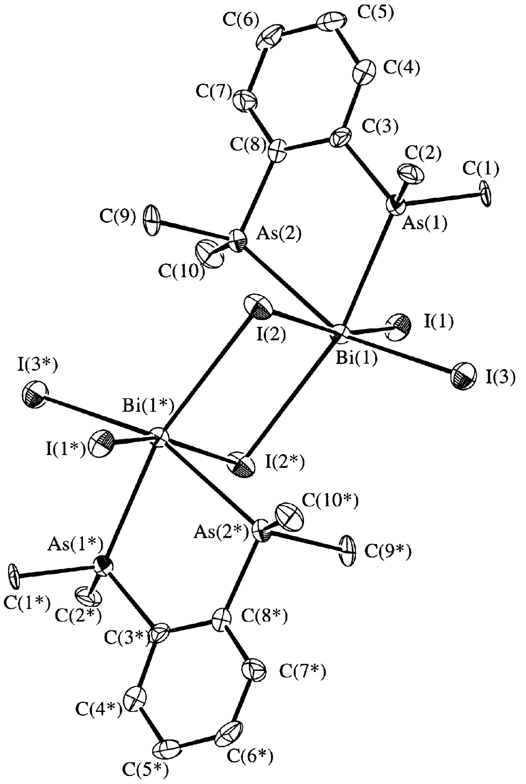

Fig. 1 View of the structure $[Bi_2I_6\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ with numbering scheme adopted. Ellipsoids are drawn at the 40% probability level. H atoms omitted for clarity.

Experimental

Infrared spectra were measured as Nujol mulls between CsI plates using a Perkin-Elmer 983 spectrometer over the range 200–4000 cm^{-1}. $^{31}P\{^1H\}$ NMR were recorded using a Bruker DPX400 spectrometer operating at 161.9 MHz referenced to external 85% H_3PO_4. All preparations used the same general

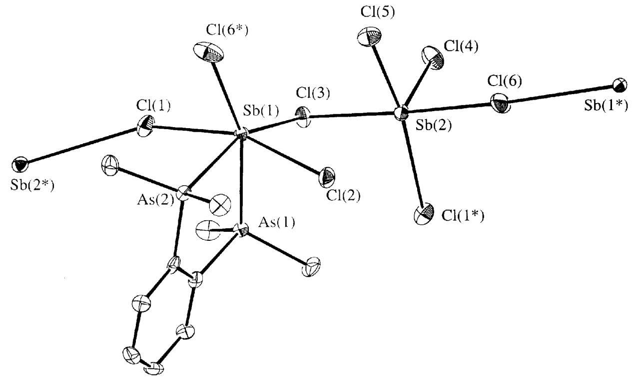

Fig. 3 View of the structure of the asymmetric unit of $[Sb_2Cl_6\text{-}\{o\text{-}C_6H_4(AsMe_2)_2\}]$, with nearest symmetry related neighbours; details as Fig. 1.

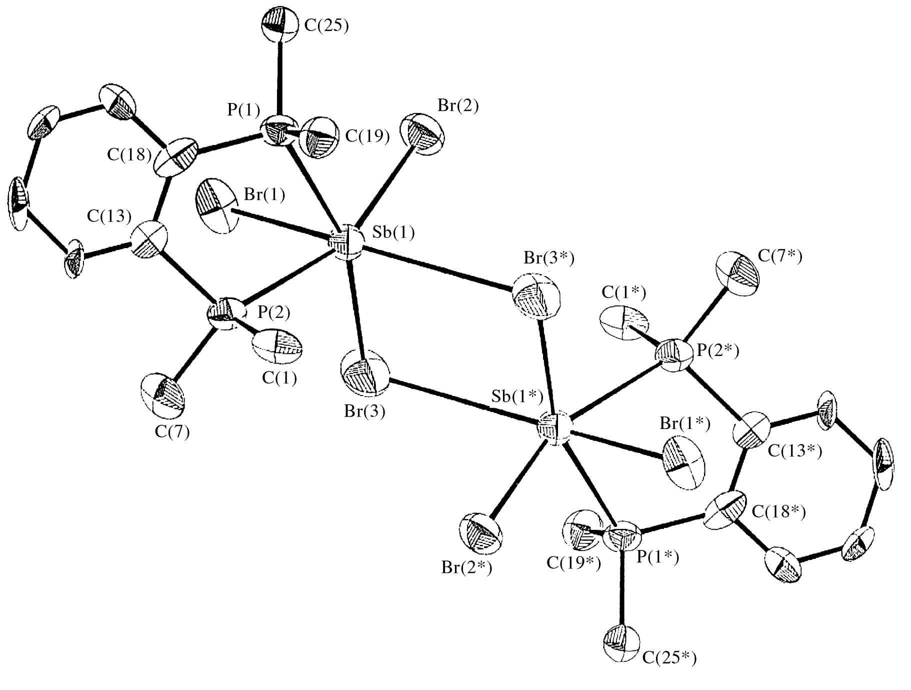

Fig. 2 View of the structure $[Sb_2Br_6\{o\text{-}C_6H_4(PPh_2)_2\}_2]$, details as Fig. 1, only *ipso*-phenyl carbons are shown. Sb(1)–Br(1) 2.540(9), Sb(1)–Br(2) 2.657(9), Sb(1)–Br(3) 2.679(8), Sb(1)–Br(3*) 3.51(1), Sb(1)–P(1) 3.01(2), Sb(1)–P(2) 2.91(2) Å.

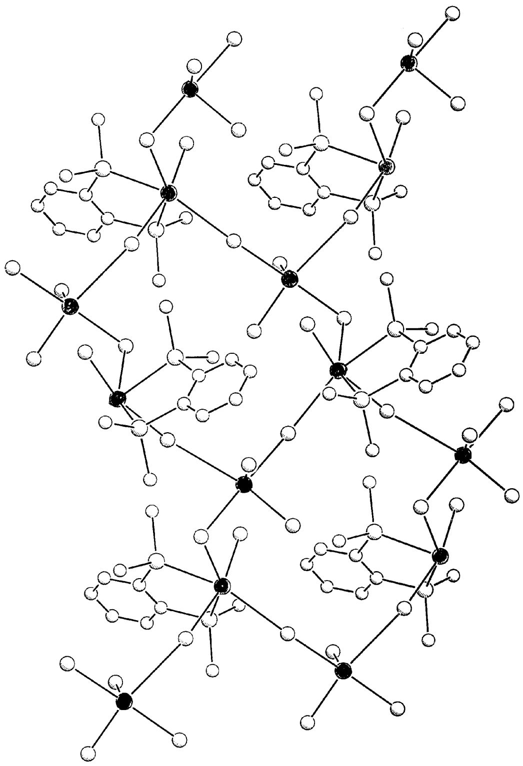

Fig. 4 View of the extended network in $[Sb_2Cl_6\{o\text{-}C_6H_4(AsMe_2)_2\}]$ (Sb atoms shaded).

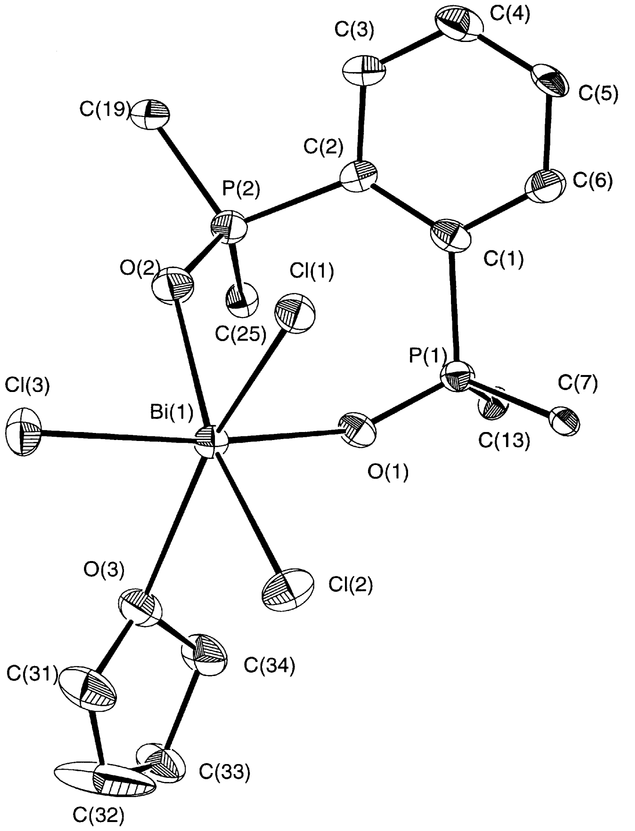

Fig. 5 View of the structure $[BiCl_3(thf)\{o\text{-}C_6H_4(P(O)Ph_2)_2\}]$ details as Fig. 1, only the *ipso*-phenyl carbons are shown.

methods, which are illustrated below, with any minor modifications noted under individual complexes. Standard Schlenk methods were used. The phosphine and arsine ligands were prepared by the literature methods,[18–21] and anhydrous bismuth and antimony halides obtained from Aldrich or Alfa, and used as received.

Preparations

$[BiCl_3\{o\text{-}C_6H_4(PPh_2)_2\}]$. A solution of o-$C_6H_4(PPh_2)_2$ (0.20 g, 0.45 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise to a stirred solution of $BiCl_3$ (0.14 g, 0.45 mmol) in MeCN (10 cm^3). The resultant bright yellow precipitate was filtered off, washed with CH_2Cl_2 and dried *in vacuo*. Yield 0.28 g, 83%. (Found: C, 47.0; H, 3.0. Calc. for $C_{30}H_{24}BiCl_3P_2$: C, 47.3; H, 3.1%). IR ν_{BiCl}/cm^{-1}: 236, 250, 260.

The following were made similarly:

$[BiBr_3\{o\text{-}C_6H_4(PPh_2)_2\}]$. Bright yellow powder. Yield 75%. (Found: C, 40.0; H, 2.6. Calc. for $C_{30}H_{24}BiBr_3P_2$: C, 40.3; H, 2.7%).

$[BiI_3\{o\text{-}C_6H_4(PPh_2)_2\}]$. Orange powder. Yield 54%. (Found: C, 34.3; H, 2.0. Calc. for $C_{30}H_{24}BiI_3P_2$: C, 34.8; H, 2.3%).

$[BiCl_3(Ph_2AsCH_2CH_2AsPh_2)]$. Pale yellow solid. Yield 71%. (Found: C, 39.0; H, 3.1. Calc. for $C_{26}H_{24}As_2BiCl_3$: C, 39.0; H, 3.0%). IR ν_{BiCl}/cm^{-1}: 229, 247, 273.

$[BiBr_3(Ph_2AsCH_2CH_2AsPh_2)]$. Yellow solid. Yield 59%. (Found: C, 32.9; H, 2.4. Calc. for $C_{26}H_{24}As_2BiBr_3$: C, 33.4; H, 2.6%).

$[BiI_3(Ph_2AsCH_2CH_2AsPh_2)]$. Yellow solid. Yield 36%. (Found: C, 29.3; H, 2.6. Calc. for $C_{26}H_{24}As_2BiI_3$: C, 29.0; H, 2.3%).

$[BiCl_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$. Yellow solid. Yield 73%. (Found: C, 19.6; H, 2.6. Calc. for $C_{10}H_{16}As_2BiCl_3$: C, 20.0; H, 2.7%). IR ν_{BiCl}/cm^{-1}: 232, 254, 268.

$[BiBr_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$. Deep orange solid. Yield 64%. (Found: C, 16.4; H, 2.2. Calc. for $C_{10}H_{16}As_2BiBr_3$: C, 16.4; H, 2.2%).

$[BiI_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$. Red solid. Yield 57%. (Found: C, 13.8; H, 2.0. Calc. for $C_{10}H_{16}As_2BiI_3$: C, 13.7; H, 1.8%).

$[BiCl_3\{MeC(CH_2AsMe_2)_3\}]$. Pale yellow solid. Yield 12%. (Found: C, 18.5; H, 4.0. Calc. for $C_{11}H_{27}As_3BiCl_3$: C, 18.9; H, 3.9%). IR ν_{BiCl}/cm^{-1}: 236, 255, 282.

$[BiBr_3\{MeC(CH_2AsMe_2)_3\}]$. Yellow solid. Yield 64%. (Found: C, 15.5; H, 3.0. Calc. for $C_{11}H_{27}As_3BiBr_3$: C, 15.9; H, 3.3%).

$[BiI_3\{MeC(CH_2AsMe_2)_3\}]$. Orange solid. Yield 47%. (Found: C, 13.7; H, 2.8. Calc. for $C_{11}H_{27}As_3BiI_3$: C, 13.6; H, 2.8%).

$[BiCl_3\{o\text{-}C_6H_4(PMe_2)_2\}]$. To an anhydrous MeCN solution (10 cm^3) of $BiCl_3$ (0.053 g, 0.17 mmol) was added a solution of the ligand (0.033 g, 0.17 mmol) in MeCN (2 cm^3). The solution was concentrated *in vacuo*, and the cream solid separated and dried. Yield 0.066 g, 75%. (Found: C, 23.2; H, 3.2. Calc. for $C_{10}H_{16}BiCl_3P_2$: C, 23.4; H, 3.1%). IR ν_{BiCl}/cm^{-1}: 237, 251, 263.

$[BiBr_3\{o\text{-}C_6H_4(PMe_2)_2\}]$. Pale brown solid. Yield 67%. (Found: C, 18.2; H, 2.4. Calc. for $C_{10}H_{16}BiBr_3P_2$: C, 18.6; H, 2.5%).

$[BiI_3\{o\text{-}C_6H_4(PMe_2)_2\}]$. Made as above, but using BiI_3 in thf. Yellow-green solid. Yield 45%. (Found: C, 15.3; H, 2.0. Calc. for $C_{10}H_{16}BiI_3P_2$: C, 15.2; H, 2.0%).

$[BiCl_3(thf)\{o\text{-}C_6H_4(P(O)Ph_2)_2\}$. A solution of o-C_6H_4-$(P(O)Ph_2)_2$ (0.14 g, 0.30 mmol) in thf (10 cm^3) was added dropwise to a stirred solution of $BiCl_3$ (0.09 g, 0.30 mmol) in MeCN (10 cm^3). Hexane (10 cm^3) was added and the solution allowed

Table 4 Crystallographic data

	$[Bi_2I_6\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$	$[Sb_2Cl_6\{o\text{-}C_6H_4(AsMe_2)_2\}]$	$[BiCl_3(thf)\{o\text{-}C_6H_4(POPh_2)_2\}]$
Formula	$C_{20}H_{32}As_4Bi_2I_6$	$C_{10}H_{16}As_2Cl_6Sb_2$	$C_{34}H_{32}BiCl_3O_3P_2$
M	1751.54	742.3	865.88
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/Å	9.009(5)	8.487(2)	12.043(2)
b/Å	12.620(4)	14.839(4)	19.467(2)
c/Å	16.765(3)	16.866(3)	14.530(2)
β/°	90.98(2)	98.93(1)	101.80(2)
U/Å^3	1906(1)	2098.2(7)	3334.7(9)
Z	2	4	4
μ(Mo-Kα)/cm^{-1}	174.59	64.54	56.47
Unique obs. reflections	3522	3855	6074
Obs. reflections with $[I_o > 2\sigma(I_o)]$	1941	3231	3648
R	0.035	0.047	0.033
R_w	0.038	0.066	0.033

$R = \Sigma(|F_{obs}|_i - |F_{calc}|_i)/\Sigma|F_{obs}|_i$, $R_w = \sqrt{[\Sigma w_i(|F_{obs}|_i - |F_{calc}|_i)^2/\Sigma w_i|F_{obs}|_i^2]}$.

to stand overnight. The resultant white solid was filtered, washed with hexane and dried *in vacuo*. Yield 0.12 g, 52%. (Found: C, 48.1; H, 4.3. Calc. for $C_{34}H_{32}BiCl_3O_3P_2$: C, 47.1; H, 3.7%). ^{1}H NMR ($CDCl_3$): δ 1.87(m), 3.7(m), 7.3–7.6(m). $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ 34.5. IR/cm^{-1}: ν_{PO} 1165sh, 1156; ν_{BiCl} 274, 236.

$[BiBr_3\{o\text{-}C_6H_4(P(O)Ph_2)_2\}]$. Pale yellow solid. Yield 65%. (Found: C, 38.4; H, 2.8. Calc. for $C_{30}H_{24}BiBr_3O_2P_2$: C, 38.8; H, 2.6%). ^{1}H NMR ($CDCl_3$): δ 7.2–7.6(m). $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ 35.0. IR/cm^{-1}: ν_{PO} 1160sh, 1148.

$[SbCl_3\{o\text{-}C_6H_4(PPh_2)_2\}]$. To a solution of $SbCl_3$ (0.09 g, 0.37 mmol) in anhydrous MeCN (5 cm^3) was added a CH_2Cl_2 (5 cm^3) solution of the ligand (0.17 g, 0.37 mmol). The resultant pale yellow solution was concentrated to yield a grey powder. Yield 0.18 g, 67%. (Found: C, 53.6; H, 3.6. Calc. for $C_{30}H_{24}Cl_3P_2Sb$: C, 53.4; H, 3.6%). IR ν_{SbCl}/cm^{-1}: 228, 240, 267.

$[SbBr_3\{o\text{-}C_6H_4(PPh_2)_2\}]$. Yellow solid. Yield 83%. (Found: C, 40.6; H, 2.7. Calc. for $C_{30}H_{24}Br_3P_2Sb.2CH_2Cl_2$: C, 39.3; H, 2.9%).

$[SbI_3\{o\text{-}C_6H_4(PPh_2)_2\}]$. As above but using BiI_3 in thf. Bright yellow solid. Yield 49%. (Found: C, 36.6; H, 2.5. Calc. for $C_{30}H_{24}I_3P_2Sb\cdot CH_2Cl_2$: C, 36.0; H, 2.5%).

$[SbCl_3\{o\text{-}C_6H_4(PMe_2)_2\}]$. To a solution of $SbCl_3$ (0.057 g, 0.25 mmol) in anhydrous thf (5 cm^3) was added a CH_2Cl_2 solution of the ligand (0.05 g, 0.25 mmol). The white precipitate was filtered off and dried *in vacuo*. Yield 0.085 g, 80%. (Found: C, 28.5; H, 3.8. Calc. for $C_{10}H_{16}Cl_3P_2Sb$: C, 28.2; H, 3.8%). $^{31}P\{^1H\}$ NMR ($MeNO_2$, 250 K): δ 4.0. IR ν_{SbCl}/cm^{-1}: 230, 243, 257.

$[SbBr_3\{o\text{-}C_6H_4(PMe_2)_2\}]$. Yellow powder. Yield 51%. (Found: C, 22.4; H, 3.0. Calc. for $C_{10}H_{16}Br_3P_2Sb$: C, 21.5; H, 2.9%). $^{31}P\{^1H\}$ NMR ($MeNO_2$, 250 K): δ −6.5.

$[SbI_3\{o\text{-}C_6H_4(PMe_2)_2\}]$. Orange powder. Yield 64%. (Found: C, 16.7; H, 2.3. Calc. for $C_{10}H_{16}I_3P_2Sb$: C, 17.1; H, 2.3%).

$[SbCl_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$. To an anhydrous ethanol solution (10 cm^3) of $SbCl_3$ (0.124 g, 0.54 mmol) was added an ethanol solution (2 cm^3) of the ligand (0.154 g, 0.54 mmol) resulting in an immediate white precipitate. Yield 0.19 g, 68%. (Found: C, 23.0; H, 3.1. Calc. for $C_{10}H_{16}As_2Cl_3Sb$: C, 23.2; H, 3.5%). IR ν_{SbCl}/cm^{-1}: 230, 240, 265.

$[SbBr_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$. Pale yellow powder. Yield 82%. (Found: C, 18.6; H, 2.4. Calc. for $C_{10}H_{16}As_2Br_3Sb$: C, 18.5; H, 2.8%).

$[SbI_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$. Bright yellow powder. Yield 60%. (Found: C, 15.3; H, 1.9. Calc. for $C_{10}H_{16}As_2I_3Sb$: C, 15.2; H, 2.3%).

$[Sb_2Cl_6\{o\text{-}C_6H_4(AsMe_2)_2\}]$. A hot ethanol solution of $[SbCl_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$ was allowed to evaporate slowly, depositing colourless blocks. (Found: C, 15.8; H, 2.0. Calc. for $C_{10}H_{16}As_2Cl_6Sb_2$: C, 16.2; H, 2.2%). IR ν_{SbCl}/cm^{-1}: 230, 251, 264.

$[SbCl_3(Ph_2AsCH_2CH_2AsPh_2)]$. Prepared as above using $SbCl_3$ in ethanol and the ligand in CH_2Cl_2. White powder. Yield 57%. (Found: C, 43.6; H, 3.1. Calc. for $C_{26}H_{24}As_2Cl_3Sb$: C, 43.7; H, 3.4%). IR ν_{SbCl}/cm^{-1}: 230, 244, 256.

$[SbBr_3(Ph_2AsCH_2CH_2AsPh_2)]$. Yellow powder. Yield 72%. (Found: C, 37.0; H, 3.2. Calc. for $C_{26}H_{24}As_2Br_3Sb$: C, 36.8; H, 2.9%).

$[SbCl_3\{MeC(CH_2AsMe_2)_3\}]$. White powder. Yield 56%. (Found: C, 21.1; H, 4.3. Calc. for $C_{11}H_{27}As_3Cl_3Sb$: C, 21.6; H, 4.5%). IR ν_{SbCl}/cm^{-1}: 232, 249, 265.

$[SbBr_3\{MeC(CH_2AsMe_2)_3]$. Yellow powder. Yield 34%. (Found: C, 17.7; H, 3.5. Calc. for $C_{11}H_{27}As_3Br_3Sb$: C, 17.7; H, 3.7%).

X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 4. Crystals of $[BiCl_3(thf)\{o\text{-}C_6H_4(P(O)Ph_2)_2\}]$ were obtained from thf by layering with Et_2O, while crystals of $[Bi_2I_6\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ were obtained by slow evaporation from a solution of the complex in MeCN. Crystals of $[Sb_2Br_6\{o\text{-}C_6H_4(PPh_2)_2\}_2]$ were obtained by slow evaporation of the synthesis solution, and crystals of $[Sb_2Cl_6\{o\text{-}C_6H_4(AsMe_2)_2\}]$ by slow evaporation of a hot ethanol solution of $[SbCl_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$. Data collection used a Rigaku AFC7S four-circle diffractometer (T = 150 K) with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Structure solution and refinement were generally routine.[22–25]

$[Bi_2I_6\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$, $[Sb_2Br_6\{o\text{-}C_6H_4(PPh_2)_2\}_2]$ Absorption correction applied using DIFABS.[25]

CCDC reference numbers 155952–155954.

See http://www.rsc.org/suppdata/dt/b0/b010179f/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the EPSRC and Southampton University for support.

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