DALTON

New square-pyramidal organoantimony(V) compounds; crystal structures of (biphenyl-2,2′-diyl)phenylantimony(V) dibromide, dichloride and diisothiocyanate, $Sb(2,2'-C_{12}H_8)PhX_2$ (X = Br, Cl or NCS), and of octahedral $SbPh(o-O_2C_6Cl_4)Cl_2\cdot OEt_2$

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Oxidative addition between (biphenyl-2,2′-diyl)phenylantimony(III), $Sb(2,2'-C_{12}H_8)Ph$ **1** and Br_2 or SO_2Cl_2 gave $Sb(2,2'-C_{12}H_8)PhBr_2$ **2** and $Sb(2,2'-C_{12}H_8)PhCl_2$ **3**, respectively, while the corresponding fluoride $Sb(2,2'-C_{12}H_8)PhF_2$ **4** and the thiocyanate $Sb(2,2'-C_{12}H_8)Ph(NCS)_2$ **5** were obtained by metathesis reactions between **3** and KF and KSCN, respectively. Compounds **2** and **3** are isostructural but, in contrast to the closely related $SbPh_3X_2$ species, individual molecules have square-pyramidal geometry. Again in contrast to $SbPh_3X_2$ compounds, secondary antimony–halogen interactions *trans* to the apical carbon atom lead to solid-state dimers, implying Lewis acidity at antimony. Antimony in the thiocyanate **5** showed similar square-pyramidal geometry with N-bonded thiocyanate groups but bridging by one thiocyanate again gives dimers in the solid. Oxidative addition between $SbPhCl_2$ and tetrachloro-*ortho*-benzoquinone in ether solution gave the tetrachlorocatechol analogue of **3** as a six-co-ordinate ether solvate, $SbPh(o-O_2C_6Cl_4)\cdot OEt_2$ **6**. If the weak bond to ether is ignored, antimony again has square-pyramidal geometry but formation of the adduct again points to antimony Lewis acidity. A non-solvated substituted catecholate, $SbPh(o-O_2C_6H_2Bu^t{}_2-3,5)Cl_2$ **8**, was also synthesized but crystals suitable for X-ray diffraction could not be obtained.

Although the vast majority of five-co-ordinate Group 15 compounds have trigonal-bipyramidal structures, the energy difference between this and the square-pyramidal alternative is small;[1] the two geometries are interconnected *via* Berry pseudorotation.[2] Nevertheless, a number of square pyramidal species have been identified. Of the Group 15 elements, phosphorus has been most widely investigated and in all structurally characterised examples[3–7] it is contained within four- or five-membered rings and indeed this geometry appears to be favoured by the presence of multiple five-membered rings. Geometric considerations suggest that this follows from the lower ring strain when the rings occupy *cis* basal positions of a square pyramid and near-perfect square-pyramidal geometry, for example, is found in $PPh(o-O_2C_6H_4)(o-O_2C_6Cl_4)$.[3] Arsenic(V) is less widely investigated, but square-pyramidal species are again found in compounds containing dioxo chelating groups, such as $AsPh(o-O_2C_6H_4)_2$.[8]

In contrast to the trigonal-bipyramidal structures of the phosphorus and arsenic analogues, $SbPh_5$ is a well known square-pyramidal molecule[9,10] although the cyclohexane solvate, $SbPh_5\cdot 0.5C_6H_{12}$,[11] the *p*-tolyl analogue, $Sb(C_6H_4Me-p)_5$,[12] and the related (biphenyl-2,2′-diyl)triphenyl analogue, $Sb(2,2'-C_{12}H_8)Ph_3$,[13] are all trigonal bipyramidal. The $SbPh_5$ structure is considered to be a solid-state packing effect.[14] Two antimony(V) compounds containing chelating groups, *e.g.* the hemihydrate $[SbPh_3(o-O_2C_6H_4)]_2\cdot H_2O$,[15] and $SbPh(o-O_2C_6Cl_4)(2,2'-C_{12}H_8)$,[16] are also square pyramidal as are $BiPh_5$ and a number of related pentaaryl compounds.[17–20] Illustrating the delicate balance between the two structural alternatives, (biphenyl-2,2′-diyl)triphenylbismuth, $Bi(2,2'-C_{12}H_8)Ph_3$, in contrast to the antimony analogue is distorted square pyramidal.[20]

This paper reports attempts to prepare new square-pyramidal organoantimony(V) compounds by a strategy involving incorporation of a chelating biphenylyl group, to give a chelate angle close to 90°, two mutually repelling groups (halogen or pseudo-halogen) expected to occupy *trans* basal positions, with the fifth site filled by a phenyl group acting as ‘spectator’. This is not, however, guaranteed to give square-pyramidal geometry as, for example, $Sb[(CH_2)_4]MeCl_2$ with a similar series of ligands is distorted trigonal bipyramidal.[21] Dioxo chelating groups are known to stabilise square-pyramidal geometry and reactions leading to compounds where such groups replace biphenylyl are also reported here. A preliminary account of one of the biphenylyl compounds has been published.[22]

Results and Discussion

Biphenyl compounds

Preparation and spectroscopy. The compound $Sb(2,2'-C_{12}H_8)Ph$ **1**, the precursor for the required antimony(V) compounds, was obtained in moderate yield by treating $SbPhCl_2$ with $2,2'-Li_2C_{12}H_8\cdot 2tmen$ in diethyl ether (tmen = $Me_2NCH_2CH_2NMe_2$); oxidative addition with either elemental bromine or sulfuryl chloride then readily gave, respectively, the dibromide **2** and dichloride **3**. The dichloride **3** was then treated with 2 mol of potassium fluoride in acetone to give the difluoride, $Sb(2,2'-C_{12}H_8)PhF_2$ **4**, and with potassium thiocyanate in acetonitrile to yield the corresponding dithiocyanate, $Sb(2,2'-C_{12}H_8)Ph(NCS)_2$ **5**.

Infrared spectra for compounds **1** to **5** are dominated by aryl modes from the phenyl and biphenylyl ligands and vary little from compound to compound. The most intense bands in the Nujol mull spectrum of $Sb(2,2'-C_{12}H_8)Ph(NCS)_2$ **5** were at 2077 and 1994 cm^{-1} and are assigned to C−N stretching modes of thiocyanate groups, probably in different environments.[23] The sharp, intense band at 2077 cm^{-1} is in a region usually associated with either 1,3 bridging or terminal S-bonding; the latter assignment is however unlikely here as hard Sb^V has a distinct preference for N-bonding.[24] The second, broad band at 1994 cm^{-1} is similar to that found for $SbPh_3(NCS)_2$ (2009 cm^{-1}) and is consistent with terminal N-bonding. A further band at 743 cm^{-1} is assigned to C−S stretching and a deformation mode occurs at 450 cm^{-1}. The C−N stretching region is, in fact, very similar to that for $SbPh_2Br(NCS)_2$,[24] where bands at 2092 and 1993 cm^{-1} were interpreted as suggesting a dimeric (or more highly polymeric) structure with antimony bonded to one terminal and one bridging thiocyanate group. Similar di- or polymeric structures are clearly possibilities for **5** and, as halogens are also potential bridging groups, for **2**–**4** also.

The ^1H NMR spectrum of $Sb(2,2'-C_{12}H_8)PhBr_2$ **2** in $CDCl_3$ solution showed multiplets centred at δ 7.56 and 8.06 (intensity ratio 7:6), with the higher field signal assigned to the *meta* and *para* phenyl protons and the H^2 and H^3 biphenylyl protons (H^1 is attached to the carbon adjacent to antimony; the remaining hydrogens H^2–H^4 are then numbered sequentially). Accordingly, the multiplet at δ 8.06 is assigned to the *ortho* phenyl protons and H^1 and H^4 of the biphenylyl group; the expected two doublets for the latter are observable.

The spectrum of $Sb(2,2'-C_{12}H_8)PhCl_2$ **3** showed greater resolution of the biphenylyl signals with two triplets [^3J(HH) 7.5 Hz] of doublets [^4J(HH) 1.4 Hz] at δ 7.55 and 7.63 assigned to the H^2 and H^3 biphenylyl protons and a complex multiplet for the *meta* and *para* phenyl protons, centred at δ 7.61. The H^4 and H^1 biphenylyl protons occurred as doublets at δ 8.02 and 8.08, respectively, with the *ortho* phenyl protons as a multiplet at δ 8.27, significantly to lower field than in **2**. The biphenylyl group in the spectrum of $Sb(2,2'-C_{12}H_8)Ph(NCS)_2$ **5** also showed a doublet, triplet, triplet, doublet pattern for the H^1 to H^4 protons, while the phenyl protons gave broad unresolved multiplets at δ 7.70 (*meta* and *para*) and 8.23 (*ortho*). The observation of only four signals for the biphenylyl group in these spectra suggests the presence of either an element of symmetry in the solution species, which makes the benzenoid rings equivalent, or a pseudo-rotation process, which leads to ligand exchange which is fast on the NMR time-scale. If the molecules are square pyramidal, the former is perhaps unlikely as the biphenylyl group is expected to span the chemically distinct axial and basal sites.

No parent ion was observed in the electron impact (EI) mass spectra of compounds **2**–**5** nor in the FAB mass spectrum of **5**. All spectra, with the exception of the EI spectrum of **5**, contained a fragment assigned to $Sb(2,2'-C_{12}H_8)PhX^+$, implying ready loss of the first halide or pseudo-halide group. Loss of the second halide or pseudo-halide is also more favourable than loss of organic groups, but for **3** the $Sb(2,2'-C_{12}H_8)Cl^+$ ion was observed. The strength of biphenylyl chelating is reflected by the presence of reasonable intensity $Sb(2,2'-C_{12}H_8)Ph^+$ and $Sb(2,2'-C_{12}H_8)^+$ ions in all spectra, while the alternative fragment $SbPh^+$ was not observed. All spectra, including that of the precursor $Sb(2,2'-C_{12}H_8)Ph$ **1**, showed high intensity for the rearrangement ion $PhC_{12}H_8^+$ (*m/z* 229), resulting from reaction between phenyl and biphenylyl. This is the analogue of Ph_2^+, invariably found in mass spectra of antimony compounds containing two or more phenyl groups.

X-Ray crystallography. Single-crystal structures have been determined for three of these compounds, $Sb(2,2'-C_{12}H_8)PhBr_2$ **2**, $Sb(2,2'-C_{12}H_8)PhCl_2$ **3** and $Sb(2,2'-C_{12}H_8)Ph(NCS)_2$ **5**.

The molecular structure of compound **2** is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. The asymmetric unit contains an antimony atom in distorted square-pyramidal geometry with the biphenylyl group spanning between apical and basal positions to give a stibole ring, while the remaining basal positions are occupied by two *trans* bromine atoms and the phenyl group. The Sb–C bond lengths are unequal with those to basal positions [Sb(1)–C(1), 2.124(6), Sb(1)–C(14), 2.119(6) Å] longer than that to the apical site [Sb(1)–C(7) 2.106(6) Å]. A shorter apical bond distance is characteristic of square-pyramidal geometry; for example, that in the five-co-ordinate molecule in $[SbPh_3(o-O_2C_6H_4)]_2 \cdot H_2O$ is 2.099(4) Å, compared with values of 2.125(4) and 2.143(4) Å for the basal bonds. Deviations from the mean plane through the basal atoms are small [Br(1), +0.031; Br(2), +0.032; C(1), −0.031; C(14), −0.032 Å] and as expected antimony lies 0.245 Å above this plane. Coplanarity of the two benzenoid rings of the biphenylyl group is illustrated by a twist angle of 3.5° between the respective best-fit planes.

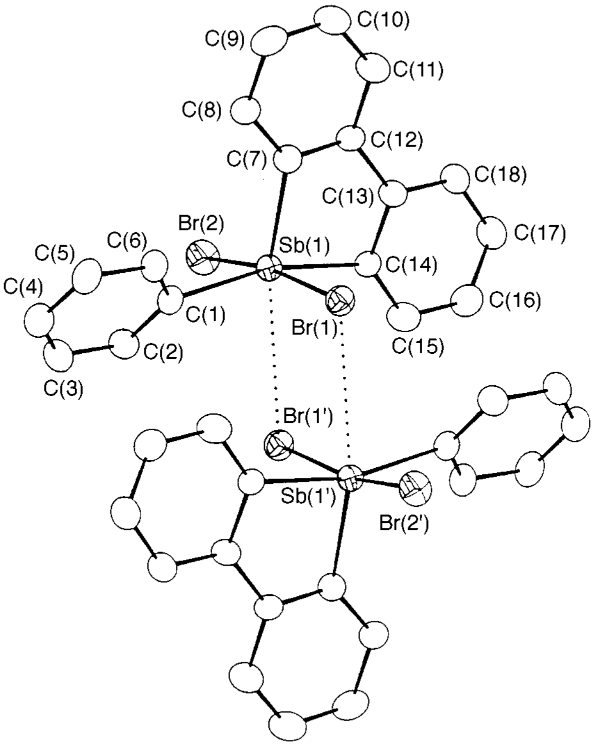

Fig. 1 Molecular structure and atom numbering scheme for $Sb(2,2'-C_{12}H_8)PhBr_2$ **2**

Table 1 Important bond distances (Å) and angles (°) for compound **2**, with estimated standard deviations (e.s.d.s) in parentheses

Sb(1)–Br(2)	2.5924(8)	Sb(1)–C(1)	2.124(6)
Sb(1)–Br(1)	2.7080(8)	Sb(1)–C(7)	2.106(6)
Sb(1)···Br(1′)*	3.346(1)	Sb(1)–C(14)	2.119(6)
Br(2)–Sb(1)–Br(1)	170.72(3)	Br(2)–Sb(1)···Br(1′)	89.42(2)
Br(2)–Sb(1)–C(1)	89.9(2)	C(7)–Sb(1)···Br(1′)	167.2(2)
Br(1)–Sb(1)–C(1)	89.7(2)	C(14)–Sb(1)···Br(1′)	85.3(2)
Br(2)–Sb(1)–C(7)	97.9(2)	C(1)–Sb(1)···Br(1′)	79.7(2)
Br(1)–Sb(1)–C(7)	90.9(2)	Sb(1)–C(1)–C(2)	122.3(5)
C(1)–Sb(1)–C(7)	110.7(3)	Sb(1)–C(1)–C(6)	115.5(5)
Br(2)–Sb(1)–C(14)	89.0(2)	Sb(1)–C(7)–C(8)	128.2(5)
Br(1)–Sb(1)–C(14)	88.9(2)	Sb(1)–C(7)–C(12)	110.1(5)
C(1)–Sb(1)–C(14)	165.0(2)	Sb(1)–C(14)–C(13)	108.2(4)
C(7)–Sb(1)–C(14)	84.3(2)	Sb(1)–C(14)–C(15)	129.7(5)
Br(1)–Sb(1)···Br(1′)	81.39(2)		

* Atoms carrying a prime are related to unprimed atoms by the symmetry operation 1 − *x*, −*y*, −*z*.

Angles at animony between the apical carbon and three of the basal atoms are greater than 90°, as expected for square-pyramidal geometry, but that between the carbons of the chelating biphenylyl group is necessarily lower [84.3(2)°]. On the other hand, *trans* basal angles [Br(2)–Sb(1)–Br(1) 170.72(3) and C(1)–Sb(1)–C(14) 165.0(2)°] are greater than expected for a simple square-pyramidal molecule (*ca.* 150°) and further the two independent Sb–Br separations are substantially different [Sb(1)–Br(1) 2.7080(8) and Sb(1)–Br(2) 2.5924(8) Å]. The Sb(1)–Br(2) bond length is comparable with that in related compounds, such as $SbPh_3Br_2$ [2.632(1) Å] where bromine is terminal.[25] These factors are a consequence of weak intermolecular Sb···Br interactions [Sb(1)···Br(1′) 3.346(1) Å], *trans* to the apical carbon atom [C(7)–Sb(1)···Br(1′) 167.2(2)°], which give centrosymmetric dimers in the solid (see Fig. 1). If these further interactions are taken into account, the antimony co-ordination number rises to six and the geometry becomes distorted octahedral.

Table 2 Important bond distances (Å) and angles (°) for compound **3**, with e.s.d.s in parentheses

Sb(1)–Cl(1)	2.544(4)	Sb(1)–C(1)	2.13(1)
Sb(1)–Cl(2)	2.444(4)	Sb(1)–C(7)	2.12(1)
Sb(1)···Cl(1′)*	3.191(4)	Sb(1)–C(14)	2.10(1)
Cl(1)–Sb(1)–Cl(2)	170.2(1)	C(7)–Sb(1)–C(14)	85.0(5)
Cl(1)–Sb(1)–C(1)	90.0(5)	C(7)–Sb(1)···Cl(1′)	165.8(5)
Cl(2)–Sb(1)–C(1)	89.3(5)	Sb(1)–C(1)–C(2)	121.0(12)
Cl(1)–Sb(1)–C(7)	90.6(4)	Sb(1)–C(1)–C(6)	116.0(12)
Cl(2)–Sb(1)–C(7)	98.9(4)	Sb(1)–C(7)–C(8)	128.7(11)
C(1)–Sb(1)–C(7)	109.6(5)	Sb(1)–C(7)–C(12)	107.4(9)
Cl(1)–Sb(1)–C(14)	89.2(4)	Sb(1)–C(14)–C(13)	108.9(10)
Cl(2)–Sb(1)–C(14)	89.0(4)	Sb(1)–C(14)–C(15)	127.7(11)
C(1)–Sb(1)–C(14)	165.4(5)		

* Atoms carrying a prime are related to unprimed atoms by the symmetry operation 1 − *x*, −*y*, −*z*.

Table 3 Important bond distances (Å) and angles (°) for compound **5**, with e.s.d.s in parentheses

Sb(1)–N(100)	2.216(4)	Sb(1)–C(14)	2.135(4)
Sb(1)–N(200)	2.146(4)	S(100)–C(100)	1.639(5)
Sb(1)···S(100′)*	3.191(4)	S(200)–C(200)	1.601(6)
Sb(1)–C(1)	2.137(4)	N(100)–C(100)	1.165(6)
Sb(1)–C(7)	2.090(4)	N(200)–C(200)	1.169(6)
N(100)–Sb(1)–N(200)	171.1(1)	Sb(1)–N(100)–C(100)	173.5(4)
N(100)–Sb(1)–C(1)	88.5(2)	Sb(1)–N(200)–C(200)	139.6(4)
N(200)–Sb(1)–C(1)	91.1(2)	Sb(1)–C(1)–C(2)	122.7(3)
N(100)–Sb(1)–C(7)	93.0(2)	Sb(1)–C(1)–C(6)	116.6(3)
N(200)–Sb(1)–C(7)	95.5(2)	C(2)–C(1)–C(6)	120.7(4)
C(1)–Sb(1)–C(7)	110.7(2)	Sb(1)–C(7)–C(8)	129.2(4)
N(100)–Sb(1)–C(14)	87.2(2)	Sb(1)–C(7)–C(12)	110.2(3)
N(200)–Sb(1)–C(14)	90.8(2)	Sb(1)–C(14)–C(13)	107.9(3)
C(1)–Sb(1)–C(14)	164.0(2)	Sb(1)–C(14)–C(15)	130.0(4)
C(7)–Sb(1)–C(14)	84.9(2)	S(100)–C(100)–N(100)	179.3(4)
C(7)–Sb(1)···S(100′)	170.6(1)	S(200)–C(200)–N(200)	178.0(5)

* Atoms carrying a prime are related to unprimed atoms by the symmetry operation 1 − *x*, 1 − *y*, 1 − *z*.

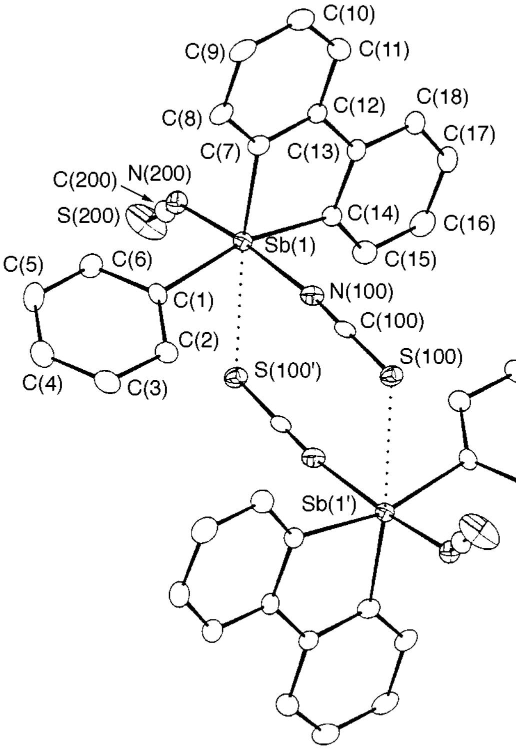

Fig. 2 Molecular structure and atom numbering scheme for $Sb(2,2'-C_{12}H_8)Ph(NCS)_2$ **5**

Two methods[26,27] have been used to define five-co-ordinate configurations and that by Muetterties and Guggenberger,[26] which is based on calculating dihedral angles relating to a number of 'shape-determining' edges, has been used here. A starting trigonal-bipyramidal conformation, similar to that in $Sb(2,2'-C_{12}H_8)Ph_3$, is defined from which Berry deviations occur to give the observed square pyramid. Three of the dihedral angles, δe_1, δe_2 and δe_3, important in assessing the geometry, are equal (53.1°) for trigonal-bipyramidal geometry but are 75.7, 75.7 and 0°, respectively, for a square pyramid. If this approach is applied to **2** there will necessarily be deviations from constraints imposed by the chelating group and the differences in Sb–C bond lengths (the bond-length ratio in this model is taken as unity). Calculations for **2**, however, give angles of 83.1, 79.2 and 3.5° for δe_1, δe_2 and δe_3, respectively, values close to those for the ideal square pyramid.

Compound **3**, the corresponding dichloride, is isostructural with **2** and the same square-pyramidal geometry is observed for the monomer. The atom numbering scheme is the same and selected bond distances and angles are included in Table 2. The biphenylyl group again spans axial and basal positions with a chelate angle C(7)–Sb(1)–C(14) of 85.0(5)°. Deviations from the mean plane through the basal atoms are again small with the chlorines above the plane [Cl(1), +0.027; Cl(2), +0.028 Å] and carbons below [C(1), −0.027; C(14), −0.028 Å]; antimony lies 0.241 Å above the plane. Confirmation of the square pyramid about antimony follows from δe_1, δe_2 and δe_3 values of 82.2, 77.3 and 3.0°, respectively. Near coplanarity of the biphenylyl ring is shown by a twist angle of 2.6°. The expected shortening of the axial Sb(1)–C(7) bond is not observed here, probably due to poorer quality data but differences in Sb–Cl bond lengths are clearly resolved [Sb(1)–Cl(2) 2.444(4), Sb(1)–Cl(1) 2.544(4) Å], with the latter involved in intermolecular bonding to a symmetry-related antimony atom. This interaction [Sb(1)···Cl(1′) 3.191(4) Å; C(7)–Sb(1)···Cl(1′) is 165.8(5)°] is weak even in comparison with similar bridges in, for example, dimeric diphenylantimony trichloride (2.839 Å).[28]

The structure of compound **5** is shown in Fig. 2 with important distances and angles collected in Table 3. As with **2** and **3**, the basic molecular unit is square pyramidal with a shorter apical Sb–C separation than those to the basal carbons. The δe_1, δe_2 and δe_3 values are 75.9, 76.9 and 6.7°, respectively, and deviations from the mean plane through the basal atoms are a little larger than those in **2** and **3** [C(1), −0.061; C(14), −0.062; N(100), +0.062; N(200), +0.061 Å], with antimony 0.231 Å above the plane. The twist angle of the biphenylyl group here is only 1.8°. As in **2** and **3**, the compound is a solid-state dimer, as suggested by IR spectroscopy, and contains both terminal and 1,3-bridging thiocyanate groups. The intermolecular Sb···S separation is 3.191(4) Å with C(7)–Sb(1)···S(100′) equal to 170.6(1)°. There are distinctly different Sb–N bond lengths [Sb(1)–N(200) 2.146(4), Sb(1)–N(100) 2.216(4) Å], presumably a consequence of bridging with the terminal separation comparable to those in $SbPh_3(NCS)_2$ (mean 2.142 Å).[24] Bridging also leads to an increase in the C–S separation [C(100)–S(100) 1.639(5), C(200)–S(200) 1.601(6) Å], but both groups, as expected, are effectively linear with angles at C(100) and C(200) of 179.3(4) and 178.0(5)°, respectively. The C–N bond lengths are short and equivalent [N(100)–C(100) 1.165(6), N(200)–C(200) 1.169(6) Å] and appear to be best described as triple bonds (*cf.* C≡N 1.16, C=N 1.30 Å).[29] One of the most striking features of this structure is the difference in angles at the thiocyanate nitrogens. That at the terminal N(200) atom is significantly lower [139.6(4)°] than any of the corresponding angles in $SbPh_3(NCS)_2$,[24] while the C(100)–N(100)–Sb(1) angle is almost linear [173.5(4)°], undoubtedly a consequence of bridging.

The structures of compounds **2**, **3** and **5** are noteworthy not only because the molecular units are square pyramidal but because dimerisation in the solid implies Lewis acidity at antimony. The compounds are direct analogues of the well known trigonal-bipyramidal species, $SbPh_3X_2$, which do not form addition compounds and the antimony Lewis acidity is clearly very low. It seems unlikely that changes in electronic effects, resulting from replacement of two of the phenyl groups in $SbPh_3X_2$ by biphenylyl, would have such a marked influence on both antimony stereochemistry and Lewis acidity. The properties could simply be a consequence of the steric requirements of the biphenylyl group in conjunction with two electronegative substituents giving square-pyramidal geometry and thus a co-ordination site *trans* to the apical carbon atom becomes available. The stereochemical non-rigidity of five-co-ordinate structures is certainly highlighted in these compounds showing that relatively small changes in substituent types can lead to considerable structural change.

Dioxo-chelate compounds

Preparation and spectroscopy. To determine if the antimony geometry would be affected by a change in the type of chelate group in compounds of this type, attempts were made to synthesize other compounds with the general formula SbPh(chelate)X_2. The first approach was oxidative addition of bromine to $SbPh(O_2C_2Me_4)$ and SbPh(*o*-$O_2C_6H_4$), but only mixtures of unidentified products were recovered. A second, more successful strategy, involved oxidation of $SbPhCl_2$ with *ortho*-benzoquinones, such as *o*-$O_2C_6Cl_4$ and *o*-$O_2C_6H_2Bu^t_2$-3,5; similar reactions have been carried out previously.[16,30] A crystalline product was obtained from a reaction with *o*-$O_2C_6Cl_4$ in diethyl ether solution and shown to be an ether adduct, SbPh(*o*-$O_2C_6Cl_4$)Cl_2·OEt_2 **6**, but pure compounds could not be prepared from reactions in solvents with no donor properties. From ^1H NMR spectroscopy, compound **6** remains unchanged on crystallisation from hot dichloromethane, while treatment with tetrahydrofuran gave the corresponding tetrahydrofuran adduct, SbPh(*o*-$O_2C_6Cl_4$)Cl_2·OC_4H_8 **7**. Solvent free five-co-ordinate species could not be obtained from 3,4,5,6-tetrachloro-*ortho*-benzoquinone, but in a reaction between $SbPhCl_2$ and *o*-$O_2C_6H_2Bu^t_2$-3,5 in dichloromethane a compound with this stoichiometry, SbPh(*o*-$O_2C_6H_2Bu^t_2$-3,5)Cl_2 **8**, was obtained.

The IR spectra of compounds **6** and **8** showed strong bands at 1249, 1242 and 1236, 1313 cm^{-1}, respectively, associated with the substituted catecholate groups. The ^1H NMR spectrum of SbPh(*o*-$O_2C_6Cl_4$)Cl_2·OEt_2 **6** clearly showed peaks due to ether [δ 1.03 (triplet), 3.74 (quartet)], shifted substantially from the free molecule positions (δ 1.20, 3.48). The phenyl protons occurred as broad, unresolved multiplets at δ 7.64 (*meta* and *para*) and 8.17 (*ortho*). Owing to poor solubility in $CDCl_3$, a ^{13}C-{^1H} DEPT-135 spectrum of **6** showed poor signal-to-noise ratio but the expected non-quaternary carbons were located. Ether signals were observed at δ 13.8 [$O(CH_2\mathit{C}H_3)_2$] and 66 [$O(\mathit{C}H_2CH_3)_2$], wheras the phenyl carbons were observed at δ 130.2 (*m*-Ph), 132.0 (*p*-Ph) and 133.0 (*o*-Ph). The ^1H spectrum of the thf adduct, SbPh(*o*-$O_2C_6Cl_4$)Cl_2·OC_4H_8 **7**, showed signals at δ 1.80 and 3.82 for thf and broad unresolved multiplets at δ 7.63 (*meta* and *para*) and 8.17 (*ortho*) for the phenyl protons.

Signals in the ^1H NMR spectrum of compound **8** were broad and poorly resolved but the spectrum was fully assigned. At high field, resonances due to the two *tert*-butyl groups were observed at δ 1.31 and 1.51 (tentatively assigned to the 3 and 5 groups, respectively) with aromatic protons at δ 6.83 and 7.07, markedly shifted from signals (δ 6.21 and 6.93) of the quinone precursor. Phenyl protons gave unresolved multiplets at δ 7.59 (*meta* and *para*) and 8.23 (*ortho*).

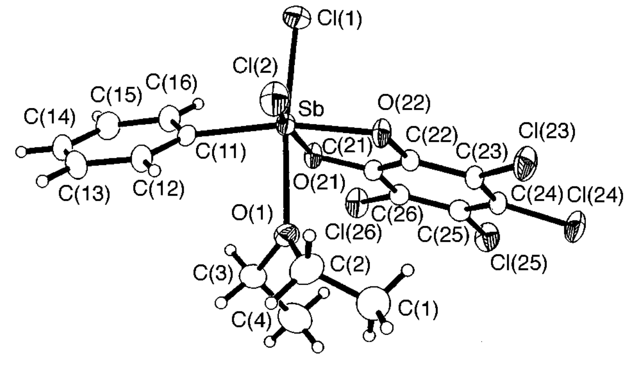

Fig. 3 Molecular structure and atom numbering scheme for SbPh(*o*-$O_2C_6Cl_4$)Cl_2·OEt_2 **6**

Table 4 Important bond distances (Å) and angles (°) for compound **6**, with e.s.d.s. in parentheses

Sb–O(22)	1.991(3)	Sb–Cl(1)	2.342(2)
Sb–O(21)	2.026(3)	Sb–Cl(2)	2.346(2)
Sb–C(11)	2.117(4)	O(21)–C(21)	1.343(5)
Sb–O(1)	2.302(3)	O(22)–C(22)	1.354(5)
O(22)–Sb–O(21)	82.15(11)	C(11)–Sb–Cl(2)	97.81(11)
O(22)–Sb–C(11)	168.86(14)	O(1)–Sb–Cl(2)	88.89(10)
O(21)–Sb–C(11)	93.88(13)	Cl(1)–Sb–Cl(2)	94.76(7)
O(22)–Sb–O(1)	81.67(13)	C(21)–O(21)–Sb	111.2(2)
O(21)–Sb–O(1)	82.56(13)	C(22)–O(22)–Sb	111.4(2)
C(11)–Sb–O(1)	87.50(14)	O(21)–C(21)–C(26)	123.5(4)
O(22)–Sb–Cl(1)	92.68(11)	O(21)–C(21)–C(22)	116.9(4)
O(21)–Sb–Cl(1)	92.58(10)	C(12)–C(11)–Sb	119.0(3)
C(11)–Sb–Cl(1)	97.91(12)	C(16)–C(11)–Sb	118.8(3)
O(1)–Sb–Cl(1)	172.98(9)	C(3)–O(1)–Sb	119.3(3)
O(22)–Sb–Cl(2)	84.69(9)	C(2)–O(1)–Sb	125.7(3)
O(21)–Sb–Cl(2)	165.20(9)		

X-Ray crystallography. The structure of SbPh(*o*-$O_2C_6Cl_4$)Cl_2·OEt_2 **6** has been determined (see Fig. 3 for the atom numbering scheme) and selected bond lengths and angles are listed in Table 4. As perhaps expected, antimony is in distorted octahedral co-ordination with the ether molecule occupying the sixth octahedral site. Three oxygen atoms from the chlorocatechol ligand and ether occupy a common triangular face to give the *fac* isomeric form. If the ether molecule is neglected, the SbPh(*o*-$O_2C_6Cl_4$)Cl_2 moiety is clearly square pyramidal but, in contrast to the biphenylyl compounds discussed above, the halogens occupy the apical position and one of the basal sites with the biphenylyl group occupying two more of the basal positions. The chelate angle [O(21)–Sb–O(22) 82.2(1)°] is similar to that in the biphenylyl compounds (mean 84.7°) and it seems probable that electronic, rather than simple geometric, effects are responsible for the different geometries. In keeping with square-pyramidal geometry, the *trans* 'basal' angles [O(22)–Sb–C(11) 168.9(1) and O(21)–Sb–Cl(2) 165.20(9)°] are significantly lower than 180° and the four atoms in the basal plane deviate only slightly from the best mean plane [C(11), −0.017; Cl(2), 0.018; O(22), −0.023; O(21), 0.022 Å] with antimony 0.171 Å above this plane.

The structure of compound **6** is similar to that of the six-co-ordinate hydrated molecule in [$SbPh_3$(*o*-$O_2C_6H_4$)]$_2$·H_2O, where the water molecule occupies a position *cis* to the catecholato oxygens giving again the *fac* isomer.[15] Bond lengths in **6** are unexceptional, although Sb–O distances to the catechol oxygens, especially that to O(22) [1.991(3) Å], are short. The slight elongation of Sb–O(21) [2.026(3) Å] can probably be ascribed to the *trans* influence of Cl(2); equivalent Sb–O separations in $SbPh_3$(*o*-$O_2C_6Cl_4$) and SbPh(2,2′-$C_{12}H_8$)(*o*-$O_2C_6Cl_4$) are *ca.* 2.051 Å.[16] The Sb–O(1) separation to the ether oxygen atom is longer [2.302(3) Å], implying a weak interaction and should be compared with Sb–O distances in diphenylantimony trichloride monohydrate (2.311 Å),[31] $SbCl_5$·$OPMe_3$ (1.94 Å)[32] and SbPh(*o*-$O_2C_6H_4$)·H_2O (2.512 Å).[15]

The ready formation and stability of the ether addition compound **6** implies Lewis acidity at antimony in the solvent-free species, as with the five-co-ordinate biphenylyl compounds discussed above, and it would clearly be of great interest to determine the structure of such a compound. Trigonal-bipyramidal geometry seems unlikely, but cannot be ruled out completely, and a square-pyramidal molecular unit forming centrosymmetric dimers *via* halide bridging, as for the biphenylyl analogues, is probably a more realistic option.

Experimental

Where necessary, reactions were carried out under a nitrogen or argon atmosphere using Schlenk methods and solvents dried by conventional methods.

Preparations

$2,2'\text{-}Li_2C_{12}H_8\cdot 2tmen$.[33] Biphenyl (1.98 g, 12.8 mmol) was added to a stirring solution of $LiBu^n$ (20 cm^3, 1.6 mol dm^{-3} in hexanes, 32 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.38 g, 33 mmol) at 0 °C under an argon atmosphere. The resulting yellow solution was stirred for 72 h at room temperature and then cooled to −30 °C for 48 h to allow crystallisation. Yellow crystals of $2,2'\text{-}Li_2C_{12}H_8\cdot 2tmen$ were isolated after decanting the supernatant liquid. Yield 2.96 g (58%).

$Sb(2,2'\text{-}C_{12}H_8)Ph$ 1. A solution of freshly prepared $2,2'\text{-}Li_2C_{12}H_8\cdot 2tmen$ (2.50 g, 6.27 mmol) in ether (20 cm^3) was slowly added to a stirring solution of $SbPhCl_2$[34] (1.69 g, 6.27 mmol) in ether (20 cm^3) at −75 °C. The resulting yellow solution was slowly warmed to room temperature and stirred for 15 h, when the mixture was filtered and added to water (50 cm^3). After separating the layers, the aqueous phase was extracted with ether (3 × 25 cm^3 portions). The combined ether fractions, after drying ($MgSO_4$), were filtered and the solvent removed under vacuum. The crude product was recrystallised from ethanol–ether to give $Sb(2,2'\text{-}C_{12}H_8)Ph$. Yield 0.70 g (32%); m.p. 95–101 °C (lit.,[35] 98–100 °C) (Found: C, 61.5; H, 3.8. Calc. for $C_{18}H_{13}Sb$: C, 61.6; H, 3.7%).

$Sb(2,2'\text{-}C_{12}H_8)PhBr_2$ 2. A solution of bromine (2.8 cm^3, 1.37 mmol) in chloroform (25 cm^3) was slowly added to a stirring solution of $Sb(2,2'\text{-}C_{12}H_8)Ph$ (0.48 g, 1.37 mmol) in chloroform (30 cm^3) at 0 °C. The resulting solution was allowed to warm to room temperature and stirred for 12 h. Volatiles were then removed in vacuum and the resulting solid crystallised from chloroform–hexane. Yield 0.50 g (72%), m.p. 211–215 °C (Found: C, 43.1; H, 2.7. Calc. for $C_{18}H_{13}Br_2Sb$: C, 42.3; H, 2.6%); δ_H[300 MHz, $CDCl_3$, room temperature (r.t.)] 7.56 [7 H, m, biphenylyl H^3, H^2, *m*- and *p*-Ph] and 8.06 [6 H, m, biphenylyl H^1, H^4, *o*-Ph]; $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1431s, 747m, 742s and 685m; *m/z* (EI) 429 (5, $[M - Br]^+$), 350 (99, $[M - 2Br]^+$, 273 {58, $[Sb(C_{12}H_8)]^+$}, 229 (100, $PhC_{12}H_8^+$) and 77 (15%, Ph^+).

$Sb(2,2'\text{-}C_{12}H_8)PhCl_2$ 3. A solution of sulfuryl chloride (0.21 g, 1.55 mmol) in dichloromethane (5 cm^3) was slowly added to a stirring solution of $Sb(2,2'\text{-}C_{12}H_8)Ph$ (0.50 g, 1.45 mmol) in dichloromethane (30 cm^3) at 0 °C. The solution was allowed to warm to room temperature and after stirring for 16 h a white precipitate formed. Removal of volatiles then gave a white solid, which was crystallised from chloroform. Yield 0.41 g (67%); m.p. 216–218 °C [lit.,[35] 220–223 °C] (Found: C, 50.4; H, 3.0. Calc. for $C_{18}H_{13}Cl_2Sb$: C, 51.3; H, 3.1%); δ_H(300 MHz, $CDCl_3$, r.t.) 7.55 [2 H, td, ^3J(HH) 7.4, ^4J(HH) 1.4, biphenylyl H^3], 7.61 (3 H, m, *m*- and *p*-Ph], 7.63 [2 H, td, ^3J(HH) 7.6, ^4J(HH) 1.4, biphenylyl H^2], 8.02 [2 H, dd, ^3J(HH) 7.4, ^4J(HH) 1.4, biphenylyl H^4), 8.08 [2 H, dd, ^3J(HH) 7.6, ^4J(HH) 1.4 Hz, biphenylyl H^1] and 8.27 (2 H, m, *o*-Ph); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1437s, 1321w, 1305w, 1286w, 1261w, 1091w (br), 1064w, 1044w (br), 1014w, 992m, 746s, 727s, 682m, 475w, 455w and 420w; *m/z* (EI) 385 (3, $[M - Cl]^+$), 350 (76, $[M - 2Cl]^+$), 308 (6, $[M - Ph - Cl]^+$), 273 (60, $[Sb(C_{12}H_8)]^+$), 229 (100, $PhC_{12}H_8^+$), 152 (98, $C_{12}H_8^+$) and 77 (12%, Ph^+).

$Sb(2,2'\text{-}C_{12}H_8)PhF_2$ 4. Potassium fluoride (0.14 g, 2.41 mmol) was added to a stirring solution of $Sb(2,2\text{-}C_{12}H_8)PhCl_2$ **3** (0.50 g, 1.18 mmol) in acetone (30 cm^3). The resulting reaction mixture was then refluxed for 16 h, after which volatiles were removed in vacuum. Crude $Sb(2,2'\text{-}C_{12}H_8)PhF_2$ was then extracted into hot chloroform and insoluble potassium chloride filtered off. Evaporation of the solvent gave a white solid which was crystallised from chloroform–hexane. Yield 0.24 g (52%) (Found: C, 54.6; H, 3.1. Calc. for $C_{18}H_{13}F_2Sb$: C, 55.6; H, 3.4%); *m/z* (EI) 369 (59, $[M - F]^+$), 350 (13, $[M - 2F]^+$), 273 (19, $[Sb(C_{12}H_8)]^+$), 229 (49, $PhC_{12}H_8^+$), 152 (61, $C_{12}H_8^+$) and 77 (30%, Ph^+).

$Sb(2,2'\text{-}C_{12}H_8)Ph(NCS)_2$ 5. A solution of potassium thiocyanate (0.23 g, 2.37 mmol) in acetonitrile (15 cm^3) was added to a stirring suspension of $Sb(2,2'\text{-}C_{12}H_8)PhCl_2$ **3** (0.50 g, 1.18 mmol) in acetonitrile (20 cm^3) and the resulting mixture stirred at room temperature for 24 h. After filtration, the solvent was removed in vacuum giving a red oily product, which was taken up in toluene, filtered and the solvent evaporated. Crystallisation of the residue from chloroform–hexane afforded crystals of the required compound. Yield 0.29 g (34%); m.p. *ca.* 180 °C (decomp.) (Found: C, 51.0; H, 2.7; N, 5.7. Calc. for $C_{20}H_{13}N_2S_2Sb$: C, 51.4; H, 2.8; N, 6.0%); δ_H(300 MHz, $CDCl_3$, r.t.) 7.56 [2 H, t, ^3J(HH) 7.3, biphenylyl H^3], 7.70 [2 H, t, ^3J(HH) 7.8, biphenylyl H^2], 7.70 [3 H, m (masked), *m*- and *p*-Ph], 7.84 [2 H, d, ^3J(HH) 7.3, biphenylyl H^4], 8.17 [2 H, d, ^3J(HH) 7.8 Hz, biphenylyl H^1] and 8.23 (2 H, m, *o*-Ph); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2077vs, 1994vs (br), 743s and 450m; *m/z* (EI) 350 (87, $[M - 2NCS]^+$), 273 (70, $[Sb(C_{12}H_8)]^+$), 229 (90, $PhC_{12}H_8^+$), 152 (100, $C_{12}H_8^+$) and 77 (15, Ph^+); (FAB) 408 (7, $[M - NCS]^+$), 367 (16, $[Sb(C_{12}H_8)PhNH_3]^+$), 350 (16, $[Sb(C_{12}H_8)Ph]^+$), 273 (44, $[Sb(C_{12}H_8)]^+$), 229 (48, $PhC_{12}H_8^+$), 152 (100, $C_{12}H_8)^+$) and 77 (43%, Ph^+).

$SbPh(o\text{-}O_2C_6Cl_4)Cl_2\cdot OEt_2$ 6. A solution of tetrachloro-*o*-benzoquinone (3.70 g, 15.0 mmol) in ether (40 cm^3) was slowly added (with immediate dissipation of the red colour) to a stirring solution of $SbPhCl_2$ (4.052 g, 15.0 mmol) in ether (20 cm^3) at 0 °C, under an argon atmosphere. Stirring for 6 h gave a yellow precipitate which was filtered off and recrystallised from dichloromethane overlayered with twice the volume of pentane. Yield 7.79 g (88%); m.p. *ca.* 140 °C (decomp.) (Found: C, 32.4; H, 2.4. Calc. for $C_{12}H_5Cl_6O_2Sb\cdot C_4H_{10}O$: C, 32.6; H, 2.6%); δ_H(250 MHz, $CDCl_3$, r.t.) 1.03 [6 H, t, ^3J(HH) 7, $O(CH_2C\mathit{H}_3)_2$], 3.73 [4 H, q, ^3J(HH) 7 Hz, $O(C\mathit{H}_2CH_3)_2$], 7.64 (3 H, m br, *m*- and *p*-Ph) and 8.17 (2 H, m br, *o*-Ph); δ_C(^{13}C-{^1H} DEPT − 135, 69 MHz, $CDCl_3$, r.t.) 13.8 [$O(CH_2\mathit{C}H_3)_2$], 65.6 [$O(\mathit{C}H_2CH_3)_2$], 130.2 (*m*-Ph), 132.0 (*p*-Ph) and 133.0 (*o*-Ph); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1429vs, 1386s, 1353w, 1332w, 1286w, 1249s, 1242s, 1086w, 1017m, 993m, 980s, 890w, 818s, 801m, 750m, 739m, 684w, 609w, 494m and 452m.

$SbPh(o\text{-}O_2C_6Cl_4)Cl_2\cdot OC_4H_8$ 7. Dissolution of $SbPh(o\text{-}O_2C_6Cl_4)Cl_2\cdot OEt_2$ (0.50 g, 0.90 mmol) in tetrahydrofuran (25 cm^3), followed by evaporation of volatiles in vacuum, gave quntitative conversion into the thf adduct $SbPh(o\text{-}O_2C_6Cl_4)Cl_2\cdot OC_4H_8$. δ_H(250 MHz, $CDCl_3$, r.t.) 1.80 (4 H, m, $OCH_2C\mathit{H}_2$), 3.82 (4 H, m, $OC\mathit{H}_2CH_2$), 7.63 (3 H, m br, *m*- and *p*-Ph) and 8.17 (2 H, m br, *o*-Ph).

$SbPh(o\text{-}O_2C_6H_2Bu^t_2\text{-}3,5)Cl_2$ 8. A solution of 3,5-di-*tert*-butyl-*o*-benzoquinone (1.96 g, 8.90 mmol) in dichloromethane (20 cm^3) was added to a stirring solution of $SbPhCl_2$ (2.40 g, 8.88 mmol) in dichloromethane (25 cm^3). The resulting green solution was then stirred at room temperature for 48 h to ensure complete reaction. Removal of volatiles in vacuum yielded a yellow-green solid. Yield 3.00 g (69%) (Found: C, 48.6; H, 4.9. Calc. for $C_{20}H_{25}Cl_2O_2Sb$: C, 49.0; H, 5.15%); δ_H(250 MHz, $CDCl_3$, r.t.) 1.31 (9 H, s br, Bu^t), 1.51 (9 H, s br, Bu^t), 6.83 (1 H,

Table 5 Crystallographic data for compounds **2**, **3**, **5** and **6**

	2	**3**	**5**	**6**
Chemical formula	$C_{18}H_{13}Br_2Sb$	$C_{18}H_{13}Cl_2Sb$	$C_{20}H_{13}N_2S_2Sb$	$C_{16}H_{15}Cl_6O_3Sb$
M	510.86	421.96	467.21	589.7
Crystal size/mm	0.50 × 0.40 × 0.20	0.30 × 0.20 × 0.15	0.20 × 0.12 × 0.08	0.80 × 0.39 × 0.21
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	11.924(2)	11.692(3)	8.832(3)	7.498(6)
b/Å	13.164(4)	12.935(4)	10.706(5)	22.32(2)
c/Å	11.067(2)	10.946(2)	10.908(3)	12.898(3)
α/°			75.65(3)	
β/°	109.83(2)	109.32(2)	70.63(2)	103.83(3)
γ/°			80.54(3)	
U/Å^3	1634.2	1562.2	938.9	2096(3)
Z	4	4	2	4
D_c/g cm^{-3}	2.077	1.794	1.653	1.869
Radiation (λ/Å)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)
μ/cm^{-1}	65.34	21.15	16.96	20.98
F(000)	968	824	460	1152
θ Limits/°	3–25	2–25	3–25	3–25
Index ranges (for unique data)	$-14 < h < 33, 0 < k < 15, 0 < l < 13$	$-13 < h < 12, 0 < k < 15, 0 < l < 12$	$-8 < h < 10, -11 < k < 11, 0 < l < 12$	$-8 < h < 8, -2 < k < 26, -1 < l < 15$
T/K	298	298	150	298
Total data collected	3022	2694	2615	4125
Unique data	3022	2694	2271	3671
R_{int}			0.0381	0.0280
Observed data [$I > 3\sigma(I)$]	2194	1495	2271	3671
Absorption correction	DIFABS	DIFABS	DIFABS	ψ Scans
minimum	0.843	0.721	0.918	0.313
maximum	1.241	1.136	1.189	0.532
Refinement	On F	On F	On F^2	On F^2
Data, variables	2194, 191	1495, 190	2271, 227	3671, 235
Goodness of fit (S)	1.120	1.022	1.129	1.146
Final difference map features/e Å^{-3}	+1.36, −0.60	+1.64, −0.86	+0.95, −0.77	+0.74, −0.49
R	0.0390	0.0793	0.0328	0.0367
R'	0.0422	0.0935	0.0668	0.0912
R observed data [$I > 2\sigma(I)$] (all data)				0.0346 (0.0429)
R' observed data (all data)				0.0880 (0.1127)

s br, benzoquinone H), 7.07 (1 H, s br, benzoquinone H), 7.59 (3 H, m br, *m*- and *p*-Ph) and 8.23 (2 H, m br, *o*-Ph); $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 1450vs (br), 1414vs, 1363s, 1313s, 1282s, 1261s, 1236vs, 1202m, 1091m, 1062m, 1027m, 996w, 975s, 862m, 827s, 808s, 751m, 734vs, 687s, 581m and 452s.

Attempted preparations

$SbPh(O_2C_2Me_4)Br_2$. A solution of pinacol (2.57 g, 21.7 mmol) in toluene (10 cm^3) was added to a stirring solution of $SbPhCl_2$ (5.86 g, 21.7 mmol) in toluene (40 cm^3). Addition of triethylamine (4.40 g, 43.4 mmol) caused immediate formation of a white precipitate. After stirring for 24 h the solid was filtered off, washed with further toluene (20 cm^3) and shaken with methanol (50 cm^3) to extract NEt_3HCl. The remaining solid was filtered off and washed with methanol. Yield 2.43 g (36%) (Found: C, 45.2; H, 5.9. Calc. for $C_{12}H_{17}O_2Sb$: C, 45.8; H, 5.4%). A solution of bromine (0.93 g, 5.82 mmol) in dichloromethane (10 cm^3) was added slowly to a stirred suspension of $SbPh(O_2C_2Me_4)$ (1.82 g, 5.76 mmol) in dichloromethane (50 cm^3). The resulting orange mixture was stirred for 12 h, after which volatiles were removed in vacuum. The expected oxidation product was not formed and ^{1}H NMR analysis showed the presence of a number of unidentified products.

$SbPh(O_2C_6H_4)Br_2$. A solution of $SbPhCl_2$ (5.21 g, 19.3 mmol) in toluene (50 cm^3) was added to a stirring suspension of catechol (2.13 g, 19.3 mmol) and toluene (20 cm^3). After stirring for 30 min, triethylamine (3.91 g, 38.6 mmol) was added giving an immediate thick white suspension. After stirring for 3 h, the precipitate was filtered off and dried under vacuum. The salt NEt_3HCl was extracted with methanol (60 cm^3) leaving insoluble $SbPh(o\text{-}O_2C_6H_4)$, which was filtered off, washed with further methanol and dried in vacuum. Yield 3.82 g (64%) (Found: C, 47.3; H, 3.6. Calc. for $C_{12}H_9O_2Sb$: C, 47.0; H, 3.0%). A solution of bromine (0.56 g, 3.50 mmol) in dichloromethane (5 cm^3) was added to a stirred suspension of $SbPh(o\text{-}O_2C_6H_4)$ (1.08 g, 3.50 mmol) in dichloromethane (50 cm^3) and the reaction mixture stirred for 16 h at reflux. The blue solution formed was evaporated to dryness, giving a green oil. The bromine oxidation product was not isolated and ^{1}H NMR analysis showed the material to be a complex mixture of unidentified products.

Crystallograhy

Crystallographic quality single crystals for compounds **2**, **3**, **5** and **6** were obtained by slow diffusion of hexane vapour into concentrated chloroform solutions of the compounds. Crystallographic data, the method of solution and refinement conditions are summarised in Table 5. Data for **2** and **3** were collected on a Hilger and Watts Y290 diffractometer, for **5** a Delft Instruments FAST TV area-detector diffractometer, equipped with a rotating anode FR591 generator was used and for **6** the diffractometer was a Stoe-Stadi four-circle instrument. The data were corrected for Lorentz-polarisation effects, merged and systematically absent reflections removed. An absorption correction, usually using DIFABS,[36] was also applied. The structures were solved either by Patterson (**2** and **3**) or direct methods [SIR 92[37] (**5**) or SHELXS 86[38] (**6**)] and refined by full-matrix least-squares methods. Hydrogen atoms were placed at their calculated positions and refined riding on their respective carbon atoms with fixed isotropic thermal parameters [usually $U_{iso}(H) = 1.2\ U_{eq}(C)$]. A standard weighting scheme was applied and corrections were made for extinction where appropriate. Crystallographic calculations used either the CRYSTALS[39] or SHELXL-93 programs[40] and neutral atom scattering factors.[41]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/537.

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