Diphenylantimony(v) Oxo/Chloro Carboxylates and Phosphinates: Crystal Structures of $\{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O$ and $[SbPh_2(O_2CPh)_2]_2O$ †

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Reaction of $SbPh_2Cl_3$ (1 mol) with the silver salt of dicyclohexylphosphinic acid (2 mol) afforded $\{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O$ **1**; a similar reaction with $AgO_2P(C_8H_{15})_2$ gave a product formulated as $\{SbPh_2Cl[O_2P(C_8H_{15})_2]\}_2O$ **2**. Similar reactions with silver carboxylates (1:3 stoichiometry) led to the crystalline derivatives $[SbPh_2(O_2CR)_2]_2O$ (R = Ph **3**, $CHPh_2$ **4**, 2,4,6-$Me_3C_6H_2$ **5**, 2-MeC_6H_4 **6** or 4-MeC_6H_4 **7**), whereas the 1:2 reaction afforded crystalline $SbPh_2Cl(O_2CR)_2$ (R = Ph **8**, 2-MeC_6H_4 **9** or 4-MeC_6H_4 **10**). Interconversion of the previously known compounds $[SbPh_2(O_2CMe)_2]O$ and $Sb_4Ph_8O_6{\cdot}3MeCO_2H$ was achieved and established by ^1H NMR spectroscopy. Compounds **1** and **3** were further characterized by X-ray diffraction; the antimony in **1** is six-co-ordinated with bridging phosphinates whereas in **3** it is seven-co-ordinated with chelating benzoates. Short Sb–O (oxo) distances (1.923 Å) and near linearity at the bridging oxygen (Sb–O–Sb 173.9°) are observed for **3**.

Compared to the large number of structurally diverse oxo carboxylate and phosphinate cages known for tin,[1,2] only a few analogous species for antimony have been reported.[3,4] Both tin and antimony in their respective higher oxidation states of +4 and +5 can be expected to achieve co-ordination numbers of six and seven readily. Thus, in the presence of oxide/hydroxide groups and bidentate ligands like carboxylates or phosphinates a variety of structures with similar skeletons, and possibly related chemistry, must be possible. It is pertinent in this context that the 'crown' structures observed for tin[2] are structurally very close to that of $Sb_4Ph_8O_6{\cdot}3MeCO_2H$ reported by Sowerby *et al.*[3] Further, the finding that tin cages exhibit structural interconversions (Scheme 1)[1] and the nature of the hydrolysis products of $SbPh_2(O_2CMe)_3$ (Scheme 2) prompted us to envisage an analogous synthetic chemistry for antimony. In addition, tin phosphinates differ structurally from the carboxylates obtained from analogous reactions.[1] Thus it can be expected that for antimony also reactions involving phosphinates and carboxylates will lead to products having different structures. Hence we investigated the reaction of the readily accessible diphenylantimony trichloride[5] with silver carboxylates and phosphinates. The crystal structures of $\{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O$ and $[SbPh_2(O_2CPh)_2]_2O$ were also determined.

Results and Discussion

Synthesis and Spectroscopy.—In the reaction of diphenylantimony trichloride with 2 mole equivalents of silver dicyclohexylphosphinate we were able to isolate only $\{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O$ **1** [$\delta(^{31}P)$ 54.6] although the reaction mixture suggests the presence of a second compound [$\delta(^{31}P)$ 60.3] in significant quantity (*ca.* 20%). It is known that $SbPh_2Cl_3$ takes up water readily;[6] this upon heating could lead to $(SbPh_2Cl_2)_2O$. The formation of the oxo bridge in our case could have occurred after the reaction with the phosphinate [equation (1)]. A similar reaction with silver dicyclooctylphosphinate also afforded a crystalline product **2** [$\delta(^{31}P)$ 58.6] which we formulate as $\{SbPh_2Cl[O_2P(C_8H_{15})_2]\}_2O$ on the basis of elemental analysis and the ^1H NMR spectrum. The compound is very soluble in common organic solvents. Attempts to obtain crystals suitable for X-ray analysis resulted in partial hydrolysis.

$$2SbPh_2Cl_3 + 2AgO_2P(C_6H_{11})_2 \xrightarrow{H_2O,\ -2HCl} \{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O + 2AgCl \quad (1)$$

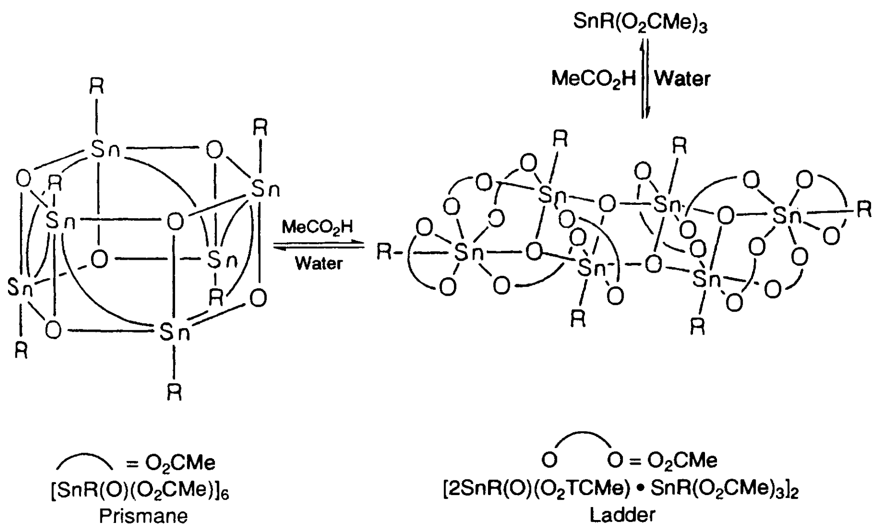
The oxo-bridged carboxylates $[SbPh_2(O_2CR)_2]_2O$ (R = Ph **3**, $CHPh_2$ **4**, 2,4,6-$Me_3C_6H_2$ **5**, 2-MeC_6H_4 **6** and 4-MeC_6H_4 **7**) were readily obtained when $SbPh_2Cl_3$ was treated with 3 mole equivalents of the respective silver carboxylates [equation (2)].

$$2SbPh_2Cl_3 + 6AgO_2CR \longrightarrow 2SbPh_2(O_2CR)_3(?) + 6AgCl$$
Not isolated
$$\downarrow H_2O\ \text{(adventitious)} \quad (2)$$
$$[SbPh_2(O_2CR)_2]_2O + 2RCO_2H$$

Compounds **3**–**7** can be crystallized from a mixture of dichloromethane and hexane (or heptane). This contrasts with the reaction of $SbPh_2Cl_3$ with silver acetate[3] where recrystallization from dichloromethane afforded the tetranuclear cage $Sb_4Ph_8O_6{\cdot}3MeCO_2H$ **II**; isolation of the oxo-bridged compound $[SbPh_2(O_2CMe)_2]_2O$ **I** required a solvent containing a water scavenger (acetic acid + acetic anhydride). Thus it is likely that the initially formed product **I** underwent hydrolysis during recrystallization from dichloromethane to give **II**. This prompted us to examine the hydrolysis of our compounds **3**–**5**. Indeed upon hydrolysis of **3** we obtained a solid **3a**, m.p. 179–183 °C, which analysed as $Sb_4Ph_8O_6{\cdot}3PhCO_2H$ (*cf.* compound **II** above). The ^1H NMR spectrum of the product from the hydrolysis of **5** corresponded to the analogous compound $Sb_4Ph_8O_6{\cdot}2,4,6\text{-}Me_3C_6H_2CO_2H$. However, the diphenylacetate derivative **4** was resistant to hydrolysis.

The formulae for compounds **I** and **II** as well as **3** and **3a** suggest that an interconversion similar to that observed for the tin carboxylates (see above) is feasible. Since removal of the excess of acid and monitoring by ^1H NMR spectroscopy is

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



$4SbPh_2(O_2CMe)_3$ → ($2H_2O$, $-4MeCO_2H$) $2[SbPh_2(O_2CMe)_2]_2O$

$4SbPh_2(O_2CMe)_3$ → ($6H_2O$, $-9MeCO_2H$) $Sb_4Ph_8O_6{\cdot}3MeCO_2H$

Scheme 2

easier for the interconversion between **I** and **II**, this pair was chosen for study. Thus the dinuclear compound $[SbPh_2(O_2CMe)_2]_2O$ **I** was converted into the tetranuclear cage $Sb_4Ph_8O_6{\cdot}3MeCO_2H$ **II** by exposing a dichloromethane solution of the former to air. More interestingly, it was possible to convert **II** back into **I** by heating it with an excess (>30 fold) of acetic acid–anhydride [equation (3)].

$$\mathbf{I} \underset{+5MeCO_2H,\ -4H_2O\ [+\text{excess}\ (MeCO)_2O]}{\overset{+4H_2O,\ -5MeCO_2H}{\rightleftharpoons}} \mathbf{II} \quad (3)$$

Three crystalline chloro derivatives $SbPh_2Cl(O_2CR)_2$ (R = Ph **8**, 2-MeC_6H_4 **9** or 4-MeC_6H_4 **10**) were also synthesized by the 1:2 stoichiometric reaction (4). The separation of the most

$$SbPh_2Cl_3 + 2AgO_2CR \longrightarrow SbPh_2Cl(O_2CR)_2 + 2AgCl \quad (4)$$

intense bands in the IR spectra ascribable to the carbonyls for sodium benzoate, $[SbPh_2(O_2CPh)_2]_2O$ **3** and $SbPh_2Cl(O_2CPh)_2$ **8** are 143, 129 and 87 cm^{-1} respectively; on this basis[7] we assign a seven-co-ordinated monomeric structure with chelating carboxylates for the chloro compound **8** (and hence for **9** and **10**). These chloro carboxylates do not undergo any appreciable hydrolysis in $CDCl_3$ solution as shown by their ^1H NMR spectra recorded over a period of several days. This feature is in contrast to that of the oxo-bridged derivatives **3**, **5** and **7** which underwent hydrolysis (see above).

Structural Aspects.—The phosphinates in $\{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O$ **1** act only as bridging ligands and the structure (Fig. 1)[8] can be compared to that of $[SbCl_3(O_2PMe_2)]_2O$. The Sb–Cl and Sb–O (P) bond distances (Table 1) [2.428 and 2.093 Å (mean) respectively] are longer than those observed for $[SbCl_3(O_2PMe_2)]_2O$ [2.333 and 2.010 Å (mean) respectively] possibly due to the presence of less electronegative phenyl groups in **1**. The bridging phosphinates around the octahedral antimony are *cis* to each other as is observed for $[SbPh_2(O_2CMe)_2]_2O$ **I** as well as $[SbCl_4(O_2PRR')]_2$ (R = R' = OMe or NMe_2, R = OMe, R' = NMe_2).[9] The three

Table 1 Selected bond distances (Å) and angles (°) for compound **1**

Sb(1)–Cl(2)	2.428(2)	Sb(2)–C(25)	2.155(5)
Sb(1)–O(2)	2.119(4)	Sb(2)–C(31)	2.131(6)
Sb(1)–O(3)	1.938(4)	P(1)–O(1)	1.528(4)
Sb(1)–O(4)	2.070(4)	P(1)–O(2)	1.526(4)
Sb(1)–C(1)	2.124(6)	P(1)–C(43)	1.829(6)
Sb(1)–C(37)	2.130(6)	P(1)–C(19)	1.805(6)
Sb(2)–Cl(1)	2.425(2)	P(2)–O(4)	1.531(4)
Sb(2)–O(1)	2.098(4)	P(2)–O(5)	1.549(5)
Sb(2)–O(3)	1.936(4)	P(2)–C(7)	1.793(6)
Sb(2)–O(5)	2.085(4)	P(2)–C(13)	1.820(6)
C(1)–Sb(1)–C(37)	100.8(2)	O(3)–Sb(2)–C(25)	167.1(2)
O(4)–Sb(1)–C(37)	91.3(2)	O(3)–Sb(2)–O(5)	86.0(2)
O(4)–Sb(1)–C(1)	88.5(2)	O(1)–Sb(2)–C(31)	89.9(2)
O(3)–Sb(1)–C(37)	92.4(2)	O(1)–Sb(2)–C(25)	88.2(2)
O(3)–Sb(1)–C(1)	166.7(2)	O(1)–Sb(2)–O(5)	85.7(2)
O(3)–Sb(1)–O(4)	89.7(2)	O(1)–Sb(2)–O(3)	88.2(2)
O(2)–Sb(1)–C(37)	175.7(2)	Cl(1)–Sb(2)–C(31)	94.0(1)
O(2)–Sb(1)–C(1)	82.1(2)	Cl(1)–Sb(2)–C(25)	95.1(2)
O(2)–Sb(1)–O(4)	85.5(2)	Cl(1)–Sb(2)–O(5)	90.4(1)
O(2)–Sb(1)–O(3)	84.7(2)	Cl(1)–Sb(2)–O(3)	87.6(1)
Cl(2)–Sb(1)–C(37)	93.4(2)	Cl(1)–Sb(2)–O(1)	174.4(1)
Cl(2)–Sb(1)–C(1)	93.0(2)	O(1)–P(1)–O(2)	113.5(2)
Cl(2)–Sb(1)–O(4)	174.7(1)	O(4)–P(2)–O(5)	113.0(3)
Cl(2)–Sb(1)–O(3)	87.7(1)	Sb(2)–O(1)–P(1)	131.3(2)
Cl(2)–Sb(1)–O(2)	89.7(1)	Sb(1)–O(2)–P(1)	135.5(3)
C(25)–Sb(2)–C(31)	99.6(2)	Sb(1)–O(4)–P(2)	133.2(3)
O(5)–Sb(2)–C(31)	175.4(2)	Sb(2)–O(5)–P(2)	137.4(2)
O(5)–Sb(2)–C(25)	81.4(2)	Sb(1)–O(3)–Sb(2)	144.7(2)
O(3)–Sb(2)–C(31)	92.8(2)		

oxygens connected to antimony are facial, a feature common to numerous oxo-bridged bimetallic compounds.[10–12]

The Sb–O–P–O–Sb–O rings have a boat conformation (Fig. 2) with phosphorus at one of the 'prow' positions;[13] it appears from molecular models that the chair conformation leads to greater steric interaction between substituents on the two phosphinate ligands. Given the boat conformation for the six-membered rings and facial arrangement for the three oxygens on antimony, four geometrical isomers are possible for $\{SbPh_2Cl[O_2P(C_6H_4)_2]\}_2O$ **1** (Fig. 3). It can be seen that steric interactions between the phenyl and cyclohexyl groups on a particular phosphorus are minimized in the observed structure **A**.

The structure of the carboxylate compound $[SbPh_2(O_2CPh)_2]_2O$ **3** (Fig. 4) is similar to that of the corresponding acetate $[SbPh_2(O_2CMe)_2]_2O$ **I**[3] with a distorted pentagonal-bipyramidal geometry around antimony. The Sb–O distances (Table 2)

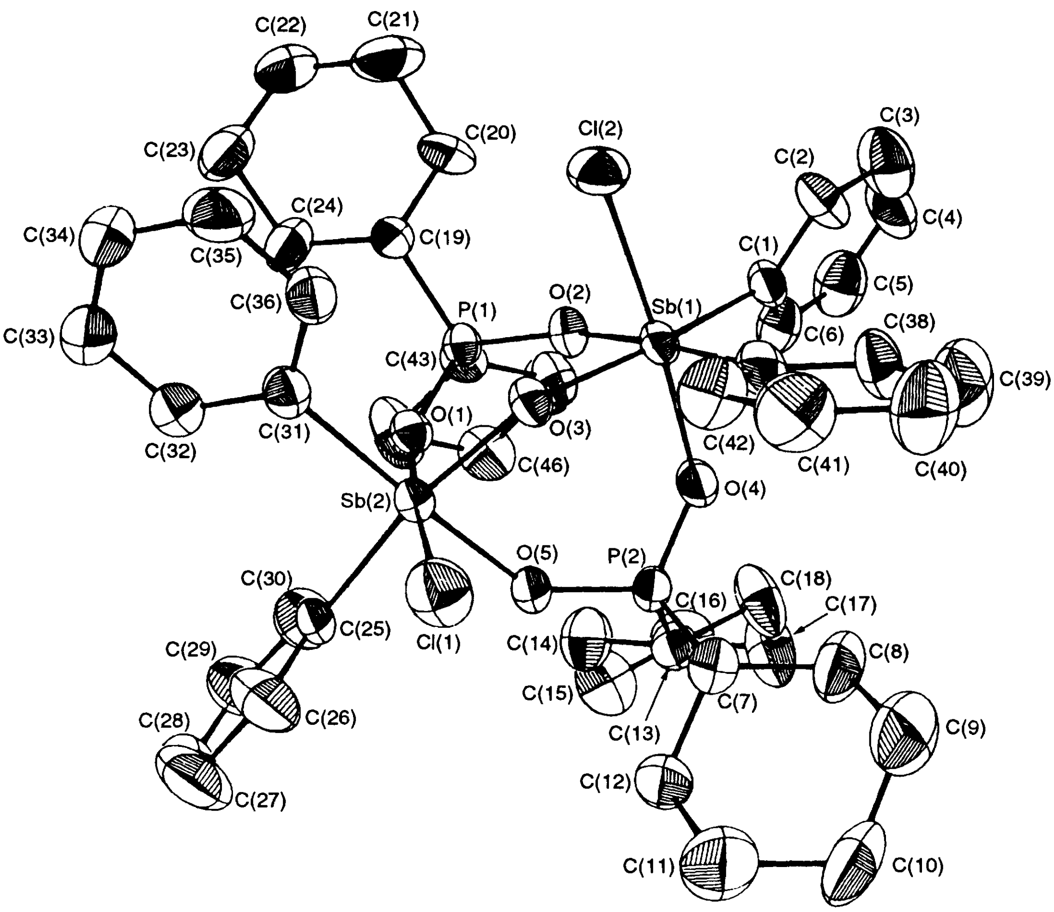


Fig. 1 An ORTEP diagram[8] of compound **1**

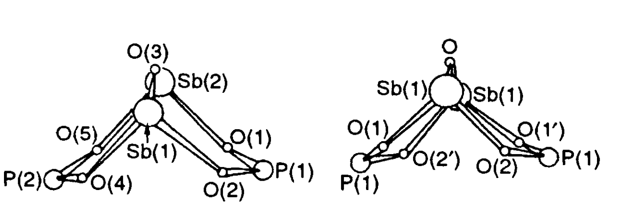


Fig. 2 The boat conformation of the Sb–O–P–O–Sb–O rings in compounds **1** and $[SbCl_3(O_2PMe_2)]_2O$

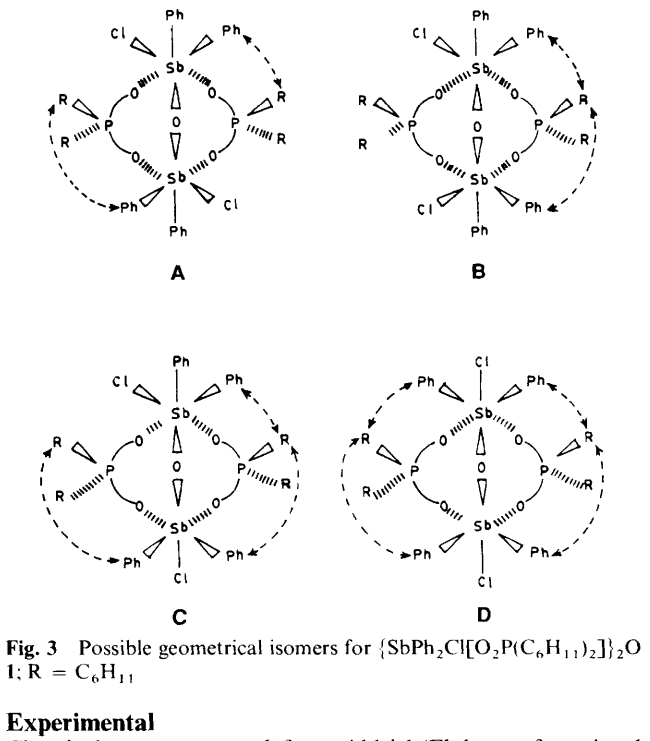


Fig. 3 Possible geometrical isomers for $\{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O$ **1**; R = C_6H_{11}

again show two sets of four with mean values of 2.188 and 2.418 Å respectively (2.16 and 2.47 Å in **I**) moving towards each other more closely than in the acetate. The five equatorial oxygen atoms and the antimony are coplanar to within ± 0.09 Å (± 0.05 Å in **I**). The diaxial disposition of the less electronegative phenyl groups in the pentagonal bipyramid contrasts with the expected diequatorial disposition in a trigonal-bipyramidal structure.

Surprisingly, the Sb–O (oxo) distance in compound **3** is shorter than that observed in **1** or $[SbCl_3(O_2PMe_2)]_2O$ (Table 3) despite the fact that antimony is seven-co-ordinated in **3** and six-co-ordinated in **1**. All these distances are shorter than the non-oxo Sb–O bonds [(mean) 2.083 in **1** and 2.303 Å in **3**]. Table 3 also gives data for oxo-bridged complexes of titanium, iron and gallium. The shortening of the Sb–O (oxo) bonds may result from the partial ionic character $M^{\delta+}O^{\delta-}$ as suggested by Cowley *et al.*[14] for the galloxane $[(2,4,6\text{-}Bu^t{}_3C_6H_2)GaMn(CO)_5]_2O$. Unlike in the case of titanium[10] or iron[11,12] complexes where the participation of the d orbitals can be invoked[11] to explain the short M–O (oxo) bonds, it is doubtful whether such a participation exists for antimony compounds.

Experimental

Chemicals were procured from Aldrich/Fluka or from local manufacturers; they were purified when required. Solvents were purified according to standard procedures.[15] Silver salts of phosphinic/carboxylic acids were prepared by treating stoichiometric quantities of the acid with aqueous sodium hydroxide followed by aqueous silver nitrate, washing the precipitate with methanol and drying *in vacuo*. All operations, unless stated otherwise, were performed under a dry nitrogen atmosphere. Proton, ^{13}C and ^{31}P-{H} NMR spectra were recorded on a Bruker 200 MHz spectrometer using $CDCl_3$ solutions with shifts referenced to $SiMe_4$ (δ 0) or 85% H_3PO_4 (δ 0), IR spectra on a JASCO FT/IR-5300 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240C CHN analyser. Chlorine and antimony were determined by known procedures.[16]

$\{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O$ **1**.—A mixture of $SbPh_2Cl_3$ (0.39 g, 1 mmol) and $AgO_2P(C_6H_{11})_2$ (0.687 g, 2 mmol) was heated in dry toluene (50 cm^3) for 2 h under reflux and then filtered. The solvent was completely removed from the filtrate and the residue crystallized from dichloromethane–hexane (1 : 5). Yield: 0.7 g, 64%; m.p. 235 °C (Found: C, 52.6; H, 5.8. Calc. for $C_{48}H_{64}Cl_2O_5P_2Sb_2$: C, 52.5; H, 5.8%). NMR: ^1H, δ 1.18–2.50 (br m, 44 H, C_6H_{11}) and 7.19–8.30 (m, 20 H, aryl); ^{13}C, δ 26.0–26.9 (many lines, C_6H_{11}, except PC), 37.8 [d, ^1J(P–C) = 99.6, PC], 39.6 [d, ^1J(P–C) = 94.0 Hz, PC], 127.7–133.6 (many lines, aryl C) and 152.6 (aryl C); ^{31}P-{^1H}, δ 54.7. IR (major bands only): 2930, 1433, 1084 [ν(P=O)], 1014, 981, 758, 731, 688, 551 and 459 cm^{-1}.

$\{SbPh_2Cl[O_2P(C_8H_{15})_2]\}_2O$ **2**.—The same procedure as for compound **1** was followed using $SbPh_2Cl_3$ (0.373 g, 0.98 mmol) and $AgO_2P(C_8H_{15})_2$ (0.773 g, 1.96 mmol) in toluene (50 cm^3). The product was recrystallized from dichloromethane–hexane (1 : 10; 4 d). Yield: 0.5 g, 43%; m.p. 221 °C (Found: C, 56.50; H, 6.65; Cl, 5.50; Sb, 20.90. Calc. for $C_{56}H_{80}Cl_2O_5P_2Sb_2$: C, 55.60; H, 6.60; Cl, 5.85; Sb, 20.15%). NMR (C_6D_6): ^1H, δ 0.85–2.35 (br m, 60 H, C_8H_{15}) and 7.23–8.40 (m, 20 H, aryl H); ^{31}P-{H}, δ 58.6. Major IR bands: 2922, 1477, 1433, 1080 [ν(P=O)], 995, 731, 688 and 461 cm^{-1}.

$[SbPh_2(O_2CPh)_2]_2O$ **3**.—The procedure was similar to that for compound **1** using $SbPh_2Cl_3$ (0.854 g, 2.24 mmol) and AgO_2CPh (1.54 g, 6.72 mmol) in toluene (70 cm^3) and overnight heating under reflux. Recrystallization was from dichloromethane–hexane (1 : 2). Yield: 1.3 g, 55%; m.p. 198 °C (Found: C, 59.50; H, 3.95. Calc. for $C_{52}H_{40}O_9Sb_2$: C, 59.30; H, 3.80%). NMR: ^1H, δ 7.00–8.40 (m, aryl H); ^{13}C, δ 128.2–133.8 (aryl C). Major IR bands: 1599, 1531vs, 1448, 1402vs, 872, 835, 721 and 686 cm^{-1}.

When a solution of compound **3** in dichloromethane was recrystallized in air a less-soluble compound **3a** was obtained; this was washed with ether to remove residual benzoic acid. Yield ≈ quantitative; m.p. 179–183 °C (Found: C, 52.25; H, 3.20; Sb, 30.50. Calc. for $C_{69}H_{56}O_{12}Sb_4$: C, 52.95; H, 3.60; Sb, 31.15%). Major IR bands: 1533, 1398, 831, 715, 690 and 455 cm^{-1}.

Compounds **4**–**7** were prepared similarly.

$[SbPh_2(O_2CCHPh_2)_2]_2O$ **4**. Quantities used: $SbPh_2Cl_3$ (1.27 g, 3.33 mmol), AgO_2CCHPh_2 (3.20 g, 10 mmol). Recrystallization from dichloromethane–hexane. Yield 2.0 g, 42.47%; m.p. 195 °C (Found: C, 68.15; H, 4.55; Sb, 17.05. Calc. for $C_{80}H_{64}O_9Sb_2$: C, 68.00; H, 4.55; Sb, 17.25%). NMR: ^1H, δ 4.95 (s, 4 H, C*H*Ph_2) and 6.90–7.90 (br m, 60 H, aryl H); ^{13}C, δ 57.4 (*C*HPh_2), 126.9–138.4 (many lines, aryl C), 147.8 (aryl C) and 178.8 (C=O). Major IR bands: 1555vs, 1493, 1400vs, 860, 802, 687, 644 and 461 cm^{-1}.

Upon exposure of a solution of compound **4** in dichloromethane–acetone to air no significant change in the ^1H NMR spectrum was observed except a broadening of the CH signal; the m.p. of the solid remained the same.

Table 2 Selected bond distances (Å) and bond angles (°) for compound **3**

Sb(1)–O(1)	2.406(2)	Sb(1)–C(21)	2.119(5)
Sb(1)–O(2)	2.187(3)	O(1)–C(1)	1.239(5)
Sb(1)–O(3)	2.429(4)	O(2)–C(1)	1.268(4)
Sb(1)–O(4)	2.189(3)	O(3)–C(8)	1.222(6)
Sb(1)–O(5)	1.923(1)	O(4)–C(8)	1.305(4)
Sb(1)–C(15)	2.115(4)		
C(15)–Sb(1)–C(21)	163.7(2)	O(2)–Sb(1)–O(3)	131.7(1)
O(5)–Sb(1)–C(21)	98.3(1)	O(1)–Sb(1)–C(21)	81.7(1)
O(5)–Sb(1)–C(15)	97.9(1)	O(1)–Sb(1)–C(15)	84.8(2)
O(4)–Sb(1)–C(21)	93.3(2)	O(1)–Sb(1)–O(5)	141.2(1)
O(4)–Sb(1)–C(15)	89.1(2)	O(1)–Sb(1)–O(4)	132.0(1)
O(4)–Sb(1)–O(5)	86.8(4)	O(1)–Sb(1)–O(3)	75.9(1)
O(3)–Sb(1)–C(21)	85.6(2)	O(1)–Sb(1)–O(2)	55.9(1)
O(3)–Sb(1)–C(15)	82.4(2)	Sb(1)–O(1)–C(1)	87.8(2)
O(3)–Sb(1)–O(5)	142.9(1)	Sb(1)–O(2)–C(1)	97.2(2)
O(3)–Sb(1)–O(4)	56.1(1)	Sb(1)–O(3)–C(8)	87.8(3)
O(2)–Sb(1)–C(21)	90.5(2)	Sb(1)–O(4)–C(8)	96.7(2)
O(2)–Sb(1)–C(15)	89.4(2)	O(1)–C(1)–O(2)	119.1(4)
O(2)–Sb(1)–O(5)	85.3(1)	O(3)–C(8)–O(4)	119.4(4)
O(2)–Sb(1)–O(4)	171.7(1)	Sb(1)–O(5)–Sb(1′)	173.9(2)

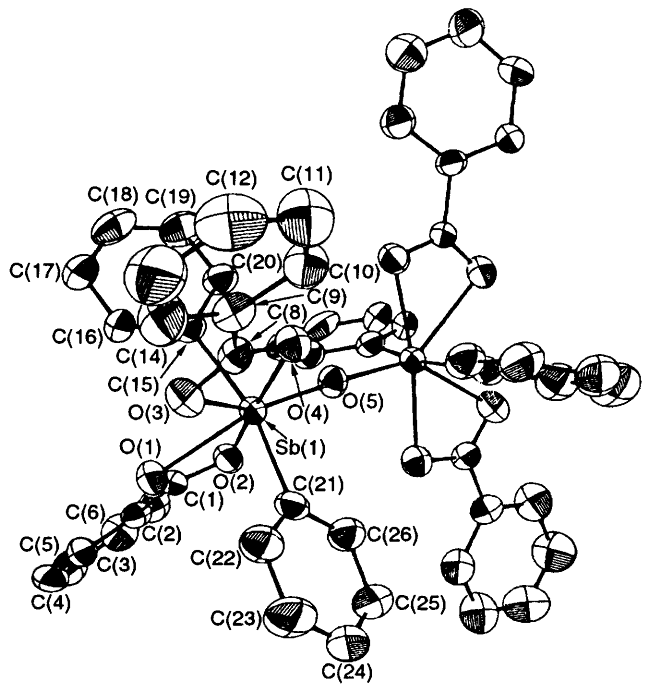


Fig. 4 An ORTEP diagram of compound **3**

Table 3 Distances (Å) M–O (oxo) and angles (°) M–O–M in selected compounds

Compound[a]	M–O	M–O–M	Ref.
1	1.937	144.7	This work
$[SbCl_3(O_2PMe_2)]_2O$	1.942	136.0	4
3	1.923	173.9	This work
I	1.911[b]	163.8[b]	3
$[\{Fe(O_2PPh_2)[HB(pz)_3]\}_2O]$	1.812 (short)	130.6	12
$[\{TiCl_2(O_2CCMe_3)(HO_2CCMe_3)\}_2O]$	1.766 (short)	138.3	10
$\{(2,4,6\text{-}Bu^t_3C_6H_2)GaMn(CO)_5\}_2O$	1.786 (short)	150.2	14

[a] pz = pyrazolyl. [b] Calculated using atomic coordinates.

Table 4 Crystal data for compounds **1** and **3***

Compound	**1**	**3**
Formula	$C_{48}H_{64}Cl_2O_5P_2Sb_2$	$C_{52}H_{40}O_9Sb_2$
M	1097.5	1052.4
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*Pbcn*
a/Å	13.989(8)	11.827(44)
b/Å	20.588(5)	18.209(18)
c/Å	17.156(3)	21.016(8)
β/°	94.95(3)	90.00
U/Å^3	4923(13)	4526(5)
D_c/g cm^{-3}	1.48	1.54
Crystal size/mm	0.4 × 0.35 × 0.15	0.4 × 0.4 × 0.45
F(000)	2192	1972
μ(Mo-Kα)/cm^{-1}	12.85	9.32
Total reflections	9379	4599
Unique reflections	8641	3962
Observed reflections [$F_o > 5\sigma(F_o)$]	6911	3336
R	0.046	0.037
R'	0.054	0.053
w	$1/[\sigma^2(F) + 0.000\,414F^2]$	$1/[\sigma^2(F) + 0.008\,488F^2]$
Residual electron density peak/e Å^{-3}	0.81	0.62

* Details in common: $Z = 4$; 20 °C; ω–2θ scans; 2θ range 2–50°; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 5 Fractional atomic coordinates for compound **1**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	0.064 35(2)	0.213 76(2)	0.905 04(2)	C(20)	0.303 1(5)	0.065 5(3)	0.892 2(4)
Sb(2)	0.173 16(2)	0.283 87(2)	0.735 55(2)	C(21)	0.404 7(6)	0.062 7(5)	0.937 5(5)
Cl(1)	0.143 65(13)	0.397 81(8)	0.759 95(11)	C(22)	0.479 7(6)	0.045 7(4)	0.880 5(5)
Cl(2)	0.205 95(12)	0.201 47(8)	0.996 10(9)	C(23)	0.480 1(5)	0.099 5(4)	0.815 7(5)
P(1)	0.185 37(10)	0.127 01(6)	0.778 14(8)	C(24)	0.380 4(5)	0.104 3(4)	0.771 2(5)
P(2)	−0.065 48(10)	0.259 12(8)	0.743 65(8)	C(1)	−0.010 3(4)	0.138 0(3)	0.958 0(3)
O(1)	0.186 8(3)	0.183 3(2)	0.720 2(2)	C(2)	−0.000 7(6)	0.132 4(3)	1.038 7(4)
O(2)	0.111 7(3)	0.135 5(2)	0.838 0(2)	C(3)	−0.045 9(6)	0.083 1(4)	1.076 5(5)
O(3)	0.141 3(3)	0.266 8(2)	0.841 2(2)	C(4)	−0.101 4(6)	0.037 7(5)	1.033 0(5)
O(4)	−0.049 2(3)	0.220 2(2)	0.819 7(2)	C(5)	−0.112 5(6)	0.043 7(4)	0.952 7(6)
O(5)	0.027 7(3)	0.269 6(2)	0.702 6(2)	C(6)	−0.067 8(4)	0.093 7(3)	0.913 3(4)
C(7)	−0.114 4(4)	0.337 5(3)	0.762 5(4)	C(37)	0.014 3(4)	0.296 3(3)	0.964 4(3)
C(8)	−0.208 3(5)	0.330 7(4)	0.804 8(5)	C(38)	−0.066 3(6)	0.290 0(3)	1.006 9(4)
C(9)	−0.241 7(7)	0.401 1(5)	0.827 3(6)	C(39)	−0.100 1(7)	0.344 2(4)	1.046 4(5)
C(10)	−0.260 0(6)	0.441 0(5)	0.747 3(7)	C(40)	−0.053 7(6)	0.403 6(4)	1.043 6(5)
C(11)	−0.166 5(7)	0.448 0(4)	0.705 4(6)	C(41)	0.025 3(6)	0.409 0(4)	1.001 2(5)
C(12)	−0.128 9(5)	0.378 1(4)	0.687 2(5)	C(42)	0.060 4(5)	0.355 6(3)	0.959 5(4)
C(13)	−0.148 6(4)	0.214 4(3)	0.676 1(4)	C(25)	0.176 5(4)	0.294 8(3)	0.610 9(3)
C(14)	−0.093 7(5)	0.177 5(4)	0.617 1(5)	C(26)	0.186 0(6)	0.355 8(4)	0.581 0(4)
C(15)	−0.164 1(7)	0.138 9(4)	0.558 0(5)	C(27)	0.193 2(7)	0.362 4(5)	0.497 8(5)
C(16)	−0.223 6(6)	0.092 7(4)	0.600 6(5)	C(28)	0.187 6(6)	0.309 6(5)	0.450 9(4)
C(17)	−0.283 1(6)	0.130 9(5)	0.658 8(5)	C(29)	0.179 3(7)	0.248 4(5)	0.484 4(4)
C(18)	−0.212 2(6)	0.168 0(5)	0.720 3(4)	C(30)	0.170 3(6)	0.241 9(4)	0.564 0(4)
C(43)	0.154 9(4)	0.052 3(3)	0.723 9(3)	C(31)	0.322 8(4)	0.290 3(2)	0.770 4(3)
C(44)	0.169 6(6)	0.061 1(3)	0.637 1(4)	C(32)	0.388 5(5)	0.285 5(3)	0.713 6(4)
C(45)	0.144 3(6)	−0.004 4(4)	0.590 1(4)	C(33)	0.485 5(5)	0.283 9(4)	0.734 2(4)
C(46)	0.044 1(6)	−0.026 4(4)	0.604 0(5)	C(34)	0.518 4(5)	0.286 8(3)	0.812 8(5)
C(47)	0.035 2(6)	−0.036 3(4)	0.692 5(5)	C(35)	0.455 3(5)	0.290 8(3)	0.869 7(4)
C(48)	0.056 4(5)	0.028 6(3)	0.736 5(4)	C(36)	0.355 9(4)	0.291 8(3)	0.848 4(4)
C(19)	0.303 8(4)	0.116 6(3)	0.827 2(3)				

$[SbPh_2(O_2CC_6H_2Me_3\text{-}2,4,6)_2]_2O$ **5**. Quantities used: $SbPb_2Cl_3$ (0.528 g, 1.38 mmol), $AgO_2CC_6H_2Me_3$-2,4,6 (1.50 g, 5.54 mmol). Recrystallization was done from dichloromethane–heptane. Yield 1.10 g, 65%; m.p. 210 °C (Found: C, 62.30; H, 5.50; Sb, 19.10. Calc. for $C_{64}H_{64}O_9Sb_2$: C, 62.95; H, 5.25; Sb, 19.95%). ^1H NMR: δ 1.84, 2.17 (two s, 36 H, CH_3) and 6.60–8.60 (many peaks, 28 H, aryl H). Major IR bands: 2970 (br), 1684, 1609, 1435vs, 1294vs, 1178, 1097, 856, 779, 603 and 453 cm^{-1}.

Exposure of a solution of compound **5** in dichloromethane–acetone to air and washing the residue with benzene after complete evaporation of the solvents afforded a solid, m.p. 181 °C. The ^1H NMR spectrum of this solid showed a large number of methyl peaks (δ 1.92, 1.98, 2.02, 2.15, 2.18, 3.46 and 3.64) along with 2,4,6-$Me_3C_6H_2CO_2H$; however the integrated intensities (CH_3: aryl H) were consistent with the formulation $Sb_4Ph_8O_6{\cdot}3(2,4,6\text{-}Me_3C_6H_2CO_2H)$.

$[SbPh_2(O_2CC_6H_4Me\text{-}2)_2]_2O$ **6**. Quantities used: $SbPh_2Cl_3$ (0.60 g, 1.58 mmol), $AgO_2CC_6H_4Me$-2) (1.166 g, 4.78 mmol). Recrystallized from dichloromethane–hexane. Yield 1.0 g, 56.4%; m.p. 205 °C (Found: C, 60.50; H, 4.20; Sb, 22.65. Calc. for $C_{56}H_{48}O_9Sb_2$: C, 60.70; H, 4.35; Sb, 22.00%). NMR: ^1H, δ 2.60 (s, 12 H, CH_3) and 7.00–8.40 (many lines, 36 H, aryl H); ^{13}C, δ 21.9 (CH_3) and 125.6–141.0 (many lines, aryl C). Major

Table 6 Fractional atomic coordinates for compound **3**

Atom	*X/a*	*Y/b*	*Z/c*
Sb(1)	0.159 11(2)	0.135 81(1)	0.231 89(1)
O(1)	0.293 4(2)	0.109 0(2)	0.149 1(1)
O(2)	0.115 4(2)	0.083 7(2)	0.141 4(1)
O(3)	0.339 8(3)	0.171 6(2)	0.277 7(2)
O(4)	0.179 1(2)	0.182 2(2)	0.327 3(1)
O(5)	0	0.130 3(2)	0.250 0(2)
C(1)	0.214 5(3)	0.081 7(2)	0.118 4(2)
C(2)	0.234 5(4)	0.044 2(2)	0.056 0(2)
C(3)	0.338 9(4)	0.052 5(3)	0.026 3(2)
C(4)	0.356 5(5)	0.016 6(3)	−0.031 5(3)
C(5)	0.276 7(5)	−0.028 3(3)	−0.058 3(2)
C(6)	0.173 7(5)	−0.037 3(3)	−0.027 3(3)
C(7)	0.150 6(4)	−0.001 1(3)	0.030 1(3)
C(8)	0.288 9(3)	0.188 9(2)	0.325 5(2)
C(9)	0.346 9(3)	0.218 0(3)	0.382 5(2)
C(10)	0.280 4(4)	0.244 6(3)	0.434 8(2)
C(11)	0.339 2(5)	0.271 9(4)	0.487 6(3)
C(12)	0.457 8(6)	0.276 7(4)	0.487 4(3)
C(13)	0.523 2(5)	0.253 1(4)	0.436 5(3)
C(14)	0.464 6(4)	0.221 4(3)	0.382 6(3)
C(15)	0.205 8(4)	0.031 9(2)	0.268 4(2)
C(16)	0.317 0(5)	0.006 5(3)	0.263 2(2)
C(17)	0.345 9(4)	−0.062 9(4)	0.288 3(3)
C(18)	0.263 4(6)	−0.104 0(3)	0.317 5(3)
C(19)	0.152 4(5)	−0.078 3(3)	0.324 1(3)
C(20)	0.122 3(4)	−0.009 5(3)	0.299 0(2)
C(21)	0.161 1(3)	0.240 2(2)	0.187 4(2)
C(22)	0.258 0(5)	0.281 9(3)	0.183 0(2)
C(23)	0.253 9(6)	0.349 4(3)	0.148 7(3)
C(24)	0.153 3(5)	0.372 7(3)	0.121 0(4)
C(25)	0.059 5(5)	0.330 1(3)	0.125 6(3)
C(26)	0.060 8(4)	0.263 9(2)	0.159 5(2)

IR bands: 1687, 1604, 1579, 1510vs [ν(C=O)], 1479, 1444vs, 1394vs, 881, 833, 734, 688, 669 and 439 cm^{-1}.

$[SbPh_2(O_2CC_6H_4Me\text{-}4)_2]_2O$ **7**. Quantities used: $SbPh_2Cl_3$ (0.64 g, 1.68 mmol), $AgO_2CC_6H_4Me$-4 (1.17 g, 4.81 mmol). Recrystallized from dichloromethane–hexane. Yield 0.9 g, 51%; m.p. 185–190 °C (Found: C, 61.40; H, 4.35; Sb, 22.35. Calc. for $C_{56}H_{48}O_9Sb_2$: C, 60.70; H, 4.35; Sb, 22.00%). NMR: ^1H, δ 2.38, 2.45 (two s, 12 H, CH_3) and 7.05–8.25 (many lines, 36 H, aryl H); ^{13}C, δ 21.6, 21.8 (CH_3), 126.8–138.6 (many lines, aryl C) and 170.3, 172.2 (both C=O). Major IR bands: 1680, 1635, 1610, 1574, 1418, 1325vs, 1288vs, 1180, 758, 733, 688, 623, 461 and 417 cm^{-1}.

A solution of compound **7** in dichloromethane on evaporation in air afforded a solid which showed two CH_3 peaks at δ 2.37 (major) and 2.44 (minor) in *ca.* 5:1 intensity ratio.

$SbPh_2Cl(O_2CR)_2$ (R = Ph **8**, 2-MeC_6H_4 **9** *or* 4-MeC_6H_4 **10**).—These compounds were prepared by a procedure similar to that for **3** using a 1:2 stoichiometry of $SbPb_2Cl_3$ (*ca.* 1.5 mmol) to AgO_2CR. They were recrystallized from dichloromethane–hexane.

Compound **8**. Yield 70%; m.p. 168 °C (Found: C, 56.40; H, 3.60; Cl, 6.80; Sb, 21.50. Calc. for $C_{26}H_{20}ClO_4Sb$: C, 56.45; H, 3.65; Cl, 6.40; Sb, 22.00%). NMR: ^1H, δ 7.20–8.50 (m); ^{13}C, δ 128.7–134.3 (many lines, aryl C) and 190.0 (C=O). Major IR bands: 1601, 1504vs [ν(C=O)], 1417vs [ν(C=O)], 875, 717, 684 and 445 cm^{-1}.

Compound **9**. Yield 78%; m.p. 192 °C (Found: C, 57.85; H, 4.10; Cl, 6.0; Sb, 21.45. Calc. for $C_{28}H_{24}ClO_4Sb$: C, 57.80; H, 4.15; Cl, 6.10; Sb, 20.95%). NMR: ^1H, δ 2.6 (s, 6 H, CH_3) and 7.10–8.45 (m, 18 H, aryl H); ^{13}C, δ 22.1 (CH_3), 126.0–133.5, 141.8, 152.0 (all aryl C) and 196.0 (very weak, C=O). Major IR bands: 1602, 1498vs [ν(C=O)], 1413vs [ν(C=O)], 885, 733 and 682 cm^{-1} (up to 600 cm^{-1}).

Compound **10**. Yield 73%; m.p. 198 °C (Found: C, 57.45; H, 4.05; Cl, 5.95; Sb, 21.85. Calc. for $C_{28}H_{24}ClO_4Sb$: C, 57.80; H, 4.15; Cl, 6.10; Sb, 20.95%). NMR: ^1H, δ 2.37 (s, 6 H, CH_3) and 7.15–8.40 (m, 18 H, aryl H); ^{13}C, δ 21.8 (CH_3), 125.0, 129.2, 131.1_0, 131.1_2, 132.5, 145.4 and 152.6 (all aryl C). Major IR bands: 1610, 1520, 1494, 1477, 1437 [ν(C=O)], 1178, 887, 762, 733, 683, 629, 459 and 419 cm^{-1}.

Interconversion of Compounds **I** *and* **II**.—Compound **I** (200 mg)[3] was dissolved in dichloromethane (30 cm^3). Upon crystallization in air **II**·CH_2Cl_2 was formed quantitatively. ^1H NMR (after drying *in vacuo* for 2 h): δ 1.76 (s, 3 H, CH_3), 1.90 (s, 6 H, CH_3) and 6.40–8.00 (m, *ca.* 43 H, aryl H + OH).

Compound **II** (150 mg)[3] was heated under reflux with acetic acid–acetic anhydride (5 + 5 cm^3) for 24 h. Upon reducing the volume of the solvent **I** (120 mg) was obtained as a crystalline solid. ^1H NMR: δ 1.98 (s, 12 H, CH_3) and 7.15–8.20 (m, 20 H, aryl H).

X-Ray Crystallography.—Single crystals of compounds **1** and **3** were grown from a mixture of dichloromethane and hexane. A suitable crystal was mounted on a glass fibre and coated with paraffin oil to protect it from air and moisture. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα (λ = 0.7107 Å) radiation. The unit-cell parameters were obtained and refined by using 25 randomly selected well centred reflections in the range 23 < 2θ < 28°. Three reflections, monitored throughout the data collection showed no significant change in intensities. The details pertaining to data collection and refinement are listed in Table 4. The structures were solved by conventional Patterson[17] and Fourier techniques and refined by full-matrix least squares.[18] The final positional parameters are listed in Tables 5 and 6. The data were corrected for Lorentz and polarization effects but not for absorption. No attempts were made to locate hydrogen atoms.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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