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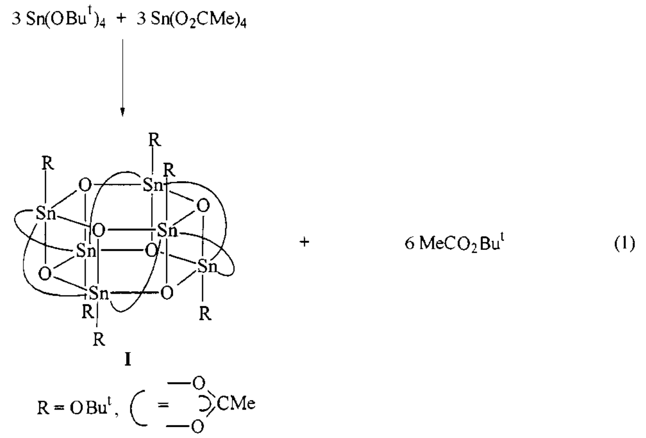
Synthesis and structures of new mono- and multi-nuclear benzyltin carboxylates and phosphinates: a novel dibenzyltin phosphinate stabilized by intramolecular hydrogen bonding

K. C. Kumara Swamy,*,†,[a] Musa A. Said,[a] S. Nagabrahmanandachari,[a] Damodara M. Poojary[b] and Abraham Clearfield[b]

[a] *School of Chemistry, University of Hyderabad, Hyderabad - 500046, A. P., India*
[b] *Department of Chemistry, Texas A & M University, College Station, Texas 77843-3255, USA*

The reaction of dibenzyltin dichloride **1** with 2 mol equivalents each of $AgO_2P(C_6H_{11})_2$ and $(C_6H_{11})_2PO_2H$ afforded the novel monometallic complex $Sn(CH_2Ph)_2[O_2P(C_6H_{11})_2]_2[HO_2P(C_6H_{11})_2]_2$ **2**. When **1** was treated with 2 mol equivalents of $AgO_2P(C_6H_{11})_2$ only the trinuclear O-capped cluster $[\{Sn(CH_2Ph)(OH)[O_2P(C_6H_{11})_2]\}_3O][O_2P(C_6H_{11})_2]$ **4** was obtained by an Sn–C bond cleavage *via* an intermediate formulated as $\{Sn(CH_2Ph)(OH)[O_2P(C_6H_{11})_2]_2\}_2$ **3**. In the reaction with silver carboxylates the type of product isolated depends on the carboxylic acid used. Thus the 'ladder' $\{[(PhCH_2)SnO{\cdot}O_2CMe]_2(PhCH_2)Sn(O_2CMe)_3\}_2$ **5**, the 'hexagonal prismanes' $[(PhCH_2)SnO{\cdot}O_2CR]_6$ (R = Me **6**, Bu^t **7**, C_5H_4N **8**, CH=CMe$_2$ **9** or $CHPh_2$ **10**) and the mononuclear compound $Sn(CH_2Ph)_2(O_2CCHPh_2)_2$ **11** have been isolated. X-Ray structural analysis confirmed the identities of **2**, **4**·$CHCl_3$, and **5**·$2CH_2Cl_2$. In **2** the mononuclear structure is stabilized by internal hydrogen bonding between P–OH and P=O of the co-ordinated phosphinic acid and the phosphinate, respectively, from the same molecule. Compound **4** has a tristannoxane ring with a capping oxygen, whereas in **5** the stannoxane skeleton is that of a 'ladder' with three different types of tin.

Several interesting multinuclear monoorganotin carboxylate/phosphinate cages and clusters that include 'drums' (hexagonal prismanes) $(RSnO{\cdot}O_2CR)_6$, 'cubanes' $(RSnO{\cdot}O_2PR_2)_4$, and 'ladders' $[(RSnO{\cdot}O_2CR)_2RSn(O_2CR)_3]_2$ have been reported during the last decade.[1–3] Most of these compounds have been prepared by either (i) condensation reactions of the appropriate carboxylic/phosphorus-based acids with stannoic acids, RSn(O)OH, or (ii) treating organotin halides with silver salts of carboxylic/phosphinic acids. In one case an ester elimination reaction which gives the hexagonal prismane **I** [equation (1)] is also used.[4]



Another route which leads to mono- and multi-nuclear tin compounds involves Sn–C bond cleavage reactions of phenyltin compounds [equations (2)–(6)].[5–8] In this connection it is

$$SnPh_2O \xrightarrow{Cl_3CCO_2H/C_6H_6,\ reflux} \tfrac{1}{6}(PhSnO{\cdot}O_2CCCl_3)_6{\cdot}3C_6H_6 \quad (2)$$

$$SnPh_3(O_2CC_6H_{11}) \xrightarrow{H_2O} \tfrac{1}{6}(PhSnO{\cdot}O_2CC_6H_{11})_6 + 2C_6H_6 \quad (3)$$

$$SnPh_3(OH) \xrightarrow{Cl_3CCO_2H/C_6H_6,\ reflux} \tfrac{1}{6}(SnPh)_6(O_2CCCl_3)_{10}O_4{\cdot}2C_6H_6 \quad (4)$$

$$SnPh_3(O_2CMe) + Hg(O_2CMe)_2 \longrightarrow HgPh_2 + \tfrac{1}{n}(PhSnO{\cdot}O_2CMe)_n \quad (5)$$

$$SnPh_4 + 4\ MeCO_2H \longrightarrow Sn(O_2CMe)_4 + 4C_6H_6 \quad (6)$$

pertinent that allyltin compounds are also prone to Sn–C bond cleavage which forms the basis of their utility in allylation reactions.[9] Since a benzyl group may be expected to behave in a manner similar to an allyl group,[10] tin–carbon bond cleavage reactions must be facile for benzyltin compounds also. Thus we chose to study the reactions of the readily prepared dibenzyltin dichloride, $Sn(CH_2Ph)_2Cl_2$ **1**,[11] with silver salts of carboxylic/phosphinic acids in order to see if the cages/clusters mentioned above can be obtained by this route, and also to explore whether products with structures other than the known types are formed.

Herein we report the synthesis and crystal structures of (a) the novel mononuclear compound $Sn(CH_2Ph)_2[O_2P(C_6H_{11})_2]_2[HO_2P(C_6H_{11})_2]_2$ **2**, (b) the O-capped cluster $[\{Sn(CH_2Ph)(OH)[O_2P(C_6H_{11})_2]\}_3O][O_2P(C_6H_{11})_2]{\cdot}CHCl_3$ **4**·$CHCl_3$, which is obtained by hydrolysis of the dimer $\{Sn(CH_2Ph)(OH)[O_2P(C_6H_{11})_2]_2\}_2$ **3** and (c) the ladder compound $\{[(PhCH_2)SnO{\cdot}O_2CMe]_2(PhCH_2)Sn(O_2CMe)_3\}_2{\cdot}2CH_2Cl_2$ **5**·$2CH_2Cl_2$. Compound **2** represents a unique structure stabilized by intramolecular hydrogen bonding. Whereas the formation of **2** involves no Sn–C bond cleavage, that of **4** or **5** involves such a cleavage. In addition to the above compounds the prismanes $[(PhCH_2)SnO{\cdot}O_2CR]_6$ (R = Me **6**, Bu^t **7**, C_5H_4N **8**, CH=CMe$_2$ **9** or $CHPh_2$ **10**) and the monometallic derivative $Sn(CH_2Ph)_2(O_2CCHPh_2)_2$ **11** have been isolated from the reaction of **1** with the corresponding silver carboxylates.

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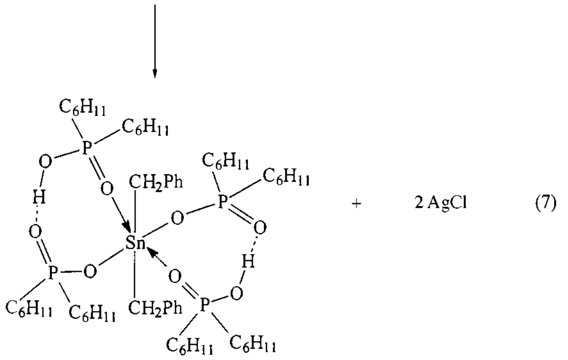
† E-Mail: kckssc@uohyd.ernet.in

Results and Discussion

Synthesis and spectroscopy

Compound **2** was synthesized according to equation (7); it is also formed as a minor product during recrystallization in the reaction of **1** with an excess (>3 mol equivalents) of silver dicyclohexylphosphinate. The ^{31}P NMR spectrum of **2** showed a broad signal at δ 54.7; in the ^{1}H NMR spectrum the expected integrated intensity ratio is observed with the phosphinic acid OH proton appearing at δ 7.95 [^{4}J(Sn–H) ≈ 25 Hz]. An analogous reaction of dicyclooctylphosphinic acid and its silver salt with **1** gave a single product [δ (^{31}P) 64.8 (br); ^{1}H NMR broad with expected integrated intensities], but no crystalline product could be isolated.

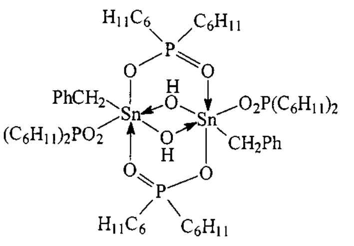
$Sn(CH_2Ph)_2Cl_2 + 2\ AgO_2P(C_6H_{11})_2 + 2\ (C_6H_{11})_2PO_2H$



$+\ 2\,AgCl$ (7)

2

In the reaction of compound **1** with 2.5 mol equivalents of $AgO_2P(C_6H_{11})_2$ alone the crystalline product **3** obtained initially showed two ^{31}P NMR signals at δ 57.2 [^{2}J(Sn–O–P) = 136.4] and 48.7 [^{2}J(Sn–O–P) = 196.4 Hz] of equal intensity. The ^{1}H NMR spectrum showed broad signals with a complex pattern but the integrated intensities showed that there are two phosphinates per benzyl group. The ^{119}Sn NMR exhibited a multiplet centred at δ −586.0. These features are analogous to those observed for the dimer $\{SnBu^n(OH)[O_2P(C_6H_{11})_2]_2\}_2$ {^{31}P NMR: δ 56.02 [^{2}J(Sn–O–P) = 124.4], 47.60 [^{2}J(Sn–O–P) = 190.8 Hz]. ^{119}Sn NMR: δ −547.47}.[12] Hence **3** is assigned an analogous structure. This product is formed most likely by cleavage of an Sn–CH$_2$Ph bond from the intermediate $Sn(CH_2Ph)_2[O_2P(C_6H_{11})_2]_2$ due to hydrolysis by adventitious moisture present.



3

Attempted crystallization of compound **3** in air led to the O-capped cluster **4** [equation (8)]. The ^{31}P NMR spectrum, although broad, shows two types of phosphinates [δ 41.5 (1P, free), 52.8 (3P, bridging)]; the ^{119}Sn NMR exhibits a triplet at δ −535.7 [^{2}J(Sn–O–P) ≈ 137 Hz] showing that all the tin atoms are equivalent and coupled to adjacent phosphorus nuclei only. It can be noted that Δδ(^{119}Sn) for **4** and the corresponding *n*-butyl compound $[\{SnBu^n(OH)[O_2P(C_6H_{11})_2]\}_3O]^+[O_2P(C_6H_{11})_2]^-$ is 36.4 ppm; the corresponding difference between our benzyl compound **3** and the *n*-butyltin compound $\{SnBu^n(OH)[O_2P(C_6H_{11})_2]_2\}_2$ is 38.5 ppm.[12] This lends credence to our assignment of the dimeric structure for **3**.

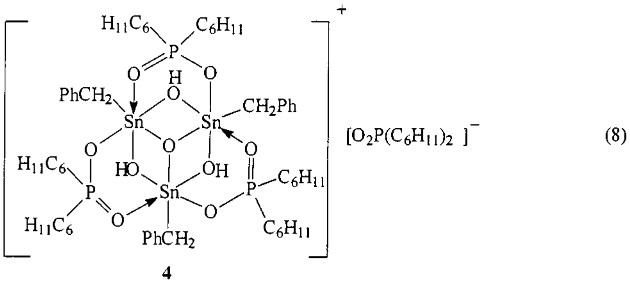
$6Sn(CH_2Ph)_2Cl_2 + 12\ AgO_2P(C_6H_{11})_2$

H_2O (?)

$3\ \{Sn(CH_2Ph)_2(OH)[(O_2P(C_6H_{11})_2]_2\}_2$

3

$2\ H_2O$ $-2\ HO_2P(C_6H_{11})_2$



$[O_2P(C_6H_{11})_2\ ]^-$ (8)

4

Treatment of compound **1** with silver carboxylates afforded different types of compounds as isolable products depending on the carboxylic acid used (Scheme 1). The NMR spectra (^{1}H, ^{13}C and ^{119}Sn) for the ladder compound **5** show broad signals. In the ^{119}Sn NMR, the signal for the prismane $[(PhCH_2)SnO\cdot O_2CMe]_6$ **6** at δ −523.1 is also seen; peaks for **5** are broad [δ −530 to −580 and −630 to −640]. This solution behaviour is reminiscent of Holmes' observations for *n*-butyltin oxide carboxylate ladders.[13] Hydrolysis of **5** to the pure prismane **6** can be readily effected [equation (9)]. Compounds **6**–**10** show characteristic singlet resonances in the ^{119}Sn NMR spectra between δ −519 and −523, upfield by *ca.* 35 ppm to those of the corresponding *n*-butyltin compounds $(Bu^nSnO\cdot O_2CR)_6$.[1,2]

(a) $Sn(CH_2Ph)_2Cl_2 + 2\ AgO_2CMe \xrightarrow{(H_2O)}$

$$\tfrac{1}{6}\underset{\mathbf{5}}{\{[(PhCH_2)SnO\cdot O_2CMe]_2(PhCH_2)Sn(O_2CMe)_3\}_2} \xrightarrow{(H_2O)} \tfrac{1}{6}\underset{\mathbf{6}}{[(PhCH_2)SnO\cdot O_2CMe]_6}$$

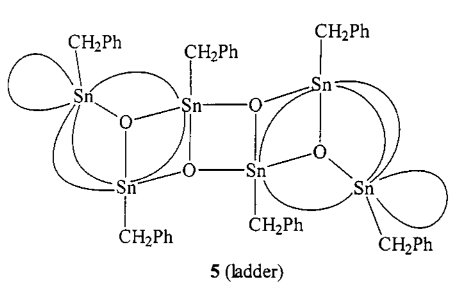
(b) $Sn(CH_2Ph)_2Cl_2 + 2\ AgO_2CR \xrightarrow{(H_2O)} \tfrac{1}{6}[(PhCH_2)SnO\cdot O_2CR]_6$

R = Bu^t **7**, C_5H_4N **8** or CH=CMe$_2$ **9**

(c) $Sn(CH_2Ph)_2Cl_2 + 2\ AgO_2CCHPh_2 \xrightarrow{(H_2O)}$

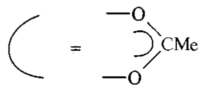
$$\underset{\mathbf{10}}{[(PhCH_2)SnO\cdot O_2CCHPh_2]_6} + \underset{\mathbf{11}}{Sn(CH_2Ph)_2(O_2CCHPh_2)_2}$$

Scheme 1

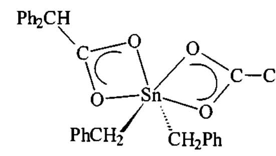


5 (ladder)

$+\ 2H_2O \longrightarrow \mathbf{6} + MeCO_2H$ (9)



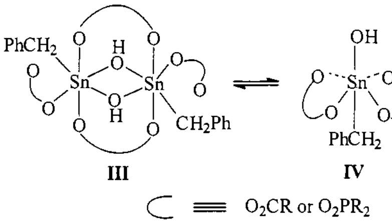
It is possible that the bulkiness of the substituents makes the diphenylacetate compound **11** readily isolable; in line with many reports on dialkyltin dicarboxylates,[14] we assign a mono-



11

meric structure for **11**. This assignment is consistent with the ^{119}Sn NMR chemical shift value of δ −235.8 which is close to that of $\mathrm{SnBu^t_2(O_2CBu^t)_2}$ [δ(^{119}Sn) −232].[14c]

The initial product formed in the reaction of compound **1** with silver phosphinates or carboxylates is of the type $\mathrm{Sn(CH_2Ph)_2(O\text{–}O)_2}$ **II** ($\mathrm{O\text{–}O = O_2PR_2}$ or $\mathrm{O_2CR}$); we isolated such a compound (**11**) in the case of diphenylacetate.‡ The second step presumably involves the attack of water on **II** leading to the dimer **III** after elimination of toluene, dimerization and ligand reorganization. Isolation of such a species was accomplished only for the phosphinates (*e.g.* **3**). It is likely that the dimer **III** is in equilibrium with the monomer **IV**. Conversion of **III** to an O-capped cluster (*e.g.* **4**) has been discussed by Holmes *et al.*[12] For the formation of a 'ladder' (*e.g.* **5**), **III** can react with its monomer **IV** with the elimination of a molecule each of water and the acid, followed by ligand reorganization and dimerization. Formation of a 'prismane' (*e.g.* **6**) from the 'ladder' (*e.g.* **5**) has been studied before and hence is not elaborated here.[13]



Structural aspects

The molecular structures of compounds **2**, **4**·CHCl$_3$ and **5**·2CH$_2$Cl$_2$ are depicted in Figs. 1–3 respectively. Selected bond distances and angles for **2** are provided in Table 1, important bond parameters for **4**·CHCl$_3$ and **5**·2CH$_2$Cl$_2$ in Figs. 2 and 3.

Compound **2** crystallizes in the space group $P\bar{1}$ with half the molecule in the asymmetric unit. It is a mononuclear six-co-ordinated tin complex containing two Sn–C, two covalently linked Sn–O (phosphinate) and two co-ordinatively linked Sn–O (phosphinic acid) bonds; the two Sn–C bonds are *trans* to each other. The two types of Sn–O bonds are nearly of the same length [2.237(2), 2.203(2) Å] but are longer than those observed in the O-capped cluster **4** (mean: 2.097 Å). The angles at the oxygens connected to tin are also nearly the same [143.6(1) and 143.7(1)°]. Distinction between the phosphinate and the phosphinic acid is best made by comparing the P–O distances, which show that P(1) belongs to the phosphinic acid.

The most important structural feature in compound **2** is the presence of hydrogen bonding between O(2) and O(4) [relevant distances and angle: O(2)–H ≈ 1.06, O(4)···H ≈ 1.37 Å, O(2)–H···O(4) ≈ 175.9°] forming an eight-membered ring that includes the hydrogen. This probably has a stabilizing effect on the observed structure. Although reports on many other diorganotin phosphates/phosphinates are available,[15,17] to our knowledge **2** is the only mononuclear diorganotin phosphinate to be structurally characterized. These tin phosphinates, in general, have a tendency to oligomerize.

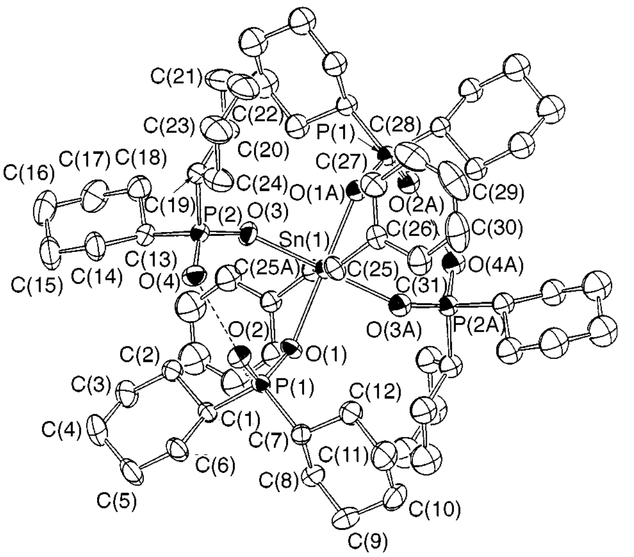


Fig. 1 An ORTEP[16] drawing of compound **2** with displacement ellipsoids at 30% probability level. Only the non-hydrogen atoms are shown

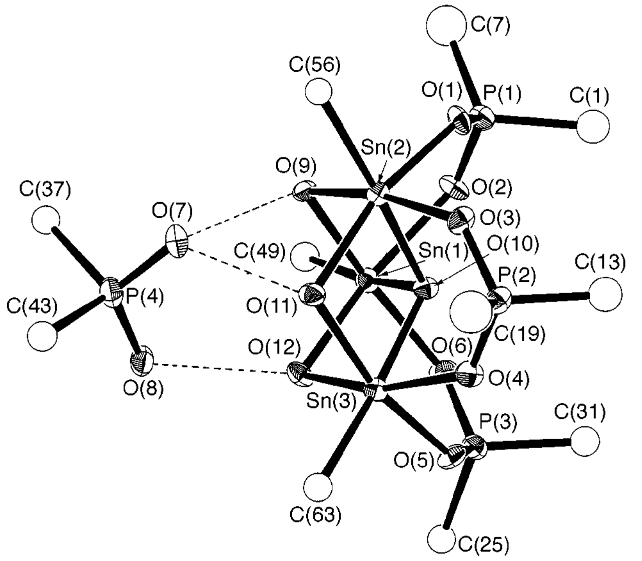


Fig. 2 An ORTEP drawing of compound **4**·CHCl$_3$ with displacement ellipsoids at 30% probability level. Only tin, oxygen, phosphorus and carbon atoms connected to tin or phosphorus are shown. Bond distances (Å) and angles (°): Sn–O 2.05(1)–2.16(1), Sn–C 2.15(2)–2.20(2); O–Sn–O(*cis*) 77.4(5)–92.4(5), O–Sn–O(*trans*) 161.4(5)–165.8(5), O–Sn–C(*cis*) 91.9(7)–105.0(7), O–Sn–C(*trans*) 171.6(7)–173.1(5), Sn–OH–Sn 98.2(6)–99.8(5), Sn(1)–O(10)–Sn(2) 104.2(6), Sn(1)–O(10)–Sn(3) 102.4(6), Sn(2)–O(10)–Sn(3) 103.4(6)

The cationic part in compound **4** consists of a tristannoxane in a chair conformation with Sn(1) and O(11) on the opposite sides of the mean plane containing Sn(2), O(9), Sn(3) and O(12); the hydroxyl groups comprise the oxygen atoms of the ring. The tin atoms are capped on one side of the tristannoxane skeleton by a three-co-ordinated oxygen atom [O(10)] at 0.87 Å above the Sn(1)–Sn(2)–Sn(3) plane. The mean Sn–O–Sn angle at the capping oxygen is ≈103.3° which is close to that in $\mathrm{[\{SnBu^n(OH)(O_2PPh_2)\}_3O]^+[O_2PPh_2]^-}$ [mean 103.6(2)°][18] but smaller than that observed in analogous titanium and zirconium carboxylates[19] (see **V** below). All the three tin atoms in **4** are equivalent and six-co-ordinated, each with two bridging phosphinates. As in $\mathrm{[\{SnBu^n(OH)(O_2PPh_2)\}_3O]^+[O_2PPh_2]^-}$,[18] the oxygen of the free phosphinate in **4** is hydrogen bonded to the hydroxyls of the tristannoxane skeleton in an essentially identical fashion; the relevant distances in **4** are O(7)···O(9) 2.71(2), O(7)···O(11) 2.69(2) and O(8)···O(12) 2.68(2) Å.

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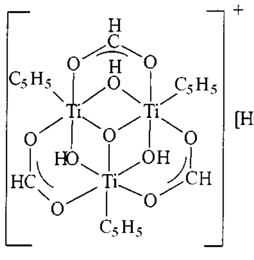
‡ The compound $\mathrm{SnMe_2[O_2P(OBu^n)_2]_2}$ has been reported; it is assigned a monomeric structure with chelating phosphates, but no crystal structure is available.[15]

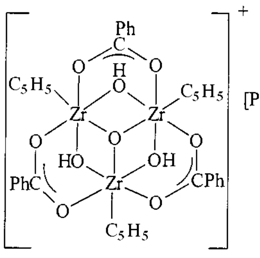
Table 1 Selected bond lengths (Å) and angles (°) for compound **2** with estimated standard deviations in parentheses

Sn–O(1)	2.237(2)	P(1)–C(7)	1.812(3)
Sn–O(3)	2.203(2)	P(2)–O(3)	1.518(2)
Sn–C(25)	2.139(3)	P(2)–O(4)	1.505(2)
P(1)–O(1)	1.509(2)	P(2)–C(13)	1.812(3)
P(1)–O(2)	1.538(2)	P(2)–C(19)	1.826(2)
P(1)–C(1)	1.809(3)		
O(1)–Sn–O(1a)	180.00	C(25)–Sn–C(25a)	180.00
O(1)–Sn–O(3)	87.40(7)	O(3)–Sn–C(25a)	89.3(1)
O(1)–Sn–O(3a)	92.60(7)	O(1)–P(1)–O(2)	114.2(1)
O(1)–Sn–C(25)	88.58(9)	O(3)–P(2)–O(4)	116.2(1)
O(1)–Sn–C(25a)	91.42(9)	Sn–O(1)–P(1)	143.6(1)
O(3)–Sn–O(3a)	180.00	Sn–O(3)–P(2)	143.7(1)
O(3)–Sn–C(25)	90.7(1)		

Hydrogen bonding appears to be a stabilizing factor for the O-capped cation. It is also found in $[\{SnBu^n(OH)[O_2P(C_6H_{11})_2]\}_3O][\{SnBu^nCl_2[O_2P(C_6H_{11})_2]\}_2(OH)]$[20] as well as in similar titanium (**Va**) and zirconium (**Vb**) carboxylate clusters.[19]



Va



Vb

The molecule of compound **5** (Fig. 3) is a dimer with the two halves related by a centre of symmetry; there are three crystallographically distinct tin atoms. The atoms Sn(1) and Sn(2) are six-co-ordinated, bonded to five oxygen atoms and one carbon; the geometry around tin is a distorted octahedron. The three bridging carboxylates on Sn(1) are meridional whereas the two bridging carboxylates on Sn(2) are *trans* to each other. The terminal Sn(3) is seven-co-ordinated and has a pentagonal bipyramidal geometry with C(25) and O(2) at the apical positions. The five oxygen atoms and Sn(3) which comprise the equatorial plane are coplanar to within ±0.11 Å. The apical angle O(2)–Sn(3)–C(25) is 173.5(3)°.

Three types of oxygen atoms are present in the molecule: (a) three-co-ordinated framework, (b) two-co-ordinated bridging carboxylate and (c) two-co-ordinated chelating carboxylate. The framework Sn–O bond lengths range from 1.999(5) to 2.138(5) Å, the longest being Sn(2)–O(2). It is interesting that this has always been the longest framework Sn–O bond in all the known structures of this type.[13,21] The shortest Sn–O bond is the one from the terminal tin to the μ_3-oxygen [Sn(3)–O(2) in **5**]. As noted by others,[13,21] the Sn–O bonds to the bridging carboxylates (mean 2.172 Å) are, in general, longer than the framework Sn–O bonds (mean 2.062 Å). The Sn(3)–O bonds to the chelating carboxylates are much longer (mean 2.258 Å) and their values are closer than those in the structures reported before.[13,21] The sum of the angles around the framework oxygen atoms is close to 360° [Σ O(1) = 356.1, Σ O(2) = 350.2]; however the geometry around O(1) is slightly non-planar and it is *ca.* 0.37 Å above the mean plane containing Sn(1), Sn(2) and Sn(3).

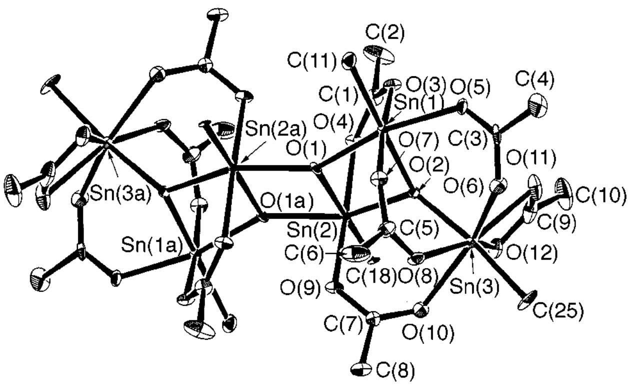
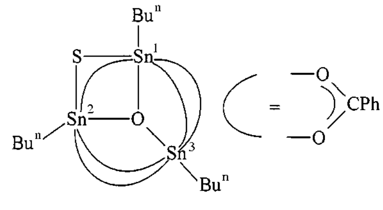


Fig. 3 An ORTEP drawing of compound $5{\cdot}2CH_2Cl_2$ with displacement ellipsoids at 30% probability level. All non-hydrogen atoms except those of the solvent and of the phenyl carbons of the $SnCH_2Ph$ group are shown. Bond distances (Å) and angles (°): Sn–O (three-co-ordinated) 1.999(5)–2.138(5), Sn–O (carboxylate) 2.115(5)–2.262(6), Sn–C 2.136(9)–2.153(9); O(1)–Sn(1)–O(2) 77.5(2), O(1)–Sn(2)–O(1a) 76.1(2), O(1)–Sn(2)–O(2) 74.8(2), O(1a)–Sn(2)–O(2) 150.9(2), Sn(1)–O(1)–Sn(2a) 149.0(3), Sn(1)–O(1)–Sn(2) 103.2(2), Sn(2)–O(1)–Sn(2a) 103.9(2), Sn(1)–O(2)–Sn(2) 100.4(2), Sn(1)–O(2)–Sn(3) 123.7(3), Sn(2)–O(2)–Sn(3) 126.1(3)

An interesting structural correlation can be made between compound **5** and the μ-S bridged compound **VI** reported by Schmid *et al.*[22] Compound **VI** essentially represents one half of the molecule of **5** with O(1) replaced by a sulfur and the chelating carboxylate on Sn(3) (in **5**) replaced by a bridging carboxylate connected to another tin.



VI

The major topological difference between the prismane (see structure **I**) and the ladder (*e.g.* **5**) is perhaps the orientation (folding) of the two peripheral Sn_2O_2 rings [Sn(1)–O(2)–Sn(2)–O(1); Sn(1a)–O(2a)–Sn(2a)–O(1a) in the ladder **5**] with respect to the central Sn_2O_2 ring [Sn(2)–O(1)–Sn(2a)–O(1a)]; whereas the folding in the ladder is transoid, in the hexagonal prismane it is cisoid. In the process of hydrolysis of the ladder, therefore, it is possible that the peripheral Sn_2O_2 rings reorient themselves.

To summarize, the present study demonstrates the utility of dibenzyltin dichloride **1** as a useful precursor to obtain monobenzyltin oxide carboxylate/phosphinate cages/clusters in addition to the novel hydrogen-bonded dibenzyltin compounds such as **2**. It remains to be seen whether a carboxylate 'cubane' $(RSnO{\cdot}O_2CR')_4$ or an 'O-capped cluster' $[\{SnR(OH)(O_2CR')\}_3O][O_2CR']$ can be isolated by a suitable choice of R and R′; the latter type of carboxylates have been isolated for titanium (**Va**) and zirconium (**Vb**). Since the O-capped cluster (*e.g.* **4**) can be viewed as a cubane with one tin corner missing it must be possible to prepare cubanes by further condensation reactions on the O-capped cluster.[1,23]

Experimental

Chemicals and solvents were from Aldrich/Fluka or from local manufacturers. Further purification was done according to standard procedures.[24] All operations, unless stated otherwise, were carried out under a dry nitrogen atmosphere using standard Schlenk techniques.[25] The ^1H, ^{13}C, ^{31}P (at 80.961 MHz) and ^{119}Sn (at 74.544 MHz) NMR spectra were recorded on a Brüker 200 MHz spectrometer in $CDCl_3$ solutions with shifts referenced to $SiMe_4$ (^1H, ^{13}C; δ 0), external 85% H_3PO_4 (δ 0) and $SnMe_4$ (δ 0) respectively. The IR spectra were recorded on either a Perkin-Elmer 1310 or a JASCO FT/IR 5300 spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240C CHN analyzer. Melting points are uncorrected.

Dicyclohexylphosphinic acid[26] and dibenzyltin dichloride **1**[11] were prepared according to literature methods. Silver salts of carboxylic acids were prepared using stoichiometric amounts of the acid, sodium hydroxide and silver nitrate.

Syntheses

$Sn(CH_2Ph)_2[O_2P(C_6H_{11})_2]_2[HO_2P(C_6H_{11})_2]_2$ 2. A mixture of compound **1** (1.50 g, 4.04 mmol) and $AgO_2P(C_6H_{11})_2$ (2.72 g, 8.07 mmol) was heated under reflux in toluene (75 cm^3) for 5 h and then dicyclohexylphosphinic acid (1.86 g, 8.07 mmol) added. The mixture was heated under reflux for 15 h and filtered. The solvent was removed and the residue washed with *n*-heptane to remove any unchanged acid. The residue was crystallized from dichloromethane–*n*-heptane (1:5) to afford **2**. Yield: 2.3 g, 55%; m.p. 180 °C (Found: 61.12; H, 8.62. Calc. for $C_{62}H_{104}O_8P_4Sn$: C, 61.03; H, 8.59%). ^1H NMR: δ 1.05–2.19 (m, 88 H, cyclohexyl), 2.70 [s, with tin satellites, ^2J(Sn–H) = 180, 176, 4 H, C*H*$_2$Ph], 6.85–7.33 (m, 10 H, aryl H) and 7.95 [s, with tin satellites, ^4J(Sn–H) = 25 Hz, 2 H, OH]. ^{31}P NMR: δ 54.7 (br).

$\{Sn(CH_2Ph)(OH)[O_2P(C_6H_{11})_2]_2\}_2$ 3 and $[\{Sn(CH_2Ph)(OH)[O_2P(C_6H_{11})_2]\}_3O][O_2P(C_6H_{11})_2]$ 4. A mixture of compound **1** (1.00 g, 2.69 mmol) and $AgO_2P(C_6H_{11})_2$ (2.27 g, 6.72 mmol) was heated in toluene (50 cm^3) under reflux for 12 h and then filtered. The solvent was completely removed from the filtrate and the residue dissolved in dichloromethane (30 cm^3). After filtering the insolubles, the volume of the solution was reduced to *ca.* 5 cm^3 and *n*-heptane added to obtain **3** as a crystalline solid. Yield: 1.1 g, 60%; m.p. 198 °C (Found: C, 54.04; H, 7.25. Calc. for $C_{62}H_{104}O_{10}P_4Sn_2$: C, 54.30; H, 7.59%). ^1H NMR: δ 0.73–2.25 (m, 88 H, cyclohexyl), 2.60–2.85 (m, 4 H, C*H*$_2$Ph), 4.90 (br, 2 H, OH) and 6.90–8.00 (m, 10 H, aryl H). ^{31}P NMR: δ 48.7 [s, with tin satellites, ^2J(Sn–O–P) = 196.4, P(dangling)] and 57.2 [s, with tin satellites, ^2J(Sn–O–P) = 134.4 Hz, P(bridging)]. ^{119}Sn NMR: δ −586.0 (m).

Upon attempted crystallization of the product **3** (chloroform + heptane) in air the O-capped cluster $[\{Sn(CH_2Ph)(OH)[O_2P(C_6H_{11})_2]\}_3O]^+[O_2P(C_6H_{11})_2]^-$ **4** as a solvate ($CHCl_3$) was obtained in >65% yield; m.p. 228–230 °C [Found: C, 51.22; H, 7.10. Calc. for $C_{69}H_{112}O_{12}P_4Sn_3$ (after removing the solvent of crystallization): C, 51.34; H, 6.99%]. ^1H NMR (after drying): δ 0.85–2.10 (m, 88 H, cyclohexyl), 2.83 [s, with tin satellites, 6 H, ^2J(Sn–H) = 166, 170 Hz, C*H*$_2$Ph], 6.95–7.40 (m, 15 H, aryl H) and 8.90 (br s, 3 H, OH). ^{13}C NMR: δ 25.8, 26.1, 26.6, 26.8 (cyclohexyl), 34.8 [^3J(P–O–Sn–C) = 30, *C*H$_2$Ph], 37.6 [^1J(P–C) = 88, cyclohexyl], 37.8 [^1J(P–C) = 84 Hz, cyclohexyl], 124.2, 127.8, 129.5 and 139.0 (aryl). ^{31}P NMR: δ 52.8 [br, 3 P, P(bridging)] and 41.5 [br, 1 P, P(free)]. ^{119}Sn NMR: δ −535.7 [t, ^2J(Sn–O–P) = 137 Hz].

$\{[(PhCH_2)SnO\cdot O_2CMe]_2(PhCH_2)Sn(O_2CMe)_3\}_2\cdot 2CH_2Cl_2$ 5·2CH_2Cl_2 and $[(PhCH_2)SnO\cdot O_2CMe]_6$ 6. A mixture of compound **1** (4.0 g, 10.7 mmol) and silver acetate (5.0 g, 29.95 mmol) was heated under reflux in toluene (80 cm^3) for 20 h. Filtration followed by removal of solvent afforded a solid which was crystallized from dichloromethane (12 cm^3) to give **5**. Yield: 0.92 g, 25%; m.p. 196–200 °C, lost crystallinity around 135 °C (Found: C, 37.44; H, 3.49. Calc. for $C_{32}H_{38}Cl_2O_{12}Sn_3$: C, 36.89; H, 3.68%). IR (KBr): 3026, 1588, 1493, 1425, 1026, 762, 737, 696 and 665 cm^{-1}. ^1H NMR: δ 1.85–2.11 (m, 30 H, CH_3), 2.95 (br m, 12 H, CH_2), 5.30 (s, 2 H, CH_2Cl_2) and 7.05–7.18 (m, 30 H, aryl). ^{13}C NMR: δ 23.8 (CH_3), 35.9 (CH_2), 54.0 (CH_2Cl_2), 124.5, 127.8, 129.2, 139.3 (aryl) and 179.4 (CO_2). ^{119}Sn NMR: δ −523.0 (assigned to **6**), −530 to −580 and −630 to −640 (many signals).

Compound **5** (0.1 g, 0.096 mmol) was dissolved in CH_2Cl_2 (2 cm^3) in air for 24 h and the solvent evaporated under reduced pressure (repeated five times) to yield **6**. Yield: 0.08 g, ≈98%; m.p. 252–256 °C (Found: C, 37.67; H, 3.63. Calc. for $C_{54}H_{60}O_{18}Sn_6$: C, 37.95; H, 3.54%). IR (KBr): 3025, 1589, 1542, 1493, 1447, 1209, 1028, 758, 696, 610, 546 and 482 cm^{-1}. ^1H NMR: δ 1.85 (s, 18 H, CH_3), 2.63 [s, with tin satellites, 12 H, ^2J(Sn–H) = 160.0, 164.0 Hz, CH_2] and 7.08–7.13 (m, 30 H, aryl). ^{13}C NMR: δ 23.7 (CH_3), 34.4 (CH_2), 124.5, 127.8, 128.2, 128.7 and 129.2 (aryl) and 179.6 (CO_2). ^{119}Sn NMR; δ −523.1.

$[(PhCH_2)SnO\cdot O_2CR]_6$ (R = Bu^t 7, C_5H_4N 8 or CH=CMe_2 9). These compounds were prepared in yields of 20–40% from the reaction of **1** (1–5 mmol) with 2 mol equivalents of appropriate silver carboxylates using the above method.

Compound **7**: M.p. >260 °C (Found: C, 44.59; H, 4.94. Calc. for $C_{72}H_{96}O_{18}Sn_6$: C, 44.12; H, 4.94%); IR (KBr) 2963, 1582, 1537, 1485, 1427, 1231, 901, 754, 693 and 640 cm^{-1}; ^1H NMR: δ 0.96 [s, with tin satellites, 54 H, $C(CH_3)_3$], 2.73 [s, with tin satellites, 12 H, ^2J(Sn–H) = 158, 152 Hz, CH_2] and 6.96–7.32 (m, 30 H, aryl); ^{13}C NMR: δ 27.1 [C(*C*H$_3$)$_3$], 34.4 (CH_2), 40.5 [*C*(CH$_3$)$_3$], 124.3, 127.9, 129.2, 139.2 (aryl) and 185.1 (CO_2); ^{119}Sn NMR: δ −523.1.

Compound **8**: m.p. 198–202 °C (Found: C, 43.92; H, 3.33; N, 4.43. Calc. for $C_{78}H_{66}N_6O_{18}Sn_6$: C, 44.58; H, 3.17; N, 4.67%); IR (KBr) 3022, 1593, 1549, 1491, 1397, 1194, 1028, 872, 756 and 696 cm^{-1}; ^1H NMR: δ 3.13 [s, with tin satellites, 12 H, ^2J(Sn–H) = 130.7, 129.8, CH_2], 6.80–7.10 (m, 30 H, aryl), 7.50 [t, 6 H, ^3J(H–H) = 4, nicotinate H^5], 8.45 [d, 6 H, ^3J(H–H) = 4, nicotinate H^6], 8.88 [d, 6 H, ^3J(H–H) = 4 Hz, nicotinate H^4] and 9.40 (s, 6 H, nicotinate H^1); ^{13}C NMR: δ 35.4 (CH_2), 123.1–153.2 (11 lines, C_6H_5 + C_5H_4N) and 172.5 (CO_2); ^{119}Sn NMR: δ −519.8.

Compound **9**: m.p. 264–266 °C (Found: C, 44.52; H, 4.56. Calc. for $C_{72}H_{84}O_{18}Sn_6$: C, 44.36; H, 4.34%); IR (KBr) 3024, 1642, 1510, 1414, 1316, 1182, 1055, 862, 760, 694, 621 and 451 cm^{-1}; ^1H NMR: δ 1.69 and 1.79 (s each, 36 H, CH_3), 2.69 [s, with tin satellites, 12 H, ^2J(Sn–H) = 156.2, 149.2 Hz, CH_2], 5.36 (s, 6 H, Me_2C=C*H*) and 6.95–7.20 (m, 30 H, aryl); ^{13}C NMR: 22.9 (CH_3), 34.9 (CH_2), 41.9 (CH_3), 124.8–130.9 (many lines, aryl), 132.7 (Me_2*C*=CH), 138.0 (Me_2C=*C*H) and 173.6 (CO_2); ^{119}Sn NMR: δ −522.9 (s).

$[(PhCH_2)SnO\cdot O_2CCHPh_2]_6$ 10 and $Sn(CH_2Ph)_2(O_2CCHPh_2)_2$ 11. The above procedure was again followed using compound **1** (0.58 g, 1.57 mmol) and silver diphenylacetate (1.0 g, 3.13 mmol) in toluene (50 cm^3). Compound **11** was isolated from a concentrated toluene (5 cm^3) solution. Yield: 0.41 g, 36%; m.p. 188–192 °C (Found: C, 70.53; H, 4.68. Calc. for $C_{42}H_{36}O_4Sn$: C, 70.70; H, 4.85%). IR (KBr): 3027, 1591, 1493, 1452, 1379, 1240, 1053, 1030, 720, 693, 652 and 453 cm^{-1}. ^1H NMR: δ 3.0 [s, with tin satellites, 4 H, ^2J(Sn–H) ≈ 95.4 Hz, CH_2), 4.90 (s, 2H, C*H*Ph$_2$) and 6.75–7.50 (m, 30 H, aryl). ^{13}C NMR: δ 54.9 (CH_2), 60.1 (*C*HPh$_2$), 124.1–138.8 (six lines, aryl) and 182.1 (CO_2). ^{119}Sn NMR: δ −235.8.

After isolation of compound **11** the mother-liquor was stripped of all the solvent and the residue crystallized from dichloromethane–diethyl ether–hexane (2:6:3) to give **10**. Yield: 0.21 g, 31%; m.p. 236–239 °C. IR (KBr): 3027, 1597, 1555, 1493 and 1412 cm^{-1}. ^1H NMR: δ 2.55 [s, 2 H, ^2J(Sn–H) = 155, 159 Hz, CH_2], 4.55 (s, 1 H, C*H*Ph$_2$) and 6.80–7.50 (m,

Table 2 Crystal data for compounds **2**, **4**·$CHCl_3$ and **5**·$2CH_2Cl_2$

	2	**4**·$CHCl_3$	**5**·$2CH_2Cl_2$
Empirical formula	$C_{31}H_{52}O_4P_2Sn_{0.5}$	$C_{70}H_{113}Cl_3O_{12}P_4Sn_3$	$C_{32}H_{38}Cl_2O_{12}Sn_3$
M	610.04	1732.98	1041.62
M.p. (°C), colour	180, colourless	228–230, colourless	252–256, colourless
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	13.267(2)	16.018(3)	18.225(4)
b/Å	13.593(2)	19.600(4)	12.954(4)
c/Å	9.757(2)	15.492(2)	18.382(4)
α/°	96.90(2)	107.18(1)	
β/°	99.71(1)	113.80(1)	118.85(2)
γ/°	114.133(9)	80.34(2)	
U/Å^3	1547.3(5)	4244(1)	3801(1)
Z	2	2	4
D_c/g cm^{-3}	1.309	1.356	1.82
λ/Å	0.710 69	0.710 69	1.541 78
T/°C	23	23	−130
μ/cm^{-1}	5.64	10.96	173.72
F(000)	650	1780	2040
Crystal size/mm	0.4 × 0.35 × 0.1	0.3 × 0.25 × 0.5	0.3 × 0.3 × 0.4
$2\theta_{max}$/°	55.1	45.1	120.2
Reflections collected	7459	11 633	6172
Independent reflections	7147	11 151	5963
R_{int}	0.032	0.026	0.135[a]
Data [$I > 3\sigma(I)$]	5883	6299	5665
Parameters	549	460	433
R[b] [$I > 3\sigma(I)$]	0.033	0.091	0.069
R'[b]	0.039	0.121	0.052
Maximum, minimum peaks in difference map/e Å^{-3}	0.38, −0.34	2.05, −1.65	1.16, −1.08

[a] The higher R_{int} is basically due to the differences in the intensities in some very low-angle reflections. High absorption from the heavier scatterers for the Cu-Kα radiation as well as the relatively significant crystal decay during the experiment probably have contributed to the R_{int} value. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(||F_o| - |F_c||)^2/\Sigma|F_o{}^2|]^{\frac{1}{2}}$.

15 H, aryl). ^{13}C NMR: δ 34.4 (CH_2), 54.9 (CHPh$_2$), 124.2–139.3 (many lines, aryl) and 179.9 (CO_2). ^{119}Sn NMR: δ −525.0.

X-Ray crystallography

A suitable crystal of compound **2** (crystallized from dichloromethane–heptane), **4** (crystallized from chloroform–heptane) or **5** (crystallized from dichloromethane–hexane) was mounted on a glass fibre. Data were collected on a Rigaku AFC5R diffractometer using graphite-monochromated Mo-Kα (for **2** and **4**) or Cu-Kα (for **5**) radiation. Three control reflections, collected every 150, showed no significant changes in intensities. The details pertaining to data collection and refinement are listed in Table 2. The structures were solved by conventional methods[27] and refined by full-matrix least squares.[28] An empirical absorption correction was applied and the data were corrected for Lorentz-polarization effects. Neutral atom scattering and anomalous-scattering correction were taken from ref. 29. The non-hydrogen atoms were refined anisotropically and the H atoms (for **2** and **5**) included at calculated positions. In the case of **4** some of the carbon atoms of the $O_2P(C_6H_{11})_2$ groups are disordered. In particular, one C_6H_{11} group of P(3) is highly disordered. On refinement its carbon atoms moved significantly, distorting the geometry. Therefore, these carbon atoms were fixed at positions found in Fourier-difference maps. Accordingly, no attempts were made to include H atoms for refinement. In addition, the final Fourier-difference map showed some minor residual densities (1–2 e Å^{-3}), possibly corresponding to a partially occupied disordered solvent molecule. These peaks could not be modelled and therefore not included in the refinement.

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