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Review

Monoorganotin(IV) phosphonates†

Vadapalli Chandrasekhar* and Kandasamy Gopal

Department of Chemistry, Indian Institute of Technology-Kanpur, Kanpur 208016, India

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Recent progress in the assembly of monoorganotin(IV) phosphonates is reviewed. The molecular structures of these compounds and their dependence on the nature of the organotin precursor and that of the phosphonic acid are discussed. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: phosphonates; organotin compounds; organotin cages; monoorganotin; phosphonic acid; molecular phosphonates

INTRODUCTION

Organotin chemistry is experiencing a renaissance with the discovery of new rings, cages and clusters containing the organooxotin motifs in general and monoorganooxotin units in particular.[1–4] Thus, a number of structural types, such as ladder,[5] drum,[6–8] cube,[9,10] O-capped cluster,[10,11] butterfly cluster,[11,12] extended cage,[13] crown cluster,[12,13] football cage,[14,15] etc., have been discovered in the recent past. Although the interrelationship between these various structural types is not immediately obvious, it is clear that the distannoxane motif, Sn_2O_2, is a predominant building block.[4] In comparison, the simple stannoxane unit Sn–O–Sn is less frequently encountered in these various structural types. Another interesting facet of the monoorganooxotin(IV) cage/cluster synthesis is the extremely subtle dependence of the eventual structural type upon the nature of the protic acid reactant.[1,4] Thus, if the monoorganotin(IV) reagent is kept constant and the protic acid is varied from carboxylic, phosphonic, phosphinic and sulfonic acids, the eventual products are dramatically different. Further, in many cases the stoichiometry of the reaction also seems to be quite crucial in directing the choice of the final product. The varied products obtained in these reactions are illustrated in Fig. 1.

The reaction of RSn(O)OH with an excess of carboxylic acid, $R'CO_2H$, leads to the formation of the tricarboxylate, $RSn(O_2CR')_3$. The latter is extremely sensitive to hydrolysis, affording the hexameric compound $\{[RSn(O)O_2CR']_2[RSn(O_2CR')_3]\}_2$. These types of compound are found to be in a ladder-type of structural arrangement[5] (Fig. 1). However, if a 6 : 6 reaction is carried out between RSn(O)OH and $R'CO_2H$, then a hexameric drum, $[RSn(O)O_2CR']_6$, is obtained. There is an intimate interrelationship between the drum and the ladder forms. Thus, further hydrolysis of the ladder affords the drum. On the other hand, reaction of the drum with more carboxylic acid leads to the ladder formation. The drum contains a cage-like structure and is made up of two fused Sn_3O_3 six-membered rings (Fig. 1). Recently the synthetic methodology for the preparation of the drum form was utilized to assemble a hexaferrocene assembly, $[n\text{-}BuSn(O)O_2CFc]_6$, in a one-pot synthesis[7] (Eqn. (1), Fig. 1):

$$6n\text{-BuSn(O)OH} + 6C_5H_5\text{–Fe–}C_5H_4CO_2H \xrightarrow[-6H_2O]{} \underset{\textbf{Drum}}{[n\text{-BuSn(O)OC(O)}C_5H_4\text{–Fe–}C_5H_5]_6} \quad (1)$$

In contrast to the reactions of monoorganotin(IV) substrates with carboxylic acids, those involving phosphorus-based acids are much more limited.[3,4] However, the variation in product type is much more diverse in the case of the phosphorus-based acids. Thus, the reaction of *n*-BuSn(O)OH with diphenylphosphinic acid leads to the formation of a trinuclear O-capped cluster, $\{[n\text{-BuSn(OH)}O_2PPh_2]_3O\}\{O_2PPh_2\}$[10] (Eqn. (2), Fig. 1):
In contrast, the reaction of *n*-BuSn(O)OH with other diorgano phosphinic acids leads to the assembly of the tetranuclear cube derivative,[10,11] $[n\text{-BuSn(O)}O_2PR_2]_4$ (R = *t*-Bu, CH_2Ph, C_6H_{11} Eqn. (2), Fig. 1):

$$3n\text{-BuSn(O)OH} + 4Ph_2PO_2H \xrightarrow[-H_2O]{}$$

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*Correspondence to: Vadapalli Chandrasekhar, Department of Chemistry, Indian Institute of Technology-Kanpur, Kanpur 208016, India.
E-mail: vc@iitk.ac.in

†Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.

$$\{[n\text{-BuSn(OH)O}_2\text{PPh}_2]_3\text{O}\}\{\text{O}_2\text{PPh}_2\} \quad \textbf{O − Capped} \tag{2}$$

$$4n\text{-BuSn(O)OH} + 4t\text{-Bu}_2\text{PO}_2\text{H} \xrightarrow[-4\text{H}_2\text{O}]{} [n\text{-BuSn(O)O}_2\text{P}(t\text{-Bu})_2]_4 \quad \textbf{Cube} \tag{3}$$

Further variations of cluster types involve the formation of a butterfly cluster,[11] $\{n\text{-BuSn(OH)}[\text{O}_2\text{P(C}_6\text{H}_{11})_2]_2\}_2$, an extended cluster,[13] $\{(n\text{-BuSn})_4(\text{OH})_2(\text{O}_2\text{PPh}_2)_6[\text{S(O)PPh}_2]_4\}$, a crown cluster,[13] $\{[n\text{-BuSn(O)O}_2\text{P}(t\text{-Bu})_2][n\text{-BuSn(OH)}_2\text{O}_2\text{P}(t\text{-Bu})_2]\}_2[\text{H}][\text{O}_2\text{P}(t\text{-Bu})_2]$, a double cube,[16] $\{[n\text{-BuSnS(O}_2\text{PPh}_2)]_3\text{O}\}_2\text{Sn}$, etc. These various forms are realized by subtle changes in the nature and stoichiometry of the phosphorous acids (Eqn (4)–(7), Fig. 1):

$$2n\text{-BuSn(O)OH} + 4(\text{C}_6\text{H}_{11})_2\text{PO}_2\text{H} \xrightarrow[-\text{H}_2\text{O}]{} \{n\text{-BuSn(OH)}[\text{O}_2\text{P(C}_6\text{H}_{11})_2]_2\}_2 \quad \textbf{Butterfly} \tag{4}$$

$$4n\text{-BuSn(O)OH} + 6\text{Ph}_2\text{PO}_2\text{H} + 4\text{Ph}_2\text{P(S)OH} \xrightarrow[-\text{H}_2\text{O}]{} \{(n\text{-BuSn})_4(\text{OH})_2(\text{O}_2\text{PPh}_2)_6[\text{S(O)PPh}_2]_4\} \quad \textbf{ExtendedCluster} \tag{5}$$

$$4n\text{-BuSn(O)OH} + 5t\text{-Bu}_2\text{PO}_2\text{H} \longrightarrow \{[n\text{-BuSn(O)O}_2\text{P}(t\text{-Bu})_2][n\text{-BuSn(OH)}_2\text{O}_2\text{P}(t\text{-Bu})_2]\}_2[\text{H}][\text{O}_2\text{P}(t\text{-Bu})_2] \quad \textbf{Crown} \tag{6}$$

$$28n\text{-BuSn(O)OH} + 24\text{Ph}_2\text{PO}_2\text{H} + 3\text{S}_8 \xrightarrow[-24\text{H}_2\text{O}]{} 4\{[n\text{-BuSnS(O}_2\text{PPh}_2)]_3\text{O}\}_2\text{Sn} \quad \textbf{DoubleCube} \tag{7}$$

The studies of monoorganotin(IV) reagents with phosphonic acids have been more limited. Recent studies of transition-metal phosphonates point to the versatility of phosphonic acids in assisting the synthesis of a variety of layered and pillared structures.[17] Molecular phosphonates have also been attracting attention, and several molecular phosphonates have recently been isolated and structurally characterized.[18–20]

This article will summarize the results obtained in recent years in the nascent field of monoorganotin(IV) phosphonates. Although these studies are still in their infancy, they already point to the enormous structural diversity that is possible for this family of compounds.

RESULTS AND DISCUSSION

Tetranuclear organooxotin phosphonate cages

Synthetic aspects

The reaction of n-BuSn(O)OH with t-BuP(O)(OH)$_2$ leads to the exclusive formation of the tetranuclear cage compound[21] $\{(n\text{-BuSn})_2\text{O}[\text{O}_2\text{P(OH)}-t\text{-Bu}]_4\}_2$ (**1**) (Scheme 1). This may be contrasted with the products formed in the reaction of n-BuSn(O)OH with t-Bu$_2$P(O)OH, where a tetrameric cube,[11] $[n\text{-BuSn(O)O}_2\text{P}(t\text{-Bu})_2]_4$, is formed (Eqn (3), Fig. 1).

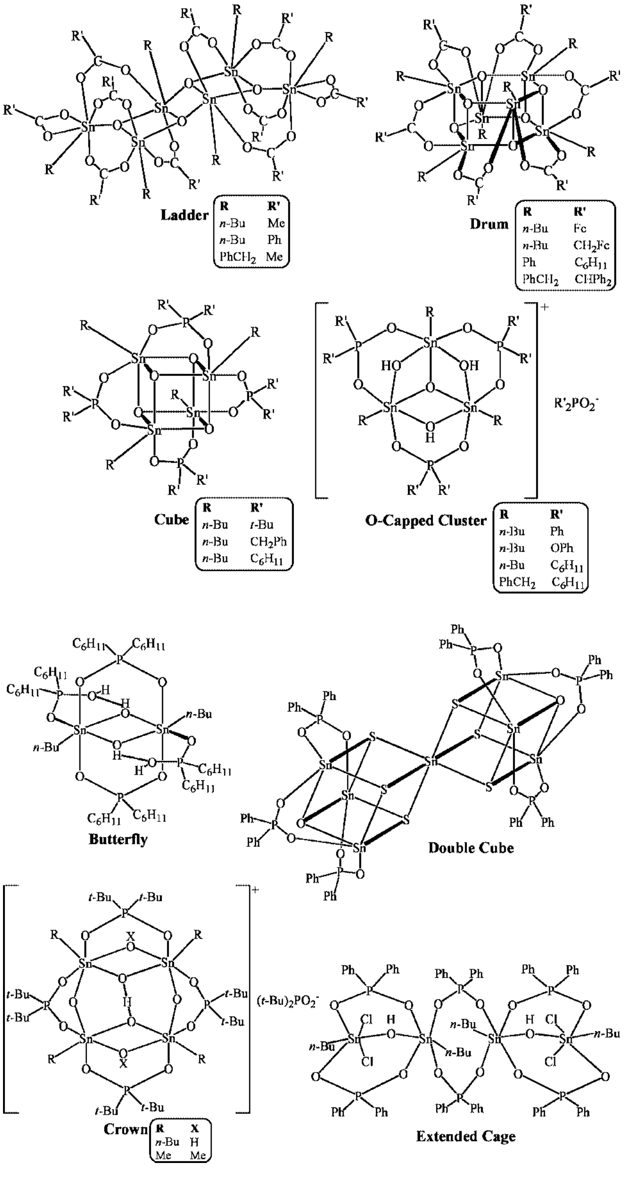
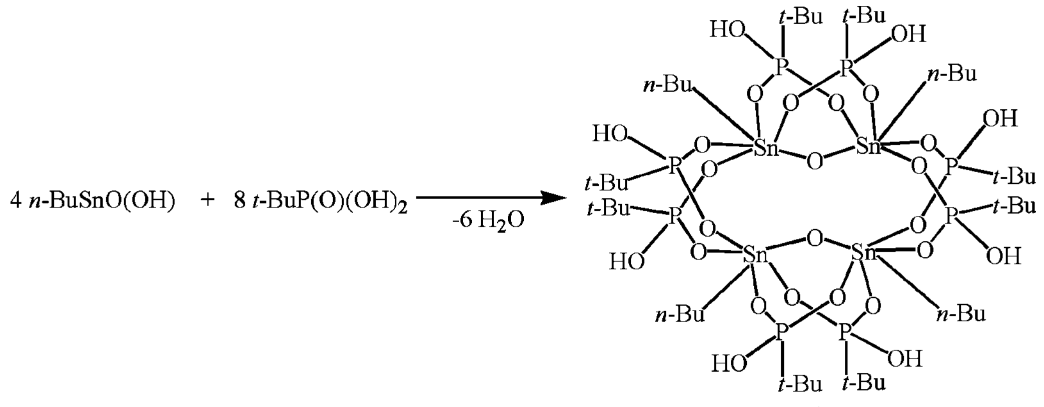


Figure 1. The various structural types formed in the reactions of monoorganotin(IV) compounds with protic acids.

The cage compound **1** is, in fact, formed in a number of reaction conditions (*vide infra*). In general, it has been observed in organooxotin chemistry that the organotin precursor assumes a structure-directing role and steers the reaction towards the eventual product.[4] For example, the reactions of mono-, di- and tri-organotin precursors with a common reactant such as a carboxylic acid leads to the formation of varied products whose molecular structures are entirely different. Even among the monoorganotin(IV) precursors, the product



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Scheme 1.

obtained tends to be different depending upon the type of precursor used. To cite a recent example, whereas the reaction of *n*-BuSn(O)OH with $FcCO_2H$ (Fc = $-C_5H_4-Fe-C_5H_5$) leads to the hexameric drum[7] [*n*-BuSn(O)O_2CFc$]_6$ (Eqn (1), Fig. 1), the analogous reaction with *n*-BuSn$(OH)_2$Cl affords the trinuclear derivative[22] {[*n*-BuSnCl$(O_2CFc)_3$](O)(OH)} (Fig. 2).

In view of these reactivity differences, the reactions of *n*-BuSn(O)OH and *n*-BuSn$(OH)_2$Cl with various kinds of phosphonate ligands, such as *t*-BuP(O)$(OH)_2$, *t*-BuP(O)(OH)$(OSiMe_3)$ and *t*-BuP(O)$(OSiMe_3)_2$, were investigated.[23] Interestingly, in all these reactions we were only able to isolate a single product, viz. compound **1** (Scheme 2; Table 1). In order to test whether the reaction proceeds in solvent-less conditions as well, we investigated the synthesis of **1** in the absence of any solvent.[24] Typically, grinding *n*-BuSn(O)OH with *t*-BuP(O)$(OH)_2$ at room temperature was quite effective for assembling **1** in over 90% yield (Table 1, entry 14).

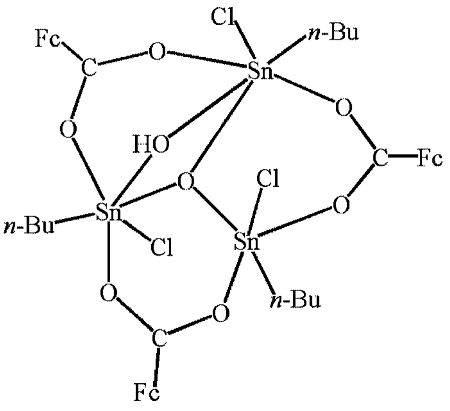
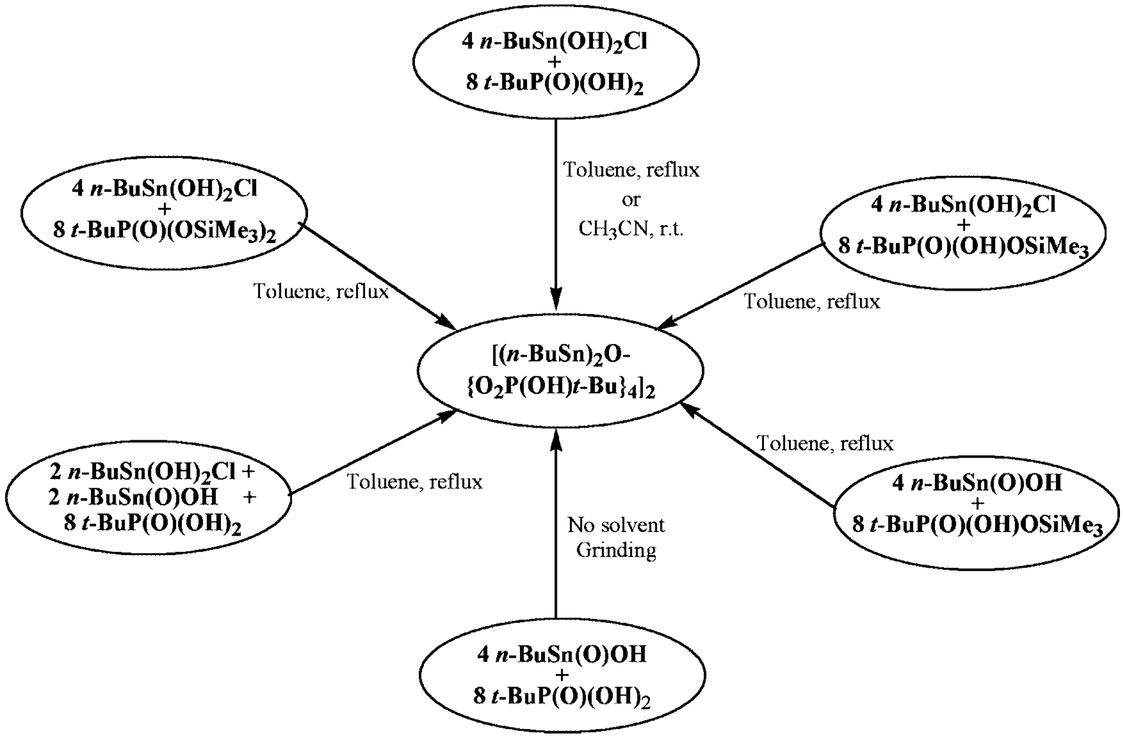


Figure 2. The trinuclear derivative {[*n*-BuSnCl$(O_2CFc)_3$](O)(OH)}.

Table 1. Formation of the tetranuclear cage under various reaction conditions

S.	Reactants		Reaction	Experimental conditions		Yield
no.	Organotin precursor	Phosphonate substrate	stoichiometry	Solvent	Conditions	(%)
1	*n*-BuSn$(OH)_2$Cl	*t*-BuP(O)$(OH)_2$	1:2	Toluene	RT	80
2	*n*-BuSn$(OH)_2$Cl	*t*-BuP(O)$(OH)_2$	1:2	Toluene	Reflux	80
3	*n*-BuSn$(OH)_2$Cl	*t*-BuP(O)$(OH)_2$	1:2	Acetonitrile	RT	78
4	*n*-BuSn$(OH)_2$Cl	*t*-BuP(O)$(OH)_2$	2:3	Toluene	Reflux	63
5	*n*-BuSn$(OH)_2$Cl	*t*-BuP(O)$(OH)_2$	2:3	Acetonitrile	RT	65
6	*n*-BuSn$(OH)_2$Cl	*t*-BuP(O)$(OH)_2$	3:4	Toluene	Reflux	57
7	*n*-BuSn$(OH)_2$Cl	*t*-BuP(O)$(OH)_2$	3:4	Acetonitrile	RT	58
8	*n*-BuSn$(OH)_2$Cl	*t*-BuP(O)$(OH)_2$	1:1	Toluene	Reflux	43
9	*n*-BuSn$(OH)_2$Cl	*t*-BuP(O)$(OH)_2$	1:1	Acetonitrile	RT	41
10	*n*-BuSn(O)OH	*t*-BuP(O)(OH)$(OSiMe_3)$	1:2	Toluene	Reflux	71
11	*n*-BuSn$(OH)_2$Cl	*t*-BuP(O)(OH)$(OSiMe_3)$	1:2	Toluene	Reflux	73
12	*n*-BuSn$(OH)_2$Cl	*t*-BuP(O)$(OSiMe_3)_2$	1:2	Toluene	Reflux	73
13	*n*-BuSn$(OH)_2$Cl and *n*-BuSn(O)OH	*t*-BuP(O)$(OH)_2$	0.5:0.5:2	Toluene	Reflux	81
14	*n*-BuSn(O)OH	*t*-BuP(O)$(OH)_2$	1:2	Solventless	RT, grinding	92



Scheme 2.

Other methods of preparing the tetranuclear cages are also known.[21] Thus, the reaction of the carboxylate ladder cluster $[(MeSn(O)O_2CCHMe_2)_2MeSn(O_2CCHMe_2)_3]_2$ with t-$BuP(O)(OH)_2$ leads to the liberation of the carboxylic acid and the formation of the phosphonate cage, $\{(MeSn)_2O[O_2P(OH)\text{-}t\text{-}Bu]_4\}_2$ (**2**) (Eqn (8)):

$$2[(MeSn(O)O_2CCHMe_2)_2MeSn(O_2CCHMe_2)_3]_2 + 24t\text{-}BuP(O)(OH)_2 \xrightarrow[-2H_2O]{} 3\{(MeSn)_2O[O_2P(OH){-}t\text{-}Bu]_4\}_2 + 20Me_2CHCO_2H \quad \underset{\mathbf{2}}{} \qquad (8)$$

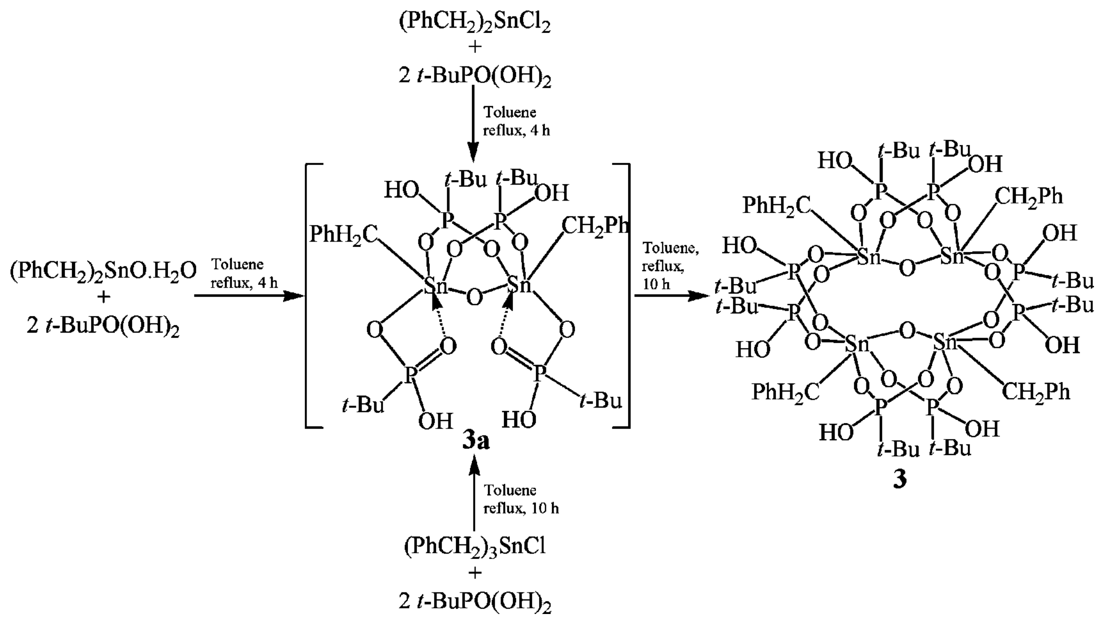
More recently, we have utilized the debenzylation reaction as a general strategy for preparing the organooxotin cage[25] $\{(PhCH_2Sn)_2O[O_2P(OH){-}t\text{-}Bu]_4\}_2$ (**3**). A controlled Sn–C bond scission reaction has been utilized as a synthetic tool for assembling many organotin compounds. Among various organotin(IV) derivatives, benzyltin compounds are most susceptible to Sn–C bond cleavage. Taking advantage of this feature, we carried out the reactions of $(PhCH_2)_2SnCl_2$, $(PhCH_2)_2SnO \cdot H_2O$ and $(PhCH_2)_3SnCl$. Interestingly, in these reactions, irrespective of the choice of the starting material (tri- or di-benzyltin(IV) derivative), the final product remains the same, viz. the tetranuclear cage **3** (Scheme 3).[25]

The ^{119}Sn NMR spectrum of the cage compound shows a triplet of triplets with a chemical shift of −661.6 ppm, indicating that all the tin centers are equivalent. The multiplet pattern in the ^{119}Sn NMR arises from the coupling of the tin centers with two equivalent sets of a pair of phosphorus centers. This is consistent with the ^{31}P NMR spectrum of **3**, which shows resonances at +32.2 and at +23.2 ppm. During the course of the conversion of the benzyltin precursors to the cage product **3**, we were able to identify, by NMR, the formation of a half-cage intermediate **3a**.[25] The latter compound shows ^{31}P NMR resonances at 33.7 and 31.8 ppm. The conversion of **3a** to the cage **3** can be monitored by the disappearance of the ^{31}P resonances (**3a**) and the appearance of new signals (**3**); ^{119}Sn NMR also can be utilized for this process. The ^{31}P and ^{119}Sn NMR data for the tetranuclear monoorganooxotin cages are summarized in Table 2.

A slightly different tetranuclear cage, $\{Me_2Sn_2(OH)[O_2P(OPh)_2]_3[O_3P(OPh)]\}_2$ (**4**),[21] is obtained in the controlled hydrolysis of $MeSn[O_2P(OPh)_2]_3$ (Scheme 4). Although all the tin centers are equivalent in this compound and show a resonance at −602.0 ppm, four different phosphorous environments are present in **4**. This compound does not have any phosphonate ligands, but it is included here because of its similarity with organotin phosphonates. Compound **4** contains six phosphinate ligands and two phosphate ligands. The coordination aspects of these ligands towards tin will be discussed *vide infra*.

Molecular structures of the tetranuclear cages

The molecular structures of compounds **1**–**3** have been determined by X-ray crystallography and are nearly similar.[21,25] Although the core structure of **4** is similar to



Scheme 3.

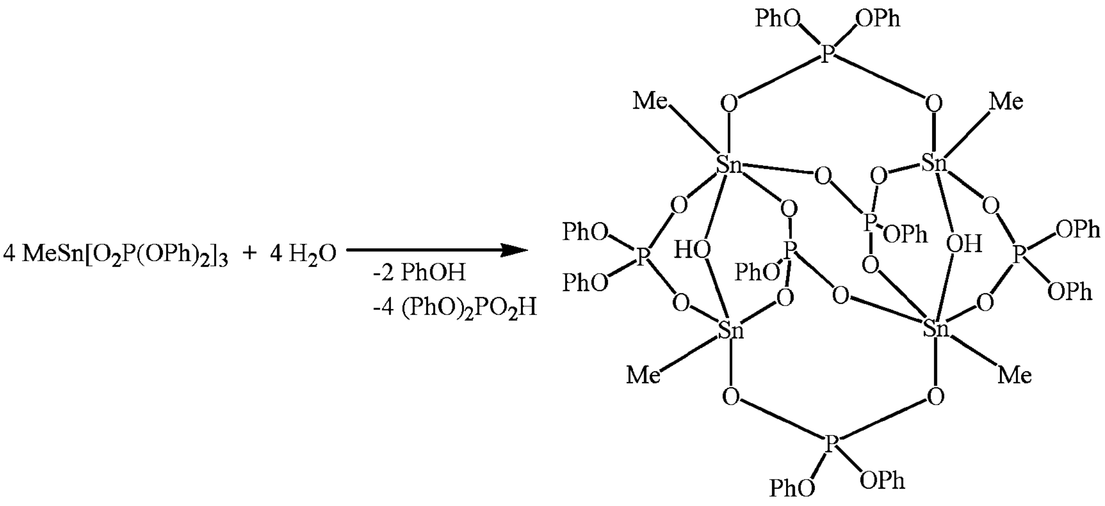
Table 2. ^{119}Sn and ^{31}P NMR data for tetranuclear organooxotin cages

Compound	δ^{119}Sn	δ^{31}P	Ref.
$\{(n\text{-BuSn})_2O[O_2P(OH)\text{-}t\text{-Bu}]_4\}_2$ (**1**)	−630.4 (tt; ^2J[Sn–O–P], 239, 287 Hz)	30.1 (s; $^2J^{119}$Sn–^{31}P, 239 Hz) 21.4 (s; $^2J^{119}$Sn–^{31}P, 286 Hz)	21, 23, 24
$\{(MeSn)_2O[O_2P(OH)\text{-}t\text{-Bu}]_4\}_2$ (**2**)	−603.5 (m)	29.8 (s; $^2J^{119}$Sn–^{31}P, 215 Hz) 21.9 (s; $^2J^{119}$Sn–^{31}P, 229 Hz)	21
$\{(PhCH_2Sn)_2O[O_2P(OH)\text{-}t\text{-Bu}]_4\}_2$ (**3**)	−661.6 (tt; ^2J[Sn–O–P], 244, 295 Hz)	32.2 (s; $^2J^{119}$Sn–^{31}P, 246 Hz) 23.2 (s; $^2J^{119}$Sn–^{31}P, 293 Hz)	25
$\{Me_2Sn_2(OH)[O_2P(OPh)_2]_3[O_3P(OPh)]\}_2$ (**4**)	−602.0 (m)	−12.6 (s; POPh; $^2J^{119}$Sn–^{31}P, 241 Hz) −17.0 (s; $P(OPh)_2$; $^2J^{119}$Sn–^{31}P, 177 Hz) −17.8 (s; $P(OPh)_2$; $^2J^{119}$Sn–^{31}P, 228 Hz) −23.9 (s; $P(OPh)_2$; $^2J^{119}$Sn–^{31}P, 243 Hz)	21

that of the cages **1**–**3**, the mode of binding of the ligands is different.[21]

The molecular structures of compounds **1**–**4** is made up of two Sn–O–Sn units. These stannoxane units are stitched together by eight phosphonate ligands. First, each half is bridged by a pair of mono deprotonated phosphonic acids, $[t\text{-BuP(OH)O}_2]^-$. These halves are further bridged by two other pairs of $[t\text{-BuP(OH)O}_2]^-$ ligands. Thus, overall, each of the eight ligands is involved in a bridging coordination mode to two tin centers. Further, one hydroxyl group remains free on each phosphorus. This arrangement leads to an overall cage-type of architecture (Scheme 3, compound **3**). A representative core structure of these cage molecules is illustrated by the example of $\{(PhCH_2Sn)_2O(O_2P(OH)\text{-}t\text{-Bu}]_4\}_2$ (**3**), as shown in Fig. 3.[25] The average Sn–O bond distances in **3** are 2.117(2) Å (for Sn–O–Sn) and 2.079(2) Å (for Sn–O–P), and the average P–O bond distances are 1.520(3) Å (for P–O–Sn) and 1.545(3) Å (for P–OH). The Sn–O–Sn bond angle in **3** is 135.17(10)°.

The structure of **4** is slightly different from that of **1** and **3**. Compound **4** also contains two ditin motifs. The two tins are, however, bridged by a μ-OH (Sn–OH–Sn). Further, all of the tin centers are connected by two symmetrical phosphonates, which function as tripodal ligands and are involved in linking three tins. This is in contrast to **1** and **3**, where the phosphonates are involved in connecting two tins



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Scheme 4.

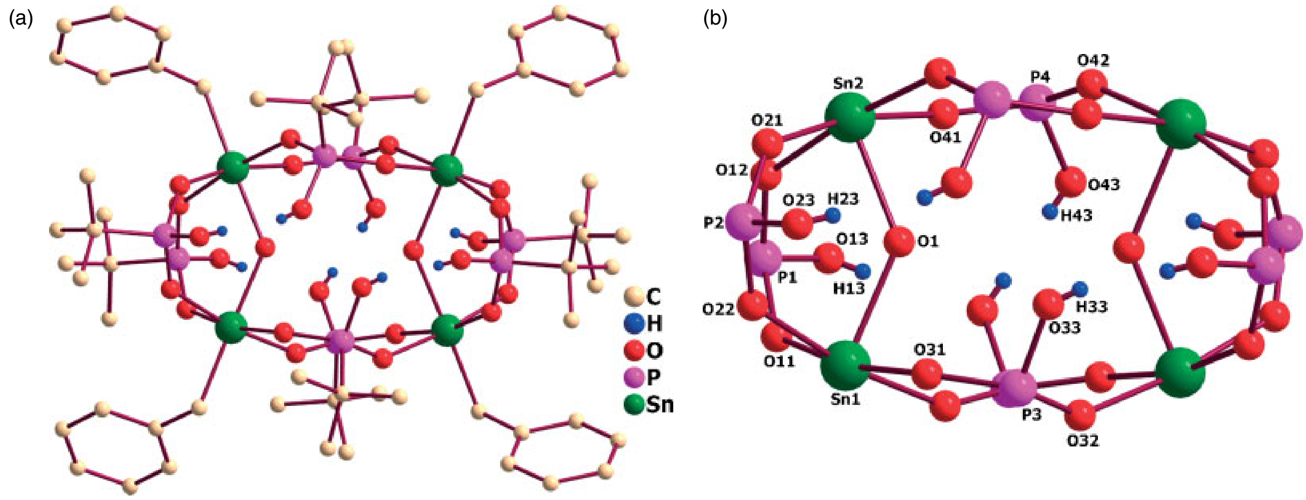


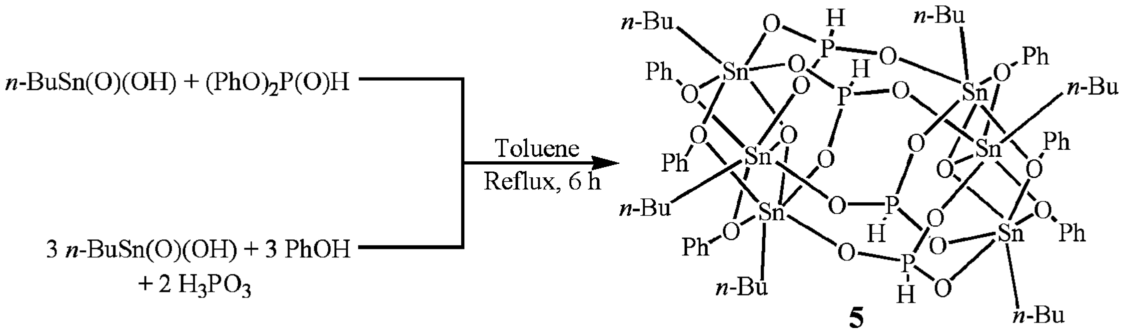
Figure 3. (a) X-ray structure of $\{(PhCH_2Sn)_2O[O_2P(OH)\text{-}t\text{-}Bu]_4\}_2$ (**3**). (b) View of the core in the X-ray structure of **3**. The unlabeled atoms are related by symmetry to the labeled atoms.

through two oxygen centers. Further, the molecular structure of **4** contains six R_2PO_2 ligands ($R = OPh$); Four of these are bidentate and are involved in connecting two adjacent tins, and two other R_2PO_2 ligands are monodentate and are present on two antipodal tin centers.

Double O-capped cluster

The reaction of *n*-BuSn(O)OH with $(PhO)_2P(O)H$ in the presence of sulfur was carried out to probe the formation of a double-cube. However, we discovered that this reaction proceeds to afford an unprecedented product involving an *in situ* P–O bond cleavage leading to the generation of an $[HPO_3]^{2-}$ ion along with phenol. The reaction of these *in-situ*-generated reagents with *n*-BuSn(O)OH leads to the formation of $\{[(n\text{-}BuSn)_3(PhO)_3O]_2(O_3PH)_4\}$ (**5**).[26] We carried out a more direct reaction involving *n*-BuSn(O)OH, phenol and H_3PO_3 and were able to isolate compound **5** in improved yields (Scheme 5).

The X-ray crystal structure of **5** revealed that it also possesses a cage-type structure (Fig. 4). Compound **5** contains two tri-tin motifs in the form of $[(n\text{-}BuSn)_3(PhO)_3O]$ that are linked to each other by four tripodal HPO_3 ligands.[26] The cage can be described as possessing two poles (in the form of the three tins held together by μ_3-O) and an equator (in the form of four HPO_3 ligands). Further, each pole also contains three phenoxide ions functioning as bridging ligands. The average Sn–O(μ_3) bond distance is 2.065 Å and the average Sn–O(μ_2) bond length is 2.172 Å.



Scheme 5.

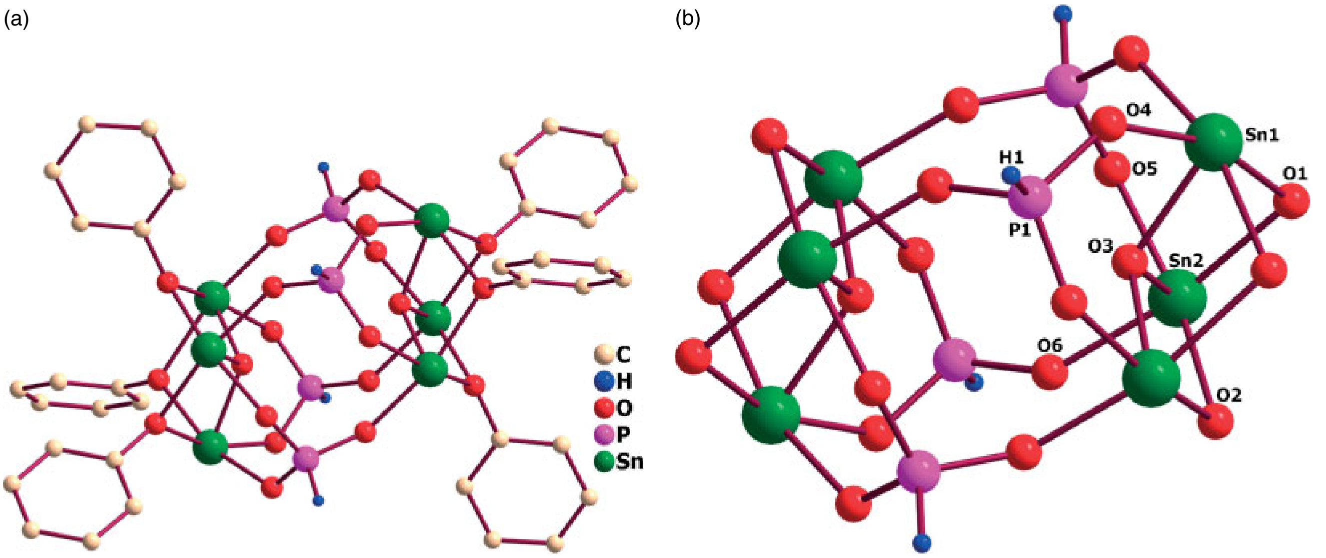


Figure 4. (a) X-ray structure of $\{[(n\text{-BuSn})_3(\text{PhO})_3\text{O}]_2(\text{O}_3\text{PH})_4\}$ (**5**). (b) View of the core in the X-ray structure of **5**. The unlabeled atoms are related by symmetry to the labeled atoms.

The molecular structure of **5** is closely related to other structural forms that are known in organooxotin chemistry.[26] Thus, the overall dimensions of cage **5** are very nearly similar to that of the football cage[14,15] $[(n\text{-BuSn})_{12}(\text{O})_{14}(\text{OH})_6][\text{X}]_2$, where $\text{X} = \text{OH}^-$, CH_3CO_2^-, 4-CH_3–C_6H_4–SO_3^-, Cl^- and $[\text{Ph}_2\text{PO}_2]^-$. Although the football cage is dodecanuclear it also possesses two poles in the form of Sn_3 units. The equator is made up of an $[(\text{RSn})_6\text{O}_{12}]$ motif.[14,15] Despite the vastly different equators in the football cage and **5**, the molecular dimensions in these two cages are very similar. Thus, the distance between diametrically opposite tin atoms (in the equator) in the football cage is 6.407 Å. In **5** the corresponding separation (between the bridging phosphorus centers) is 6.337 Å. The inter-polar μ_3-O distance in the football cage is 3.778 Å and in **5** it is 3.987 Å. The structure of **5** is also related to other structural types known in organooxotin compounds, in particular to the O-capped cluster. Thus, the reaction of n-BuSn(O)OH with $\text{Ph}_2\text{P(O)OH}$ affords the trinuclear O-capped cluster $\{[n\text{-BuSn(OH)O}_2\text{PPh}_2]_3\text{O}\}\{\text{O}_2\text{PPh}_2\}$ (Eqn (2), Fig. 1). The same structural motif is present in the pole region of cage **5**.

SUMMARY

Monoorganotin phosphonates are an emerging family of compounds possessing interesting molecular structures. The multiple functionality of the phosphonic acid and the resultant phosphonate ligands allows these versatile ligands to bind in diverse modes to the organotin motifs. The intrinsic structural plasticity of the organostannoxane units is greatly augmented by the varied binding modes of the phosphonate ligands. This favorable combination is likely to yield rewarding results in terms of new structural types for this family of compounds.

Acknowledgments

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