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Asymmetric Pentameric and Tetrameric Organooxotin Clusters: Insights into Their Formation through Partial Dearylation

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The reaction between diphenyltin dichloride and 2,6-diisopropylphenylphosphate (dippH_2) in ethanol affords a highly asymmetric pentameric organotin cluster, $[Sn_5Ph_7(\mu_3\text{-dipp})_4(\mu\text{-dippH})(\mu_3\text{-O})(\mu\text{-OEt})(EtOH)(H_2O)Cl]\cdot H_2O$ (**1**), that contains Ph^-, EtO^-, Cl^-, O^{2-}, $ROPO_3^{2-}$, $ROPO_3H^-$, OH_2, and EtOH ligands. The same reaction when carried out in *i*PrOH, under otherwise identical conditions, results in the formation of another pentamer, $[Sn_5Ph_7(\mu_3\text{-dipp})_4(\mu\text{-dippH})(\mu_3\text{-O})(\mu\text{-OH})(i\text{PrOH})(H_2O)Cl]\cdot i\text{PrOH}$ (**2**). Change of the phosphate ligand to sterically less bulky 2,6-dimethylphenylphosphate in the above reaction carried out in ethanol results in the formation of a tetrameric cluster, $[Sn_4Ph_5(\mu_3\text{-dmpp})_2(\mu\text{-dmpp})(\mu\text{-dmppH})_2(\mu_3\text{-O})(\mu\text{-OEt})(EtOH)]\cdot EtOH$ (**3**). Isolation of **3** provides useful insights into the formation of the pentamers **1** and **2**. Compounds **1**−**3** have been characterized by means of their analytical data, IR, and multinuclear NMR (^1H, ^{31}P, and ^{119}Sn) spectral data. The solid-state structures of **1**−**3** have been determined by X-ray diffraction studies.

Introduction

The last few decades have seen intense activity in the area of organooxotin clusters in view of the structural diversity shown by this type of compound, their use as building blocks in supramolecular chemistry, and their ability to catalyze organic transformations.[1,2] Exploiting the reaction between a suitable organotin precursor and protic acids (such as carboxylic, phosphinic, phosphonic, phosphoric, and sulfonic acids), several types of organooxtin clusters having a tin-oxo core resembling ladder, double-ladder, triple-ladder, drum, cube, butterfly, and football structures have been synthesized.[1–5] The nuclearity of these clusters often varies from trimeric to octadecameric. While clusters made up of an even number of tin atoms are very common, clusters with an odd number of tin atoms are conspicuous by their absence or rarity (e.g., 5, 7, and 9 clusters). Similarly, irrespective of the nuclearity of the cluster, almost all examples reported are symmetric structures incorporating mirror planes and inversion centers.

While the cluster-forming reactions involving phosphinic and phosphonic acids have been well investigated in organooxotin chemistry,[4,5] the usage of monoester phosphoric acid for this purpose is largely unexplored.[6–8] Although both RPO_3H_2 and $(RO)PO_3H_2$ are very similar in terms of their ability to bind to metal ions through the $-PO_3^{2-}$ fragment, the actual structures obtained from these two types of compounds are very different, as shown by us recently in the case of zinc and aluminum phosphate chemistry.[9,10] In order to explore the possibility of unravelling newer structural types in organooxotin chemistry, we have now investigated the reactions of Ph_2SnCl_2 with phosphate monoesters. The results of this investigation are reported herein.

Results and Discussion

Synthesis and Characterization of 1 and 2. An equimolar reaction between 2,6-diisopropylphenyl phosphate (dippH_2) and Ph_2SnCl_2 in ethanol at room temperature leads to the formation of the pentameric tin cluster $[Sn_5Ph_7(\mu_3\text{-dipp})_4(\mu\text{-dippH})(\mu_3\text{-O})(\mu\text{-OEt})(EtOH)(H_2O)Cl]\cdot H_2O$ (**1**) in 60% yield as single crystals (Scheme 1). The IR spectrum of **1** shows a strong absorption at 1131 cm^{-1} corresponding to the Sn−O−P stretching vibration. The broad absorption observed at 3435 cm^{-1} is indicative of the presence of either H_2O and/or OH groups in the molecule. The NMR spectra (^1H, ^{31}P, and ^{119}Sn)

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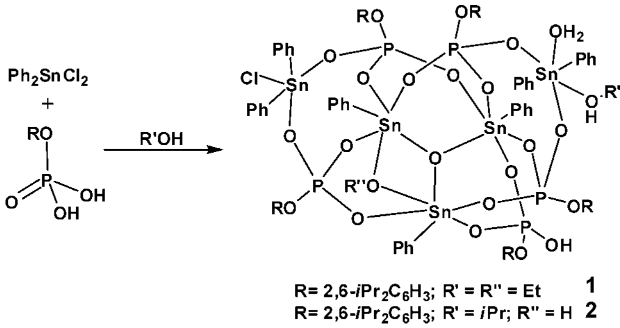
Scheme 1. Synthesis of 1 and 2



of **1** show very broad resonances with unresolved coupling constants (*vide infra*). The integrated intensities of various resonances in the ^{1}H NMR spectrum however match with the formulation of the cluster.

Due to the asymmetric structure of **1**, we sought to examine the generality of this reaction. Since the solvent ethanol also participates in the product formation in **1**, we chose to vary the solvent medium (to 2-propanol) and carried out the reaction under otherwise identical conditions (Scheme 1). The reaction proceeds in a similar fashion, and compound $[Sn_5Ph_7(\mu_3\text{-dipp})_4(\mu\text{-dippH})(\mu_3\text{-O})(\mu\text{-OH})(i\text{PrOH})\,(H_2O)Cl]\cdot i\text{PrOH}$ (**2**) has been isolated in 42% yield. Compound **2** not only crystallizes in the same space group but also possesses similar structural and spectroscopic features to those of **1**.

Molecular Structure of 1 and 2. Compound **1**, which crystallizes in the orthorhombic space group $P2_12_12_1$, is a hitherto unknown pentameric cluster in organooxotin chemistry (Figure 1). Unlike many large clusters of tin known in the literature, compound **1** lacks any mirror or rotational symmetry (C_1). The fact that the five tin atoms in the molecule exhibit five different coordination geometries explains the extent of asymmetry in the molecule. The first set of tin atoms, Sn1, Sn2, and Sn3, not only has undergone a partial dearylation reaction by the loss of one phenyl ring each[11] but has also formed a central $Sn_3(\mu_3\text{-O})$ unit around which the entire cluster is built. The tin atoms Sn4 and Sn5 form the second set where both phenyl rings on the tin remain intact in the product (although the final geometries of these two tin atoms are very different). In order to maintain the charge balance due to the loss of phenyl rings, additional ligands such as O^{2-} and EtO^- coordinate to the central Sn_3 unit. The coordinative unsaturation on the periphery of the cluster is compensated by additional neutral ligands (water and ethanol). As a result, the cluster contains, apart from five metals and four dipp and one dippH, additional ligands such as oxide, ethoxide, water, chloride, and phenyl groups.

Tin atoms Sn1, Sn2, Sn3, and Sn5 are octahedral. Although Sn1 and Sn2 seem to have identical coordination environments, one of the three phosphate oxygen atoms bound to Sn2 originates from a singly deprotonated dippH ligand (P5). Similarly, Sn3 is different from Sn1 and Sn2 by the absence of OEt coordination, which is however compensated by an extra phosphate oxygen binding. The peripheral Sn5 is bound to one ethanol and one water molecule apart from two phosphate oxygen atoms and two phenyl rings. The second peripheral tin (Sn4) is the only pentacoordinate metal (*tbp*) in the cluster, which is surrounded by two phenyl and chloride ligands apart from the two phosphate oxygen atoms (Figure 1). The Sn−O distances involving the μ_3-O^{2-} ion are similar, although not equal (Sn(1)−O(1) 2.099(5), Sn(2)−O(1) 2.103(5), and Sn(3)−O(1) 2.066(5) Å). The P(5)−O(24) distance (1.550(6) Å) of the dippH ligand is longer than all other P−O(Sn) distances (av 1.517 Å) in the molecule. The average Sn−O distance involving the μ_2-OEt is 2.089 Å. The Sn−O bond distance involving the terminal EtOH (2.330(7) Å) is longer than the Sn−O distance involving the bridging EtOH. Two of the three Sn−O−Sn bond angles in the tritin subunit are different from the third angle (Sn(1)−O(1)−Sn(2) 104.0(2)°, Sn(1)−O(1)−Sn(3) 126.2(2)28°, Sn(2)−O(1)−Sn(3) 126.9(2)°). The Sn(1)−O(2)−Sn(2) bond angle involving μ_2-OEt is 104.1(3)°, which is smaller than that of the tritin subunit.

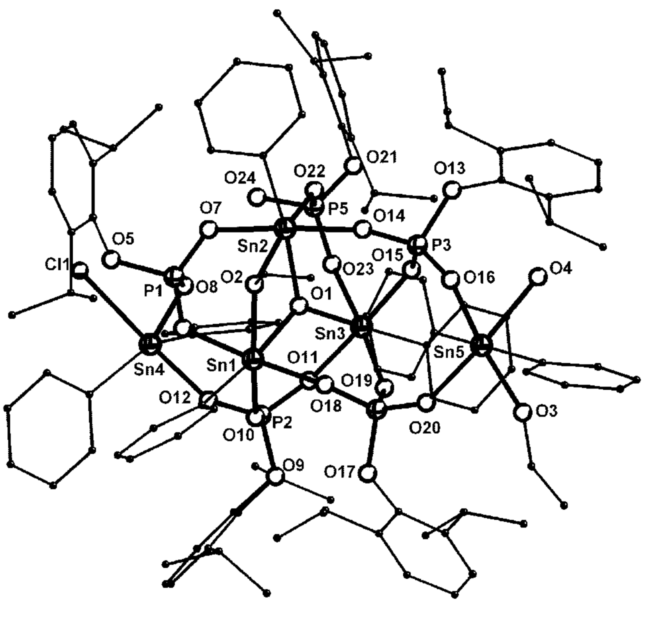


Figure 1. Molecular structure of **1**. The solvent molecule and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)−O(1) 2.092(5), Sn(1)−O(2) 2.116(6), Sn(1)−O(6) 2.116(5), Sn(1)−O(10) 2.054(6), Sn(1)−O(18) 2.057(5), Sn(2)−O(14) 2.051(5), Sn(2)−O(22) 2.081(5), Sn(2)−O(2) 2.086(5), Sn(2)−O(1) 2.105(5), Sn(2)−O(7) 2.115(5), Sn(3)−O(19) 2.066(5), Sn(3)−O(1) 2.071(5), Sn(3)−O(11) 2.077(5), Sn(3)−O(15) 2.097(6), Sn(3)−O(23) 2.113(5), Sn(4)−O(8) 2.016(7), Sn(4)−O(12) 2.097(6), Sn(4)−Cl(1) 2.549(3), Sn(5)−O(16) 2.065(5), Sn(5)−O(20) 2.091(5), Sn(5)−O(3) 2.328(7), Sn(5)−O(4) 2.326(7); O(10)−Sn(1)−O(18) 94.0(2), O(10)−Sn(1)−O(1) 90.3(2), O(18)−Sn(1)−O(1) 88.6(2), O(10)−Sn(1)−O(2) 163.5(2), O(18)−Sn(1)−O(2) 92.0(2), O(1)−Sn(1)−O(2) 74.6(2), O(10)−Sn(1)−O(6) 86.1(2), O(18)−Sn(1)−O(6) 175.2(2), O(1)−Sn(1)−O(6) 86.6(2), O(2)−Sn(1)−O(6) 86.6(2), O(14)−Sn(2)−O(22) 90.6(2), O(14)−Sn(2)−O(2) 94.0(2), O(22)−Sn(2)−O(2) 164.2(2), O(14)−Sn(2)−O(1) 90.3(2), O(22)−Sn(2)−O(1) 90.0(2), O(2)−Sn(2)−O(1) 74.9(2), O(14)−Sn(2)−O(7) 174.3(2), O(22)−Sn(2)−O(7) 85.1(2), O(2)−Sn(2)−O(7) 89.1(2), O(1)−Sn(2)−O(7) 86.0(2), O(19)−Sn(3)−O(1) 89.0(2), O(19)−Sn(3)−O(11) 90.1(2), O(1)−Sn(3)−O(11) 89.0(2),O(19)−Sn(3)−O(15) 91.6(2), O(1)−Sn(3)−O(15) 88.4(2), O(11)−Sn(3)−O(15) 176.9(2), O(19)−Sn(3)−O(23) 175.1(2), O(1)−Sn(3)−O(23) 86.3(2), O(11)−Sn(3)−O(23) 88.3(2), O(15)−Sn(3)−O(23) 89.8(2), O(8)−Sn(4)−O(12) 88.8(2), O(16)−Sn(5)−O(20) 95.5(2), O(16)−Sn(5)−O(3) 173.4(2), O(20)−Sn (5)−O(3) 91.1(2), O(16)−Sn(5)−O(4) 80.6(2), O(20)−Sn(5)−O(4) 175.6(2), O(3)−Sn(5)−O(4) 92.8(2), Sn(3)−O(1)−Sn(1) 126.3(2), Sn(3)−O(1)−Sn(2) 126.6(2), Sn(1)−O(1)−Sn(2) 104.2(2), Sn(2)−O(2)−Sn(1) 104.0(2).

The crystal structure determination of compound **2** reveals the replacement of the −OEt ligand by a bridging −OH group

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[11] Cleavage of Sn−Ph bonds has been recently reviewed. See ref 4a. In the present case the phenyl groups are lost as benzene.

[12] Under identical reaction conditions using the same concentration of reactants, compound **3** crystallizes out within 4 days, while compound **1** crystallizes only after 6 days.

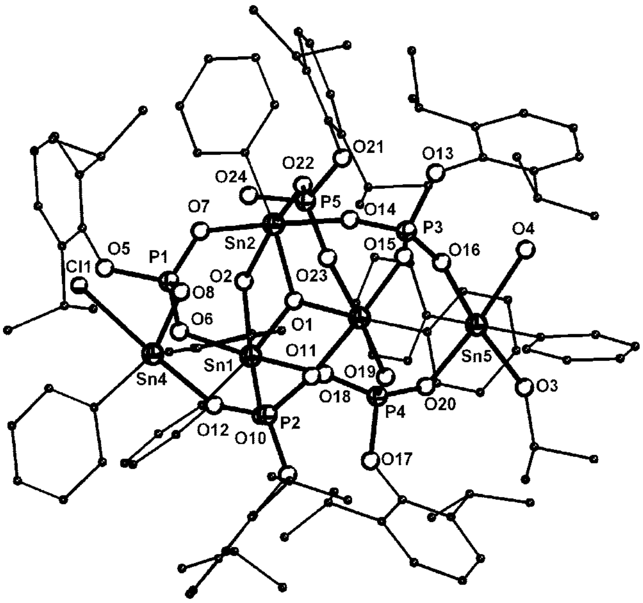
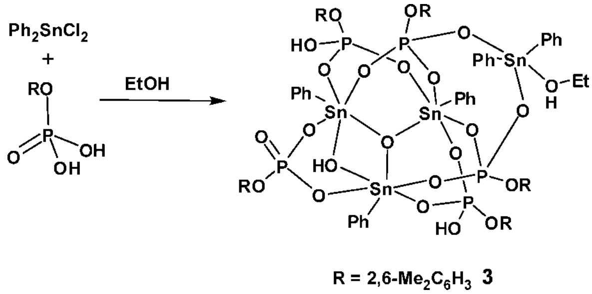


Figure 2. Molecular structure of **2**. The solvent molecule and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)−O(10) 2.060(5), Sn(1)−O(18) 2.081(5), Sn(1)−O(1) 2.100(4), Sn(1)−O(2) 2.110(5), Sn(1)−O(6) 2.120(5), Sn(2)−O(14) 2.060(5), Sn(2)−O(22) 2.076(4), Sn(2)−O(7) 2.092(5), Sn(2)−O(1) 2.102(4), Sn(2)−O(2) 2.114(5), Sn(3)−O(1) 2.063(4), Sn(3)−O(11) 2.094(5), Sn(3)−O(19) 2.096(5), Sn(3)−O(15) 2.099(5), Sn(3)−O(23) 2.122(5), Sn(4)−O(8) 2.006(6), Sn(4)−O(12) 2.104(5), Sn(4)−Cl(1) 2.563(2), Sn(5)−O(16) 2.077(5), Sn(5)−O(20) 2.096(5), Sn(5)−O(3) 2.311(6), Sn(5)−O(4) 2.348(6); O(10)−Sn(1)−O(18) 93.6(2), O(10)−Sn(1)−O(1) 89.84(18), O(18)−Sn(1)−O(1) 87.90(18), O(10)−Sn(1)−O(2) 164.9(2), O(18)−Sn(1)−O(2) 91.5(2), O(1)−Sn(1)−O(2) 76.15(17), O(10)−Sn(1)−O(6) 87.6(2), O(18)−Sn(1)−O(6) 174.82(19), O(1)−Sn(1)−O(6) 87.09(18), O(2)−Sn(1)−O(6) 86.1(2), O(14)−Sn(2)−O(22) 90.98(19), O(14)−Sn(2)−O(7) 174.45(19), O(22)−Sn(2)−O(7) 84.95(19), O(14)−Sn(2)−O(1) 90.26(18), O(22)−Sn(2)−O(1) 90.12(17), O(7)−Sn(2)−O(1) 85.97(19), O(14)−Sn(2)−O(2) 93.6(2), O(22)−Sn(2)−O(2) 165.45(19), O(7)−Sn(2)−O(2) 89.5(2), O(1)−Sn(2)−O(2) 76.01(18), O(1)−Sn(3)−O(11) 88.96(18), O(1)−Sn(3)−O(19) 89.17(18), O(11)−Sn(3)−O(19) 90.2(2), O(1)−Sn(3)−O(15) 88.12(17), O(11)−Sn(3)−O(15) 176.62(19), O(19)−Sn(3)−O(15) 91.4(2), O(1)−Sn(3)−O(23) 86.78(18), O(11)−Sn(3)−O(23) 88.57(19), O(19)−Sn(3)−O(23) 175.8(2), O(15)−Sn(3)−O(23) 89.6(2), O(8)−Sn(4)−O(12) 89.84(19), O(16)−Sn(5)−O(20) 94.86(19), O(16)−Sn(5)−O(3) 173.0(2), O(20)−Sn(5)−O(3) 91.8(2), O(16)−Sn(5)−O(4) 79.8(2), O(20)−Sn(5)−O(4) 174.0(2), O(3)−Sn(5)−O(4) 93.6(2), Sn(3)−O(1)−Sn(1) 126.7(2), Sn(3)−O(1)−Sn(2) 127.1(2), Sn(1)−O(1)−Sn(2) 103.29(19), Sn(1)−O(2)−Sn(2) 102.5(2).

Scheme 2. Synthesis of 3



and the substitution of an ethanol molecule on Sn5 by a 2-propanol molecule (Figure 2). Since the other structural features are very similar, a more detailed discussion on the structure of **2** is not warranted.

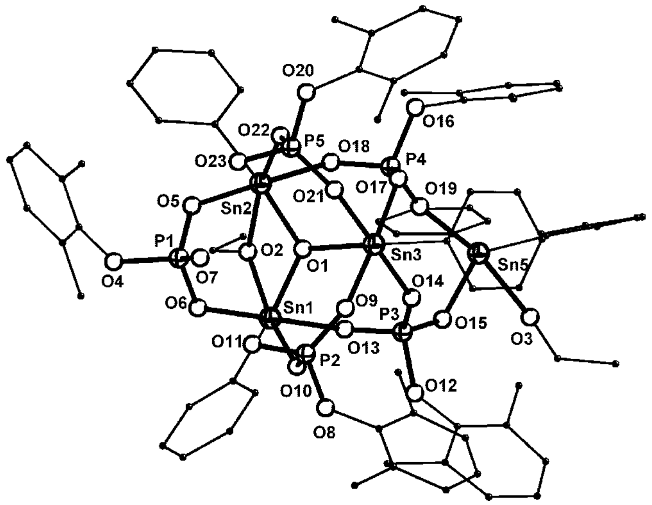


Figure 3. Molecular structure of **3**. The solvent molecule and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)−O(10) 2.087(5), Sn(1)−O(13) 2.092(5), Sn(1)−O(2) 2.094(5), Sn(1)−O(6) 2.117(5), Sn(1)−O(1) 2.120(4), Sn(2)−O(18) 2.058(4), Sn(2)−O(22) 2.072(4), Sn(2)−O(5) 2.098(4), Sn(2)−O(2) 2.102(5), Sn(2)−O(1) 2.135(4), Sn(3)−O(1) 2.081(5), Sn(3)−O(17) 2.086(4), Sn(3)−O(14) 2.090(4), Sn(3)−O(21) 2.092(4), Sn(3)−O(9) 2.101(4), Sn(5)−O(15) 2.019(4), Sn(5)−O(19) 2.080(4), Sn(5)−O(3) 2.266(5); O(10)−Sn(1)−O(13) 90.55(18), O(10)−Sn(1)−O(2) 163.18(17), O(13)−Sn(1)−O(2) 93.79(18), O(10)−Sn(1)−O(6) 85.83(18), O(13)−Sn(1)−O(6) 175.86(18), O(2)−Sn(1)−O(6) 89.12(18), O(10)−Sn(1)−O(1) 89.48(17), O(13)−Sn(1)−O(1) 89.42(17), O(2)−Sn(1)−O(1) 74.34(17), O(6)−Sn(1)−O(1) 88.54(17), O(18)−Sn(2)−O(22) 92.31(17), O(18)−Sn(2)−O(5) 176.21(18), O(22)−Sn(2)−O(5) 84.84(17), O(18)−Sn(2)−O(2) 92.95(18), O(22)−Sn(2)−O(2) 161.03(18), O(5)−Sn(2)−O(2) 88.99(18), O(18)−Sn(2)−O(1) 89.83(17), O(22)−Sn(2)−O(1) 87.89(17), O(5)−Sn(2)−O(1) 87.58(17), O(2)−Sn(2)−O(1) 73.91(17), O(1)−Sn(3)−O(17) 88.89(17), O(1)−Sn(3)−O(14) 90.07(17), O(17)−Sn(3)−O(14) 90.29(17), O(1)−Sn(3)−O(21) 87.87(17), O(17)−Sn(3)−O(21) 88.88(17), O(14)−Sn(3)−O(21) 177.79(18), O(1)−Sn(3)−O(9) 88.36(17), O(17)−Sn(3)−O(9) 176.59(18), O(14)−Sn(3)−O(9) 91.72(18), O(21)−Sn(3)−O(9) 89.01(17), O(15)−Sn(5)−O(19) 87.75(17), O(15)−Sn(5)−O(3) 82.23(18), O(19)−Sn(5)−O(3) 168.8(2), Sn(3)−O(1)−Sn(1) 127.3(2), Sn(3)−O(1)−Sn(2) 127.0(2), Sn(1)−O(1)−Sn(2) 102.95(19), Sn(1)−O(2)−Sn(2) 104.9(2).

Due to the fact that the molecule possesses no symmetry, the five different phosphate groups in **1** should give rise to five different signals in the ^{31}P NMR spectrum. Further, since the environment around the five phosphate groups do not change appreciably, these five signals should also appear very close to each other. Further, each of these phosphorus atoms would couple with three tin atoms (two in the case of P5) to different extents because the tin atoms themselves are not equivalent. Hence, the actual ^{31}P NMR spectrum should contain five sets of closely appearing signals with a large number of $^{117/119}$Sn satellite peaks. Indeed the spectrum recorded in $CDCl_3$ contains five closely appearing sets of signals with not well-resolved tin coupling constants, impeding any further analysis of the spectrum. The ^{119}Sn NMR spectrum shows two totally unresolved very broad signals ($w_{1/2} \approx 1665$ Hz) due to the two types of tin atoms discussed *vide supra.*

Synthesis and Characterization of 3. Although it is obvious from the molecular structures of **1** and **2** that the cluster growth would have started with a central [Sn$_3$(μ_3-O)] unit, the solution NMR studies could not be employed to prove this point due to poor solubility of these compounds. Alternatively, the use of a

Table 1. Crystal Data for 1−3

	1	2	3
formula	$C_{106}H_{136}O_{25}P_5Sn_5Cl$	$C_{108}H_{140}O_{25}P_5Sn_5Cl$	$C_{76}H_{89}O_{24}P_5Sn_4$
fw	2593.90	2621.95	2016.08
temp, K	150(2)	150(2)	150(2)
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$C2/c$
a, Å	15.6035(5)	15.7555(2)	50.9261(17)
b, Å	22.6982(5)	22.6489(3)	13.6704(17)
c, Å	32.5487(9)	32.5870(5)	24.9438(9)
α, deg	90	90	90
β, deg	90	90	91.687(6)
γ, deg	90	90	90
V, Å^3	11527.8(6)	11628.5(3)	17358(2)
Z	4	4	8
D(calcd), Mg/m^3	1.495	1.498	1.543
abs coeff, mm^{-1}	1.228	1.218	1.300
F(000)	5256	5320	8096
cryst size, mm^3	0.36 × 0.34 × 0.30	0.27 × 0.22 × 0.21	0.33 × 0.27 × 0.22
θ range, deg	2.99 to 28.00	2.96 to 28.00	2.95 to 28.00
data (R_{int})	26432(0.0567)	28019(0.0484)	20926(0.0927)
completeness to 2θ (%)	98.9	99.7	99.8
no. of restraints/params	8/1195	36/1285	42/967
GoF on F^2	0.984	1.113	1.069
R_1 [$I > 2\sigma(I)$]	0.0579	0.0555	0.0683
wR_2 [$I > 2\sigma(I)$]	0.1242	0.1276	0.1290
R_1 (all data)	0.1013	0.0711	0.1194

smaller organic substituent on the phosphate monoester can further reduce the solubility of the intermediates, and hence it should be possible to isolate these intermediate species during the slow crystallization. Thus, the use of 2,6-dimethylphenylphosphate (dmppH$_2$) instead of dippH$_2$ (in an identical reaction that previously led to the formation of **1**) produced [$Sn_4Ph_5(\mu_3$-dmpp)$_2$(μ-dmpp)(μ-dmppH)$_2$(μ_3-O)(μ-OEt)(EtOH)]·EtOH (**3**) in 69% yield (Scheme 2). The IR spectrum of **3** shows absorption at 1131 cm^{-1}, corresponding to the presence of Sn−O−P stretching frequencies. The broad absorption observed at 3526 cm^{-1} is indicative of the presence of either H_2O and/or OH groups in the molecule. The NMR spectra (^{1}H, ^{31}P, and ^{119}Sn) of **3** show very broad resonances, as in the case of **1** and **2**, thus precluding deriving structural information from the coupling pattern.

A single-crystal diffraction study revealed that compound **3** is a tetrameric tin phosphate with one of the tin atoms of **1** (the *Sn4* Ph$_2$SnCl unit) missing from the structure (Figures 3). In common with the structures of **1** and **2**, compound **3** also contains a central [$Sn_3(\mu_3$-O)] unit that is supported by five phosphate ligands. The Sn5 is pentacordinate (*tbp*) in **3** because of the absence of water coordination. The other structural parameters of **3** are comparable to those found in **1**. The Sn−O distances involving the μ_3-O^{2-} ion in compound **3** are not equal (Sn(1)−O(1) 2.120(5) Å, Sn(2)−O(1) 2.135(5) Å, and Sn(3)−O(1) 2.079(5) Å). The average P−O distance of the unreacted P−OH groups (1.543(5) Å) is longer than all other P−O distances (av 1.515 Å). The average Sn−O distance involving the μ_2-OEt is 2.099(5) Å. The Sn−O bond distance involving the terminal EtOH (2.263(5) Å) is longer than the Sn−O distance involving bridging EtOH, while two of the Sn−O−Sn bond angles in the tritin subunit are wider than the third angle (Sn(1)−O(1)−Sn(2) 102.9(2)°, Sn(1)−O(1)−Sn(3) 127.4(2)°, Sn(2)−O(1)−Sn(3) 127.0(2)°). The Sn(1)−O(2)−Sn(2) bond angle involving μ_2-OEt is 104.9(2)°.

Summary

We have shown that by varying the substituent on the phosphate ester, it is possible to isolate either pentameric or tetrameric organooxotin clusters and establish a mechanism for their formation. It appears that the dearylation is the key step in this reaction, which opens up room for several other types of ligands to be incorporated in the cluster, which eventually leads to a higher asymmetry of the cluster. While pentameric clusters are unknown in organo-stannoxane chemistry, the previously reported tetrameric structures have a highly symmetric core. Hence it can be concluded that the cluster architecture found in both the pentamer and the tetramer is unprecedented in organo-stannoxane chemistry.

Experimental Section

General Comments. The ^{1}H (Me$_4$Si internal standard), ^{31}P (85% H_3PO_4 external standard), and ^{119}Sn (Ph$_4$Sn external standard) NMR spectra were recorded on a Varian VXR 400S spectrometer. Infrared spectra were obtained from a Nicolet Impact-400 FT-IR spectrometer. Microanalyses were performed on a Thermo Finnigan (FLASH EA 1112) or a Carlo Eraba 1106 microanalyzer. Thermogravimetric analysis was carried out at IIT, Bombay, on a Perkin-Elmer thermal analysis system, under a stream of nitrogen gas. X-ray powder diffraction data were obtained with a Philips X'Pert Pro X-ray diffraction system using monochromated Cu Kα1 radiation (λ = 1.5406 Å). All reactions were carried out in the presence of air in a beaker; precautions however were taken to avoid contact of all tin compounds. The products were stable to normal atmosphere, excluding air or moisture in any of the reactions described. Commercially available starting materials such as diphenyltin dichloride (Aldrich) were used as received. 2,6-Diisopropylphenyl phosphate (dmpp-H$_2$) and 2,6-dimethylphenyl phosphate (dmpp-H$_2$) were synthesized using a previously reported procedure.[13]

Synthesis of 1. A solution of dippH$_2$ (258 mg, 1 mmol) in ethanol (25 mL) was added to a solution of Ph$_2$SnCl$_2$ (344 mg, 1 mmol) in 25 mL of ethanol. The reaction mixture was stirred at 25 °C for 6 h. The solution was filtered and left to crystallize at room temperature. The colorless crystals were formed from this solution after 6 days. Yield: 318 mg (60%). Mp: >250 °C. Anal.Calcd for $C_{106}H_{136}O_{25}P_5Sn_5Cl$ (M_r = 2593.90): C 49.08; H 5.28. Found: C

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48.86; H 5.11. IR (KBr, cm^{-1}): 3785(w), 3435(br), 3054(w), 2965(s), 2923(w), 2869(w), 1634(br), 1517(w), 1462(w), 1433(w), 1383(w), 1336(w), 1257(m), 1168(w), 1131(w), 1091(w), 1048(w), 1025(w), 938(m), 880(w), 796(w), 771(m), 749(w), 731(w), 695(w), 666(w), 598(w), 520(w) 458(w). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.40−1.10 (m, 3H, ^{i}Pr-CH$_3$ and EtOH), 2.90−3.77 (m, H, ^{i}Pr-CH), 6.7−7.1 (m, 6H, Sn-Ph), 7.30−7.70 (m, 3H, ArH). ^{31}P NMR (C$_6$D$_6$, 400 MHz, ppm): δ −5.35 to −5.08 (d), −9.47 to −9.06 (d), −12.21 to −11.54 (d), −17.22 to −14.41 (m). ^{119}Sn NMR (CDCl$_3$, ppm): −625 (br), −682 (br). MS (ESI, 70 eV): *m/z* 2475.53. TGA: temp range °C (weight loss): 155−281 (12.8%), 281−487 (40.3%).

Synthesis of 2. A solution of dippH$_2$ (258 mg, 1 mmol) in 2-propanol (25 mL) was added to a solution of Ph$_2$SnCl$_2$ (344 mg, 1 mmol) in 25 mL of 2-propanol. The reaction mixture was stirred at 25 °C for 6 h. The solution was filtered and left to crystallize at room temperature. The colorless crystals were formed from this solution after 6 days. Yield: 253 mg (42%). Mp: >250 °C. Anal. Calcd for C$_{108}$H$_{140}$O$_{25}$P$_5$Sn$_5$Cl (M_r = 2621.95): C 49.47; H 5.38. Found: C 49.34; H 4.87. IR (KBr, cm^{-1}): 3532(w), 3412(br), 3065(w), 2966(s), 2928(w), 2869(w), 2418(br), 1959(w), 1623(br), 1464(w), 1432(w), 1383(w), 1362(w), 1337(w), 1257(m), 1168(w), 1133(s), 1048(w), 1026(m), 938(m), 798(w), 773(m), 751(w), 731(m), 695(m), 666(w), 598(w), 585(w), 573(w), 515(w), 504(w), 456(w). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.60−1.20 (m, 6H, CH$_3$-^{i}Pr(dipp) and ^{i}PrOH), 3.2−3.6 (m, H, CH-^{i}Pr(^{i}PrOH)), 3.8−4.0(m, H, CH-^{i}Pr(dipp)), 6.8−7.1 (m, 6H, Sn-Ph), 7.4−8.0 (m, 3H, ArH). ^{31}P NMR (C$_6$D$_6$, 400 MHz, ppm): δ −5.62, −9.21, −15.83. ^{119}Sn NMR (CDCl$_3$,ppm): −625 (br), −683 (br). MS (ESI, 70 eV): *m/z* 2448.09. TGA: temp range °C (weight loss): 70−250 (19.8%); 250−510 (55.2%).

Synthesis of 3. A solution of dmppH$_2$ (202 mg, 1 mmol) in ethanol (25 mL) was added to a solution of Ph$_2$SnCl$_2$ (344 mg, 1 mmol) in 25 mL of ethanol. The reaction mixture was stirred at 25 °C for 4 h. The solution was filtered and left to crystallize at room temperature. The colorless crystals were formed from this solution after 4 days. Yield: 379 mg (69%). Mp: >250 °C. Anal. Calcd for C$_{76}$H$_{89}$O$_{24}$P$_5$Sn$_4$ (M_r = 2016.08): C 45.28; H 4.45. Found: C 45.04; H 4.07. IR (KBr, cm^{-1}): 3526(br), 3049(w), 2971(w), 2926(w), 2328(br), 1610(br), 1476(s), 1432(m), 1382(w), 1268(w), 1152(s), 1131(s), 1094(w), 1034(s), 987(m), 937(m), 891(w), 782(m), 768(m), 732(m), 697(m), 662(w), 596(w), 510(m). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.1−1.3 (s, 3H, EtOH-CH$_3$), 1.5−2.4 (b, 3H, Ar-CH$_3$), 3.1−3.3 (b, 2H, EtOH-CH$_2$), 5.2−5.4 (s, H, P-OH), 6.6−6.8 (b, 6H, Sn-Ph), 7.30−7.60 (b, 3H, ArH). ^{31}P NMR (CDCl$_3$, 400 MHz, ppm): δ −4.67, −7.84, −9.92, −16.70. ^{119}Sn NMR (CDCl$_3$, ppm): −623 (br), −685 (br). MS (ESI, 70 eV): *m/z* 1924.39. TGA: temp range °C (weight loss): 88−210 (22.0%), 210−455 (27%); 410−552 (5.0%).

Single Crystal X-ray Diffraction Studies. Intensity data for all three samples were collected on an Oxford XCalibur CCD diffractometer. All calculations were carried out using the programs in the WinGX module.[14] The structure solution was achieved by direct methods in most cases using programs implemented in SIR-92.[15] The final refinement of the structure was carried out using full-matrix least-squares methods on F^2 using SHELXL-97.[16] The crystal data and refinement details are listed in Table 1.

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Supporting Information Available: Details of single-crystal X-ray diffraction studies of compounds **1**−**3** (CIF) and core structures of compounds **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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