Synthesis of a Tetranuclear Organooxotin Cage by Debenzylation Reactions: X-ray Crystal Structure of $[(PhCH_2)_2Sn_2O(O_2P(OH)\text{-}t\text{-}Bu)_4]_2$

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Received July 8, 2002

The reactions of $(PhCH_2)_2SnCl_2$, $(PhCH_2)_2SnO\cdot H_2O$, and $(PhCH_2)_3SnCl$ with 2 equiv of t-BuP(O)(OH)$_2$ afford the tetranuclear organooxotin cage $[(PhCH_2)_2Sn_2O(O_2P(OH)\text{-}t\text{-}Bu)_4]_2$ (**4**) in good yields. The formation of the half-cage intermediate $[(PhCH_2)_2Sn_2O(O_2P(OH)\text{-}t\text{-}Bu)_4]$ (**4a**) en route to **4** has been detected by ^{119}Sn and ^{31}P NMR. The molecular structure of compound **4** as determined by single-crystal X-ray analysis shows a tetranuclear cage structure containing two Sn−O−Sn motifs connected by bridging $[t\text{-}BuP(OH)(O)_2]^-$ ligands. The solid-state structure of **4** is retained in solution.

Introduction

A rich cluster chemistry comprising a variety of structural forms is known for monoorganooxotin compounds.[1,2] Holmes and others have found that several types of clusters with varied geometric frameworks are known, such as drums or prismanes,[3,4] cubes,[5,6] oxygen-capped clusters,[6−8] etc. Most of these are obtained principally by adopting a single synthetic route consisting of a condensation of n-butylstannonic acid (n-BuSn(O)OH) with carboxylic, sulfonic, phosphinic, phosphoric, and phosphonic acids. This strategy, although valuable, is severely restrictive in view of the fact that modulation of the organic group on tin remains difficult. In view of this, in recent years there have been efforts to develop other synthetic methods for the preparation of organotin clusters. In this regard dearylation[3,9] and dealkylation[10] reactions appear promising, although the numbers and types of clusters obtained from these routes are still very limited. To explore the utility of debenzylation[10] reactions for the formation of a specific monoorganotin cluster, viz., the tetranuclear organooxotin cage[11] $[(n\text{-}C_4H_9)_2Sn_2O(O_2P(OH)\text{-}t\text{-}Bu)_4]_2$, we have studied the reactions of dibenzyl- and tribenzyltin derivatives[12] with *tert*-butylphosphonic acid, where we have replaced an n-butyl group on tin with a benzyl group. This was prompted by the consideration that, in contrast to other cluster types, very few examples of tetranuclear organooxotin cages are known in the literature[11] and it was of interest to examine the possibility of isolating such compounds using a completely different preparative route. Our investigations reveal that, irrespective of the type of benzyltin derivative used, the debenzylation reaction proceeds effectively and affords the tetranuclear organooxotin cage $[(PhCH_2)_2Sn_2O(O_2P(OH)\text{-}t\text{-}Bu)_4]_2$ (**4**) in good yield. Further, we have been able to characterize spectroscopically the intermediate product **4a**, which is eventually converted into **4**. These results are discussed herein.

Results and Discussion

Synthesis and Spectra. It has been noted earlier that benzyltin compounds can be compared to allyltin compounds in terms of the sensitivity of the Sn−C bond cleavage reaction.[10] The latter compounds are routinely used as allyl transfer reagents.[13] In fact, the labile nature of the Sn−C bond in these classes of compounds has impeded their use in organotin cluster chemistry. However, we reasoned that in the reaction using benzyltin compounds if at least one Sn−benzyl group remains intact in the final product, this would be an effective way of generating monoorganooxotin clusters.

The reaction of $(PhCH_2)_2SnCl_2$ (**1**) or $(PhCH_2)_2SnO\cdot H_2O$ (**2**) with 2 equiv of t-BuP(O)(OH)$_2$ in boiling toluene for 20 h affords the tetranuclear organooxotin cage $[(PhCH_2)_2Sn_2O(O_2P(OH)\text{-}t\text{-}Bu)_4]_2$ (**4**) in good yield (Scheme 1). In this reaction one of the benzyl groups on tin is eliminated as toluene. A similar reaction time

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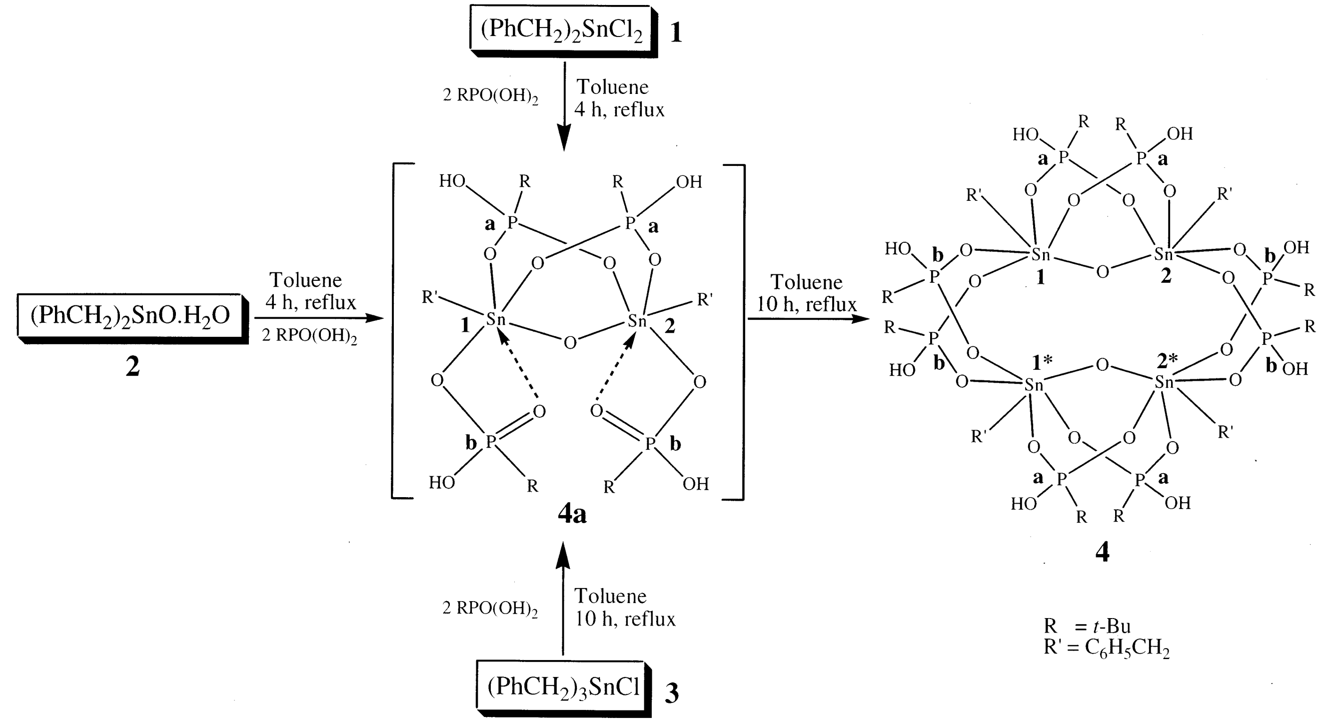
10.1021/om020531r CCC: $22.00
Publication on Web 09/20/2002

Scheme 1



is required to generate **4** from a double-debenzylation reaction involving the use of (PhCH$_2$)$_3$SnCl (**3**) as the source of tin. Importantly, in all three reactions, despite the harsh reaction conditions, one of the Sn−benzyl bonds remains intact. This reaction is also versatile, since the dibenzyltin compounds used can be in the form of the chloride or the oxide. It is noted that in **4** the ratio of Sn to O is 1:6.5. Consequently, for the reactions starting from **1** and **3**, respectively, the trace amount of water present in commercial *tert*-butylphosphonic acid is likely to be the source of the extra oxygen. Such an involvement of the residual moisture in *tert*-butylphosphonic acid has also been noted earlier.[14,15]

The ^{119}Sn NMR spectrum of the cage-type compound **4** shows a triplet of triplets with a chemical shift of −661.6 ppm (Figure 1c). All the tin atoms are chemically equivalent, and the multiplet pattern arises from each tin being coupled to two sets of two equivalent phosphorus nuclei. This is the result of the cage structure of **4**, where two pairs of phosphonates are linked to each tin (Scheme 1). The chemical shift observed for **4** may be compared with that of the *n*-butyl analogue,[11] which appears at −630.4 ppm. Comparison of these chemical shifts with some other geometric forms of monoorganooxotin clusters (Supporting Information) reveals that the chemical shifts in the tetranuclear cages are the most upfield shifted.

The ^{31}P NMR spectrum of **4** shows two resonances at 32.2 and 23.2 ppm with ^{119}Sn and ^{117}Sn satellites (Figure 2c). These are assigned to the two types of phosphonates. These values are also similar to those of the *n*-butyl analogue.[11] The peak at 32.2 ppm is assigned to the phosphorus atoms labeled **a**, and the peak at 23.2 ppm is assigned to the phosphorus atoms **b**. This assignment has been possible due to the isolation of the

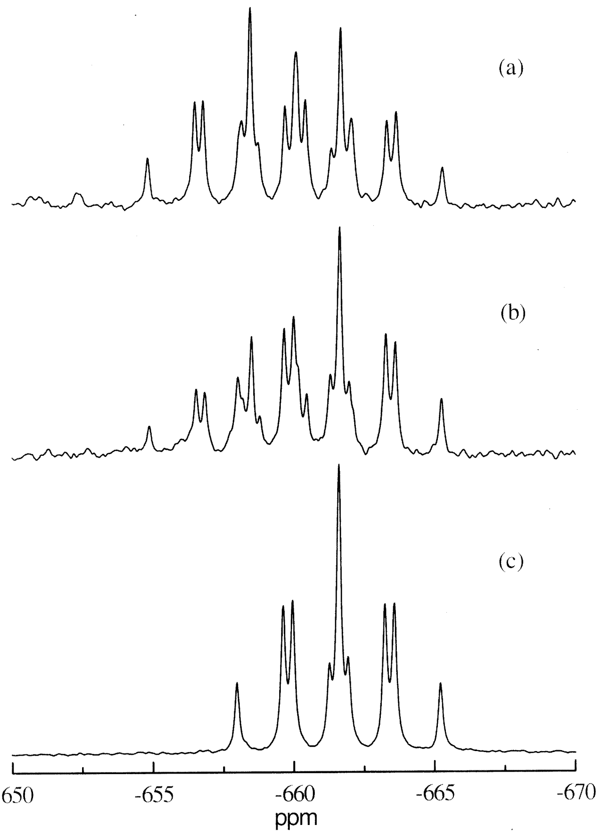


Figure 1. (a) ^{119}Sn NMR of a mixture of half-cage **4a** and full-cage **4** taken immediately after refluxing **1** with 2 equiv of *t*-BuPO(OH)$_2$ for 10 h, showing a 15-line pattern. (b) ^{119}Sn NMR of the same sample taken after 4 days at room temperature, showing an increase in concentration of full-cage **4**. (c) ^{119}Sn NMR of the sample taken after 8 days at room temperature showing complete conversion of **4a** to **4**.

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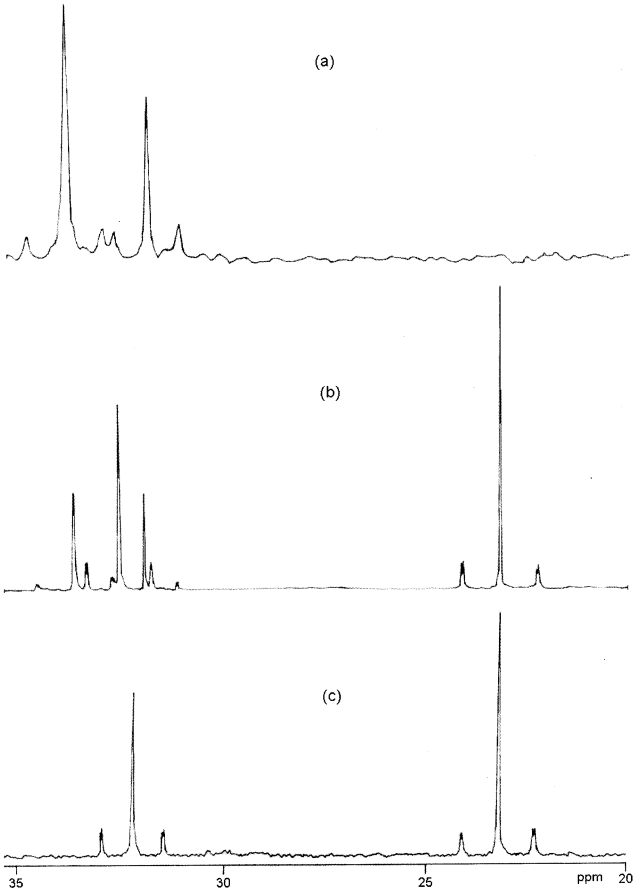

Figure 2. (a) ^{31}P NMR of the half-cage **4a** showing peaks at 33.67 and 31.76 ppm with tin satellites. (b) ^{31}P NMR of a mixture of half-cage **4a** and full-cage **4** showing peaks at 33.67, 32.17, 31.76, and 23.21 ppm with tin satellites. (c) ^{31}P NMR of full-cage **4** showing peaks at 32.17 and 23.21 ppm with tin satellites.

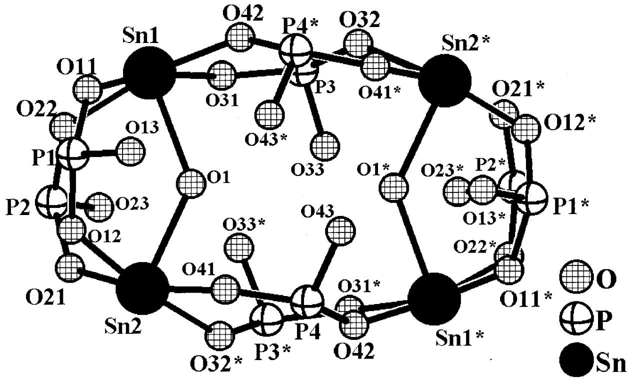

Figure 3. DIAMOND view of the core of the cage **4**. The benzyl group on tin and the *tert*-butyl group on phosphorus have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) in 4

	Bond Lengths		
Sn1−O1	2.116(2)	Sn1−O11	2.074(2)
Sn1−O22	2.085(2)	Sn1−O31	2.088(2)
Sn1−O42	2.065(2)	Sn2−O1	2.117(2)
Sn2−O21	2.075(2)	Sn2−O12	2.083(2)
Sn2−O32	2.068(2)	Sn2−O41	2.095(2)
P1−O11	1.527(2)	P1−O12	1.519(2)
P1−O13	1.555(3)	P2−O21	1.523(2)
P2−O22	1.518(2)	P2−O23	1.556(3)
P3−O31	1.521(2)	P3−O32	1.520(2)
P3−O33	1.540(3)	P4−O41	1.519(2)
P4−O42	1.516(2)	P4−O43	1.527(3)
	Bond Angles		
O11−Sn1−O31	169.4(8)	O11−Sn1−O42	88.84(8)
O32−Sn1−O31	90.86(8)	O22−Sn1−O42	170.89(8)
Sn1−O1−Sn2	135.17(10)	O12−Sn2−O32	173.63(8)
O12−Sn2−O41	89.08(8)	O21−Sn2−O32	89.43(8)
O21−Sn2−O41	168.84(8)	O11−P1−O12	112.82(13)
O21−P2−O22	112.96(13	O31−P3−O32	113.36(12)
O41−P4−O42	113.61(12)		

half-cage intermediate **4a**. We monitored the reaction between $(PhCH_2)_2SnCl_2$ or $(PhCH_2)_2SnO{\cdot}H_2O$ and 2 equiv of *t*-BuP(O)(OH)$_2$ by ^{31}P NMR. After 4 h of reaction time two peaks were observed at 33.7 and 31.8 ppm (Figure 2a). Both of these showed ^{119}Sn and ^{117}Sn satellites. The reaction was continued for a further 6 h. At this time the ^{31}P NMR showed four prominent peaks at 33.4, 32.4, 31.8, and 23.4 ppm (Figure 2b). It may be noted that two of these, viz., those at 32.4 and 23.4 ppm, correspond with the chemical shifts of the cage **4**. After the reaction is continued for a further period of 6 h, the peaks at 33.4 and 31.8 ppm completely disappear and the final spectrum is reminiscent of the cage **4** (Figure 2c). We propose that the initial product formed is the half-cage **4a**. In accordance with the proposed structure the ^{119}Sn NMR of **4a** is a triplet of doublets with the tin chemical shift being seen at −657.6 ppm (^2J(Sn−O−P) = 251, 291 Hz). Further, ^{119}Sn NMR of the mixture containing both the cage **4** and the half cage **4a** shows the expected 15-line pattern (Figure 1a). Attempts to grow single crystals of **4a** did not succeed because during the course of crystal growth (6−8 days) the half-cage **4a** was fully converted at room temperature to the cage **4**. This transformation can be monitored at room temperature in an NMR tube by carrying out ^{119}Sn NMR studies. Thus, the half-cage is converted gradually into a full cage over a period of 8 days. The ^{119}Sn NMR spectra at different stages of the conversion are shown in Figure 1. Thus, it appears that in the reaction of the benzyltin compounds a half-cage containing an Sn−O−Sn bond supported by chelating and bridging phosphonates is initially formed. Such a compound dimerizes to afford the tetranuclear cage **4** (Scheme 1).

Crystal and Molecular Structure of 4. The DIAMOND view of **4** (the core) is shown in Figure 3. Selected metric parameters for this compound are summarized in Table 1. In order for electrical neutrality to be maintained in **4**, there must be eight hydrogen atoms bonded to oxygen atoms. As it was not possible to locate all these hydrogen atoms from the difference map, their positions were fixed by using the atom riding model. Thus, each of the eight phosphonates is monodeprotonated and functions as a bridging ligand, $[t\text{-BuP(OH)O}_2]^-$. An inspection of the structure reveals that **4** contains equivalent basket-like halves comprising a Sn−O−Sn motif. This motif is bridged by a pair of $[t\text{-BuP(OH)O}_2]^-$ ligands. The halves of the structure are further bridged by two other pairs of $[t\text{-BuP(OH)O}_2]^-$ ligands. This arrangement leads to an overall cage type of architecture. Each phosphonate has two types of P−O bond lengths. The shorter bond length (average 1.520(3) Å) is associated with the bridging P−O, and the longer one (average 1.547(3) Å) is associated with the P−OH unit. Further, the P−O bond lengths of the

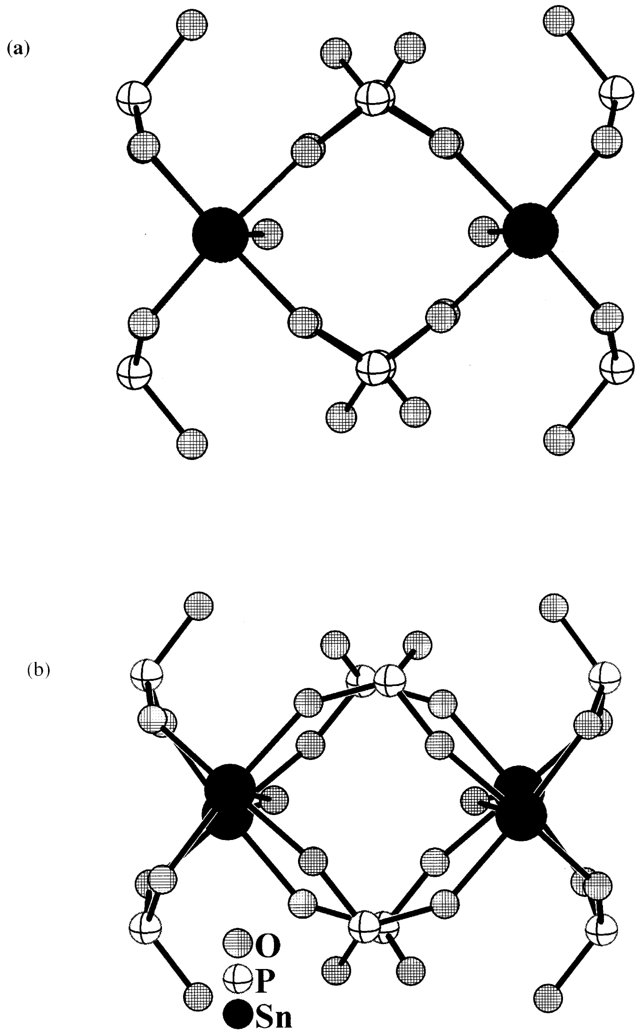

Figure 4. Views of (a) $[(n\text{-BuSn})_2O(O_2P(OH)\text{-}t\text{-Bu})_4]_2$ and (b) $[(PhCH_2)_2Sn_2O[O_2P(OH)\text{-}t\text{-Bu})_4]_2$ (**4**) through the Sn−O−Sn motif. In (a) complete eclipsing of the tin atoms and the bridging phosphonate moieties may be seen. In (b) the tin atoms and the bridging phosphonate groups deviate away from each other. The butyl and benzyl groups on tin and the *tert*-butyl group on phosphorus have been omitted for clarity.

bridging phosphonate within a half-cage (for example, P(1)−O(11) = 1.527(2) Å and P(1)−O(12) = 1.519(2) Å) are slightly longer than the bridging P−O bonds involved in linking the halves (for example, P(4)−O(41) = 1.519(2) Å and P(4)−O(42) = 1.516(2) Å). A similar trend is also seen for the P−O bond of the P−OH unit (for example, P(1)−O(13) = 1.555(3) Å and P(4)−O(43) = 1.537(3) Å). Each tin in **4** is hexacoordinate with a CO_5 coordination environment. The two Sn−O bond lengths within the Sn_2O distannoxane unit are identical (2.117(2) Å). The Sn−O−Sn bond angle is 135.17°.

A view of the molecule through the two opposite pairs of tin atoms (Sn1 and Sn1′; Sn2 and Sn2′) is shown in Figure 4b. This reveals that the opposite pairs of tins are slightly tilted away in the halves of the molecule and are only partially eclipsed. A similar situation is also found for the two pairs of phosphonates bridging the two Sn−O−Sn motifs (Figure 4b). This may be contrasted with the situation found for the analogous *n*-butyl cage,[11] where the opposite pairs of tin atoms as well as the two pairs of phosphonates bridging the Sn−O−Sn motifs along with the bridging oxygens are perfectly eclipsed (Figure 4a). The slight tilt observed in the present instance appears to have important ramifications in the supramolecular formation in **4**. Thus in the *n*-butyl cage, analysis for the presence of weak hydrogen bonds[16−18] up to a limit of 2.70 Å for O···H interactions (the sum of van der Waals radii for "O" and "H" is 2.7 Å)[19] revealed that meaningful intermolecular interactions are absent. However, in the present instance prominent intermolecular hydrogen bonding interactions are seen between one C−H of the $-C(CH_3)_3$ group on phosphorus and a neighboring P−O moiety. The two pairs of phosphonates bridging the tins within the Sn−O−Sn motifs are involved in these interactions. Thus, each cage is involved in two proton-donor and two proton-acceptor interactions, leading to the formation of a supramolecular two-dimensional sheetlike[20] network (Supporting Information).

In summary, we report a clean dealkylation route for the preparation of the elusive tetranuclear cage structures. We were also able to identify a half-cage from spectroscopic evidence, which is presumably an intermediate in the formation of the cage structure. The solid-state structure of **4** is retained in solution. A closer inspection of the molecular structure of compound **4** shows the formation of a C−H···O-assisted supramolecular assembly.

Experimental Section

All of the reactions were performed under a dry nitrogen atmosphere by employing standard Schlenk techniques. Solvents were dried over sodium benzophenone ketyl and were collected from the still at the time of reaction. Dibenzyltin dichloride, dibenzyltin oxide hydrate, and tribenzyltin chloride were prepared by literature methods.[12] *tert*-Butylphosphonic acid (Fluka) was used as received without any further purification. It has been noted previously that *tert*-butylphosphonic acid contains trace amounts of water which cannot be removed.[14,15] Melting points were measured using a JSGW melting point apparatus and are uncorrected. Elemental analyses were carried out using a Thermoquest CE Instruments Model EA/110 CHNS-O elemental analyzer. ^1H, ^{31}P, and ^{119}Sn NMR spectra were obtained on a JEOL-JNM LAMBDA Model 400 spectrometer using $CDCl_3$ solutions with the corresponding chemical shifts referenced to tetramethylsilane, 85% H_3PO_4, and tetramethyltin, respectively. ^{31}P and ^{119}Sn NMR were recorded under broad-band decoupled conditions.

Synthesis. Preparation of the Cage Cluster $[(PhCH_2)_2Sn_2O(O_2P(OH)\text{-}t\text{-Bu})_4]_2$ (4). The title compound has been prepared by using three different tin precursors.

(a) $(PhCH_2)_2SnCl_2$ (**1**; 0.13 g, 0.36 mmol) and *tert*-butylphosphonic acid (0.10 g, 0.72 mmol) were refluxed in toluene (30 mL) for 20 h. The reaction mixture was warmed to room temperature and filtered to remove insoluble impurities. The filtrate was evaporated to obtain a white solid. This was dissolved in toluene (20 mL), and the solution on slow evaporation at room temperature over a period of 2 days yielded crystals of compound **4**. Yield: 0.15 g (85%). Mp: 260

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Table 2. Crystal Data and Structure Refinement Parameters for 4

empirical formula	$C_{44.67}H_{72}O_{17.33}P_{5.33}Sn_{2.67}$
fw	1368.04
temp	150(2) K
wavelength	0.710 73 Å
cryst syst	orthorhombic
space group	*Pnna*
unit cell dimens	$a = 21.774(4)$ Å
	$b = 24.507(5)$ Å
	$c = 16.699(3)$ Å
	$\alpha = 90°$
	$\beta = 90°$
	$\gamma = 90°$
V	8911(3) Å^3
Z	6
density (calcd)	1.530 Mg/m^3
abs coeff	1.320 mm^{-1}
$F(000)$	4152
cryst size	$0.2 \times 0.3 \times 0.4$ mm^3
θ range for data collecn	1.48−22.49°
index ranges	$-23 \leq h \leq 23$
	$-26 \leq k \leq 26$
	$-10 \leq l \leq 17$
no. of rlfns collected	30 976
no. of indep rflns	5513 (R(int) = 0.0310)
completeness to $\theta = 22.49°$	94.7%
abs cor	semiempirical from equivalents
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	5513/47/470
goodness of fit on F^2	1.082
final R indices ($I > 2\sigma(I)$)	R1 = 0.0233, wR2 = 0.0649
R indices (all data)	R1 = 0.0410, wR2 = 0.0720
largest diff peak and hole	1.000 and −0.989 e Å^{-3}

°C dec. Anal. Calcd for $C_{60}H_{108}O_{26}P_8Sn_4$: C, 36.62; H, 5.53; Found: C, 36.40; H, 5.20. ^{1}H NMR ($CDCl_3$, ppm): 1.10 (d), 0.78 (d) (two types of *t*-Bu group protons, 36 H each), 2.60 (s, with $^{117/119}$Sn satellites, CH_2, 8H), 6.80−7.29 (m, aryl, 20H). ^{31}P NMR ($CDCl_3$, ppm): 32.17 (s, with $^{117/119}$Sn satellites, 232.8, 245.7 Hz), 23.21 (s, with $^{117/119}$Sn satellites, 281.3, 292.6 Hz). ^{119}Sn NMR ($CDCl_3$, ppm): −661.6 (tt, ^2J[Sn−O−P] = 244, 295 Hz).

(b) $(PhCH_2)_2SnO\cdot H_2O$ (**2**; 0.27 g, 0.80 mmol) and *tert*-butylphosphonic acid (0.22 g, 1.6 mmol) were refluxed in toluene (30 mL) for 20 h with a Dean−Stark apparatus to remove the water formed in the reaction by azeotropic distillation. Filtration of the reaction mixture followed by the removal of solvent in vacuo afforded the title product **4**, as indicated by its analytical and spectroscopic data, which match those obtained in the first preparation. Yield: 0.28 g (72%).

(c) $(PhCH_2)_3SnCl$ (**3**; 0.50 g, 1.2 mmol) and *tert*-butylphosphonic acid (0.32 g, 2.3 mmol) were reacted in a manner similar to that described in (a) to afford the title product **4**, as indicated by its analytical and spectroscopic data, which match those obtained in the first preparation. Yield: 0.45 g (79%);

X-ray Crystallography. Crystals of **4** (obtained in the first preparation) were grown by slow evaporation of toluene at room temperature. Colorless blocklike crystals suitable for single-crystal X-ray diffraction were loaded on a Bruker AXS Smart Apex CCD diffractometer. Details pertaining to the data collection and refinement are given in Table 2. The carbon atoms of one of the benzyl groups and the carbon atoms of the solvent molecule toluene were disordered. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97.[21,22] All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters.

Acknowledgment. We are grateful to the Department of Science and Technology, New Delhi, India, for financial support. A.S. and S.Z. thank the Engineering and Physical Sciences Research Council of the United Kingdom for financial support.

Supporting Information Available: Tables giving ^{119}Sn NMR chemical shifts for butyltin and benzyltin oxo clusters and additional X-ray crystallographic data for compound **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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