Organometallics **2007,** *26,* 4386−4388

Formation of a Double-Bicapped Hexatin Phosphate Cage by a De-arylation Reaction. Synthesis and Structure of $[(PhSn)_6(\mu\text{-}OH)_2(\mu_3\text{-}O)_2(\mu\text{-}OEt)_4\{(ArO)PO_3\}_4]$ (Ar = 2,6-*i*-$Pr_2C_6H_3$)

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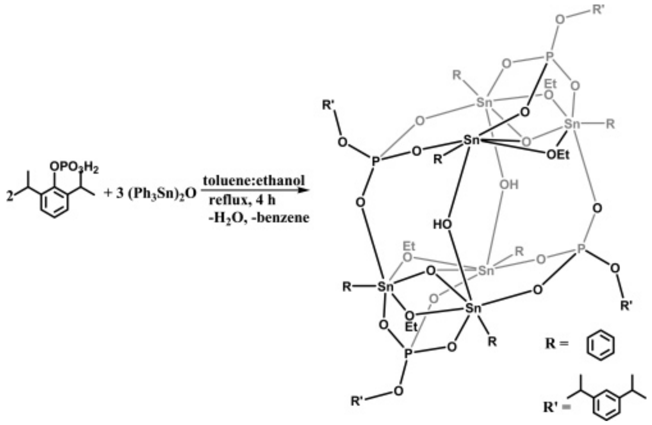
Received May 1, 2007

Summary: The reaction of bis(triphenyl)tin oxide, $(Ph_3Sn)_2O$, with 2,6-diisopropylphenylphosphate, $(ArO)PO_3H_2$ (Ar = 2,6-i-Pr_2-C_6H_3), leads to the formation of a novel double-bicapped hexanuclear monoorganooxotin cage, $[(PhSn)_6(\mu\text{-}OH)_2(\mu_3\text{-}O)_2(\mu\text{-}OEt)_4\{(ArO)PO_3\}_4]$. This reaction proceeds by a de-arylation reaction involving the cleavage of Sn−C bonds.

Reactions of organotin oxides and organotin oxide-hydroxides with phosphinic acids have been very well investigated.[1,2] This is because subtle modulation in terms of the nature of phosphinic acid has a profound effect on the structure of the resultant organostannoxane compound. In contrast to this situation, the reactions of organotin precursors with phosphonic acids have not been studied very well.[3,4] Research work from the lab of Holmes and ours have shown that the tetranuclear cages $[\{(RSn)_2(\mu\text{-}O)\}[O_2P(OH)\text{-}t\text{-}Bu]_4\}_2$ (R= *n*-Bu, $C_6H_5CH_2$) are formed in the reactions of butyl/benzyltin precursors with *tert*-butylphosphonic acid.[4c,g] In these cages the phosphonic acid acts as a monoanionic bidentate ligand. Recently, we have discovered that three-component reactions involving H_3PO_3, phenol, and $[n\text{-}BuSn(O)OH]_n$ result in the formation of double-O-capped clusters of the type $[\{(n\text{-}BuSn)_3(\mu_3\text{-}O)(\mu\text{-}OPh)_3(HPO_3)_2\}_2]$.[5] In these compounds the $[HPO_3]^{2-}$ unit functions as a dianionic tridentate ligand. In view of the varying reaction behavior of *t*-$BuPO_3H_2$ and H_3PO_3 toward organotin substrates we were interested in probing the reactions of other types of diprotic phosphorus-based acids such as $(RO)PO_3H_2$ with organotin oxides. We report herein an unusual de-arylation in the reaction between $(Ph_3Sn)_2O$ and $(ArO)PO_3H_2$ (R= 2,6-*i*-Pr_2-C_6H_3) to afford an unprecedented double-bicapped hexatin phosphate cage, $[(PhSn)_6(\mu\text{-}OH)_2(\mu_3\text{-}O)_2(\mu\text{-}OEt)_4\{(ArO)PO_3\}_4]$ (**1**).

Scheme 1. Synthesis of 1



The reaction of $(ArO)PO_3H_2$ with bis(triphenyltin)oxide in toluene/ethanol (16:1) under reflux conditions afforded **1** in an excellent yield (Scheme 1).[6] X-ray quality crystals were obtained by recrystallization of **1** from a 1:1 mixture of dichloromethane and ethanol at room temperature.[7] Single-crystal X-ray structure

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(6) Synthesis of **1**: A mixture of $ArP(O)_2(OH)_2$ (0.25 g, 0.97 mmol) and $(Ph_3Sn)_2O$ (0.69 g, 0.97 mmol) was taken in 80 mL of dry toluene and 5 mL of ethanol. The final mixtures were heated to reflux under dry nitrogen atmosphere for 4 h. The solvent was removed in vacuo to afford a sticky white solid, which was treated with dichloromethane (2 × 5 mL), and the solvent was removed to obtain the white solid, which upon recrystallization from a dry ethanol and dichloromethane mixture at room temperature by slow evaporation yielded colorless crystals suitable for X-ray analysis. Yield: 0.52 g (88 % based on $ArOPO_3H_2$); mp 173−175 °C; ^1H NMR (ppm) 0.71(m), 3.70(m), 3.30(m), and 7.19(m); ^{31}P NMR (ppm) 1.98 (s, with $^{117/119}Sn$ satellites and −17.26 (s, with $^{117/119}Sn$ satellites); ^{119}Sn NMR ($CDCl_3$, ppm) −590.0 (dd, J[Sn−O−P] = 102.8 Hz, 257.7 Hz) and −607.9 (dd, J[Sn−O−P] = 106.5 Hz, 204.1 Hz.). Anal. Calcd for $C_{92}H_{120}O_{24}P_4$-Sn_6 (2446.03): C, 45.02; H, 4.93. Found: C, 44.91; H, 5.01. IR (KBr, cm^{-1}): 1262 cm^{-1} [P−O−C (aromatic)], 1092 [vs, (ν_{aym} PO_3)], 1022 [vs, ($\nu_{sym}PO_3$)]. TGA, temperature ranges (°C) (weight loss %): 30−160 (2.4); 130−320 (33.0); 320−400 (18); 400−560 (10); 560−760 (3).

(7) Crystal data for $C_{46}H_{60}O_{12}P_2Sn_3$ (**1**): fw = 1222.9; monoclinic, *P*2-(1)/*n*; a = 15.913(5) Å, b = 16.520(5) Å, c = 19.837(5) Å, α = 90.000-(5)°, β = 95.946(5)°, γ = 90.000(5)°; V = 5187(3) $Å^3$; Z = 4; D_x = 1.565 Mg/m^3; μ = 1.551 mm^{-1}; crystal size 0.2 × 0.2 × 0.2; θ_{max} = 26.0°; 28 785 reflections collected at 273 K, 10 286 unique reflections ($I > 2\sigma(I)$); 342 parameters; R1 = 0.0512; wR2 = 1264. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELX-97. See: Scheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Analysis (release 97-2); University of Göttingen: Göttingen, Germany, 1998. All hydrogen atoms were included in idealized positions, and a riding model was used.

10.1021/om700421b CCC: $37.00

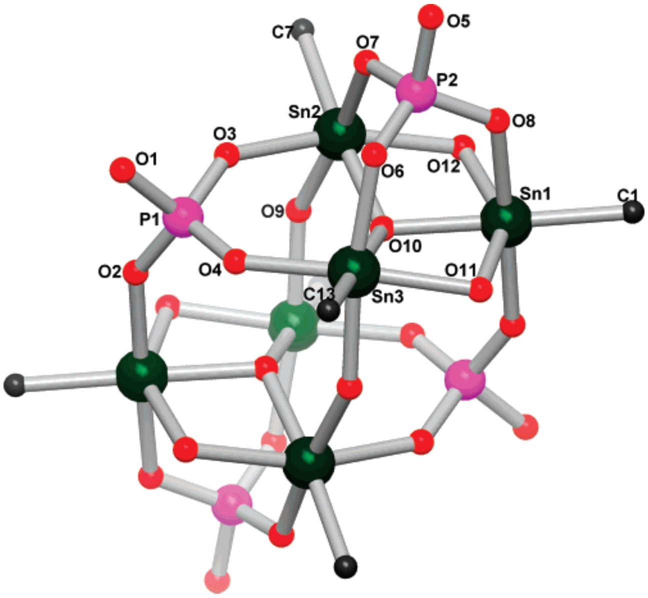
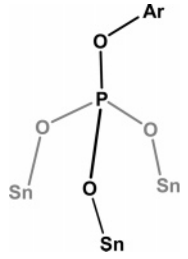


Figure 1. View of the core of **1**. All the carbon and hydrogen atoms have been removed for the sake of clarity. Selected bond lengths [Å] and angles [deg] for half of the molecule: Sn(1)−O(10) 2.077(4), Sn(1)−O(2) 2.086(4), Sn(1)−O(12) 2.117(4), Sn(1)−O(11) 2.118(4), Sn(1)−C(1) 2.129(4), Sn(1)−O(8) 2.129(4), Sn(2)−O(10) 2.062(4), Sn(2)−O(3) 2.072(4), Sn(2)−O(7) 2.100(4), Sn(2)−O(9) 2.118(4), Sn(2)−O(12) 2.141(4), Sn(2)−C(7) 2.144(3), Sn(3)−O(4) 2.035(4), Sn(3)−O(10) 2.064(4), Sn(3)−O(6) 2.103(4), Sn(3)−O(9) 2.119(4), Sn(3)−C(13) 2.125(3), Sn(3)−O(11) 2.145(4); O(10)−Sn(1)−O(11) 74.19(14), O(10)−Sn(1)−O(2) 91.41(15), O(10)−Sn(1)−O(12) 73.55(14), O(10)−Sn(1)−O(8) 87.22(15), O(10)−Sn(1)−C(1) 175.46(16), O(2)−Sn(1)−O(11) 90.46(16), O(2)−Sn(1)−O(12) 95.88(16), O(2)−Sn(1)−O(8) 176.11(16), O(2)−Sn(1)−C(1) 91.82(17), O(12)−Sn(1)−O(8) 87.23(16), O(12)−Sn(1)−O(11) 147.24(15), O(12)−Sn(1)−C(1) 109.27(17), O(11)−Sn(1)−C(1) 102.59(17), O(11)−Sn(1)−O(8) 85.66(16), C(1)−Sn(1)−O(8) 89.35(17), O(10)−Sn(2)−C(7) 175.14(16), O(10)−Sn(2)−O(12) 73.35(14), O(10)−Sn(2)−O(9) 92.24(14), O(10)−Sn(2)−O(3) 89.40(15), O(10)−Sn(2)−O(7) 86.84(14), O(3)−Sn(2)−O(7) 89.93(17), O(3)−Sn(2)−O(9) 82.87(17), O(3)−Sn(2)−O(12) 162.37(15), O(3)−Sn(2)−C(7) 93.54(17), O(7)−Sn(2)−C(7) 89.29(16), O(7)−Sn(2)−O(9) 172.75(17), O(7)−Sn(2)−O(12) 92.66(16), O(9)−Sn(2)−O(12) 93.96(16), O(9)−Sn(2)−C(7) 91.96(15), O(12)−Sn(2)−C(7) 103.92(16), O(4)−Sn(3)−C(13) 91.76(17), O(6)−Sn(3)−C(13) 91.42(16), O(10)−Sn(3)−C(13) 176.43(16), O(11)−Sn(3)−C(13) 104.81(17), O(9)−Sn(3)−C(13) 95.08(16), O(6)−Sn(3)−O(9) 171.10(16), O(6)−Sn(3)−O(11) 90.32(16), O(6)−Sn(3)−O(10) 85.30(14), O(6)−Sn(3)−O(4) 98.37(16), O(10)−Sn(3)−O(9) 88.04(14), O(10)−Sn(3)−O(11) 73.87(14), O(10)−Sn(3)−O(4) 90.10(15), O(4)−Sn(3)−O(9) 87.52(16), O(4)−Sn(3)−O(11) 161.12(15), O(9)−Sn(3)−O(11) 82.15(16).

analysis of **1** showed that it possesses a remarkable hexanuclear cage structure (Figure 1) that is quite unprecedented among organostannoxanes and merits a detailed description. The hexanuclear cage **1** contains two symmetrically related tri-tin halves. Each tri-tin subunit is *doubly capped* (Figure 1). On one side a μ_3 bridging oxide ligand, O10, caps the three tin atoms Sn1, Sn2, and Sn3. On the other side these three tin atoms are capped by a tridentate phosphate ligand (O6, O7, and O8). The capping oxygen atom, O10, is displaced from the mean plane of the three tin atoms by 0.49 Å, giving a pyramidal topology to the Sn_3O unit. The Sn−O bond distances involving O10 are nearly equal (av 2.068(4) Å). The Sn−O distances involving the capping phosphate ligand are slightly longer (av 2.111(4) Å). Among the three Sn−O−Sn bond angles involving the capping oxide O10, two (Sn2−O10−Sn1 and Sn3−O10−Sn1) are smaller (av 106.69(16)°), while the third angle (Sn2−O10−Sn3) is much wider (132.25(18)°). The three tin atoms are further bridged in the sides by two ethoxide ligands (O11 and O12). This bridging action of the ethoxide ligands generates two four-membered Sn_2O_2 rings. Of the three tin atoms, Sn2 and Sn3 are not bridged to each other by the ethoxide ligands.

Chart 1. Harris Notation of the Coordination Mode of the Phosphate Ligand in 1



The two phosphate and oxygen-capped tri-tin subunits, described above, are interlinked to each other by a pair of symmetrically related phosphate and hydroxide ligands. The coordination mode of the two phosphate ligands can be described as 3.111 according to the Harris notation (Chart 1).[8] The phosphate ligands (P1 and P1′) are involved in a tripodal coordination action (O2, O3, O4 and symmetrically related O2′, O3′, O4′) and join the two halves of the molecule. This action is augmented by the two hydroxide ligands (O9 and O9′; Sn2−O9−Sn3′ 148.9 (2)°; av Sn−O 2.119(4) Å), which further interconnect two pairs of tin atoms (Sn2 and Sn3′; Sn3 and Sn2′). The final coordination achieved around each of the six tin atoms is six (1C, 5O), and each tin is present in a distorted octahedral environment (see Supporting Information). The concerted bridging coordination of the phosphate and the hydroxide ligands results in the realization of the double-bicapped cage structure for **1**. The cage structure of **1**, thus formed, contains six puckered Sn_3O_4P eight-membered rings, as the faces of a distorted cubic manifold with the tin and phosphorus atoms occupying the vertices of the cube and the oxygen atoms bridging the cube edges (Scheme 1). This cubic manifold can be structurally compared with the D4R (double four ring) building units found in zeolites.[9] The overall structure of **1**, thus, is completely unusual among organostannoxanes and represents a new structural form. Previously known hexanuclear compounds possessed the open ladder structures ($[\{(PhCH_2)Sn(O)O_2CMe\}_2\{(PhCH_2)Sn(O_2CMe)_3\}]_2$),[10] drum structure ($[n\text{-}BuSn(O)O_2CR]_6$),[11] double-O-capped cluster structure ($[\{(n\text{-}BuSn)_3(\mu_3\text{-}O)(\mu\text{-}OPh)_3(HPO_3)_2\}_2]$),[5] or the prismane structure $\{[\{n\text{-}BuSn(OH)R\}_6\cdot 6H_2O\cdot 6R'OH\cdot CHCl_3]$ (R = 9-hydroxyfluorene-9-carboxylic, R′ = *p*-iodophenol)$\}$.[12] The structural relationship between **1** and the well-known O-capped cluster becomes obvious from the following discussion. It is known

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[8] Harris notation describes the binding mode as [$X_{Y1Y2Y3---Yn}$], where X is the overall number of metals bound by the whole ligand and each value of Y refers to the number of metal atoms attached to the different donor atoms. See: Coxall, R. A.; Harris, S. G.; Henderson, S.; Parsons, S.; Taskar, R. A.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **2000**, *14*, 2349.

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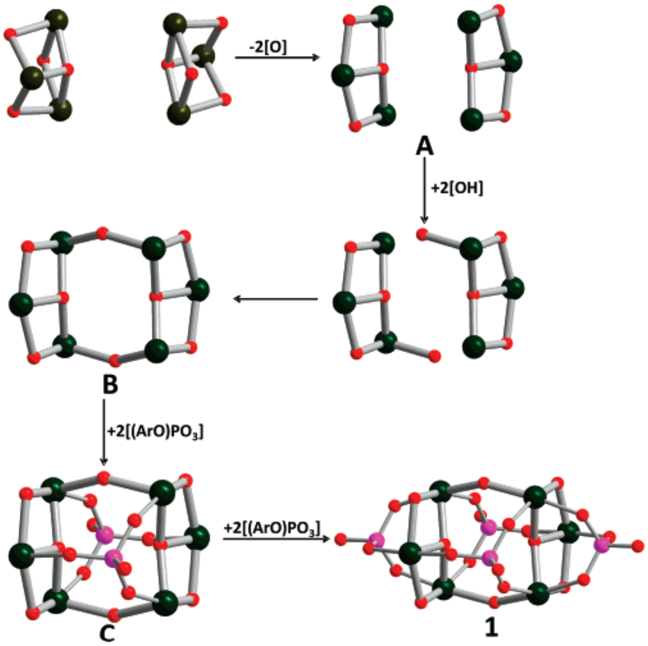
Scheme 2. Stepwise "Structural" Construction of 1



from our work that the O-capped Sn_3 cluster is an important building block of organostannoxanes and serves as a structural construct for many types of organostannoxanes such as drums, double-O-capped clusters, and football cages.[1] It is possible to envisage a stepwise structural buildup of **1** from the O-capped cluster. Subrogating one of the oxygen atoms from the classical O-capped cluster affords the motif **A** (Scheme 2). A pair of tin atoms from each unit is now bridged by two hydroxide ligands to generate **B**. This is followed by joining the remaining tin atoms with two phosphate ligands to assemble the cage **C**. Finally, the two ends of the cage, each containing a trinuclear motif, are capped further by two phosphate ligands, completing the construction of **1** (Scheme 2).

NMR studies on **1** are consistent with its molecular structure. The $^{119}Sn\{^1H\}$ NMR of **1** revealed two types of tin signals (each a doublet of doublets as a result of coupling to phosphorus), which are seen centered at −590.0 and −607.9 ppm (see Supporting Information). The $^{31}P\{^1H\}$ NMR spectrum of **1** shows two signals at 2.0 and −17.3 ppm, with the corresponding tin satellites (see Supporting Information).

Thermogravimetric analysis of **1** was carried out to ascertain the thermal stability of this cage. The weight loss for this compound starts at fairly low temperatures, the final decomposition occurring at 510 °C (final char yield, 37.7%; see Supporting Information). We are investigating the possibility of utilizing **1** as a possible single-source precursor for the formation of tin phosphates such as SnP_2O_7.

In conclusion, we report an unprecedented double-bicapped hexanuclear organostannoxane cage that is formed by a de-arylation involving the reaction between bis(triphenyltin)oxide and $(ArO)PO_3H_2$. The structural formation of **1** can be understood in a stepwise manner starting from the ubiquitous O-capped cluster building block. The synthesis of **1** points out the potential of using phosphates as reagents in organostannoxane synthesis. We are currently modulating the stereoelectronic features of the phosphate ligands and investigating their influence on the structural features of organostannoxane assemblies. We are also investigating the potential applications of de-arylation reactions, as planned synthetic strategies, for the construction of organostannoxane clusters.[1b,13]

Acknowledgment. We are thankful to the Department of Science and Technology, India, for financial support. V.C. is a Lalith Kapoor Professor of Chemistry at the Indian Institute of Technology. V.C. is grateful for the J. C. Bose fellowship of the Department of Science and Technology, New Delhi, India. P.S. and P.T. gratefully acknowledge the CSIR, New Delhi, India, for Research Fellowships.

Supporting Information Available: CIF file for **1** and Figures S1−S8. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700421B

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