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MONOORGANO (CHLORO) OXO-TIN CLUSTERS WITH PHOSPHINATE LIGANDS

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Abstract Reaction of *n*-butyltin dihydroxy chloride, $\text{n-BuSn(OH)}_2\text{Cl}$, with the phosphinic acids, $\text{R}_2\text{P(O)OH}$ [$\text{R} = \text{C}_6\text{H}_{11}$, Bu^t , and Ph], affords the novel chloro(oxo) tin clusters, $[\{\text{n-BuSn(OH)} \cdot \text{O}_2\text{P(C}_6\text{H}_{11})_2\}_3\text{O}][\{\text{n-BuSnCl}_2\text{O}_2\text{P(C}_6\text{H}_{11})_2\}_2\text{OH}]$ (1), $[\{\text{n-BuSn(O)O}_2\text{PBu}^t_2\}(\text{n-BuSn(OH)}_2\text{O}_2\text{PBu}^t_2)]_2[\text{H}][\text{Cl}][\text{n-BuSnCl(OH)(O}_2\text{PBu}^t_2)]_2$ (2), and $[\{\text{n-BuSnCl}_2(\text{O}_2\text{PPh}_2)\}(\text{n-BuSn(OH)(O}_2\text{PPh}_2)]_2 \cdot 2\text{CH}_2\text{Cl}_2$ (3), respectively. The Sn-O skeleton in 1-3, as revealed by X-ray crystallography, contains 4, 6 and/or 8 membered rings. The ^{119}Sn NMR spectra in benzene- d_6 are consistent with the structures observed in the solid state.

From a structural point of view, mono(organo)tin(IV) compounds are more versatile than diorgano or triorgano tin(IV) compounds. Our recent success in structurally characterizing a diverse series of mono(organo)tin(IV) oxo-carboxylate,^{1,2} phosphinate,²⁻⁵ and phosphate⁶ compounds prompted us to explore the synthetic utility of a new substrate, *n*-butyltin dihydroxy chloride, $\text{n-BuSn(OH)}_2\text{Cl}$. This paper reports the syntheses and structures of the products obtained from the reaction of the latter chloride with the phosphinic acids, $\text{R}_2\text{P(O)OH}$, where $\text{R} = \text{C}_6\text{H}_{11}$, Bu^t or Ph . These include $[\{\text{n-BuSn(OH)O}_2\text{P(C}_6\text{H}_{11})_2\}_3\text{O}][\{\text{n-BuSnCl}_2\text{O}_2\text{P(C}_6\text{H}_{11})_2\}_2\text{OH}]$ (1), $[\{\text{n-BuSn(O)O}_2\text{PBu}^t_2\}(\text{n-BuSn(OH)}_2\text{O}_2\text{PBu}^t_2)]_2[\text{H}][\text{Cl}][\text{n-BuSnCl(OH)(O}_2\text{PBu}^t_2)]_2$ (2), and $[\{\text{n-BuSnCl}_2\text{O}_2\text{PPh}_2\}(\text{n-BuSn(OH)(O}_2\text{PPh}_2)]_2 \cdot 2\text{CH}_2\text{Cl}_2$ (3). Although the reaction mixtures showed complex ^{119}Sn NMR spectra in the hexacoordinated region [-400 to -620 ppm, TMT ref.] indicative of the presence of species other than 1-3, none have been isolated thus

far. The reactions were carried out in toluene with the azeotropic removal of water followed by crystallization of the products from a suitable combination of the solvents dichloromethane, diethyl ether, and methyl cyanide. Yields of about 25% were obtained.

A view of 1 (mp 182–195°C) in Figure 1 indicates that the structure of the cationic portion is similar to that for the oxygen-capped cluster, $[\{n\text{-BuSn}(\text{OH})\text{O}_2\text{PPh}_2\}_3\text{O}][\text{O}_2\text{PPh}_2]$, reported previously.³ It consists of a six-membered $[\text{Sn}-\text{O}(\text{H})]_3$ ring with the three tin atoms capped by an oxygen and connected to each other by phosphinate ligands. The anion contains two hexacoordinated tin atoms connected by an $-\text{OH}$ bridge and two phosphinate ligands. Each tin has two chlorines which are hydrogen-

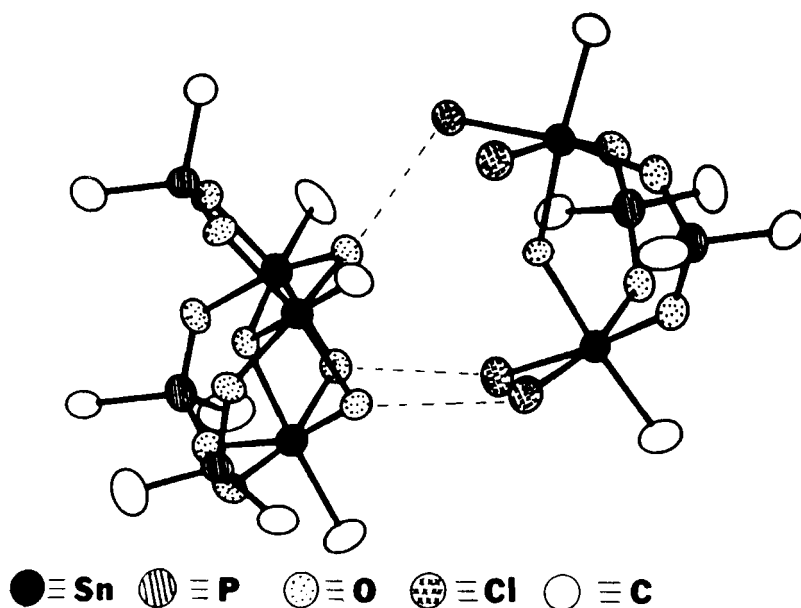


FIGURE 1 ORTEP plot of $[\{n\text{-BuSn}(\text{OH})\text{O}_2\text{P}(\text{C}_6\text{H}_{11})_2\}_3\text{O}][\{n\text{-BuSnCl}_2\text{O}_2\text{P}(\text{C}_6\text{H}_{11})_2\}_2\text{OH}]$ (1). Pendant atoms of the five $n\text{-Bu}$ groups and of the ten cyclohexyl groups are omitted for purposes of clarity.

bonded to the hydroxy protons of the cation. The ^{119}Sn NMR spectrum (C_6D_6) of 1 shows two triplets, one at -517.29 ppm and the other at -525.81 ppm, with $^2J(\text{Sn}-\text{O}-\text{P})$ values of 136.0 Hz and 209.1 Hz. These signals are assigned to the cationic and the anionic portions, respectively, based on their relative intensities.

A representation of compound 2 (mp $167\text{--}172^\circ\text{C}$) in Figure 2 shows that the behavior of di-*t*-butyl phosphinic acid is different from that of dicyclohexyl phosphinic acid. The structure consists of two neutral molecules, one tetranuclear and one dinuclear tin entity, held together by "hydrogen chloride" via hydrogen bonding. The tetrameric unit has a crown shape⁴ with two four-membered $[(\text{Sn}-\text{O})(\text{Sn}-\text{OH})]$ rings linked by two hydroxyl groups. A proton resides in between two oxygens of the two four-membered rings.

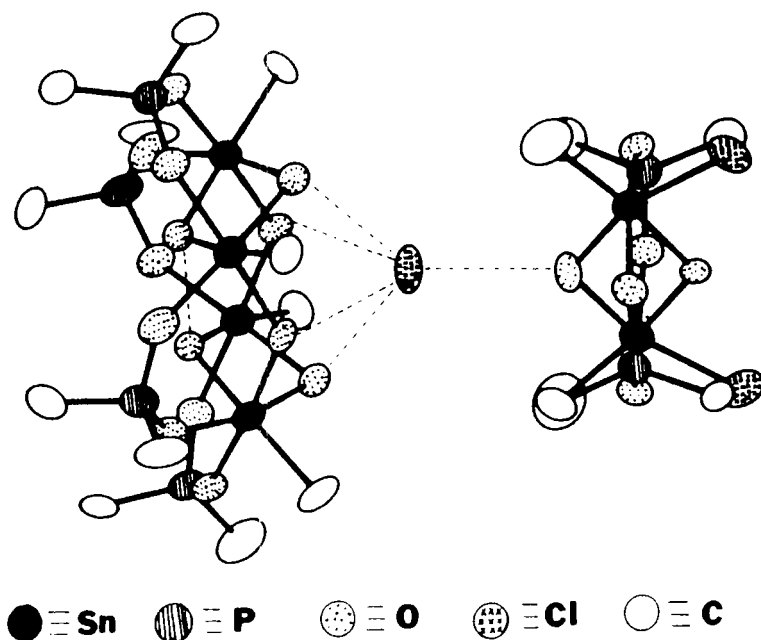


FIGURE 2 ORTEP drawing of $[\underline{n}\text{-BuSn}(\text{O})\text{O}_2\text{PBu}^t_2)(\underline{n}\text{-BuSn}(\text{OH})_2\text{O}_2\text{PBu}^t_2)]_2[\text{H}][\text{Cl}][(\underline{n}\text{-BuSnCl}(\text{OH})(\text{O}_2\text{PBu}^t_2))]_2$ (2). Pendant atoms of the six *n*-Bu groups and of the six *t*-Bu groups are omitted for purposes of clarity.

The chloride is then H-bonded to the O-H of the crown and also to an O-H of the dimeric unit, $[\text{BuSnCl}(\text{OH})(\text{O}_2\text{P}^t\text{Bu}_2)]_2$. The ^{119}Sn NMR of 2 exhibits a doublet of doublets at -535.2 ppm with $^2J(\text{Sn}-\text{O}-\text{P})$ values of 148.5 and 193.0 Hz and is assigned to the crown portion. A broad signal of lower intensity at -500 ppm is attributed to the dimeric unit.

Like 2, the oxotin product containing the diphenyl phosphinic acid ligand, 3 (mp 258-260°C), shown in Figure 3 contains a tetrameric unit but it is in the form of an extended unit with a central eight membered ring rather than a crown arrangement. Although the reaction stoichiometry was 1:1 (Sn:P), the formation of 3 has a Sn:P ratio of 2:3 showing additional phosphinate coupling compared to 1 and 2. The two kinds of tin are clearly

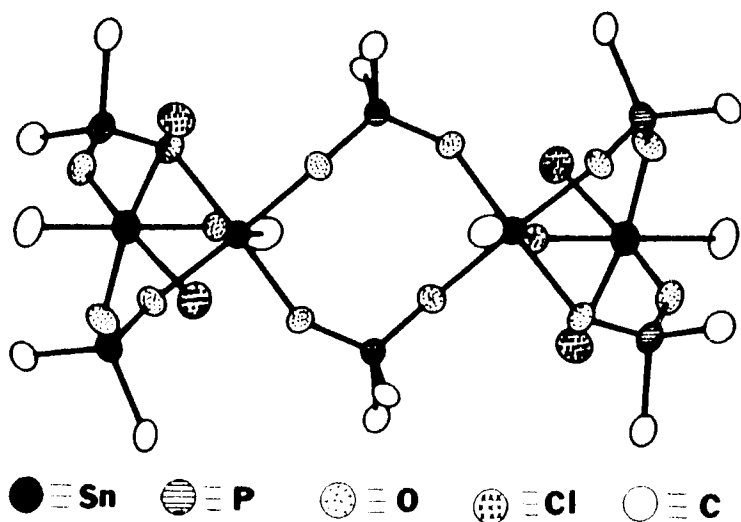
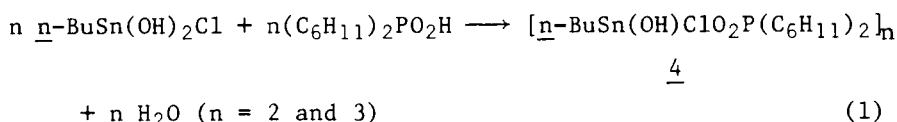


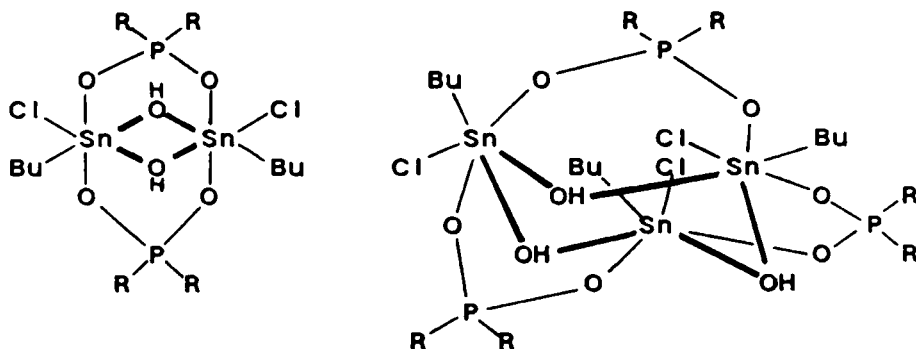
FIGURE 3 ORTEP plot of $[(n\text{-BuSnCl}_2\text{O}_2\text{PPh}_2)n\text{-BuSn}(\text{OH})(\text{O}_2\text{PPh}_2)_2]_2 \cdot 2\text{CH}_2\text{Cl}_2$ (3). Pendant atoms of the four $n\text{-Bu}$ groups and of the twelve phenyl groups are omitted for purposes of clarity.

distinguished in the ^{119}Sn NMR spectrum. Signals appear at -507.39 ppm ($^2J(\text{Sn}-\text{O}-\text{P}) = 222.8$ Hz; central tin atoms) and at -615.36 ppm (m, terminal tin atoms).

A possible route for the formation of 1-3, possessing different structures but originating from the common reactant, n-BuSn(OH)₂Cl, is suggested by the initial formation of the likely phosphinate derivatives, [n-BuSn(OH)Cl(O₂PR₂)]_n [n = 2,3], [n-BuSn(OH)₂(O₂PR₂)]₂, or [n-BuSn(OH)(O₂PR₂)₂] followed by rearrangement or condensation. For example, in the case of 1, an initial condensation reaction, eq. 1,



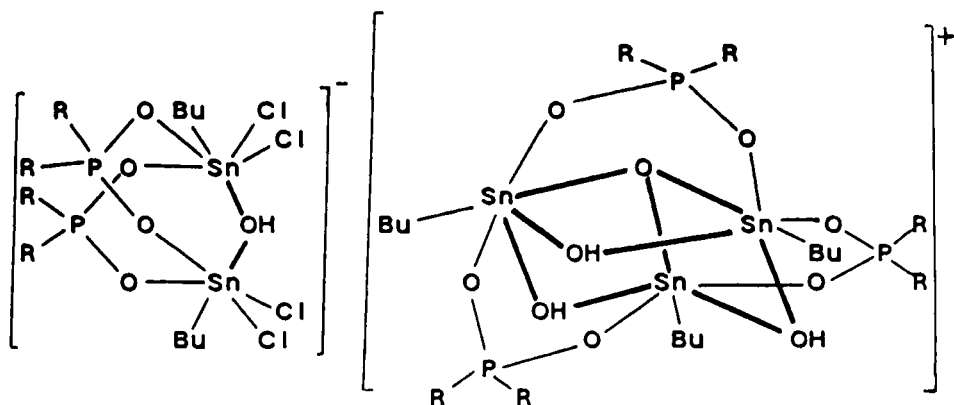
is postulated to give the cyclic dimeric and trimeric ring formulations.



(Postulated intermediates, 4 (R = C₆H₁₁), in forming 1)

Formally, elimination of a molecule of HCl between these two species must occur as well as a transfer of an oxygen atom from the dimer to the trimer and a transfer of two chlorine atoms from the trimer to the dimer to obtain the two components of 1.

Attempts to replace the residual chloride functionalities on tin in 1-3 either by use of the latter as starting materials or increasing the reactant phosphinic acid to n-BuSn(OH)₂Cl mole ratio may lead to additional new cluster and cage derivatives.



(Schematic representation of 1; R = C₆H₁₁)

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REFERENCES

1. R. R. Holmes, C. G. Schmid, V. Chandrasekhar, R. O. Day, and J. M. Holmes, *J. Am. Chem. Soc.*, **109**, 1408 (1987).
2. R. R. Holmes, R. O. Day, V. Chandrasekhar, C. G. Schmid, K. C. Kumara Swamy, and J. M. Holmes, in *Inorganic and Organometallic Polymers*, edited by M. Zeldin, K. J. Wynne and H. R. Allcock (ACS Monograph 360, 1988), Chapter 38, pp. 470-482.
3. R. O. Day, J. M. Holmes, V. Chandrasekhar, and R. R. Holmes, *J. Am. Chem. Soc.*, **109**, 940 (1987).
4. K. C. Kumara Swamy, C. G. Schmid, R. O. Day, and R. R. Holmes, *J. Am. Chem. Soc.*, **110**, in press (1988).
5. R. R. Holmes, K. C. Kumara Swamy, C. G. Schmid, and R. O. Day, *J. Am. Chem. Soc.*, **110**, in press (1988).
6. R. O. Day, V. Chandrasekhar, K. C. Kumara Swamy, J. M. Holmes, S. D. Burton, and R. R. Holmes, *Inorg. Chem.*, **27**, in press (1988).