Solventless Reactions for the Synthesis of Organotin Clusters and Cages§

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Organotin clusters and cages have been synthesized in quantitative yields by using a benign solventless synthetic methodology. Using this method a variety of structural forms, which include the *drum*, *O-capped cluster*, *tetranuclear oxo cage*, *discrete*, and *polymeric* compounds, have been synthesized. All these compounds (**1**−**11**) have been characterized by spectroscopic and analytical techniques. The new compounds, which include the hexameric drum [*n*-BuSn(O)OCOAd]$_6$ (Ad = adamantyl) **9**, a triorganotin-based discrete structure Ph_3SnO_2C-C_6H_2-2,4,6-Me_3 (**10**), and a polymer Ph_3SnOSO_2-C_6H_3-2,5-Me_2 (**11**), have been characterized by single-crystal X-ray crystallography.

Introduction

Traditionally solid-state synthesis has been used primarily for alloys or for inorganic solids such as ceramics, and most of these are high-temperature syntheses.[1−3] The application of a solventless synthetic methodology for organic compounds that were conventionally synthesized in a solvent medium is becoming more common in recent years.[4] Thus, well-known organic reactions such as the Wittig reaction, aldol condensation, and the pinacol rearrangement have been found to occur even in the absence of a solvent.[4] In contrast, there are virtually no reports on the application of solventless methods for the preparation of simple inorganic or organometallic molecules, although recently there have been some efforts on the preparation of coordination polymers and supramolecular arrays using this approach. However, the latter pertain to specific examples and are not general methods of synthesis.[5,6] In the following we demonstrate a solventless synthetic strategy that is applicable for general families of organotin compounds that are traditionally synthesized by the use of high-boiling solvents under reflux conditions. All of these reactions are considerably complex and involve several bond-breaking and bond-forming processes.[7] Organotin cages and clusters are a particularly attractive target because of the large structural diversity that is present in this family and also because of their importance in catalysis and other applications.[7,8] By the use of solventless methodology, at ambient temperature, we were able to synthesize in nearly quantitative yields *six different* structural types; these include cages and clusters as well as discrete and supramolecules. We have chosen to utilize this method for the synthesis of various known examples from literature (**1**−**8**) and showed that solid-state synthesis can be readily applied to these systems. In addition we have also used this synthetic methodology for the preparation of three new compounds, **9**, **10**, and **11**. The latter have also been characterized by X-ray crystallography.

Results and Discussion

Typically the synthesis protocol consisted of grinding the organotin reagent such as *n*-BuSn(O)OH, *n*-BuSn-

§ This paper is dedicated to Prof. R. R. Holmes on the occasion of his 75th birghday.

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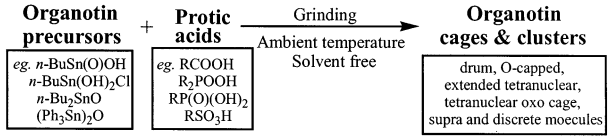
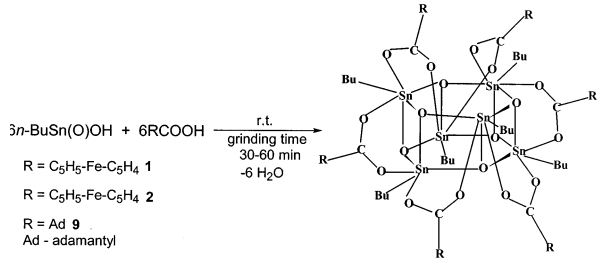
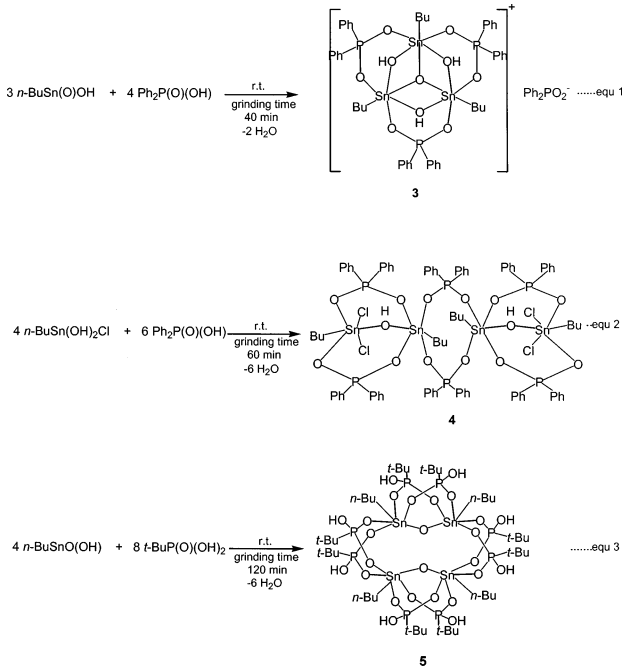
Scheme 1



Scheme 2



Scheme 3

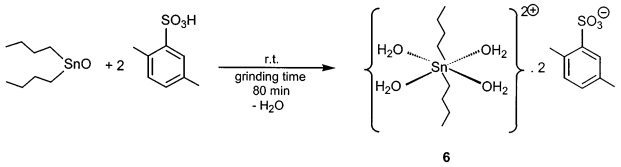


(OH)$_2$Cl, *n*-Bu$_2$SnO, or (Ph$_3$Sn)$_2$O with appropriate protic reagents such as a carboxylic acid, phosphinic acid, or a sulfonic acid (Scheme 1).

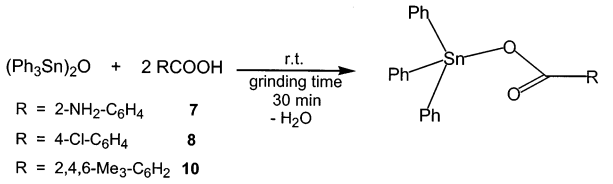
In each case the tin reagent is a polymeric solid except for (Ph$_3$Sn)$_2$O, which is a molecular solid. The protic reagents themselves are all solids. The reactions were monitored by ^{119}Sn and/or ^{31}P NMR. At the completion of the reaction the solid mixture was extracted with dichloromethane at room temperature and the organotin compound was isolated by crystallization. Each of these reactions leads to the formation of a unique organotin compound, each representing a different structural type (Schemes 2−6). Remarkably in every case the isolated yields of the product are in excess of 90%. It is of interest to note that conventionally these compounds have been prepared by carrying out the reaction in boiling benzene or toluene and also by using a Dean−Stark apparatus for the dynamic removal of water formed in the reaction.

The generality of the synthetic procedure can be widely appreciated if one considers the diversity of the organotin precursor and the protic acid employed. Thus, the reaction of *n*-BuSn(O)OH with FcCOOH (Fc = Ferrocenyl) is completed in 1 h to afford in about 90% yield the hexameric drum [*n*-BuSn(O)OCOFc]$_6$, **1** (Scheme 2).[9a] To assess if the water formed in the above reaction is enabling a solvent type medium, we ground the substrates in the presence of activated alumina for scavenging the extruded water. No difference in reactivity was noted. A similar reaction was also observed with ferrocene acetic acid to afford the drum [*n*-BuSn(O)-OCOCH$_2$Fc]$_6$, **2** (Scheme 2).[9b] It is to be noted that the products **1** and **2** represent rare examples of hexaferrocene arrays supported on the central stannoxane core and possess remarkable thermal and electrochemical stability.

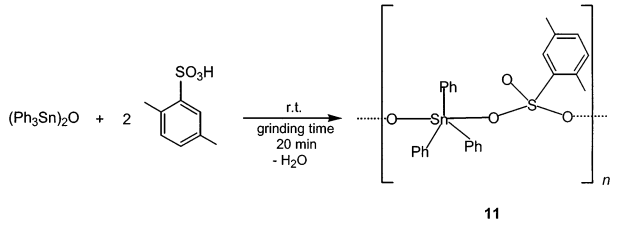
Scheme 4



Scheme 5



Scheme 6



The reactions of tin reagents with phosphorus-based acids are more complex, and the nature of the product isolated in these reactions is extremely sensitive to the stoichiometry of the reagents and the nature of the phosphorus-based acid.[7] This remarkable product preference is also retained in the present solventless synthetic methodology. Thus, the reaction of *n*-BuSn(O)OH with Ph$_2$P(O)OH in a 3:4 ratio afforded the O-capped cluster {[*n*-BuSn(OH)O$_2$PPh$_2$]$_3$O}[O$_2$PPh$_2$], **3**, in 91% yield (Scheme 3, eq 1).[9c] In contrast the reaction of *n*-BuSn(OH)$_2$Cl with Ph$_2$P(O)OH affords the extended tetranuclear cage {(*n*-Bu)$_2$Sn$_2$Cl$_2$(OH)(O$_2$PPh$_2$)$_3$}$_2$, **4**, in 95% yield (Scheme 3, eq 2).[9d] Interestingly in this cluster four terminal Sn−Cl bonds are retained. A different tetranuclear oxo tin cage {(*n*-Bu)$_2$Sn$_2$O[O$_2$P(OH)-*t*-Bu]$_4$}$_2$, **5**, is formed in the reaction of *n*-BuSn(O)OH with *t*-BuP(O)OH)$_2$ (Scheme 3, eq 3).[9e]

In another variation the reaction of *n*-Bu$_2$SnO with xylyl sulfonic acid afforded the dication [*n*-Bu$_2$Sn-

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$(H_2O)_4]^{2+}$, **6** (Scheme 4), which has a supramolecular architecture in the solid state.[10a] In this reaction, not only is water eliminated in the first step of the reaction, but subsequently the eliminated water also serves as the ligand for the dication. While this is not so unusual in solution, the facility with which this dual process happens in the solid state also suggests that this methodology can be very useful even for complex situations. Further it is of interest to note that though only one molecule of water is eliminated in the reaction, the final product contains four molecules of coordinated water. It is highly possible that the other water molecules might have been absorbed from atmospheric moisture due to the high stability encountered with the dication.[10b]

Even with triorganotin substrates such as $(Ph_3Sn)_2O$ the reactions are equally facile. Thus as shown in Scheme 5, triorganotin carboxylates with discrete molecular structures (**7** and **8**) are formed.[11a,b]

In any of the above reactions (Schemes **1**−**5**), no visible melt was observed during any stage of the reaction and the solid powder was completely free flowing during the entire reaction condition. This is in contrast to most organic solventless reactions, where a eutectic melt has been detected.[4a,c] As observed in the recently reported phosphonium bromide[4f] synthesis, we believe that mechanical grinding provides sufficiently close proximity and contact between reactants for mass transfer to occur. To check if the solid-state reactions proceed by loss of crystallinity, we have chosen a test case. Thus, in the preparation of the extended tetranuclear cage $\{(n\text{-Bu})_2Sn_2Cl_2(OH)(O_2PPh_2)_3\}_2$, **4**, the powder X-ray diffraction at various time intervals (Figure 1) shows the evolution of peaks corresponding to the formation of the product. The final XRD compares well with that of the authentic sample. It is to be noted that at all stages the crystalline nature of the reaction mixture is maintained, as indicated by the presence of clear diffraction pattern. In the reactions leading to products **7** and **8** (Scheme 5), the solid mixtures, although they did not turn into a melt, were marked by a slight amount of stickiness. The progress of the formation of the cages $\{(n\text{-Bu})_2Sn_2Cl_2(OH)(O_2PPh_2)_3\}_2$, **4**, and $\{(n\text{-Bu})_2Sn_2O[O_2P(OH)\text{-}t\text{-Bu}]_4\}_2$, **5**, has been monitored by ^{31}P NMR. In the preparation of the extended cluster **4** it was observed that the reaction progresses rapidly in the first 30 min and is completed after 1 h. ^{31}P NMR spectra (in $CDCl_3$) of the solid obtained by grinding *n*-$BuSn(OH)_2Cl$ with $Ph_2P(O)(OH)$ at various time intervals are shown in Figure 2. The chemical shifts observed in the ^{31}P NMR spectrum (60 min) match with those of the authentic sample **4** prepared conventionally. Similarly the tetranuclear cage $\{(n\text{-Bu})_2Sn_2O[O_2P(OH)\text{-}t\text{-Bu}]_4\}_2$, **5**, also is formed quite rapidly and is complete in 2 h (Figure 3).

Although the efficacy of the solventless methodology is proven beyond doubt (as shown vide supra) for the preparation of a variety of known organotin compounds,

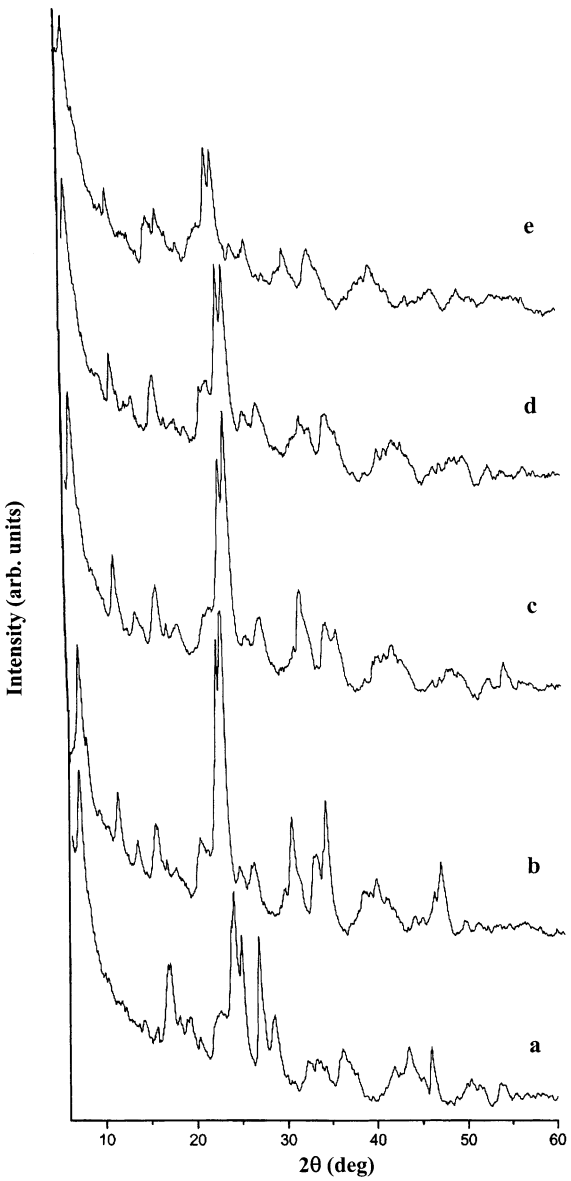

Figure 1. Powder X-ray diffraction pattern of the solid obtained on grinding *n*-$BuSn(OH)_2Cl$ with $Ph_2P(O)(OH)$: (a) immediately after mixing the reactants, (b) after 15 min, (c) after 25 min, (d) after 40 min, and (e) after 60 min of grinding. The pattern (e) matches exactly with the powder XRD pattern of the product **4** synthesized by conventional methods.[9d]

we wished to extend this methodology to new compounds as well. Accordingly the reaction of *n*-BuSn(O)OH was carried out with adamantane carboxylic acid by using both solventless and conventional techniques. Similarly the reactions of $Ph_3SnOSnPh_3$ with 2,4,6-$Me_3C_6H_2COOH$ or 2,5-$Me_2C_6H_3SO_3H$ were also carried out by both methods (Schemes 2, 5, 6). Irrespective of the method used, a unique product was isolated in high yields from each reaction. The products formed in these reactions, viz., $[n\text{-BuSn(O)OC(O)Ad}]_6$ (**9**), $Ph_3SnO_2C\text{-}C_6H_2\text{-}2,4,6\text{-}Me_3$ (**10**), and $Ph_3SnOSO_2\text{-}C_6H_3\text{-}2,5\text{-}Me_2$ (**11**), were characterized by spectroscopic methods as well as by X-crystallography.

Thus, ^{119}Sn NMR chemical shifts of **9**, **10**, and **11** are characterized by singlets at −486.7, −112.5, and −238.1 ppm, respectively. The molecular structures of these compounds were confirmed by X-ray crystal structures.

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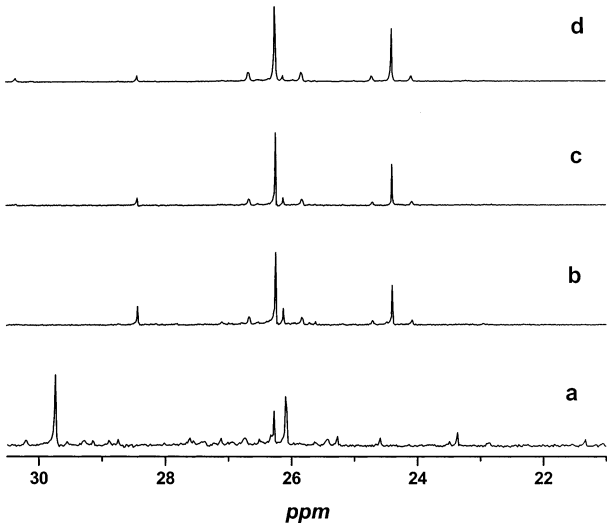

Figure 2. ^{31}P NMR spectra (in $CDCl_3$) of the solid obtained by grinding *n*-$BuSn(OH)_2Cl$ with $Ph_2P(O)(OH)$: (a) after 15 min, (b) after 30 min, (c) after 45 min, and (d) after 60 min of grinding. The chemical shifts in spectrum (d) match that of the cage $\{(n\text{-}Bu)_2Sn_2Cl_2(OH)(O_2PPh_2)_3\}_2$, **4**, prepared by conventional methods.[9d]

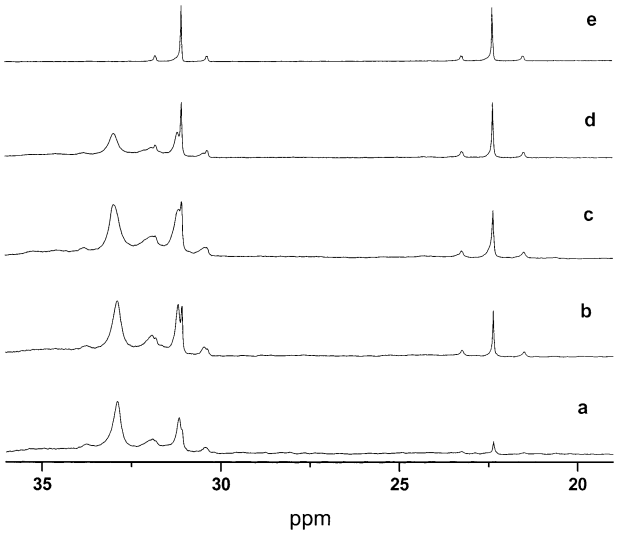

Figure 3. ^{31}P NMR spectra (in $CDCl_3$) of the solid obtained by grinding *n*-BuSn(O)OH with *t*-$BuP(O)(OH)_2$: (a) after 10 min, (b) after 25 min, (c) after 50 min, (d) after 80 min, and (e) after 120 min of grinding. The chemical shifts in spectrum (e) match that of the cage $\{(n\text{-}Bu)_2Sn_2O[O_2P(OH)\text{-}t\text{-}Bu]_4\}_2$, **5**, prepared by conventional methods.[9e]

Molecular Structures of 9, 10, and 11. The molecular structures of **9**, **10**, and **11** are shown in Figures 4, 5, and 6, respectively. The molecular structure of **9** shows that it possesses the well-known drum type of architecture.[7,9a] Thus the organotin cluster consists of a Sn_6O_6 core. This core is comprised of two puckered Sn_3O_3 units that serve as top and bottom faces of the drum. The fusion of the two Sn_3O_3 units leads to the generation of six Sn_2O_2 distannoxane rings which form the sides of the drum. Alternate tin centers in the Sn_6O_6 core are bridged by the adamantane carboxylate in a symmetrical isobidentate manner. The metric parameters found for this compound are normal and are summarized in the caption of Figure 4.

The molecular structure of **10** shows that the triorganotin carboxylate adopts a discrete structure (Figure 5). The tin is involved in four covalent bonds having a distorted tetrahedral geometry about the tin center. The carboxyl oxygen is involved in a fifth weaker bonding interaction with tin along a tetrahedral face. Accordingly, two types of Sn−O distances are seen. Thus, the Sn1−O1 distance is 2.071(6) Å and corresponds to the Sn−O covalent bond. The bond distance between the tin center and the carboxyl oxygen (Sn1−O2) is 2.769(7) Å. The sum of the van der Waals radii of tin and oxygen is 3.7 Å.[12] In view of this and also in view of literature precedents[7] it can be proposed that a coordi-

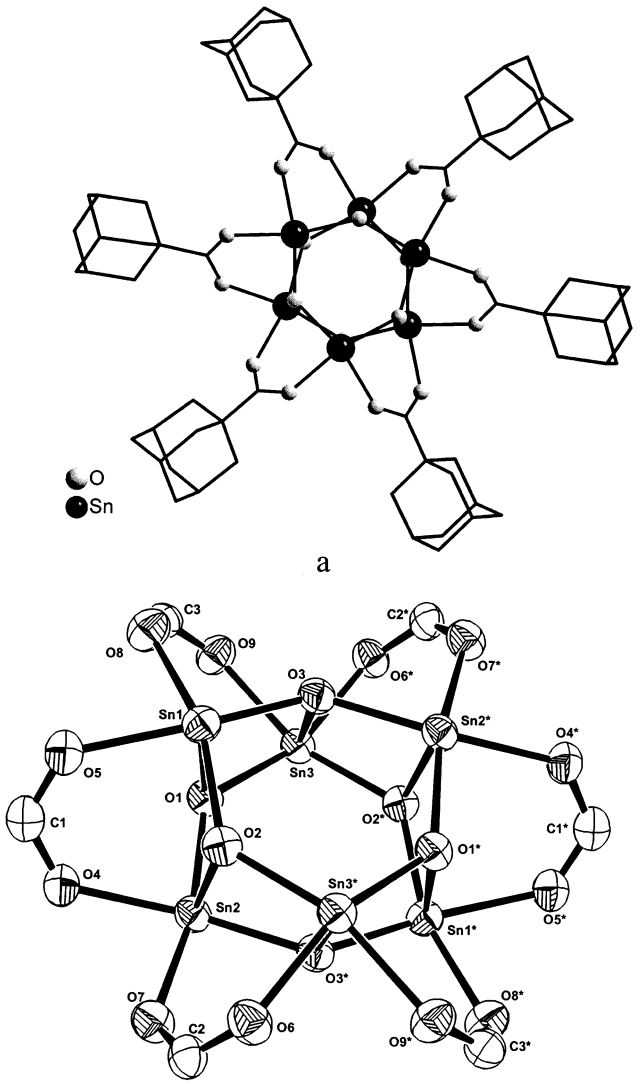

Figure 4. (a) DIAMOND view of the drum **9** (*n*-butyl groups on tin have been omitted for clarity) and (b) ORTEP view of the Sn_6O_6 core are shown. Selected bond lengths (Å) and bond angles (deg) for **9**: Sn2−O1 2.078(15), Sn1*−O2* 2.078(9), Sn3−O2* 2.088(20), Sn3−O1 2.094(4), Sn2−O3* 2.092(25), Sn1*−O3* 2.090(13), Sn3−O3 2.098(3), Sn2*−O2* 2.094(5), Sn2*−O3* 2.092(25), Sn3−O9 2.162(15), Sn1−O8 2.168(4), Sn1−O5 2.181(17), Sn2−O4 2.161(28), Sn2−O7 2.162(14), Sn3*−O6 2.160(11), Sn1−O2−Sn3* 132.93(16), Sn3*−O1*−Sn2* 131.47(16), Sn2*−O3−Sn1 133.69(17), Sn1−O3−Sn3 100.18(14), Sn3−O1−Sn1 100.29(14), Sn1−O1−Sn2 99.90(13), Sn2−O2−Sn1 99.78(13), O2−Sn2−O3* 78.11(13), O2−Sn3*−O3* 78.12(13).

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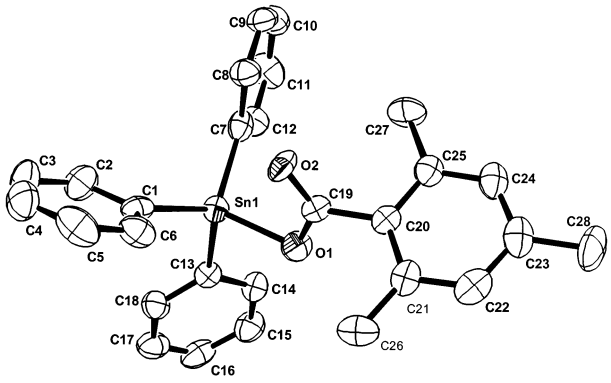

Figure 5. ORTEP view of **10**. Selected bond lengths (Å) and bond angles (deg): Sn1−O1 2.071(6), Sn1−O2 2.769(7), Sn1−C1 2.110(9), Sn1−C7 2.120(9), Sn1−C13 2.135(8), C19−O1 1.309(11), C19−O2 1.230(12), O1−C19−O2 122.85(86), O1−Sn1−C13 95.20(28), O1−Sn1−C1 114.6(3), O1−Sn1−C7 105.75(31), C7−Sn1−C1 116.19(32), C13−Sn1−C1 112.25(31).

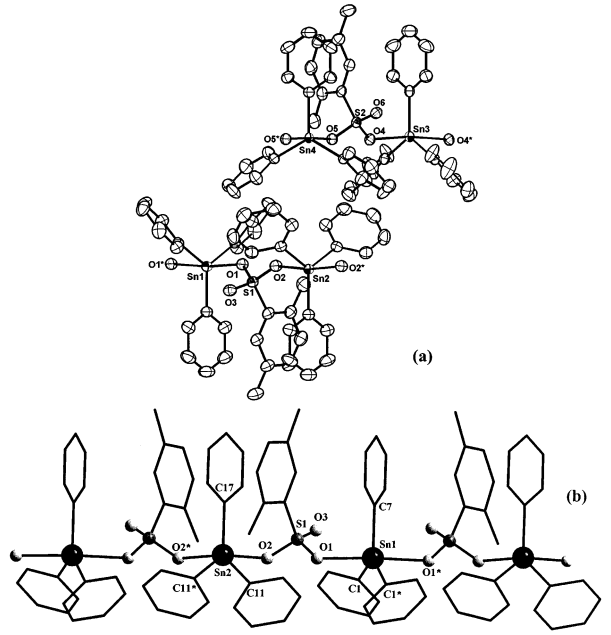

Figure 6. (a) ORTEP view of **11** shown at 50% probability level. The asymmetric unit contains two molecules. (b) DIAMOND view showing the propagation of **11** into a linear polymeric chain. Selected bond lengths (Å) and bond angles (deg): Sn1−O1 2.273(3), Sn2−O2 2.280(3), Sn1−C7 2.114(5), Sn1−C1 2.124(6), Sn1−C1* 2.124(6), Sn2−C11 2.109(6), Sn2−C11* 2.109(6), Sn2−C17 2.110(5), Sn1−O3 1.435(5), O1−Sn1−O1* 174.38(9), C1−Sn1−C1* 117.31(18), C1−Sn1−C7 121.35(10), C7−Sn1−C1 121.35(10), O2−S1−O1 107.56(15), O2−Sn2−O2* 172.53(9), C11*−Sn2−C11 119.88(19), C11−Sn2−C17 120.06(10), C17−Sn2−C11* 120.06(10).

native interaction exists between O2 and Sn1. It is known that discrete structures are preferred for triphenyltin arylcarboxylates.[7]

The molecular structure of **11** is shown in Figure 6. Two molecules are present in the asymmetric unit cell. The molecule adopts a polymeric structure in the solid state. Successive triphenyltin units are linked by a bridging sulfonate moiety. Unlike many polymeric triorganotin carboxylates which adopt zigzag conformations, it may be noticed that the tin centers in the polymeric chain of **11** are arranged in a linear manner. Each tin has trigonal bipyramidal geometry with the axial positions being taken up by the oxygen atoms.

Conclusion

In summary, we have shown that an ambient temperature, solventless solid-state synthesis is a convenient way for the preparation of various types of organotin clusters. Both known and new organotin compounds have been prepared in excellent yield by the use of this methodology. This is the first example of the application of such a benign solid-state solvent-free synthetic methodology for the construction of complicated clusters.

Experimental Section

The following chemicals were purchased and used as such without further purification: ferrocenemonocarboxylic acid (Aldrich), *n*-butyltin hydroxide oxide (Aldrich), *n*-butyltin chloride dihydroxide (Aldrich), *n*-dibutyltin oxide (Aldrich), bis(triphenyltin) oxide (Aldrich), *tert*-butylphosphonic acid (Aldrich), diphenyl phosphinic acid (Aldrich), 2-aminobenzoic acid (Fluka), 4-chlorobenzoic acid (Fluka), 2,6-dimethylbenzoic acid (Aldrich), 2,4,6-trimethylbenzoic acid (Fluka).

Ferroceneacetic acid[13] and 2,5-dimethylbenzene sulfonic acid[14] were prepared using literature procedures. 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. ^{1}H, ^{31}P, and ^{119}Sn NMR spectra were obtained on a JEOL-JNM LAMBDA 400 model spectrometer using $CDCl_3$ solutions (unless specified) with shifts referenced to tetramethylsilane (^{1}H), 85% H_3PO_4 (^{31}P), and tetramethyltin (^{119}Sn), respectively. ^{31}P and ^{119}Sn NMR were recorded under broad-band decoupled conditions.

Synthesis. General Procedure. A typical synthesis involves grinding the organotin precursor with a protic acid (in stoichiometric ratio) at room temperature using a mortar and a pestle. Most of the organotin starting materials are insoluble white solids. Increase in solubility of the mixture with time along with noticeable morphological changes reveals the progress of the reaction. When the solid is completely soluble, a minimum amount of dichloromethane is added and filtered through a G4 frit to remove any insoluble impurities present. Evaporation of the filtrate affords the product. The products **1**−**8** were characterized by spectroscopic techniques (^{1}H, ^{119}Sn, and where required ^{31}P NMR) and elemental analysis. The new compounds **9**−**11** were characterized by spectroscopic, analytical, and single-crystal X-ray diffraction techniques.

The stoichiometric ratios of the reactants, the yield of the product, and the ^{119}Sn chemical shifts (in $CDCl_3$) are given below.

1. [*n*-BuSn(O)OCOFc]$_6$: *n*-BuSn(O)OH (0.10 g, 0.47 mmol), ferrocene carboxylic acid (0.11 g, 0.47 mmol), grinding time: 60 min. Product yield: 0.18 g (90%). Mp: 244 °C (dec) (lit[9a] mp: 244 °C (dec)). ^{119}Sn NMR ($CDCl_3$, ppm): −486.6 (lit. −486.6).[9a]

2. [*n*-BuSn(O)OCOCH$_2$Fc]$_6$: *n*-BuSn(O)OH (0.10 g, 0.47 mmol), ferrocene carboxylic acid (0.12 g, 0.49 mmol), grinding time: 50 min. Product yield: 0.19 g (91%). Mp: 93 °C (lit.[9b] mp: 92 °C). ^{119}Sn NMR ($CDCl_3$, ppm): −483.2 (lit. −483.2).[9b]

3. {[*n*-BuSn(OH)O$_2$PPh$_2$]$_3$O}[O$_2$PPh$_2$]: *n*-BuSn(O)OH (0.19 g, 0.90 mmol), diphenylphosphinic acid (0.26 g, 1.19 mmol), grinding time: 40 min. Product yield: 0.40 g (91%). Mp: 196

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Table 1. Crystal Data and Structure Refinement Parameters for 9, 10, and 11

	9	10	11
empirical formula	$C_{90}H_{132}O_{18}Sn_6$	$C_{28}H_{26}O_2Sn$	$C_{26}H_{24}O_3SSn$
fw	2214.10	513.18	535.20
temperature	213(2) K	213(2) K	150(2) K
wavelength	0.71073 Å	0.71073 Å	0.71073 Å
cryst syst	monoclinic	orthorhombic	monoclinic
space group	*P*2(1)/*c*	*Iba*2	*C*2/*c*
unit cell dimens	$a = 14.885(3)$ Å, $\alpha = 90°$ $b = 16.787(4)$ Å, $\beta = 104.26(2)°$ $c = 19.457(3)$ Å, $\gamma = 90°$	$a = 17.662(3)$ Å, $\alpha = 90°$ $b = 40.678(6)$ Å, $\beta = 90°$ $c = 6.6149(8)$ Å, $\gamma = 90°$	$a = 18.7581(11)$ Å, $\alpha = 90°$ $b = 49.196(3)$ Å, $\beta = 132.6500(10)°$ $c = 13.7580(8)$ Å, $\gamma = 90°$
volume	4712.0(15) Å^3	4752.4(12) Å^3	9338.1(9) Å^3
Z	2	8	16
density (calcd)	1.561 Mg/m^3	1.434 mg/m^3	1.523 Mg/m^3
abs coeff	1.628 mm^{-1}	1.096 mm^{-1}	1.209 mm^{-1}
F(000)	2232	2080	4320
cryst size	0.1 × 0.1 × 0.2 mm^3	0.4 × 0.4 × 0.3 mm^3	0.4 × 0.3 × 0.15 mm^3
θ range for data collection	1.86 to 24.28°	1.89 to 24.17°	1.53 to 25.02°
index ranges	$-17 \le h \le 17$, $-19 \le k \le 19$, $-22 \le l \le 22$	$-20 \le h \le 20$, $-46 \le k \le 46$, $-7 \le l \le 7$	$-22 \le h \le 22$, $-58 \le k \le 38$, $-15 \le l \le 16$
no. of reflns collected	29 646	14 807	24 453
no. of ind reflns	7469 [*R*(int) = 0.0490]	3697 [*R*(int) = 0.1383]	8271 [*R*(int) = 0.0220]
completeness to θ	97.8%	98.3%	99.8%
abs corr	none	none	semiempirical from equivalents
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least-squares on F^2
no. of data/restrains/ params	7469/1305/624	3697/1/283	8271/0/569
goodness-of-fit on F^2	1.026	0.959	1.149
final *R* indices [$I>2\sigma(I)$]	R1 = 0.0428, wR2 = 0.0966	R1 = 0.0489, wR2 = 0.1093	R1 = 0.0358, wR2 = 0.0847
R indices (all data)	R1 = 0.0520, wR2 = 0.1065	R1 = 0.0717, wR2 = 0.1182	R1 = 0.0400, wR2 = 0.0865
largest diff peak and hole	0.675 and −0.856 e Å^{-3}	0.878 and −0.934 e Å^{-3}	0.887 and −0.449 e Å^{-3}

°C (dec) (lit.[9c] mp: 198 °C (dec)). ^{119}Sn NMR ($CDCl_3$, ppm): −498.5 (t, ^2J(Sn−O−P) = 132 Hz) (lit. −498.5).[9c]

4. {(n-Bu)$_2$Sn$_2$Cl$_2$(OH)(O$_2$PPh$_2$)$_3$}$_2$: *n*-BuSn(OH)$_2$Cl (0.10 g, 0.40 mmol), diphenylphosphinic acid (0.13 g, 0.60 mmol), grinding time: 60 min. Product yield: 0.21 g (95%). Mp: 256 °C (lit.[9d] mp: 258−260 °C). ^{119}Sn NMR ($CDCl_3$, ppm): −507.4 (t, ^2J(Sn−O−P) = 222 Hz), −615.4 (m); (lit. −507.4, −615.4).[9d]

5. {(n-Bu)$_2$Sn$_2$O[O$_2$P(OH)-t-Bu]$_4$}$_2$: *n*-BuSn(O)OH (0.10 g, 0.47 mmol), *tert*-butylphosphonic acid (0.13 g, 0.95 mmol), grinding time: 120 min. Product yield: 0.20 g (92%). Mp: 278 °C (dec) (lit.[9e] mp: 280 °C (dec)). ^{119}Sn NMR ($CDCl_3$, ppm): −630.4 (tt, ^2J(Sn−O−P) = 239, 286 Hz) (lit. −630.4).[9e]

6. {n-Bu$_2$Sn(H$_2$O)$_4$}$^{2+}$2{2,5-Me$_2$-C$_6$H$_3$SO$_3$}$^-$: *n*-Bu$_2$SnO (0.10 g, 0.40 mmol), 2,5-dimethylbenzene sulfonic acid (0.15 g, 0.80 mmol), grinding time: 80 min. Product yield: 0.24 (90%). Mp: 273 °C (lit.[10a] mp: 273 °C). ^{119}Sn NMR (in CD_3OD): −360.0 (s) (lit. −360.04).[10a]

7. Ph$_3$SnOC(O)-C$_6$H$_4$-2-NH$_2$: (Ph$_3$Sn)$_2$O (0.13 g, 0.18 mmol), 2-aminobenzoic acid (0.05 g, 0.36 mmol), grinding time: 30 min. Product yield: 0.17 g (96%). Mp: 108 °C (lit.[11a] mp: 108−109 °C). ^{119}Sn NMR ($CDCl_3$, ppm): −119.5 (s) (lit. −119.5).[11a]

8. Ph$_3$SnOC(O)-C$_6$H$_4$-4- Cl: (Ph$_3$Sn)$_2$O (0.11 g, 0.18 mmol), 4-chlorobenzoic acid (0.05 g, 0.31 mmol), grinding time: 30 min. Product yield: 0.15 g (96%). Mp: 129−133 °C (lit.[11b] mp: 128−135 °C). ^{119}Sn NMR ($CDCl_3$, ppm): −108.2 (s) (lit. −108.2).[11b]

9. Synthesis of [n-BuSn(O)OCO-Ad]$_6$. (a) Solventless Method. The general procedure as described above was followed. The quantities of the reactants are *n*-BuSn(O)OH (1.00 g, 4.7 mmol) and adamantane-1-carboxylic acid (0.86 g, 4.7 mmol). Grinding time: 30 min. Crystals suitable for single-crystal X-ray diffraction were obtained by the slow evaporation of a solution of **9** in $CHCl_3$ at room temperature. Yield: 0.97 g (93%). Mp: 280 °C (dec). Anal. Calcd for $C_{90}H_{144}O_{18}Sn_6$: C, 48.55; H, 6.52. Found: C, 48.51; H, 6.40. ^{1}H NMR ($CDCl_3$, ppm): 0.84 (t, 3H, butyl CH_3); 1.07−1.11 (m, 2H, butyl CH_2); 1.28−1.37 (m, 2H, butyl CH_2); 1.56−1.64 (m, br, 8H, adamantly CH_2 and $SnCH_2$); 1.78 (d, 6H, adamantly CH_2); 1.91 (s, br, 3H, adamantly CH). ^{119}Sn NMR ($CDCl_3$, ppm): −486.7 (s).

(b) Conventional Method. A mixture of *n*-BuSn(O)OH (0.63 g, 3.00 mmol) and adamantane-1-carboxylic acid (0.54 g, 3.00 mmol) in toluene (70 mL) was heated under reflux for 6 h. The water formed in the reaction was removed by using a Dean−Stark apparatus. The reaction mixture was filtered and evaporated to afford a white solid whose analytical and spectroscopic data matched with the sample obtained in the preparative route 9a. Yield: 0.92 g (83%).

10. Synthesis of Ph$_3$SnOC(O)-C$_6$H$_2$-2,4,6- Me$_3$. (a) Solventless Method. The procedure described vide supra was followed. The quantities of the reactants are $Ph_3SnOSnPh_3$ (0.29 g, 0.40 mmol) and 2,4,6-trimethylbenzoic acid (0.13 g, 0.80 mmol). Grinding time: 30 min. Crystals suitable for single-crystal X-ray diffraction were obtained by vapor diffusion of *n*-hexane into the solution of **10** in CH_2Cl_2 at room temperature. Yield: 0.38 g (93%). Mp: 110 °C. Anal. Calcd for $C_{28}H_{26}O_2Sn$: C, 65.53; H, 5.11. Found: C, 65.21; H, 5.01. ^{1}H NMR ($CDCl_3$, ppm): 2.16 (s, 9H, CH_3); 6.72 (s, 2H, aromatic); 7.37−7.38 and 7.71−7.73 (m, 15H, aromatic). ^{119}Sn NMR ($CDCl_3$, ppm): −112.5 (s).

(b) Conventional Method. The procedure given in 9b was followed. The quantities of the reactants used are $Ph_3SnOSnPh_3$ (0.72 g, 1.00 mmol) and 2,4,6-trimethylbenzoic acid (0.33 g, 2.00 mmol). Yield: 0.95 g (93%). Analytical and spectroscopic data of this product were exactly similar to those obtained from the preparative route 10a.

(11) Synthesis of [Ph$_3$SnOSO$_2$-C$_6$H$_3$-2,5-Me$_2$]$_n$. (a) Solventless Method. The procedure as described above was followed. The quantities of the reactants taken are $Ph_3SnOSnPh_3$ (0.20 g, 0.27 mmol) and 2,5-dimethylbenzene sulfonic acid (0.10 g, 0.55 mmol). Grinding time: 20 min. Crystals suitable for single-crystal X-ray diffraction were obtained by the slow evaporation of a solution of **11** in a mixture of methanol and toluene. Yield: 0.25 g (85%). Mp: 238 °C. Anal. Calcd for $C_{26}H_{24}O_3SSn$: C, 58.34; H, 4.51. Found: C, 58.11; H, 4.24. ^{1}H NMR: 2.27 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 7.09−7.90 (m, 18H, aromatic). ^{119}Sn (DMSO-d_6, ppm): −238.1.

(b) Conventional Method. A mixture of $Ph_3SnOSnPh_3$ (1.00 g, 1.40 mmol) and 2,5-dimethylbenzene sulfonic acid (0.52 g, 2.80 mmol) in toluene (60 mL) was heated under reflux for 6 h using a Dean−Stark apparatus to remove the water formed in the reaction by azeotropic distillation. A white solid formed in the reaction was filtered by a sintered funnel and dried.

Analytical and spectroscopic data of the white solid matched with the sample obtained from the procedure 11a. Yield: 1.15 g (77%).

X-ray Crystallography. Colorless blocklike crystals of **9**, **10**, and **11** suitable for single-crystal X-ray diffraction were loaded on a Bruker AXS Smart Apex CCD diffractometer. The details pertaining to the data collection and refinement are given in Table 1. In the crystal structure of **9** two adamantyl framework carbons and two butyl carbons were disordered. All the structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97.[15,16] All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. Powder X-ray diffraction patterns were recorded using a Rich-Seifert X-ray diffractometer (model Isodebyeflux 2002) with Cu Kα radiation and a Ni filter.

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