# Oxo Carboxylate Tin Ladder Clusters. A New Structural Class of Organotin Compounds[1]

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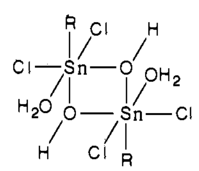
**Abstract:** The hexameric *n*-butyloxotin benzoate, $[n\text{-}BuSn(O)O_2CC_6H_4NO_2\text{-}2]_6\cdot 3C_6H_6$, **1**, and the dimeric methyloxotin cyclohexanoate, $[(MeSn(O)O_2CC_6H_{11})_2MeSn(O_2CC_6H_{11})_3]_2$, **4**, were prepared by condensing the stannoic acid with the respective carboxylic acid. Reaction of *n*-butyltin trichloride with the silver salt of the respective carboxylic acid gave the dimeric *n*-butyloxotin carboxylate compositions, $[(n\text{-}BuSn(O)O_2CR)_2\text{-}n\text{-}BuSn(O_2CR)_3]_2$, **2** (R = Ph) and **3** (R = Me). These represent new substances and, as found by X-ray analysis, form a new structural class of organotin compounds for **2–4** having "unfolded drum" or "ladder" structures. The hexamer composition **1** exists in "drum" form. $^{119}Sn$ NMR data show that the drum and ladder structures interconvert reversibly. **1** crystallizes in the rhombohedral/space group $R\bar{3}$ with $a_H$ = 15.283 (4) Å, $c_H$ = 34.683 (9) Å, and $Z$ = 3. **2** crystallizes in the triclinic space group $P\bar{1}$ with $a$ = 13.657 (6) Å, $b$ = 14.104 (2) Å, $c$ = 14.559 (4) Å, $\alpha$ = 99.14 (2)°, $\beta$ = 111.73 (3)°, $\gamma$ = 101.57 (3)°, and $Z$ = 1. **3** crystallizes in the orthorhombic space group *Pbca* with $a$ = 10.721 (1) Å, $b$ = 23.833 (5) Å, $c$ = 25.138 (5) Å, and $Z$ = 4. **4** crystallizes in the triclinic space group $P\bar{1}$ with $a$ = 12.549 (2) Å, $b$ = 13.368 (3) Å, $c$ = 15.301 (4) Å, $\alpha$ = 82.12 (2)°, $\beta$ = 67.24 (1)°, $\gamma$ = 72.80 (2)°, and $Z$ = 1. The conventional unweighted residuals were 0.037 (**1**), 0.033 (**2**), 0.043 (**3**), and 0.077 (**4**).

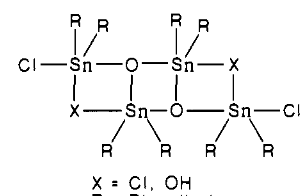
Recently, we reported[3] the first example of a new structural form of tin octahedrally coordinated in a drum-shaped molecule. An X-ray structure of hexameric phenyloxotin cyclohexanecarboxylate, $[PhSn(O)O_2CC_6H_{11}]_6$, showed that the faces of the drum are comprised of six-membered $(\text{–Sn–O–})_3$ tristannoxane rings, and the sides contain four-membered $(\text{–Sn–O–})_2$ distannoxane rings. The hexameric composition apparently formed as a result of slow hydrolysis of triphenyltin cyclohexanoate, $Ph_3SnO_2C(C_6H_{11})$, the major reaction product of $Ph_3SnOH$ and cyclohexane carboxylic acid.

Formation of distannoxane rings seems to be an integral component of hydrolysis products of many organotin compounds.[4] For example, monoalkyltin halides hydrolyze to give distannoxanes of the type




R = *n*-Bu,[5] Et[6]

whereas diorganotin halides give dimeric distannoxanes as end products. These possess "ladder"[4,7,8] or "stair case"[9] structures. Here the tin atoms are pentacoordinated.




X = Cl, OH
R = Ph, alkyl

Similar structural units are found in aluminum chemistry. In the series, $(R_xAlNR)_n$,[10] where $n$ = 4, 6, 7, 8, all the observed structures have components consisting of four- and six-membered rings, including drum compounds[10a,11] ($n$ = 6) analogous to the tin derivative, cubane structures, expanded drums, and an unique heptamer cage structure, $(MeAlNMe)_7$.[10b]

The cubane structure, observed for $(R_2AlNR)_4$[12] so far has no counterpart in stannoxane chemistry. However, an unstable organostannylphosphine, $Ph_4Sn_4P_4$,[13] exists with a proposed cubane form. Further, for tin–sulfur derivatives, admantyl structures are known, e.g., $(MeSn)_4S_6$,[14] which possess six-membered $(\text{–Sn–S–})_3$ rings, as does the cyclic structure found for trimeric $(R_2SnS)_3$ compounds.[8] The latter are similar to the structure of oxygen analogues, e.g., $(t\text{-}Bu_2SnO)_3$.[15]

The above analogies suggest that additional structural forms for tin are possible containing either four- or six-membered rings or both.[26] Toward that end, we have characterized condensation products resulting from the reaction of either a stannoic acid, RSn(O)OH (R = *n*-Bu, Me), with a carboxylic acid or caused coupling between $n\text{-}BuSnCl_3$ and silver salts of benzoic acid and acetic acid.

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(2) This work represents in part a portion of the Ph.D. Thesis of Charles G. Schmid, University of Massachusetts, Amherst, MA.

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The latter reaction was used by Anderson[16] and led to the isolation of tricarboxylates, $R'Sn(O_2CR)_3$. The former reaction is one employed earlier by Lambourne[17] in the synthesis of crystalline $Me_3Sn_3(O)_2(O_2CR)_5$ derivatives.

We report the reaction of *n*-BuSn(O)OH with *o*-nitrobenzoic acid which resulted in a drum derivative, [*n*-BuSn(O)($O_2CC_6H_4NO_2$-2]$_6$·$3C_6H_6$, **1**, sparingly soluble in hot THF. The other reactions reported here produced new derivatives with the composition described by Lambourne.[17] However, as a result of X-ray analysis, this formulation is better represented as a mixed oxycarboxylate–tricarboxylate, $[(R'Sn(O)O_2CR)_2R'Sn(O_2CR)_3]_2$. Accordingly, the compounds we prepared with this formula represent members of this new structural class of oxycarboxylate tin compounds. Relative to this formula, the members are R′ = *n*-Bu and R = Ph, **2**; R′ = *n*-Bu and R = Me, **3**; R′ = Me and R = $C_6H_{11}$, **4**. All of these are found to have an open-drum or "ladder" structure.

$^{119}$Sn NMR data indicate that the compounds retain their structures in chloroform solution in the absence of perturbing influences. Additional NMR evidence indicates that these ladder forms can be made to undergo a reversible reaction leading to the drum form.

## Experimental Section

Chemicals were obtained from Aldrich and Ventron and used without further purification. Methylstannoic acid was prepared according to the procedure given by Lambourne.[17] *n*-Butylstannoic acid was a gift from Koriyama Kasei Co., LTD. (Japan) and was purified by using excess KOH in $CHCl_3$ to remove a small amount of *n*-BuSn(OH)$Cl_2$ and/or *n*-BuSn(OH)$_2$Cl suspected[18] as a contaminant. Solvents used were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.

$^1$H and $^{119}$Sn NMR spectra (proton decoupled) were recorded on a Varian X-L 300 FT/NMR spectrometer equipped with a multinuclear broadband probe and operated at 300 MHz and 11.862 MHz, respectively. Resonances are referenced vs. tetramethylsilane ($^1$H) and tetramethyltin (external standard, $^{119}$Sn). Infrared spectra were recorded by using KBr windows on a Perkin-Elmer Model 180 spectrometer.

**Synthesis. Hexameric *n*-Butyloxotin *o*-Nitrobenzoate [*n*-BuSn(O)$O_2CC_6H_4NO_2$-2]$_6$·$3C_6H_6$ (1).** *n*-Butylstannoic acid, *n*-BuSn(O)OH, (2.17 g, 10.4 mmol) was added to a stirred solution of methylene chloride (50 mL) and benzene (80 mL). *o*-Nitrobenzoic acid (1.74 g, 11.4 mmol) was added, and the mixture was refluxed for 18 h. A Dean-Stark separator was used to azeotropically remove the water generated in the reaction. The clear yellow solution originally present turned to a cream-white cloudy suspension. Upon standing 24 h, a white powder containing small clear crystals was present. This was filtered and washed with benzene. On standing, larger crystals grew from the filtrate. These were isolated. Both the crystals and the powder had the same melting point: mp 295–305 °C dec (total yield 3.65 g, 98%); IR (Nujol) (cm$^{-1}$) 1530, 1550 $\nu_{COO}$; 563, $\nu_{Sn-O}$ 530. Prior to analysis the solid was dried. Anal. Calcd for $C_{66}H_{78}O_{30}N_6Sn_6$: C, 36.91; H, 3.66; N, 3.91. Found: C, 36.43; H, 3.43; N, 3.82.

**Dimeric Bis(*n*-butyloxotin benzoato)-*n*-butyltin Tribenzoate, [(*n*-BuSn(O)$O_2$CPh)$_2$-*n*-BuSn($O_2$CPh)$_3$]$_2$ (2).** *n*-Butyltin trichloride (1.44 g, 5.09 mmol) was dissolved in carbon tetrachloride (50 mL), and to this solution was added silver benzoate (3.75 g, 16.37 mmol). Reflux of this heterogeneous mixture under nitrogen for 3 h and filtration of the silver chloride gave a clear solution. Removal of the solvent yielded a soft, cream-colored solid assumed to be *n*-BuSn($O_2$CPh)$_3$. From a small portion of this solid dissolved in a $CH_2Cl_2$/hexane mixture, two types of crystals grew long clear needlelike crystals, identified as benzoic acid, and large clear chunky crystals of [(*n*-BuSn(O)$O_2$CPh)$_2$-*n*-BuSn($O_2$CPh)$_3$]$_2$. Hydrolysis of the remaining soft solid with wet acetonitrile precipitated a white powder which was collected, washed with cold acetonitrile and dried. This powder had an identical melting point and infrared spectrum to the large chunky crystals [mp 302–303 °C dec (yield 1.68 g, 85.0%); $^{119}$Sn NMR ($CDCl_3$) (ppm) −520 (m), −536 (s), −548 (m), −606 (br)]. The signal at −536 ppm suffered a relative decrease in intensity with time: IR (Nujol) (cm$^{-1}$) 1560, 1535 $\nu_{COO}$, 610, 580 $\nu_{Sn-O}$. Anal. Calcd for $C_{94}H_{104}O_{24}Sn_6$: C, 48.45; H, 4.50. Found: C, 48.23; H, 4.53.

**Dimeric Bis(*n*-butyloxotin acetato)-*n*-butyltin Triacetate, [(*n*-BuSn(O)$O_2$CMe)$_2$-*n*-BuSn($O_2$CMe)$_3$]$_2$ (3).** *n*-Butyltin trichloride (1.23 g, 4.38 mmol) was dissolved in $CH_2Cl_2$ (40 mL) followed by the addition of silver acetate (2.24 g, 13.43 mmol). The mixture was refluxed 4 h. The silver chloride formed was filtered off, and the solvent was removed to give a tan colored solid. Upon sitting for 2 days in the reaction flask, clear crystals grew. These were removed and washed with cold ether. The rest of the tan colored solid was hydrolyzed with 95% ethanol to give additional crystals and a white powder. Both the white powder and the crystals had the same melting point and infrared spectra: mp 292–295 °C dec (total yield 1.07 g, 86.2%); $^{119}$Sn NMR ($CDCl_3$) (ppm) recorded on a sample one week after preparation; −486 (s), −522 (s), −533 (s), −549 (s); IR (Nujol) (cm$^{-1}$) 1595, 1560 $\nu_{COO}$, 610, 575 $\nu_{Sn-O}$, 543. Anal. Calcd for $C_{44}H_{84}O_{24}Sn_6$: C, 30.92; H, 4.95. Found: C, 30.94; H, 4.84.

**Dimeric Bis(methyloxotin cyclohexanoato)methyltin Tricyclohexanoate, [(MeSn(O)$O_2CC_6H_{11}$)$_2$MeSn($O_2CC_6H_{11}$)$_3$]$_2$ (4).** Methylstannoic acid, MeSn(O)OH (1.0 g, 6.0 mmol), was taken in a conical flask under an atmosphere of nitrogen. Cyclohexanecarboxylic acid (2.31 g, 18.0 mmol) was added to it, and the mixture was heated to 100 °C. More cyclohexanecarboxylic acid (4.6 g, 36.0 mmol) was added to the reaction mixture, and heating was continued up to a temperature of 160 °C when a clear solution was formed. It was kept at this temperature for 2 h and allowed to cool. A thick oily mass was the the product. It was heated with 50 mL of anhydrous ether to remove excess cyclohexanecarboxylic acid and filtered. The residue was heated with methylene chloride and filtered. A whitish semicrystalline material was obtained, both from the ether extract and the methylene chloride extract. They both had a melting point of 200–260 °C. They were recrystallized separately, both from a mixture of methylene chloride and Skelly B (1:1) at room temperature, to yield needle like crystals. Crystals obtained from both batches were found to be the same: mp 268–270 °C (total yield of the crystalline solid 0.75 g, 35%); $^1$H NMR ($CDCl_3$) (ppm) 1.24–2.24 (m, aliphatic resonances of cyclohexyl group), 0.60 (s, Sn–C$H_3$); $^{119}$Sn NMR ($CDCl_3$) (ppm) −500.9 (s), −527.0 (s), −607.4 (s); two additional lines of low intensity appeared at −465.9 and −515.6; IR (Nujol) (cm$^{-1}$) 1580, 1545 $\nu_{COO}$, 590, 560 $\nu_{Sn-O}$. Anal. Calcd for $C_{76}H_{128}O_{24}Sn_6$: C, 42.70; H, 6.03. Found: C, 41.70; H, 5.90.

**X-ray Studies.** All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite monochromated molybdenum radiation (λ K$\alpha_1$ = 0.70930, λ K$\alpha_2$ = 0.71359 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[19]

Crystals were mounted inside of thin-walled glass capillaries which were sealed as a precaution against moisture. The structures were solved by using standard Patterson and difference Fourier techniques and were refined by using full-matrix least-squares.[20]

**X-ray Crystallographic Study for [*n*-BuSn(O)$O_2CC_6H_4NO_2$-2]$_6$·$3C_6H_6$ (1).** The colorless crystal used for the X-ray study was cut from a larger polycrystal and was nearly a triangular prism with edge lengths of 0.23 mm and a height of 0.13 mm.

**Crystal Data.** ($C_{11}H_{13}O_5NSn$)$_6$·$3C_6H_6$, rhombohedral space group $R\bar{3}$ [$C^2_{3i}$—No. 148],[21] hexagonal setting, $a_H$ = 15.283 (4) Å, $c_H$ = 34.683 (9) Å, $Z$ = 3 and $\mu_{Mo\ K\alpha}$ = 1.671 mm$^{-1}$. A total of 3052 independent reflections (+$h$,+$k$,±$l$) was measured by using the $\theta$–$2\theta$ scan mode for 3° ≤ $2\theta_{Mo\ K\alpha}$ ≤ 50°. No corrections were made for absorption.

The 21 independent non-hydrogen atoms were refined anisotropically. The 13 hydrogen atoms with positions which could be inferred from the molecular geometry were included in the refinement as fixed isotropic scatterers whose coordinates were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. Positions for the three independent methyl hydrogen atoms were obtained from a difference Fourier synthesis, and these atoms were also included in the refinement as fixed isotropic scatterers. The final agreement factors[22] were $R$ = 0.037 and $R_w$ = 0.049 for the 2187 reflections having $I \geq 2\sigma_I$.

**X-ray Crystallographic Study for [(*n*-BuSn(O)$O_2$CPh)$_2$-*n*-BuSn($O_2$CPh)$_3$]$_2$ (2).** The colorless crystal used for the X-ray study was cut from a larger polyfaceted crystal and had dimensions of 0.20 × 0.28 × 0.33 mm.

**Crystal Data.** [(*n*-BuSn(O)$O_2$CPh)$_2$-*n*-BuSn($O_2$CPh)$_3$]$_2$, **2**, triclinic space group $P\bar{1}$ [$C^1_i$—No. 2],[23] $a$ = 13.657 (6) Å, $b$ = 14.104 (2) Å,

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(20) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean atomic scattering factors were taken from ref 21, 1974, Vol. IV, pp 72–98. Real and imaginary dispersion corrections for Sn and O were taken from the same source, pp 149–150.
(21) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 252.
(22) $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.
(23) Reference 21, p 75.

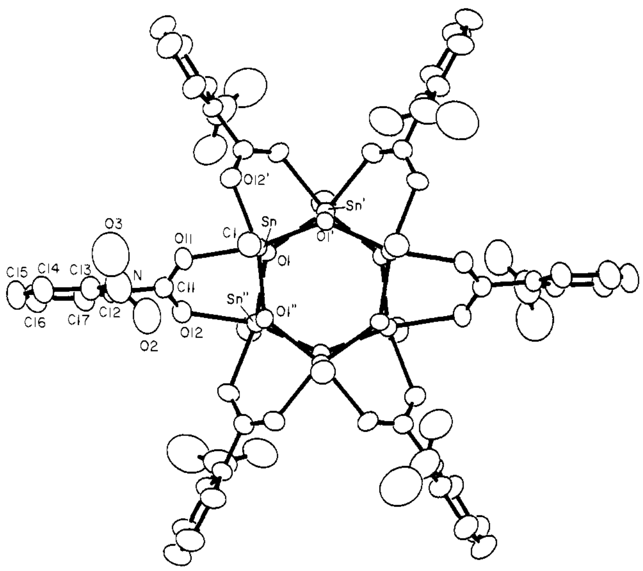


**Figure 1.** ORTEP plot of $[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_4\text{NO}_2\text{-2}]_6\cdot 3\text{C}_6\text{H}_6$, **1** with thermal ellipsoids at the 30% probability level. The three terminal atoms of the *n*-Bu groups (C2, C3, and C4) and the benzene of solvation have been omitted for purposes of clarity. The coordinates of the labeled symmetry related atoms are derived from those in the coordinate list by $' = y, y - x, -z$ and $'' = x - y, x, -z$.

$c$ = 14.559 (4) Å, $\alpha$ = 99.14 (2)°, $\beta$ = 111.73 (3)°, $\gamma$ = 101.57 (3)°, $Z$ = 1, and $\mu_{\text{Mo K}\alpha}$ = 1.566 mm$^{-1}$. A total of 5628 independent reflections ($+h,\pm k,\pm l$) was measured by using the $\theta$–$2\theta$ scan mode for 3° ≤ $2\theta_{\text{MoK}\alpha}$ ≤ 43°. No corrections were made for absorption.

The 62 independent non-hydrogen atoms were refined anisotropically. Hydrogen atoms were omitted from the refinement. The final agreement factors[22] were $R$ = 0.033 and $R_w$ = 0.047 for the 4715 reflections having $I \geq 2\sigma_I$.

**X-ray Crystallographic Study for $[(n\text{-BuSn(O)O}_2\text{CMe})_2\text{-}n\text{-BuSn(O}_2\text{CMe})_3]_2$ (3).** The colorless crystal used for the X-ray study was cut from a fused mass of chunky crystals and had dimensions of 0.23 × 0.24 × 0.25 mm.

**Crystal Data.** $[(n\text{-BuSn(O)O}_2\text{CMe})_2\text{-}n\text{-BuSn(O}_2\text{CMe})_3]_2$, **3**, orthorhombic space group *Pbca* [$D^{15}_{2h}$—No. 61],[24] $a$ = 10.721 (1) Å, $b$ = 23.833 (5) Å, $c$ = 25.138 (5) Å, $Z$ = 4, and $\mu_{\text{Mo K}\alpha}$ = 2.375 mm$^{-1}$. A total of 3666 independent reflections ($+h,+k,+l$) was measured by using the $\theta$–$2\theta$ scan mode for 3° ≤ $2\theta_{\text{Mo K}\alpha}$ ≤ 43°. No corrections were made for absorption.

Of the 37 independent non-hydrogen atoms, 35 were refined anisotropically in full occupancy. Two sets of positions were found for CA2 and CA3 of the *n*-Bu group attached to Sn1, and these two atoms were refined anisotropically in half occupancy for each of their two positions. Hydrogen atoms were omitted from the refinement. The final agreement factors[22] were $R$ = 0.043 and $R_w$ = 0.054 for the 2323 reflections having $I \geq 2\sigma_I$.

**X-ray Crystallographic Study for 4.** The crystal used for data collection was cut from an elongated hexagonal prism, which was a twin, and had dimensions of 0.15 × 0.30 × 0.35 mm.

**Crystal Data.** $[(\text{MeSn(O)O}_2\text{CC}_6\text{H}_{11})_2\text{MeSn(O}_2\text{CC}_6\text{H}_{11})_3]_2$, **4**, triclinic space group $P\bar{1}$,[23] $a$ = 12.549 (2) Å, $b$ = 13.368 (3) Å, $c$ = 15.301 (4) Å, $\alpha$ = 82.12 (2)°, $\beta$ = 67.24 (1)°, $\gamma$ = 72.80 (2)°, $Z$ = 1. A total of 5162 independent reflections ($+h,\pm k,\pm l$) was measured for 2° ≤ $2\theta_{\text{Mo K}\alpha}$ ≤ 43°. Of the 53 independent non-hydrogen atoms, the 23 which were not part of cyclohexyl groups were refined anisotropically. Although it was possible to find positions for the 30 carbon atoms of the five independent cyclohexyl groups which had marginally reasonable initial geometry, refinement including these atoms as isotropic scatterers would not converge. The agreement factors[22] converged to $R$ = 0.077 and $R_w$ = 0.106 for the 3356 reflections having $I \geq 2\sigma_I$.

## Results

The molecular geometry and atom labeling scheme for **1** is shown in the ORTEP plot of Figure 1. Atomic coordinates are given in Table I, while selected bond lengths and angles are given in Table II. The corresponding information for **2** and **3** is given in Figures 2 and 3 and Tables III, IV, and V. Figure 4 displays the structural form of **4**. The basic structure of **1** resembles a "drum" whereas **2–4** are "unfolded drums" or, more descriptively, "ladders".

(24) Reference 21, p 150.

**Table I.** Atomic Coordinates in Crystalline $[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_4\text{NO}_2]_6\cdot 3\text{C}_6\text{H}_6$ (**1**)[a]

| atom[b] | $10^4x$ | $10^4y$ | $10^4z$ |
|---|---|---|---|
| Sn1 | 1639.4 (3) | 1066.5 (3) | 336.8 (1) |
| O1 | 1427 (3) | 931 (3) | −259 (1) |
| O2 | 2452 (6) | 3840 (5) | 858 (2) |
| O3 | 3935 (7) | 4171 (6) | 1018 (2) |
| O11 | 2686 (3) | 2688 (3) | 251 (1) |
| O12 | 1938 (3) | 3090 (3) | −219 (1) |
| N | 3350 (7) | 4232 (5) | 799 (2) |
| C1 | 1820 (5) | 1230 (5) | 947 (2) |
| C2 | 2640 (7) | 1076 (7) | 1119 (2) |
| C3 | 2411 (8) | 5 (7) | 1119 (3) |
| C4 | 3213 (9) | −150 (9) | 1310 (3) |
| C11 | 2589 (5) | 3298 (5) | 41 (2) |
| C12 | 3364 (5) | 4404 (5) | 93 (2) |
| C13 | 3770 (5) | 4821 (5) | 449 (2) |
| C14 | 4526 (6) | 5818 (6) | 490 (3) |
| C15 | 4880 (7) | 6398 (6) | 167 (3) |
| C16 | 4516 (7) | 6022 (6) | −188 (3) |
| C17 | 3733 (6) | 5020 (5) | −229 (2) |
| CA | 2903 (10) | 5637 (7) | 1670 (4) |
| CB1 | 491 (36) | 982 (13) | 2051 (5) |
| CB2 | 1023 (12) | 504 (34) | 2044 (4) |

[a] Numbers in parentheses are esd's. [b] Atoms are labeled to agree with Figure 1. The terminal atoms of the independent *n*-Bu group omitted from Figure 1 are C2–C4. The independent carbon atom for the benzene of solvation having crystallographic $S_6$ symmetry is CA. The two independent carbon atoms for the benzene of solvation having crystallographic $C_3$ symmetry are CB1 and CB2.

**Table II.** Selected Bond Lengths (Å) and Bond Angles (deg) for $[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_4\text{NO}_2]_6\cdot 3\text{C}_6\text{H}_6$ (**1**)[a]

| | | | |
|---|---|---|---|
| Sn–O1 | 2.085 (3) | Sn–O11 | 2.197 (4) |
| Sn–O1′ | 2.088 (4) | Sn–O12′ | 2.193 (4) |
| Sn–O1″ | 2.097 (4) | C11–O11 | 1.249 (7) |
| Sn–C1 | 2.132 (6) | C11–O12 | 1.259 (7) |
| C1–Sn–O1 | 177.8 (2) | C1–Sn–O11 | 91.4 (2) |
| O1′–Sn–O11 | 160.2 (2) | C1–Sn–O12′ | 96.3 (2) |
| O12′–Sn–O1″ | 155.7 (2) | C1–Sn–O1′ | 103.0 (2) |
| O1′–Sn–O1″ | 105.0 (2) | C1–Sn–O1″ | 100.0 (2) |
| O1′–Sn–O1 | 78.0 (2) | O11–Sn–O12′ | 76.3 (2) |
| O1″–Sn–O1 | 77.8 (1) | O11–Sn–O1″ | 85.3 (2) |
| Sn′–O1–Sn″ | 131.5 (2) | O11–Sn–O1 | 77.8 (1) |
| Sn′–O1–Sn | 100.3 (2) | O12′–Sn–O1′ | 88.6 (2) |
| Sn″–O1–Sn | 100.6 (2) | O12′–Sn–O1 | 85.7 (2) |

[a] Numbers in parentheses are esd's. Atoms are labeled to agree with Figure 1.

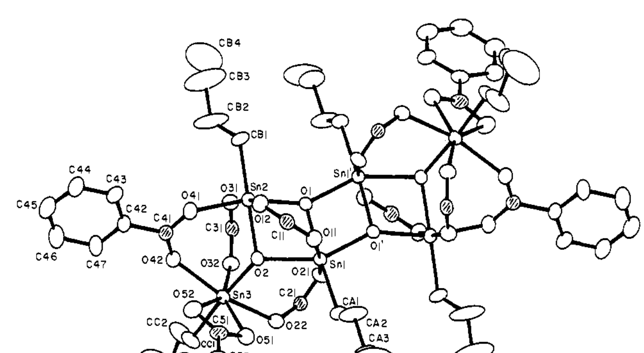


**Figure 2.** ORTEP plot of $[(n\text{-BuSn(O)O}_2\text{CPh})_2\text{-}n\text{-BuSn(O}_2\text{CPh})_3]_2$, **2**, with thermal ellipsoids at the 30% probability level. Six of the ten phenyl group have been omitted for purposes of clarity. Carbon atoms of the carboxyl groups are shaded. Primed atoms are related to unprimed ones by the inversion operation.

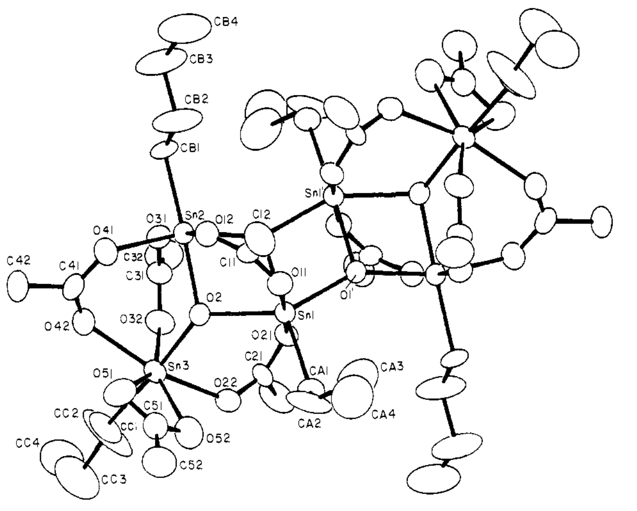


**Figure 3.** ORTEP plot of $[(n\text{-BuSn(O)O}_2\text{CMe})_2\text{-}n\text{-BuSn(O}_2\text{CMe})_3]_2$, **3**, with thermal ellipsoids at the 30% probability level. Primed atoms are related to unprimed ones by the inversion operation. For purposes of clarity, only one set of positions for the disordered CA2 and CA3 is shown.

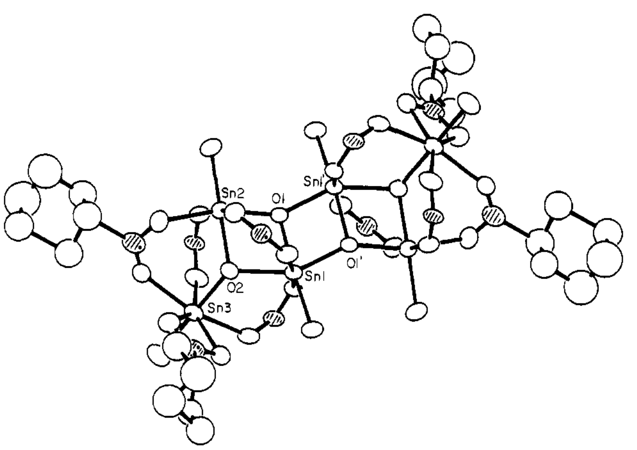


**Figure 4.** ORTEP plot showing the partially refined structure of $[(\text{MeSn(O)}_2\text{CC}_6\text{H}_{11})_2\text{MeSn(O}_2\text{CC}_6\text{H}_{11})_3]_2$, **4**, with thermal ellipsoids at the 20% probability level. Six of the ten cyclohexyl groups are omitted for purposes of clarity. Carbon atoms of the carboxyl groups are shaded. Primed atoms are related to unprimed ones by the inversion operation.

Thermal parameters and additional bond lengths and angles for **1**, **2**, and **3** and hydrogen atom parameters for **1** are provided as Supplementary Material.

## Discussion

**Synthesis.** Two routes were used to prepare the oxocarboxylates **1**–**4**. For the derivatives having the drum composition **1** or the ladder formulation **4** a condensation reaction between the stannoic acid and carboxylic acid proceeded according to eq 1 and 2, respectively.

$$6n\text{-BuSn(O)OH} + 6\text{HO}_2\text{CC}_6\text{H}_4\text{NO}_2\text{-2} \xrightarrow{\text{C}_6\text{H}_6} [n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_4\text{NO}_2\text{-2}]_6\cdot3\text{C}_6\text{H}_6 + 6\text{H}_2\text{O} \quad (1)$$

$$6\text{MeSn(O)OH} + 10\text{C}_6\text{H}_{11}\text{CO}_2\text{H} \rightarrow [(\text{MeSn(O)O}_2\text{CC}_6\text{H}_{11})_2\,\text{MeSn(O}_2\text{CC}_6\text{H}_{11})_3]_2 + 8\text{H}_2\text{O} \quad (2)$$

In contrast, the preparation of **2** and **3** was achieved by reacting $n$-butyltin trichloride with the silver salt of the corresponding acid, followed by hydrolysis as expressed in eq 3. Anderson[16] has shown

$$6n\text{-BuSnCl}_3 + 10\text{Ag}^+\text{RCO}_2^- + 4\text{H}_2\text{O} \rightarrow [(n\text{-BuSn(O)O}_2\text{CR})_2\text{-}n\text{-BuSn(O}_2\text{CR})_3]_2 + 10\text{AgCl} + 8\text{HCl} \quad (3)$$

that organotin tricarboxylates can be distilled in high yield from the reaction of organotin trichlorides and silver salts of carboxylic acids. Further, he established that the tricarboxylates readily hydrolyze in a reversible reaction leading to an oxycarboxylate composition of unspecified degree of polymerization, e.g., eq 4.

$$n\text{-BuSn(O}_2\text{CR)}_3 + \text{H}_2\text{O} \rightarrow {}^1/_x(n\text{-BuSn(O)O}_2\text{CR})_x + 2\text{RCO}_2\text{H} \quad (4)$$

**Table III.** Atomic Coordinates in Crystalline $\{[n\text{-BuSn(O)O}_2\text{CPh}]_2[n\text{-BuSn(O}_2\text{CPh)}_3]\}_2$ (**2**)[a]

| atom[b] | $10^4x$ | $10^4y$ | $10^4z$ |
|---|---|---|---|
| Sn1 | 40.7 (3) | 154.1 (3) | 1152.7 (3) |
| Sn2 | 1738.5 (4) | 2173.3 (3) | 1261.0 (3) |
| Sn3 | 387.8 (4) | 2485.9 (3) | 1956.1 (3) |
| O1 | 564 (3) | 903 (3) | 242 (3) |
| O2 | 906 (3) | 1663 (3) | 2101 (3) |
| O11 | 1686 (3) | -99 (3) | 1733 (3) |
| O12 | 2859 (3) | 1366 (3) | 1978 (3) |
| O21 | -1472 (3) | 567 (3) | 610 (3) |
| O22 | -1241 (3) | 1318 (3) | 2177 (3) |
| O31 | 668 (4) | 3075 (3) | 769 (3) |
| O32 | -491 (4) | 2918 (3) | 1527 (3) |
| O41 | 2802 (4) | 3367 (3) | 2598 (3) |
| O42 | 1597 (4) | 3863 (3) | 3124 (3) |
| O51 | 552 (4) | 1374 (3) | 3889 (3) |
| O52 | 1987 (4) | 2663 (4) | 4478 (4) |
| C11 | 2637 (5) | 489 (5) | 2102 (5) |
| C12 | 3561 (5) | 135 (5) | 2716 (5) |
| C13 | 4622 (6) | 807 (6) | 3215 (6) |
| C14 | 5487 (7) | 474 (8) | 3798 (6) |
| C15 | 5308 (7) | -493 (7) | 3912 (6) |
| C16 | 4252 (8) | -1167 (7) | 3407 (6) |
| C17 | 3377 (7) | -841 (6) | 2817 (6) |
| C21 | -1816 (5) | 994 (5) | 1220 (5) |
| C22 | -2937 (5) | 1107 (5) | 789 (4) |
| C23 | -3523 (6) | 867 (6) | -272 (5) |
| C24 | -4553 (7) | 1019 (8) | -695 (6) |
| C25 | -5006 (7) | -1421 (8) | 56 (7) |
| C26 | -4422 (7) | 1651 (8) | 1009 (6) |
| C27 | -3394 (6) | 1478 (6) | 1430 (5) |
| C31 | -232 (6) | 3116 (4) | 824 (5) |
| C32 | -1051 (6) | 3417 (5) | -13 (5) |
| C33 | -730 (8) | 3751 (6) | -751 (6) |
| C34 | -1509 (9) | 3999 (8) | -1557 (7) |
| C35 | -2574 (10) | 3891 (8) | -1616 (7) |
| C36 | -2880 (8) | 3559 (8) | -847 (8) |
| C37 | -2097 (6) | 3332 (6) | -28 (6) |
| C41 | 2514 (5) | 3994 (5) | 3106 (4) |
| C42 | 3387 (5) | 4968 (5) | 3720 (5) |
| C43 | 4429 (6) | 5124 (5) | 3738 (5) |
| C44 | 5243 (7) | 6021 (6) | 4310 (6) |
| C45 | 5011 (8) | 6749 (6) | 4867 (7) |
| C46 | 3954 (8) | 6610 (6) | 4842 (7) |
| C47 | 3119 (7) | 5692 (5) | 4270 (6) |
| C51 | 1498 (5) | 1856 (5) | 4572 (5) |
| C52 | 1974 (5) | 1457 (5) | 5475 (4) |
| C53 | 1495 (6) | 473 (6) | 5425 (5) |
| C54 | 1908 (6) | 106 (6) | 6301 (6) |
| C55 | 2777 (6) | 725 (7) | 7186 (6) |
| C56 | 3259 (6) | 1710 (7) | 7225 (6) |
| C57 | 2858 (6) | 2083 (6) | 6362 (5) |
| CA1 | -424 (6) | -731 (5) | 2079 (5) |
| CA2 | 251 (9) | -1426 (7) | 2431 (8) |
| CA3 | -173 (10) | -2035 (7) | 3073 (9) |
| CA4 | 599 (16) | -2591 (13) | 3608 (13) |
| CB1 | 2702 (7) | 2623 (6) | 448 (6) |
| CB2 | 2846 (18) | 3580 (11) | 297 (16) |
| CB3 | 3636 (24) | 3853 (15) | -169 (22) |
| CB4 | 3247 (22) | 4238 (24) | -952 (19) |
| CC1 | -296 (6) | 3286 (6) | 3808 (5) |
| CC2 | -1012 (8) | 3898 (8) | 3265 (7) |
| CC3 | -1678 (9) | 4203 (9) | 3882 (9) |
| CC4 | -2407 (14) | 4796 (14) | 3352 (9) |

[a] Numbers in parentheses are esd's. [b] Atoms are labeled to agree with Figure 2. The carbon atoms of the three independent phenyl groups omitted from Figure 2 are labeled C12–C17 (C12 bonded to C11), C22–C27 (C22 bonded to C21), and C32–C37 (C32 bonded to C31).

Table IV. Atomic Coordinates in Crystalline $\{[n\text{-BuSn(O)O}_2\text{CMe}]_2[n\text{-BuSn(O}_2\text{CMe)}_3]\}_2$ (3)[a]

| atom[b] | $10^4x$ | $10^4y$ | $10^4z$ |
|---|---|---|---|
| Sn1 | 733.7 (8) | -34.4 (4) | 567.9 (3) |
| Sn2 | 1907.5 (9) | 1040.0 (3) | -28.2 (3) |
| Sn3 | 1906.4 (9) | 1102.4 (4) | 1411.4 (3) |
| O1 | 474 (7) | 471 (3) | -82 (3) |
| O11 | 2321 (8) | -364 (3) | 134 (3) |
| O12 | 3199 (8) | 380 (4) | -227 (3) |
| O2 | 1850 (8) | 691 (3) | 726 (3) |
| O21 | -857 (8) | 356 (3) | 949 (3) |
| O22 | 196 (8) | 636 (4) | 1655 (3) |
| O31 | 659 (8) | 1694 (3) | 214 (3) |
| O32 | 309 (9) | 1602 (4) | 1082 (4) |
| O41 | 3560 (8) | 1482 (4) | 213 (4) |
| O42 | 2990 (9) | 1770 (3) | 1027 (4) |
| O52 | 4093 (11) | 864 (5) | 1494 (4) |
| O51 | 2657 (10) | 351 (4) | 1831 (4) |
| C11 | 3110 (13) | -138 (6) | -157 (5) |
| C12 | 4046 (13) | -520 (6) | -425 (6) |
| C21 | -824 (14) | 555 (5) | 1411 (5) |
| C22 | -2022 (12) | 681 (8) | 1703 (6) |
| C31 | 56 (14) | 1785 (6) | 628 (6) |
| C32 | -1149 (16) | 2107 (8) | 569 (7) |
| C41 | 3738 (14) | 1755 (6) | 639 (7) |
| C42 | 4939 (14) | 2098 (7) | 666 (6) |
| C51 | 3776 (17) | 451 (7) | 1748 (6) |
| C52 | 4775 (14) | 51 (7) | 1985 (7) |
| CA1 | 1048 (13) | -601 (6) | 1213 (5) |
| CA2[c] | 1519 (31) | -1194 (12) | 1021 (11) |
| CA2'[c] | 2291 (44) | -957 (16) | 1210 (12) |
| CA3[c] | 2931 (31) | -1186 (18) | 1167 (16) |
| CA3'[c] | 2070 (45) | -1440 (16) | 871 (19) |
| CA4 | 3331 (23) | -1774 (9) | 921 (10) |
| CB1 | 1986 (14) | 1426 (5) | -802 (5) |
| CB2 | 2727 (22) | 1108 (9) | -1206 (6) |
| CB3 | 2655 (28) | 1442 (10) | -1724 (8) |
| CB4 | 2985 (39) | 1129 (11) | -2150 (10) |
| CC1 | 1882 (16) | 1603 (7) | 2111 (6) |
| CC2 | 835 (22) | 1869 (12) | 2270 (8) |
| CC3 | 751 (21) | 2176 (10) | 2806 (9) |
| CC4 | 0 (28) | 2618 (12) | 2745 (10) |

[a] Numbers in parentheses are esd's. [b] Atoms are labeled to agree with Figure 3. [c] Half occupancy.

In one instance, Lambourne[17a] isolated $(\text{MeSn(O)O}_2\text{CMe})_3$ for which the trimer formulation was given based on cryoscopic measurements in phenol.

For $[\text{MeSn(O)O}_2\text{CR}]_6$, R = Et, Pr, *i*-Pr, Lambourne[17b] obtained hexamer compositions from cryoscopic molecular weight determinations in benzene. The isolation of different reaction products by us and by Anderson[16] using similar reactants, according to eq 3, suggest that the tricarboxylate formulation, $\text{R'Sn(O}_2\text{CR)}_3$, is an intermediate in the reaction sequence leading to the oxocarboxylate compositions, **1**–**4**.

Not only do the tricarboxylate compositions readily hydrolyze, eq 4, but as our NMR data show, a reversible reaction is established in some cases between the drum and ladder forms. Subtraction of eq 2 from eq 1, in general form, leads to the hydrolysis reaction in eq 5. Hence, the drum is a hydrolysis product further

$$[(\text{R'Sn(O)O}_2\text{CR})_2\text{R'Sn(O}_2\text{CR)}_3]_2 + 2\text{H}_2\text{O} \rightarrow [\text{R'Sn(O)O}_2\text{CR}]_6 + 4\text{RCO}_2\text{H} \quad (5)$$

along the sequence from the tricarboxylate composition than is the ladder. Whereas it takes 1 mol of $H_2O$ per mol of tricarboxylate to form the drum structure (eq 4), only $^2/_3$ of a mol of $H_2O$ are required to form the ladder.

**$^{119}$Sn NMR Data.** NMR evidence showing partial conversion of ladders to drums has been obtained for the mixed oxocarboxylate tricarboxylates **2**–**4**. For example, three major $^{119}$Sn signals for **4** at −500.9, −527.0, and −607.4 ppm are assignable to the three nonequivalent tin sites in this ladder structure. The most shielded tin atoms are obviously the pair of terminal tins which are seven-coordinated. It seems reasonable to assign the successively observed lower field peaks to pairs of tin atoms located

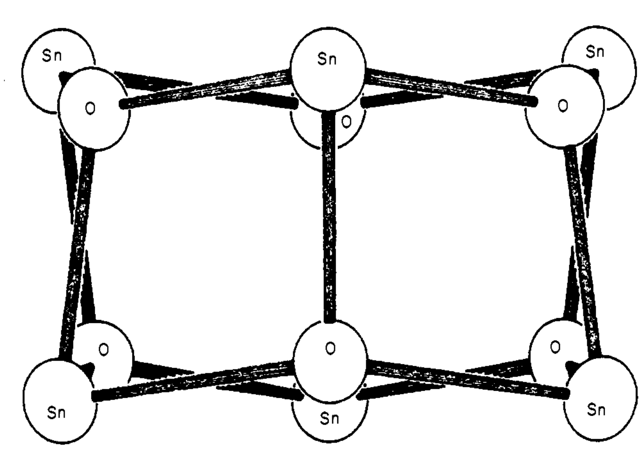


Figure 5. ORTEP plot showing the Sn–O framework of the "drum" in $[n\text{-BuSn(O)}_2\text{CC}_6\text{H}_4\text{NO}_2\text{-2}]_6\cdot 3\text{C}_6\text{H}_6$, **1**.

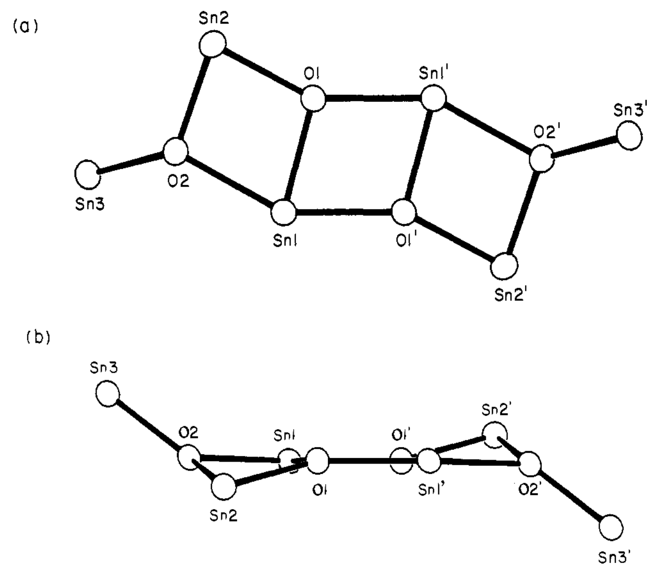


Figure 6. ORTEP plot showing the Sn–O framework of the "unfolded drum" in $[(n\text{-BuSn(O)O}_2\text{CPh})_2\text{-}n\text{-BuSn(O}_2\text{CPh)}_3]_2$, **2**: (a) viewed normal to the central $Sn_2O_2$ plane and (b) viewed parallel to the central $Sn_2O_2$ plane.

progressively toward the center of the ladder structure. Two additional $^{119}$Sn signals of low intensity are present at −465.9 and −515.6 ppm. The former signal may be due to the drum, $[\text{MeSn(O)O}_2\text{CC}_6\text{H}_{11}]_6$, formed by loss of carboxylic acid, eq 5, whereas the signal at 515.6 ppm may be due to an intermediate on the way to the formation of the drum.

The range of $^{119}$Sn chemical shifts observed for drums[18] is −478 to −485 ppm for butylstannoic acid derivatives. It is reasonable that the lower field signal at −465.9 ppm for **4** is due to the drum formed in the hydrolysis of eq 5. Addition of carboxylic acid to a solution of pure drum causes the appearance of $^{119}$Sn NMR signals associated with the ladder formulation.[18]

These data are in agreement with earlier work of Lambourne[17a] suggesting the presence of the reversibility of eq 5. He found that the "pentacetyl" derivative, $\text{Me}_3\text{Sn}_3\text{(O)}_2\text{(O}_2\text{CMe)}_5$, (identified in our work as the ladder structure, $[(\text{R'Sn(O)O}_2\text{CR})_2\ \text{R'Sn(O}_2\text{CR)}_3]_2$) underwent partial hydrolysis to produce a much more stable "triacetyl" compound, $(\text{MeSn(O)O}_2\text{CMe})_3$ (in our work, we have established drum compositions $[\text{R'Sn(O)O}_2\text{CR}]_6$). Further he showed that the original "pentacetyl" compound was formed by prolonged action of excess glacial acetic acid on the "triacetyl" derivative.

Similar to **4**, the three $^{119}$Sn NMR signals recorded as broad at −606 ppm and as multiplets at −548 and −520 ppm for the benzoate derivative **2** are assigned to the "ladder", and the signal at −536 ppm is assigned to an intermediate. The components of the multiplet at −548 ppm are −545, −548, and −550 ppm while

**Table V.** Selected Bond Lengths (Å) and Bond Angles (deg) for $[(n\text{-BuSn(O)O}_2\text{CR})_2\text{-}n\text{-BuSn(O}_2\text{CR})_3]_2$ (**2**), (R = Ph) and (**3**) R = Me[a]

| compound | 2 | 3 | compound | 2 | 3 |
|---|---|---|---|---|---|
| O1–Sn1 | 2.051 (4) | 2.049 (7) | O41–Sn2 | 2.147 (5) | 2.148 (9) |
| O1–Sn2 | 2.060 (4) | 2.054 (7) | O42–Sn3 | 2.189 (5) | 2.194 (9) |
| O1–Sn1′ | 2.079 (5) | 2.061 (7) | O51–Sn3 | 2.218 (5) | 2.229 (10) |
| O2–Sn1 | 2.161 (4) | 2.140 (7) | O52–Sn3 | 2.407 (5) | 2.421 (12) |
| O2–Sn2 | 2.067 (4) | 2.072 (7) | C11–O11 | 1.253 (8) | 1.241 (4) |
| O2–Sn3 | 1.985 (4) | 1.983 (7) | C11–O12 | 1.268 (8) | 1.251 (14) |
| Sn1–CA1 | 2.154 (7) | 2.137 (12) | C21–O21 | 1.275 (9) | 1.254 (13) |
| Sn2–CB1 | 2.143 (8) | 2.153 (11) | C21–O22 | 1.257 (8) | 1.269 (14) |
| Sn3–CC1 | 2.129 (7) | 2.126 (12) | | | |
| O11–Sn1 | 2.210 (4) | 2.169 (9) | C31–O31 | 1.272 (8) | 1.243 (15) |
| O12–Sn2 | 2.149 (5) | 2.159 (8) | C31–O32 | 1.264 (8) | 1.252 (14) |
| O21–Sn1 | 2.161 (4) | 2.166 (8) | C41–O41 | 1.263 (8) | 1.267 (16) |
| O22–Sn3 | 2.242 (5) | 2.230 (9) | C41–O42 | 1.252 (8) | 1.264 (16) |
| O31–Sn2 | 2.130 (5) | 2.143 (8) | C51–O51 | 1.269 (8) | 1.241 (17) |
| O32–Sn3 | 2.232 (4) | 2.244 (9) | C51–O52 | 1.242 (8) | 1.221 (17) |
| Sn1–O1–Sn1′ | 104.8 (2) | 105.2 (3) | O2–Sn2–O41 | 87.9 (2) | 87.9 (3) |
| Sn1–O1–Sn2 | 103.7 (2) | 103.5 (3) | O2–Sn2–O12 | 84.7 (2) | 86.5 (3) |
| Sn2–O1–Sn1′ | 148.2 (2) | 147.4 (4) | O2–Sn2–O31 | 90.4 (2) | 90.7 (3) |
| Sn1–O2–Sn2 | 99.7 (2) | 99.8 (3) | CB1–Sn2–O1 | 103.0 (3) | 104.6 (4) |
| Sn3–O2–Sn2 | 126.0 (2) | 126.6 (4) | CB1–Sn2–O41 | 95.1 (3) | 90.8 (5) |
| Sn3–O2–Sn1 | 125.9 (2) | 125.3 (4) | CB1–Sn2–O12 | 89.7 (3) | 94.4 (4) |
| CA1–Sn1–O1 | 174.5 (2) | 176.4 (4) | CB1–Sn2–O31 | 91.7 (3) | 88.3 (4) |
| O11–Sn1–O21 | 173.7 (2) | 174.8 (3) | O1–Sn2–O12 | 93.5 (2) | 89.1 (3) |
| O2–Sn1–O1′ | 150.4 (2) | 150.4 (3) | O1–Sn2–O31 | 91.6 (2) | 91.8 (3) |
| O1–Sn1–O2 | 75.2 (1) | 75.5 (3) | O41–Sn2–O12 | 83.2 (2) | 83.9 (3) |
| O1–Sn1–O1′ | 75.2 (2) | 71.8 (3) | CC1–Sn3–O2 | 175.2 (3) | 174.9 (5) |
| O1–Sn1–O11 | 85.5 (2) | 85.3 (3) | O51–Sn3–O2 | 86.8 (2) | 91.4 (3) |
| O1–Sn1–O21 | 90.1 (1) | 89.6 (3) | O52–Sn3–O2 | 91.9 (2) | 89.3 (4) |
| CA1–Sn1–O2 | 107.7 (2) | 106.3 (4) | O51–Sn3–O22 | 76.1 (20) | 76.5 (4) |
| CA1–Sn1–O1′ | 101.9 (2) | 103.3 (4) | O52–Sn3–O22 | 131.7 (2) | 131.0 (3) |
| CA1–Sn1–O11 | 90.1 (1) | 91.7 (4) | O51–Sn3–O42 | 129.5 (2) | 126.9 (4) |
| CA1–Sn1–O21 | 94.5 (2) | 93.4 (4) | O52–Sn3–O42 | 73.9 (2) | 72.3 (4) |
| O2–Sn1–O11 | 84.5 (2) | 87.0 (3) | O51–Sn3–CC1 | 92.3 (2) | 93.7 (5) |
| O2–Sn1–O21 | 90.1 (2) | 90.6 (3) | O52–Sn3–CC1 | 91.5 (2) | 94.2 (5) |
| | | | O51–Sn3–O52 | 55.7 (2) | 54.6 (4) |
| O1′–Sn1–O11 | 94.8 (2) | 90.7 (3) | O32–Sn3–O2 | 85.0 (2) | 85.3 (3) |
| O1′–Sn1–O21 | 88.5 (2) | 89.1 (3) | O32–Sn3–O22 | 75.5 (2) | 74.8 (3) |
| CB1–Sn2–O2 | 174.4 (3) | 178.3 (4) | O32–Sn3–O42 | 79.0 (2) | 81.8 (4) |
| O12–Sn2–O31 | 171.9 (2) | 176.8 (3) | O32–Sn3–CC1 | 93.5 (3) | 89.9 (5) |
| O1–Sn2–O41 | 165.0 (2) | 163.6 (3) | O2–Sn3–O42 | 92.1 (2) | 89.6 (3) |
| O2–Sn2–O1 | 77.1 (2) | 76.9 (3) | O2–Sn3–O22 | 87.3 (2) | 88.1 (3) |
| O41–Sn2–O31 | 90.2 (2) | 94.5 (3) | CC1–Sn3–O42 | 92.1 (3) | 87.9 (5) |
| O32–Sn3–O51 | 150.7 (2) | 151.2 (4) | CC1–Sn3–O22 | 87.8 (3) | 92.4 (5) |
| O32–Sn3–O52 | 152.5 (2) | 153.5 (4) | | | |
| O22–Sn3–O42 | 154.4 (2) | 156.6 (3) | | | |

[a] Numbers in parentheses are esd's. Atoms are labeled to agree with Figures 3 and 4.

the components of the multiplet at −520 ppm are −517, −520, −522, and −523 ppm.

For the week old sample of the acetate compound **3** the high field signal assignable to the terminal tin atoms of the ladder was not observed. This agrees with the presence of only weak intensity signals at −522 and −549 ppm which are assigned to the two other types of tin atoms in **3**. Correspondingly, a strong signal at −486 ppm supports the formation of the drum structure in this sample according to eq 5. The relatively weak signal at −533 ppm is assigned to an intermediate.

**IR Data.** Infrared bands corresponding to the bridging carboxyl groups and the Sn–O stretching vibration are very useful in discriminating between the drum and ladder forms. For drum structures, the carboxyl absorption, $\nu_{COO}$, appears as a symmetrical doublet centered near 1550 $cm^{-1}$, whereas the ladders have an unsymmetrical doublet absorption in this same region. A very strong band around 600 $cm^{-1}$, characteristic of the Sn–O–Sn linkage,[25] is assigned to $\nu_{Sn-O}$ for the drum form. Ladders, however, give two bands in this region of the spectrum. The infrared data recorded here for **1–4** are consistent with these patterns that have been observed on additional derivatives of both structural forms.[18]

**Structural Details.** The drum compound **1** has crystallographic $S_6$ symmetry, so that the six tin atoms are both crystallographically and chemically equivalent. The hexacoordinated tin atoms have distorted octahedral geometry. For each hexamer in the unit cell there are three benzene molecules of solvation, one with crystallographic $S_6$ symmetry and two with crystallographic $C_3$ symmetry.

The ladder or "unfolded drum" compounds **2** and **3** have crystallographic $C_i$ symmetry, which corresponds to the idealized molecular symmetry. There are, therefore, three chemically nonequivalent types of Sn atoms in the molecules. Both compounds have similar geometries in which Sn1 and Sn2 are both hexacoordinated and have distorted octahedral geometry. The terminal Sn3, however, is heptacoordinated and has pentagonal bipyramidal geometry with O2 and CC1 in axial positions. For **2**, the five ligand atoms and the Sn3 atom comprising the equatorial plane are coplanar to within ±0.081 Å, while the axial angle O2–Sn3–CC1 is 175.2 (3)°. For **3**, these values are ±0.057 Å and 174.9 (5)°.

The general structural features of the methyloxotin cyclohexanoate **4** are very similar to those of **2** and **3**, as shown in Figure 4. This compound also has crystallographic $C_i$ symmetry.

The Sn–O framework of the "drum" in **1** is shown in Figure 5. The general features of this framework are the same as for

(25) Brown, M. P.; Okawara, R.; Rochow, E. G. Spectrochimica *Acta* **1960**, *16*, 595–601. Ford, B. F. E.; Liengme, B. V.; Sams, J. R. *J. Organomet. Chem.* **1969**, *19*, 53–65.

(26) **Note Added In Proof.** Recently, we reported a new structural form of tin as an oxygen-capped cluster. Day, R. O.; Holmes, J. M.; Chandrasekhar, V.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 940–941.

the other drum shaped molecules which have been structurally characterized:[3,18] the six-membered rings have a chair conformation while the four-membered rings are not planar due to the fact that the oxygen atoms are tilted toward the center of the cavity, relative to the tin atoms. The Sn–O bond lengths in the framework are 2.088 (4) and 2.097 (4) Å for the six-membered rings and 2.085 (3) Å for the four-membered rings. The bonds are shorter than the Sn–O bonds to the bridging carboxyl oxygen atoms which have values of 2.197 (4) and 2.193 (4) Å.

The Sn–O framework for the unfolded species **2** is shown in Figure 6. In Figure 6b deviations from planarity for this framework can be visualized. Atom Sn1, O1, Sn1′, and O1′ are required by symmetry to be copolanar. The symmetry related O2 atoms lie very nearly in this plane while the Sn2 atoms and the Sn3 atoms are progressively more displaced from this plane in opposite directions. The geometry about the trivalent oxygen atoms, however, tends toward planarity. For **2**, the sum of the angles about O1 is 356.7° and about O2 is 351.6°. For **3**, these values are 356.1° and 351.7°.

As in the case of the drum **1** the framework Sn–O bonds tend to be shorter than the Sn–O bonds to bridging carboxylate groups, with the exception of the Sn1–O2 framework bond. For **2**, the framework Sn–O bonds range from 1.985 (4) to 2.067 (4) Å except for the Sn1–O2 bond length of 2.161 (4) Å, while the bridging Sn–O bond lengths range from 2.189 (5) to 2.242 (5) Å. For **3**, these values are 1.983 (7) to 2.072 (7), 2.140 (7), and 2.143 (8) to 2.244 (9) Å. For both **2** and **3**, the shortest Sn–O bond length is the axial bond of the heptacoordinated Sn3.

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**Supplementary Material Available:** Listings of anisotropic thermal parameters, hydrogen atom parameters, and additional bond lengths and angles (Tables S1–S3, respectively, for **1**), anisotropic thermal parameters and additional bond lengths and angles (Tables S4 and S5, respectively, for **2**, and Tables S6 and S7, respectively, for **3**), deviations from selected least-squares mean planes (Tables S8 and S9 for **2** and **3**, respectively) (13 pages); a listing of observed and calculated structure factors for **1–3** (36 pages). Ordering information is given on any current masthead page.

# Clusters Containing Carbene Ligands. 1. Novel Transformations of Carbene Ligands at Multinuclear Metal Sites. α-Activation of C–H and S–C Bonds in Carbene Containing Thiolatotriosmium Carbonyl Cluster Compounds

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**Abstract:** Treatment of the (arenethiolato)triosmium carbonyl cluster compounds $Os_3(CO)_{10}(\mu\text{-SAr})(\mu\text{-H})$ (**1a**, Ar = $C_6H_5$; **1b**, Ar = $C_6F_5$; **1c**, Ar = $p\text{-}C_6H_4Me$) with the diamines $H_2C(NR_2)_2$ (R = Me or Et) at 97 °C has yielded the new thiolatotriosmium cluster compounds $Os_3(CO)_9[C(H)NR_2](\mu\text{-SAr})(\mu\text{-H})$ (**2a**, R = Me, Ar = $C_6H_5$; **2b**, R = Me, Ar = $C_6F_5$; **2c**, R = Me, Ar = $p\text{-}C_6H_4Me$; **2d**, R = Et, Ar = $p\text{-}C_6H_4Me$) which contain a secondary (dialkylamino)carbene ligand substituted for a carbonyl ligand in the compounds **1a–c**. The structure of **2a** was established by a single-crystal X-ray diffraction analysis. When subjected to UV irradiation the compounds **2a–d** are decarbonylated and transformed into the products $Os_3(CO)_8[\mu\text{-CNR}_2](\mu\text{-SAr})(\mu\text{-H})_2$ (**3a–d**) and isomeric pairs of products $Os_3(CO)_8[\mu\text{-CNR}_2](\mu\text{-SAr})(\mu\text{-H})_2$ (**4a**, **4c**, and **4d** and **5a**, **5c**, and **5d**). Compounds **3a** and **5d** were characterized by single-crystal X-ray diffraction analyses. Compound **3a** contains a triangular cluster of three osmium atoms with bridging benzenethiolato and (dimethylamino)carbyne ligands along adjacent edges of the cluster. Compounds **3** were formed by an α-CH activation of the aminocarbene ligand in the compound **2**. In compound **5d** the arenethiolato ligand was orthometalated at the third metal atom. The secondary aminocarbene ligand was not changed. The compounds **3a–d** were converted into the new carbene containing cluster compounds $Os_3(CO)_8[C(Ar)NR_2](\mu_3\text{-S})(\mu\text{-H})_2$ (**6a–d**) by heating to reflux in octane solvent for 1 h. Compound **6a** was characterized by a single-crystal X-ray diffraction analysis. It contains a triangular cluster of three metal atoms with a triply bridging sulfido ligand and a terminally coordinated phenyl(dimethylamino)carbene ligand. These compounds were formed by the transfer of the aryl group from the thiolato ligand to the carbon atom of the bridging carbyne ligand. A crossover experiment established that the transfer occurred by an intramolecular process. A mechanism which involves a sigmatropic shift of the phenyl group is proposed.

Studies of transition-metal cluster compounds are revealing an increasing number of new and unusual ligand transformations that involve interactions at two or more metal sites.[1,2] An understanding of the scope and mechanisms of these rearrangements will play a central role in developing the potential of these compounds to serve as reaction catalysts.[3]

In our recent studies we have discovered that the osmium cluster complex $Os_3(CO)_9(\mu_3\text{-CO})(\mu_3\text{-S})$ will react with $NMe_3$ by a double C–H activation process to yield the product $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-S})(\mu\text{-H})_2$ which contains a terminally coordi-

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