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# A Spacer-Linked Molecular Diorganotin Oxide

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*Summary: The synthesis and molecular structure are reported of the first example of a diorganotin oxide, {p-[R(O)SnCH$_2$SiMe$_2$]$_2$C$_6$H$_4$}$_3$ (**3**) (R = (Me$_3$Si)$_2$CH), in which two six-membered Sn$_3$O$_3$ units are linked by three −CH$_2$Si(Me)$_2$C$_6$H$_4$Si(Me)$_2$CH$_2$− spacers.*

## Introduction

Diorganotin oxides (R$_2$SnO)$_n$ have been known for many years. Generally they are polymeric ($n = \infty$, R = Me, Et, Bu, vinyl, Ph).[1,2] However, some molecular species have been characterized for diorganotin oxides containing bulky substituents. When R = (Me$_3$Si)$_2$CH, a dimer ($n = 2$)[3] is formed, whereas trimers ($n = 3$) have been reported for cases where R = CH$_2$SiMe$_3$,[4] *t*-Bu, Me$_2$EtC,[5] (Me$_3$Si)$_3$C/Me,[6] 2,6-Me$_2$-C$_6$H$_3$,[7] 2,6-Et$_2$-C$_6$H$_3$,[8] 2,4,6-(CF$_3$)$_3$-C$_6$H$_2$,[9] and 2,4,6-*i*-Pr-C$_6$H$_2$.[10] Furthermore, for R = Me$_3$SiCH$_2$, the existence in solution of a tetramer ($n = 4$) was proposed on the basis of NMR studies.[4] A convenient synthesis of diorganotin oxides is the complete hydrolysis of diorganotin dihalides, R$_2$SnX$_2$ (X = Cl, Br). Dimeric tetraorganodistannoxanes of the type [R$_2$(X)SnOSn(Y)R$_2$]$_2$ (X, Y = Cl, Br, OH) are formed along the hydrolysis path. In addition to some interesting structural features such as the almost perfect planarity of the Sn$_4$O$_2$X$_2$Y$_2$ layer, the latter class of compound is of high practical value, as representatives are efficient catalysts for a variety of organic reactions.[11]

Recently, we used the concept of the preassembly of suitably architectured precursors containing two or three tins to generate larger molecular units. Such precursors in which the tin atoms are connected by flexible oligomethylene-bridged spacers could be transformed to double- and triple-ladders of types **C** and **D**, respectively (Chart 1).[12,13a,b] For example, double ladders of type **C** were obtained by reaction of a spacer-bridged diorganotin dichloride of type **A** with the corresponding spacer-bridged diorganotin oxide of type **B** (Chart 1).

The spacer-linked oxide species **B** have hitherto been amorphous solids and poorly characterized. The use of more rigid spacers such as −CH$_2$Si(Me)$_2$C$_6$H$_4$Si(Me)$_2$CH$_2$− can give rise to different molecular architectures, for example, a unique twisted DL-double-ladder containing eight chiral tin atoms.[14] We now report the use of a more rigid spacer that has enabled characterization for the first time of a spacer-linked molecular tin oxide (**3**).

## Results and Discussion

Compound **3** has been obtained in a multistep procedure as shown in Scheme 1. It is a colorless, crystalline solid that does not melt or decompose until 345 °C and which is only slightly soluble in chloroform, hot benzene, or toluene. Crystals suitable for X-ray crystallography were obtained as the tri-toluene solvate.

The molecular structure of the spacer-bridged diorganotin oxide **3** is illustrated in Figure 2, and key geometric parameters are listed in the caption;[15] there is no molecular symmetry in the structure. The structure features two Sn$_3$O$_3$ units, each of which adopts a flattened chair conformation, that are linked by the three −CH$_2$Si(Me)$_2$C$_6$H$_4$Si(Me)$_2$CH$_2$− spacers that adopt extended conformations as seen in the range of Sn−C−Si−C torsion angles of 163.0(3)−173.4(2)°. The links are arranged so that the tin atoms are directed

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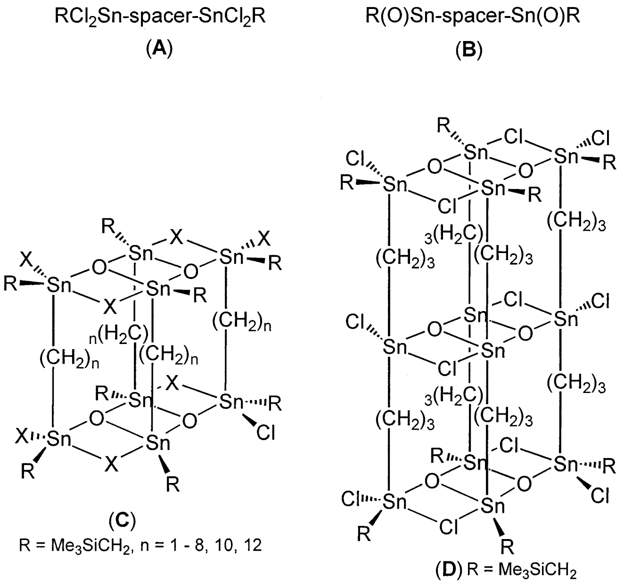
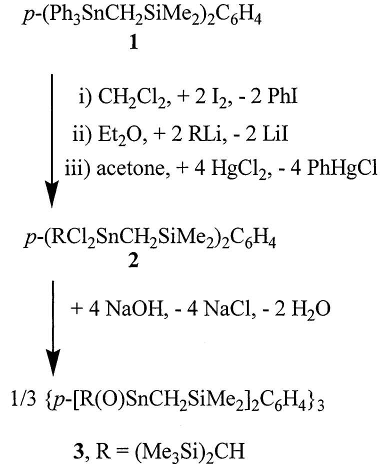
## Chart 1



## Scheme 1



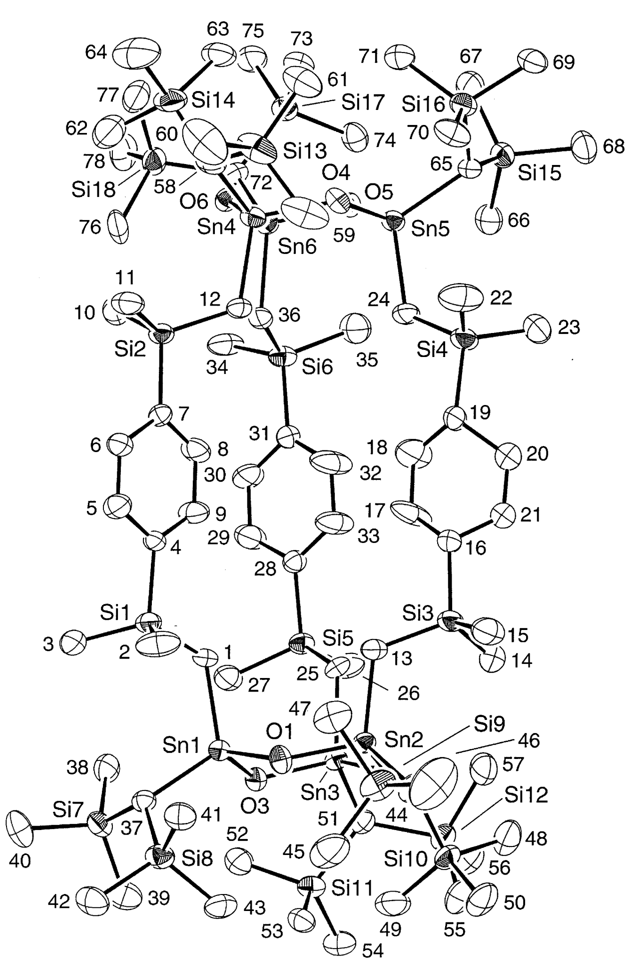


**Figure 1.** Molecular structure of **3** showing the crystallographic numbering scheme. The O2 atom is obscured, only the major conformation of the disordered C20 and C21 atoms is shown, all hydrogen atoms and the three toluene molecules of solvation have been omitted for clarity, and atoms otherwise not indicated are carbons. Selected ranges for bond lengths (Å) and angles (deg): Sn−O 1.964(3)−1.974(3), Sn−C 2.134(6)−2.163(5), O−Sn−O 103.6(1)−104.6(1), O−Sn−C 106.1(2)−111.9(2) and C−Sn−C 116.1(2)−119.0(2).

toward the center of the cavity thus formed and the silicon-bound methyl groups are oriented outside the cavity, the latter presumably so as to minimize steric interactions. The triangles formed by the two sets of tin atoms are almost parallel (dihedral angle 4.1°) and projecting through the molecule, $Sn_3$ triangle to $Sn_3$ triangle, showing that each tin atom of one $Sn_3O_3$ ring is superimposable upon an oxygen of the second ring. The average separation between the two triangles is approximately 12.2 Å, and the twist between them is estimated to be 37°. In terms of a solid geometry and to a first approximation, the tin oxide/spacer framework may be described as a molecular prism, the aforementioned twist not withstanding. The coordination geometry about each tin atom is completed by a $CH(SiMe_3)_2$ substituent, each of which is directed away from the central part of the molecule. The tin atoms exist in distorted $C_2O_2$ tetrahedral geometries with the narrowest angles (approximately 104°) involving endocyclic oxygen atoms and the widest subtended by the exocyclic organic substituents (approximately 117°).

## Conclusion

The results reported confirm the utility of the preassembly concept and opens the way to rational design of other new high-nuclearity organotin oxides. Control over the nuclearity and interlaminar spacing offers new opportunities for catalytic and other practical applications.

## Experimental Section

All solvents were dried and purified by standard procedures. NMR spectra were obtained using a Varian 300 MHz Unity

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(15) Crystal data for $C_{78}H_{174}O_6Si_{18}Sn_6{\cdot}3C_7H_8$: $M_r = 2702.3$, triclinic, $P\bar{1}$, $a = 15.234(1)$ Å, $b = 20.056(1)$ Å, $c = 23.854(1)$ Å, $\alpha = 77.180(1)°$, $\beta = 77.455(1)°$, $\gamma = 79.989(1)°$, $V = 6876.1(6)$ Å$^3$, $Z = 2$, $D_x = 1.305$ g cm$^{-3}$, $\mu = 12.71$ cm$^{-1}$. Intensity data (47 270) were collected at 153(2) K on a Nonius KappaCCD fitted with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ 0.71073 Å) so that $\theta_{max}$ was 25.0°. Data were corrected for absorption using SADABS,[16] solved with SHELXLS97,[17] and refined on $F^2$ using SHELXL97.[17] The H atoms were included in their geometric positions using a riding model approximation. One of the phenyl rings of the spacer groups, i.e., C16−C21, was found to be disordered, but two positions were discernible for the C20 and C21 atoms only. These were refined isotropically with site occupancy factors of 0.7 and 0.3 (determined from refinement). Similarly, severe disorder was found in one of the three solvent toluene molecules, and this was refined isotropically as a rigid group. The final $R$ values were $R_1 = 0.038$ (for 12 619 data with $I > 2\sigma(I)$) and $wR_2 = 0.082$ (for 22 366 unique data). The diagram was drawn with ORTEP at the 50% probability level.[18]

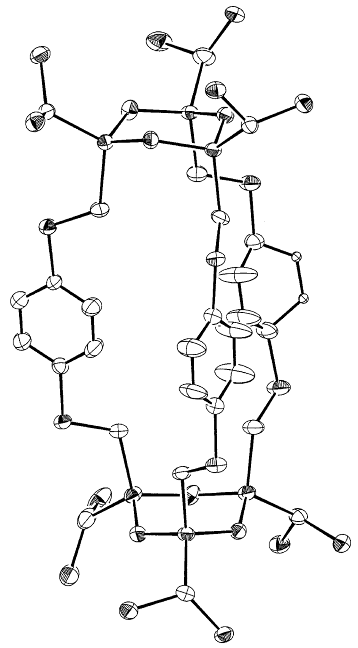

**Figure 2.** Tilted view of **3** highlighting the framework in the molecular diorganotin oxide. Only the major conformation of the disordered C20 and C21 atoms is shown. All methyl groups, hydrogen atoms, and the three toluene molecules of solvation have been omitted for clarity.

Plus NMR spectrometer. $^{1}$H, $^{13}$C, and $^{119}$Sn chemical shifts $\delta$ are given in ppm and are referenced against $Me_4Si$ and $Me_4Sn$, respectively. Coupling constants $J$ are given in Hz. Uncorrected melting points were determined on a Kofler hot stage. Microanalyses were performed using a CE 1106 elemental analyzer. The synthesis of compound **1** has been described elsewhere.[14]

**Synthesis of 1,4-Bis[bis(trimethylsilyl)methyldichlorostannylmethyldimethylsilyl)]benzene (2).** To a magnetically stirred and cooled (0 °C) solution of 1,4-bis(triphenylstannylmethyldimethylsilyl)benzene (**1**) (2.6 g, 2.83 mmol) in $CH_2Cl_2$ (30 mL) was added in small portions $I_2$ (1.435 g, 5.65 mmol) during 30 min. The reaction mixture was stirred for 2 h, and the solvent and all volatile byproducts were removed in vacuo (3 h at 130 °C and $10^{-3}$ mm/Hg) to give 1,4-bis(iododiphenylstannylmethyldimethylsilyl)benzene as a yellow oil ($\delta$ $^{119}$Sn (111.85 MHz, $CDCl_3$) −58.7, $^{1}J(^{13}\mathrm{C}-^{119}\mathrm{Sn})$ = 538, 269 Hz), which was used for the subsequent reaction without further purification.

To a solution of $LiCH(SiMe_3)_2$[19] in $Et_2O$ (23 mL, $c = 0.4$ mol/L) was added at room temperature a solution of 1,4-bis(iododiphenylstannylmethyldimethylsilyl)benzene (4.43 g, 4.35 mmol) in $Et_2O$ (40 mL) during 40 min. The reaction mixture was stirred overnight and hydrolyzed with saturated $NH_4Cl$ solution. The organic layer was separated, washed twice with water, and dried over $Na_2SO_4$. After filtration the organic solvent was evaporated in vacuo, and the resulting yellow oil was kept 1 h at 130 °C and $10^{-3}$ Torr to remove all volatile byproducts to give 4.32 g of 1,4-bis[bis(trimethylsilyl)methyldiphenylstannylmethyldimethylsilyl)]benzene ($\delta$ $^{29}$Si (59.6 MHz, $CDCl_3$) −2.01 (s, $^{2}J(^{117/119}\mathrm{Sn}-^{29}\mathrm{Si})$ = 22, $SiMe_2$); 1.57 (s, $^{2}J(^{117/119}\mathrm{Sn}-^{29}\mathrm{Si})$ = 31, $^{1}J(^{13}\mathrm{C}-^{29}\mathrm{Si})$ = 51, $SiMe_3$); $\delta$ $^{119}$Sn (111.85 MHz, $CDCl_3$) −55.2 $^{1}J(^{13}\mathrm{C}-^{119}\mathrm{Sn})$ = 479, $^{1}J(^{13}\mathrm{C}-^{119}\mathrm{Sn})$ = 256), which was used for the subsequent reaction without further purification.

To a magnetically stirred and cooled (0 °C) solution of the latter compound (4.32 g, 3.99 mmol) in acetone (50 mL) was added dropwise a solution of $HgCl_2$ (5.50 g, 20.26 mmol) in acetone (50 mL) during 30 min. The reaction mixture was stirred for 7 days and the acetone removed in vacuo. Hexane (100 mL) was added to the residue, and the suspension was heated at reflux for 10 min. The hot solution was filtered to remove PhHgCl, and the organic solvent of the filtrate was evaporated in vacuo to give 3.74 g of a yellow oil, which was recrystallized from $CHCl_3$ (15 mL) to give 1.96 g (51%) of 1,4-bis[bis(trimethylsilyl)methyldichlorostannylmethyldimethylsilyl)]benzene, mp 133−136 °C. $^{1}$H NMR (299.98 MHz, $CDCl_3$): $\delta$ −0.11 [s, 1H, $^{2}J(^{117/119}\mathrm{Sn}-^{1}\mathrm{H})$ = 101/106, CH]; 0.16 (s, 18H, $SiMe_3$); 0.51 (s, 6H, $SiMe_2$); 1.00 (s, 2H, $^{2}J(^{117/119}\mathrm{Sn}-^{1}\mathrm{H})$ = 84/89, $CH_2$); 7.59 (s, 2H, $C_6H_4$). $^{13}$C NMR (75.44 MHz, $CDCl_3$): $\delta$ $SiMe_2$ −0.67 $^{3}J(^{117/119}\mathrm{Sn}-^{13}\mathrm{C})$ = 20, $^{1}J(^{29}\mathrm{Si}-^{13}\mathrm{C})$ = 55; $SiMe_3$ 2.77 $^{3}J(^{117/119}\mathrm{Sn}-^{13}\mathrm{C})$ = 27, $^{1}J(^{29}\mathrm{Si}-^{13}\mathrm{C})$ = 52; CH 14.81, $^{1}J(^{117/119}\mathrm{Sn}-^{13}\mathrm{C})$ = 314/329, $^{1}J(^{29}\mathrm{Si}-^{13}\mathrm{C})$ = 46; $CH_2$ 18.24, $^{1}J(^{117/119}\mathrm{Sn}-^{13}\mathrm{C})$ = 204/213, $^{1}J(^{29}\mathrm{Si}-^{13}\mathrm{C})$ = 35; $C_o$ 133.21; $C_i$ 140.66. $^{119}$Sn NMR (111.85 MHz, $CDCl_3$): $\delta$ 123.7. Anal. Calcd for $C_{26}H_{58}Cl_4Si_6Sn_2$: C, 34.00; H, 6.36. Found: C, 33.99; H, 6.38.

**Synthesis of the Diorganotin Oxide (3).** To a magnetically stirred solution of 1,4-bis[bis(trimethylsilyl)methyldichlorostannylmethyldimethylsilyl)]benzene (**2**) (400 mg, 0.44 mmol) in toluene (6 mL) at 70−80 °C was added dropwise a solution of NaOH (1.3 g, 32.50 mmol) in water (6 mL) during 2 min. The reaction mixture was stirred at 80 °C for 12 h followed by addition of a further 3 mL of hot toluene. The organic layer was separated and the solvent evaporated in vacuo to give 380 mg of a white solid, which was recrystallized from hot toluene (15 mL) to give the diorganotin oxide **3** (240 mg, 68%) as colorless crystals that do not melt or decompose below 345 °C. Upon exposure to air, these crystals within minutes become opaque, indicating the loss of solvent. $^{1}$H NMR (299.98 MHz, $CDCl_3$): $\delta$ −0.04 [s, $^{2}J(^{117/119}\mathrm{Sn},^{1}\mathrm{H})$ = 96/102 Hz, 6H, CH]; 0.22 (s, 108H, $SiMe_3$), 0.34 (s, 36H, $SiMe_2$), 0.73 [s, $^{2}J(^{117/119}\mathrm{Sn},^{1}\mathrm{H})$ = 87/92 Hz, 12H, $CH_2$], 7.58 (s, 12H, $C_6H_4$). $^{13}$C{$^{1}$H} NMR (75.44 MHz, $CDCl_3$): $\delta$ 0.93 [$^{1}J(^{29}\mathrm{Si},^{13}\mathrm{C})$ = 52 Hz, $SiMe_2$], 3.35 [$^{3}J(^{117/119}\mathrm{Sn},^{13}\mathrm{C})$ = 22 Hz, $^{1}J(^{29}\mathrm{Si},^{13}\mathrm{C})$ = 51 Hz, $SiMe_3$], 11.06 [$^{1}J(^{117/119}\mathrm{Sn},^{13}\mathrm{C})$ = 299/311 Hz, CH], 14.93 [$^{1}J(^{117/119}\mathrm{Sn},^{13}\mathrm{C})$ = 303/318 Hz, $^{1}J(^{29}\mathrm{Si},^{13}\mathrm{C})$ = 37 Hz, $CH_2$], 132.46 ($C_o$), 141.82 ($C_i$). $^{119}$Sn{$^{1}$H} NMR (111.85 MHz, $CDCl_3$): $\delta$ 38.0 [$^{2}J(^{117}\mathrm{Sn},^{119}\mathrm{Sn})$ = 415 Hz]. Anal. Calcd for $C_{78}H_{174}O_6Si_{18}Sn_6$: C, 38.62; H, 7.23. Found: C, 38.51; H, 7.21.

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**Supporting Information Available:** Tables of all coordinates, anisotropic displacement parameters, and geometric data for compound **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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