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Molecular Dynamics within Diorganotin Systems: Solution and Solid State Studies of New Mixed Distannoxane Dimers $[^{t}Bu_2(Cl)SnOSn(Cl)R_2]_2$[†]

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Di-*tert*-butyltin oxide, $(^{t}Bu_2SnO)_3$, reacts with R_2SnCl_2 to give mixed distannoxanes $[^{t}Bu_2(Cl)SnOSn(Cl)R_2]_2$ (**1**, R = Me; **2**, R = Et; **3**, R = ^{i}Pr; **4**, ^{n}Bu) whereas di-*tert*-butyltin hydroxide chloride, $[^{t}Bu_2Sn(OH)Cl]_2$, reacts with $[^{n}Bu_2SnO]_n$ to give the chlorohydroxydistannoxane $[^{t}Bu_2(OH)SnOSn(Cl)^{n}Bu_2]_2$, **5**; the dimeric nature of these tetraorganodistannoxanes was confirmed by crystal structure determinations of **1** and **4**. Although stable in the solid state, compounds **1**−**4** rearrange to give a number of distannoxanes in solution. Addition of R_2SnCl_2 (R = Me, ^{i}Pr, ^{n}Bu) to solutions of **1**, **3**, and **4**, respectively, causes displacement of $^{t}Bu_2SnCl_2$ with concomitant formation of $[(^{t}Bu_2SnCl_2)(R_2SnO)_2(R_2SnCl_2)]$ and $[(R_2SnCl_2)(R_2SnO)_2(R_2SnCl_2)]$. Thus **1**−**4** can be regarded as $(R_2SnO)_2$ units which are stabilized by two $^{t}Bu_2SnCl_2$ molecules. NMR data indicate that reaction between $(^{t}Bu_2SnO)_3$ and $^{t}Bu_2SnCl_2$ gives rise to an equilibrium involving linear $[^{t}Bu_2Sn(Cl)OSn(Cl)^{t}Bu_2]$ and the novel three-quarter ladder compound $[^{t}Bu_2SnCl_2][^{t}Bu_2SnO]_2$. Formation of trinuclear tin species is also evident from electrospray mass spectrometric studies.

Introduction

Tetraorganodistannoxanes of the types $R_2(X)SnOSn(X)R_2$ and $R_2(OH)SnOSn(X)R_2$ (R = alkyl, Ph; X = halide, OAc, NCS, OR) have been known for some years.[1] Derivatives with X = halide are usually prepared by the controlled hydrolysis of diorganotin dihalides[2,3] or from reaction between equimolar amounts of diorganotin oxide and diorganotin dihalide.[1] Only symmetrically substituted compounds have been fully characterised so far[3−7] although there is one early report of the synthesis of the nonsymmetric tetraorganodistannoxane $Et_2(Br)SnOSn(Br)Pr_2$.[8] A characteristic feature of symmetric tetraorganodistannoxanes in the solid state is their dimerization which results in the so-called ladder-type arrangement which contains a central planar Sn_2O_2 four-membered ring; tin-119 NMR investigations favor retention of this structure in solution.[9]

Asymmetric distannoxanes in the ladder configuration, where the anionic X groups provide the asymmetry, were reported recently.[10] There was evidence for monomer−dimer equilibria of these compounds in solution. These equilibria were rapid on the preparative time scale but slow on the NMR time scale. Although formation of monomeric species $R_2(X)SnOSn(X)R_2$ have been postulated,[11] to date structural details have appeared only for the compound $(R_f)_2(Cl)SnOSn(Cl)(R_f)_2$, which resulted from the fortuitous oxidation and hydrolysis of $(R_f)_2Sn$ (R_f = 2,4,6-tris(trifluoromethyl)phenyl).[12]

The trimer $(^{t}Bu_2SnO)_3$ has been well characterized structurally,[13] and its use as a convenient oxide transfer reagent was recently described.[14] We now report NMR and electrospray mass spectrometric studies of reactions of $(^{t}Bu_2SnO)_3$ with a number of diorganotin dihalides, R_2SnCl_2 (R = Me, Et, ^{i}Pr, ^{n}Bu, ^{t}Bu) as well as the reaction of $[^{t}Bu_2Sn(OH)Cl]_2$ with $[^{n}Bu_2SnO]_n$. We also report the crystal structures of $[^{t}Bu_2(Cl)SnOSn(Cl)R_2]_2$ for R = Me (**1**) and R = ^{n}Bu (**4**).

Experimental Section

General Methods. All solvents were dried by standard methods. Dibutyltin oxide, dimethyltin dichloride, and dibutyltin dichloride were purchased from Aldrich. Di-*tert*-butyltin dichloride[15], di-*tert*-butyltin oxide,[13] and di-*tert*-butyltin hydroxide chloride[16] were prepared by published procedures. Elemental analyses were carried out by the Microanalytical Laboratory of the Australian National University, Canberra. Molecular weights were determined osmometrically using a Hitachi Perkin-Elmer 115 molecular weight apparatus and a Knaur osmometer (AO 280). Compounds **1** and **4** were measured at a concentration of 0.660 g/100 g of $CHCl_3$ solvent; compound **3** was measured in the concentration range 0.200−0.400 g/100 g of $CHCl_3$.

[†] Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.

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NMR Spectroscopy. Solution NMR spectra (typically of 0.5−1.0 M solutions) were recorded on either a 500 Varian Unity or a JEOL GX 270 FT NMR spectrometer at 500 and 270.17 (^{1}H), 125.697 and 67.84 (^{13}C), and 186.409 and 100.75 (^{119}Sn) MHz. The chemical shifts are relative to external Me_4Si (^{1}H, ^{13}C) and Me_4Sn (^{119}Sn). Solid-state ^{119}Sn MAS (149.16 MHz) and ^{13}C (100.44 MHz) CPMAS NMR spectra were acquired on a Bruker MSL 400 spectrometer. For ^{119}Sn NMR spectra, MAS high-power ^{1}H decoupling and fast MAS (>10 kHz) were used with a 4 mm double-bearing MAS probe. Spectra were referenced to an external secondary standard of solid tetracyclohexyltin at −97.4 ppm.

Electrospray Mass Spectrometry. Solutions of the compounds (approximately 2×10^{-4} M) were prepared in methanol/water (50:50). Electrospray mass spectra were obtained using a VG Bio-Q triple quadrupole mass spectrometer (VG BioTech, Altrincham, Cheshire, U.K.) with a water/methanol (50:50) mobile phase. Solutions of the compounds were injected directly into the spectrometer via a Rheodyne injector equipped with a 10 μL loop. A Phoenix 20 micro LC syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 3 μL min^{-1}. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 3 L min^{-1} and 100 mL min^{-1}, respectively. Pressure in the mass analyzer region was about 3×10^{-5} Torr. Typically, about 20 signal-averaged spectra were required to give a good signal to noise ratio. Measurements were made at a first-skimmer (B1) voltage of 40 V.

Synthesis of [^{t}Bu$_2$(Cl)SnOSn(Cl)Me$_2$]$_2$ (1). A mixture of (^{t}Bu$_2$SnO)$_3$ (7.59 mmol, 5.67 g) and Me_2SnCl_2 (22.70 mmol, 5.00 g) was refluxed in toluene (100 mL) until the solution became clear. The mixture was then left to cool slowly, and the colorless crystals which formed were filtered off and dried in air to give 9.1 g (85%) of **1**; mp 250 °C. Anal. Calcd for $C_{20}H_{48}Cl_4O_2Sn_4$ ($M_r = 937.25$): C, 25.64; H, 5.18. Found: C, 25.32; H, 5.31.

Synthesis of [^{t}Bu$_2$(Cl)SnOSn(Cl)Et$_2$]$_2$ (2). A mixture of (^{t}Bu$_2$SnO)$_3$ (0.45 mmol, 0.33 g) and Et_2SnCl_2 (1.33 mmol, 0.33 g) was refluxed for 15 min in 10 mL of toluene. The reaction mixture was then filtered, and the filtrate was stored at −5 °C for 5 days, after which the colorless crystals that formed were filtered off and dried to give 0.46 g (70%) of **2**; mp 200 °C. Anal. Calcd for $C_{24}H_{56}Cl_4O_2Sn_4$ ($M_r = 993.28$): C, 29.02; H, 5.68; Cl, 14.28. Found: C, 29.33; H, 5.55; Cl, 14.45. δ(^{119}Sn) (major peaks in toluene): −152.9; −163.9 (^{2}J(^{119}SnO$^{117/119}$Sn) = 90 Hz, J(^{119}Sn−C) = 663 Hz).

Synthesis of [^{t}Bu$_2$(Cl)SnOSn(Cl)^{i}Pr$_2$]$_2$ (3). A sample of ^{i}Pr$_2$SnCl$_2$ (16.40 mmol, 4.54 g) was reacted with (^{t}Bu$_2$SnO)$_3$ (5.49 mmol, 4.09 g) in toluene in a manner analogous to that for **2**. The colorless solid **3** (5.0 g, 58%) precipitated from toluene: mp 175−189 °C. Anal. Calcd for $C_{28}H_{64}Cl_4O_2Sn_4$ ($M_r = 1049.46$): C, 32.04, H, 6.15; Cl, 13.51. Found: C, 31.93; H, 6.18; Cl, 13.12. δ(^{119}Sn) (major peaks in CDCl$_3$): −165.3 (^{2}J(^{119}SnO$^{117/119}$Sn) = 114 Hz); −180.2 (^{2}J(^{119}SnO$^{117/119}$Sn) = 98 Hz).

Synthesis of [^{t}Bu$_2$(Cl)SnOSn(Cl)^{n}Bu$_2$]$_2$ (4). A sample of ^{n}Bu$_2$SnCl$_2$ (16.46 mmol, 5.00 g) was reacted with (^{t}Bu$_2$SnO$_3$) (5.49 mmol, 4.09 g) in toluene in a manner analogous to that for **2**. The colorless solid **4** (8.15 g, 90%) was recrystallized from toluene; mp 178−181 °C. Anal. Calcd for $C_{32}H_{72}Cl_4O_2Sn_4$ ($M_r = 1105.56$): C, 34.78; H, 6.58. Found: C, 35.74; H, 7.40. δ(^{119}Sn) (major peaks in CDCl$_3$): −150.7 (^{2}J(^{119}SnO$^{117/119}$Sn) = 81 Hz, J(^{119}Sn−C) = 517 Hz); −157.6 (^{2}J(^{119}SnO$^{117/119}$Sn) = 89 Hz, J(^{119}Sn−C) = 614 Hz).

Synthesis of [^{t}Bu$_2$(OH)SnOSn(Cl)^{n}Bu$_2$]$_2$ (5). A mixture of 1/*n* (Bu$_2$SnO)$_n$ (1.39 mmol, 0.35 g) and ^{t}Bu$_2$Sn(OH)Cl (1.39 mmol, 0.40 g) was refluxed for 45 min in 15 mL of toluene. The solution was filtered and the solvent evaporated *in vacuo*. The residue was dissolved in dichloromethane and the solution stored at −5 °C for 5 days to give 0.55 g (74%) of **5** as colorless crystals: mp 200−208 °C. Anal. Calcd for $C_{32}H_{74}Cl_2O_4Sn_4$ ($M_r = 1068.10$): C, 35.97; H, 6.98; Cl, 6.64. Found: C, 36.33; H, 7.21; Cl, 6.59. δ(^{119}Sn) (in CDCl$_3$): −181.7 (^{2}J(^{119}SnO$^{117/119}$Sn) = 38 and 222 Hz, J(^{119}Sn−C) = 625 Hz); −220.9 (^{2}J(^{119}SnO$^{117/119}$Sn) = 38 and 220 Hz, J(^{119}Sn−C) = 605 Hz).

Crystallography. Intensity data for transparent crystals of **1** and **4** were obtained at room temperature on an Enraf-Nonius CAD4F diffractometer fitted with Mo Kα radiation (graphite monochromator), $\lambda = 0.7107$ Å, employing the $\omega-2\theta$ scan technique. The size of the crystal of **1** was $0.23 \times 0.58 \times 0.58$ mm and that of the multifaceted **4** was approximately 0.5 mm in diameter. The net intensity values of two standard reflections, monitored after every 7200 s of X-ray exposure time, showed no change for **1** but indicated a linear decrease during the course of the data collection for **4**. At the conclusion of the latter data collection, the intensity standards had decreased to 85% of their original values and the data set was scaled accordingly. Lorentz and polarization corrections[17] were applied, and for **1**, an analytical absorption correction was applied.[18] Crystal data are summarized in Table 1.

Table 1. Crystal Data and Refinement Details for **1** and **4**

	1	**4**
formula	$C_{20}H_{48}Cl_4O_2Sn_4$	$C_{32}H_{72}Cl_4O_2Sn_4$
fw	937.1	1105.5
cryst system	monoclinic	monoclinic
space group	$C2/m$,	$P2_1/n$
a, Å	8.306(1)	13.320(2)
b, Å	15.916(2)	10.813(1)
c, Å	12.810(1)	16.493(4)
β, deg	96.61(1)	101.38(1)
V, Å^3	1682.2	2328.8
Z	2 (tetramers)	2 (tetramers)
D_{calcd}, g cm^{-3}	1.850	1.577
F(000)	904	1096
λ, Å	0.71073	0.71073
μ, cm^{-1}	30.31	21.96
transm: max, min	0.511, 0.250	n/a
hkl range	$\pm h,+k,-l$	$\pm h,+k,-l$
T, K	293	293
no. of data collcd	1654	6823
θ max, deg	25.0	27.5
no. of unique data	1545	5349
R_{amal}^{a}	0.037	0.016
no. of unique data used with $I \geq 2.5\sigma(I)$	1311	2883
R	0.049	0.031
g	0.013	0.002
R_w	0.048	0.038
residual ρ, e Å^{-3}	2.23	0.68

^{a} $R_{amal} = \{\sum[N\sum[w(F_{mean} - |F_o|)^2]]/\sum[(N-1)\sum(w|F_o|^2)]\}^{1/2}$, where the inner summation is over N equivalent reflections averaged to give F_{mean}, the outer summation is over all unique reflections, and the weight, w, is taken as $[\sigma(F_o)]^{-2}$.

Each structure was solved by direct methods[19] and refined by full-matrix least-squares procedures based on F.[18] Anisotropic displacement parameters were employed for all non-H atoms, and H atoms were included in each model at their calculated positions. Disorder was noted in the positions of the C atoms of the *n*-butyl groups in **4**, and hence these groups were refined with C−C bond distances constrained to 1.50(2) Å. A weighting scheme of the form $w = [\sigma^2(F) + |g|F^2]^{-1}$ was introduced, and the refinements were continued until convergence; final refinement details are listed in Table 1. The analysis of variance for each structure showed no special features, indicating that an appropriate weighting scheme had been employed. The numbering schemes employed are shown in Figure 1, which was drawn with the ORTEP[20] program at 25% probability ellipsoids. Scattering factors for all atoms were those incorporated in SHELX76.[18]

Results and Discussion

Synthesis. Reaction of equimolar amounts of di-*tert*-butyltin oxide (^{t}Bu$_2$SnO)$_3$ with diorganotin dichlorides R_2SnCl_2 (R = Me, Et, ^{i}Pr, ^{n}Bu) in dichloromethane or toluene results in formation of clear solutions from which colorless crystals of

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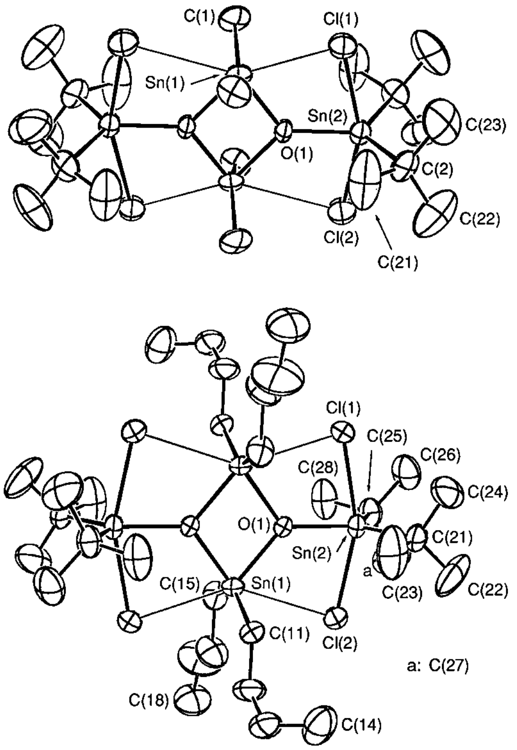


Figure 1. Molecular structures of **1** (upper) and **4** (lower).

formulation $^tBu_2(Cl)SnOSn(Cl)R_2$ were isolated (eq 1).

$$^1/_3(^tBu_2SnO)_3 + R_2SnCl_2 \xrightarrow{CH_2Cl_2 \text{ or } C_7H_8} {}^tBu_2(Cl)SnOSn(Cl)R_2 \quad (1)$$

1: R = Me
2: R = Et
3: R = ^iPr
4: R = ^nBu

Interestingly, compound **4** can also be obtained by reaction of di-*tert*-butyltin dichloride and di-*n*-butyltin oxide (eq 2).

$$^tBu_2SnCl_2 + (1/n)(^nBu_2SnO)_n \xrightarrow{CH_2Cl_2 \text{ or } C_7H_8} {}^tBu_2(Cl)SnOSn(Cl)^nBu_2 \quad (2)$$

4

In a similar manner, di-*tert*-butyltin hydroxide chloride reacts with di-*n*-butyltin oxide to give **5** (eq 3).

$$^1/_2[^tBu_2Sn(OH)Cl]_2 + (1/n)(^nBu_2SnO)_n \xrightarrow{CH_2Cl_2 \text{ or } C_7H_8} {}^tBu_2(OH)SnOSn(Cl)^nBu_2 \quad (3)$$

5

Compounds **1**−**5** have satisfactory elemental analyses; all are colorless solids which are soluble in solvents such as dichloromethane, chloroform, and toluene.

Molecular Structures of 1 and 4. The molecular structures of **1** and **4** are shown in Figure 1, and selected interatomic parameters for these compounds are given in Table 2. The structures are essentially molecular although in **1** there is a weak intermolecular contact between the Sn(1) atom and a symmetry-related Cl(1) atom (symmetry operation: −*x*, −*y*, 1 − *z*) of 3.597(3) Å. Both compounds feature centrosymmetric dimers situated about a crystallographic center of inversion at ($^1/_2$, 0, $^1/_2$) for **1** and at ($^1/_2$, $^1/_2$, $^1/_2$) for **4**. Connected to the central Sn_2O_2 unit are two exocyclic $^tBu_2Sn$ groups so that each O atom is triply bridging; further links between the Sn atoms are provided by the Cl atoms. In addition to the center of inversion, **1** has a crystallographic *m* symmetry such that the $Sn_4O_2Cl_4$ atoms lie on this plane and the organic substituents are related to each other across this plane. Although mirror symmetry is not crystallographically imposed in **4**, the $Sn_4O_2Cl_4$ atoms are planar to ±0.034(2) Å.

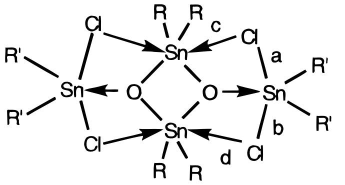
Table 2. Selected Bond Distances (Å) and Angles (deg) for **1** and **4**[a]

compd **1**		compd **4**	
Sn(1)−Cl(1)	2.802(2)	Sn(1)−Cl(1)′	2.907(2)
Sn(1)−Cl(2)	3.126(2)	Sn(1)−Cl(2)	3.013(2)
Sn(1)−O(1)	2.074(5)	Sn(1)−O(1)	2.075(3)
Sn(1)−O(1)′	2.104(5)	Sn(1)−O(1)′	2.080(3)
Sn(1)−C(1)	2.130(6)	Sn(1)−C(11)	2.107(6)
Sn(1)−C(1)″	2.130(6)	Sn(1)−C(15)	2.109(7)
Sn(2)−Cl(1)	2.675(2)	Sn(2)−Cl(1)	2.598(2)
Sn(2)−Cl(2)	2.516(2)	Sn(2)−Cl(2)	2.574(2)
Sn(2)−O(1)	2.028(5)	Sn(2)−O(1)	2.034(3)
Sn(2)−C(2)	2.191(5)	Sn(2)−C(21)	2.183(6)
Sn(2)−C(2)″	2.191(5)	Sn(2)−C(25)	2.177(7)
Cl(1)−Sn(1)−Cl(2)	158.8(1)	Cl(1)′−Sn(1)−Cl(2)	144.8(1)
Cl(1)−Sn(1)−O(1)	73.1(1)	Cl(1)′−Sn(1)−O(1)	146.3(1)
Cl(1)−Sn(1)−O(1)′	148.4(1)	Cl(1)′−Sn(1)−O(1)′	72.1(2)
Cl(1)−Sn(1)−C(1)	88.4(2)	Cl(1)′−Sn(1)−C(11)	84.0(2)
Cl(1)−Sn(1)−C(1)″	88.4(2)	Cl(1)′−Sn(1)−C(15)	85.9(2)
Cl(2)−Sn(1)−O(1)	66.7(1)	Cl(2)−Sn(1)−O(1)	68.9(1)
Cl(2)−Sn(1)−O(1)′	142.3(1)	Cl(2)−Sn(1)−O(1)′	144.0(1)
Cl(2)−Sn(1)−C(1)	81.8(2)	Cl(2)−Sn(1)−C(11)	81.2(2)
Cl(2)−Sn(1)−C(1)″	81.8(2)	Cl(2)−Sn(1)−C(15)	84.3(2)
O(1)−Sn(1)−O(1)′	75.4(1)	O(1)−Sn(1)−O(1)′	75.2(2)
O(1)−Sn(1)−C(1)	106.3(2)	O(1)−Sn(1)−C(11)	108.7(2)
O(1)−Sn(1)−C(1)″	106.3(2)	O(1)−Sn(1)−C(15)	106.4(2)
O(1)′−Sn(1)−C(1)	100.5(2)	O(1)′−Sn(1)−C(11)	106.2(3)
O(1)′−Sn(1)−C(1)″	100.5(2)	O(1)′−Sn(1)−C(15)	104.7(2)
C(1)−Sn(1)−C(1)″	144.7(2)	C(11)−Sn(1)−C(15)	137.8(3)
Cl(1)−Sn(2)−Cl(2)	158.8(1)	Cl(1)−Sn(2)−Cl(2)	158.6(1)
Cl(1)−Sn(2)−O(1)	76.7(2)	Cl(1)−Sn(2)−O(1)	79.0(1)
Cl(1)−Sn(2)−C(2)	92.6(2)	Cl(1)−Sn(2)−C(21)	95.3(2)
Cl(1)−Sn(2)−C(2)″	92.6(2)	Cl(1)−Sn(2)−C(25)	94.3(2)
Cl(2)−Sn(2)−O(1)	82.1(2)	Cl(2)−Sn(2)−O(1)	79.7(1)
Cl(2)−Sn(2)−C(2)	97.3(2)	Cl(2)−Sn(2)−C(21)	95.2(2)
Cl(2)−Sn(2)−C(2)″	97.3(2)	Cl(2)−Sn(2)−C(25)	94.9(2)
O(1)−Sn(2)−C(2)	117.9(2)	O(1)−Sn(2)−C(21)	118.1(2)
O(1)−Sn(2)−C(2)″	117.9(2)	O(1)−Sn(2)−C(25)	117.1(2)
C(2)−Sn(2)−C(2)″	123.7(2)	C(21)−Sn(2)−C(25)	124.8(3)
Sn(1)−O(1)−Sn(2)	126.4(2)	Sn(1)−O(1)−Sn(2)	126.5(2)
Sn(1)−O(1)−Sn(1)′	104.6(2)	Sn(1)−O(1)−Sn(1)′	104.8(2)
Sn(2)−Cl(1)−Sn(1)′	83.9(1)	Sn(2)−Cl(1)−Sn(1)′	83.4(1)
Sn(1)′−Cl(2)−Sn(2)	82.0(1)	Sn(1)−Cl(2)−Sn(2)	82.8(1)

[a] Primed atoms are related by a center of inversion, and doubly-primed atoms are related by a mirror plane.

From an inspection of Table 2 it is clear that the Cl atoms bridge the Sn atoms with relatively long and disparate Sn−Cl bond distances so that assignment of coordination numbers to the Sn atoms is ambiguous, in particular for the endocyclic Sn atoms. For **1**, the exocyclic Sn atom, Sn(2), is coordinated by two organic substituents, the O(1) atom and two Cl atoms at 2.675(2) and 2.516(2) Å. The Sn(2)−Cl bond distances are somewhat longer than the sum of the covalent radii of Sn and Cl, at 2.39 Å, but are short enough to be considered as bonding interactions, thereby leading to a distorted trigonal bipyramidal geometry. The trigonal plane is defined by the O(1) atom and two C atoms of the ^tBu groups, and the Cl(1)−Sn(2)−Cl(2) axial angle is 158.8(1)°. The deviation from the ideal axial angle and the elongation of the Sn(2)−Cl bond distances may be due, in part, to the interaction of the Cl atoms with the endocyclic Sn atoms. The immediate geometry about the Sn(1) atom is defined by the two O atoms of the Sn_2O_2 core and two C atoms of the methyl substituents which define a distorted tetrahedral

Table 3. Sn−Cl Bond Distances (Å) in $[(R_2Sn(Cl)OSn(Cl)R'_2]_2$



R	R′	a	b	c	d	ref
Me	Me	2.445(2)	2.789(2)	3.409(2)	2.702(2)	24
^{i}Pr	^{i}Pr	2.462(6)	2.803(5)	3.473(3)	2.675(6)	5
Ph	Ph	2.430(1)	2.697(1)	3.355(2)	2.688(1)	26
Me	^{t}Bu	2.516(2)	2.675(2)	3.126(2)	2.802(2)	this work
^{n}Bu	^{t}Bu	2.574(2)	2.598(2)	3.013(2)	2.907(2)	this work

geometry. The Sn(1) atom also forms two close contacts with the Cl atoms, Sn(1)−Cl(1) = 2.802(2) and Sn(1)−Cl(2) = 3.126(2) Å, and while the former distance is indicative of some bonding interaction, the latter is quite long but nevertheless shorter than the sum of the van der Waals radii for these atoms of 4.0 Å.[21] The environment about the Sn(1) atom is thus best described as being based on a skew-trapezoidal planar geometry with the methyl groups lying over the weaker, i.e. Sn−Cl, bonds. The different Sn(1)−Cl bond distances are reflected in the associated Sn(2)−Cl bond distances. Thus, the more tightly held Cl(2) atom (Sn(2)−Cl(2) = 2.516(2) Å) forms the weaker intramolecular contact to the Sn(1) atom (3.126(2) Å) and conversely the less tightly held Cl(1) atom (2.675(2) Å) forms a shorter contact to the Sn(1) atom of 2.802(2) Å. From these variations it can be seen that the Cl(1) atom forms the more symmetrical bridge between the Sn atoms.

The geometry about the Sn(2) atom in **4** is the same as that in **1** and the axial Cl(1)−Sn(2)−Cl(2) angle is equivalent, at 158.6(1)°. As in **1**, there are weak Sn(1)−Cl interactions of 2.907(7) and 3.013(3) Å for Sn(1)−Cl(1)′ and Sn(1)−Cl(2), respectively. Consequently, the geometry about Sn(1) is as described for the comparable atom in **1**. In **4**, where the same trends in the Sn−Cl bond distances as above are found, the disparity in the Sn(2)−Cl bond distances (2.574(2), 2.598(2) Å) is much less and the difference between the Sn(1)−Cl interactions (3.013(2) and 2.907(2) Å) reflects this fact.

The basic structural type found for **1** and **4** has been observed previously in other $[(R_2SnX)_2O]_2$ compounds, for example, where X = NCS[22] and X = O_2CR' [23] and, particularly relevant to the present study, where X = Cl;[5,24−26] selected interatomic parameters for the X = Cl derivatives are listed in Table 3. The structure of the $[(Me_2SnCl)_2O]_2$ compound has been determined on three occasions,[5,24,26] and the most recent parameters have been included in Table 3. In the $[(R_2SnX)_2O]_2$ compounds that have been structurally characterized, the R groups are the same for both the endo- and exocyclic Sn atoms, and thus these may be termed symmetrical tetraorganodistannoxanes, whereas the present series are examples of asymmetric tetraorganodistannoxanes.

There is a substantial difference between the structures found for the symmetric and asymmetric $[(R_2SnCl)_2O]_2$ compounds. Whereas in the asymmetric compounds both Cl atoms are involved in weak, but significant, interactions with the endocyclic Sn atom, in the symmetric compounds one Cl atom forms a symmetric bridge and the other is essentially terminal. This has the consequence that in the symmetric $[(R_2SnX)_2O]_2$ species both Sn atoms are five-coordinate and trigonal bipyramidal.

Table 4. ^{119}Sn NMR Data (186.409 MHz) for **1** (Analytically Pure Sample) in $CDCl_3$ Solution at 25 °C

$\delta(^{119}Sn)$, ppm	integral	$^2J(^{119}SnO^{117/119}Sn)$, Hz	$^1J(^{119}Sn-^{13}C)$, (Hz)	assign^b
54.5	8			$^tBu_2SnCl_2$
−75.9	1			
−81.8	3	br	610	B
−110.0	0.5	175		
−112.4	0.5			
−112.7	0.5			
−120.0	6.5	72, 188		
−126.6	6	67	680	B′
−134.1	2.5	br		B″
−135.1	5	br, ∼100		
−138.3	46	79	693 (394)	A
−145.6	46	br^a		A′
−163.6	6	br, 105	708 (400)	
−216.0	0.5			
−220.4	4	188		
−222.3	0.5			

[a] Sharpens at −55 °C; $^2J(^{119}SnO^{117/119}Sn)$ = 75 Hz. [b] A = $[(^tBu_2SnCl_2)(Me_2\mathit{Sn}O)_2(^tBu_2SnCl_2)]$; A′ = $[(^tBu_2\mathit{Sn}Cl_2)(Me_2SnO)_2(^tBu_2SnCl_2)]$; B = $[(^tBu_2SnCl_2)(Me_2SnO)_2(Me_2\mathit{Sn}Cl_2)]$; B′ = $[(^tBu_2SnCl_2)(Me_2\mathit{Sn}O)_2(Me_2SnCl_2)]$; B″ = $[(^tBu_2\mathit{Sn}Cl_2)(Me_2SnO)_2(Me_2SnCl_2)]$.

NMR Studies. The solid state ^{119}Sn NMR spectrum of **1** contains two resonances at −145.8 and −172.0 ppm. The ^{13}C CPMAS NMR spectrum of **1** (same sample as ^{119}Sn) shows resonances at 17.9 ppm, $^1J(^{119}Sn-^{13}C)$ = 732 Hz ($SnCH_3$), 32.0 ppm (CH_3), and 45.6 ppm, $^1J(^{119}Sn-^{13}C)$ = 504 Hz (SnC). The solid state ^{119}Sn NMR spectrum of **4** shows two signals, of nearly equal intensity, at −153.5 and −169.0 ppm.

The ^{119}Sn NMR spectrum of an analytically pure sample of **1** in $CDCl_3$ at 25 °C (Table 4) contains two major resonances at −138.3 and −145.6 ppm which show $^2J(^{119}Sn-O-^{117/119}Sn)$ satellites of 79 Hz. The resonance at −138.3 ppm displays a $J(^{119}Sn-^{13}C)$ coupling of 693 Hz. These two resonances account for about 68% of the total integrated signal intensity of the ^{119}Sn spectrum. In addition, the ^{119}Sn NMR spectrum contains 14 weaker resonances between 55 and −220 ppm (Figure 2). These 14 resonances contribute approximately 32% toward the total signal intensity of the spectrum, and the origin of these signals is discussed further below.

The ^{13}C NMR spectrum of **1** in $CDCl_3$ (the same solution ^{119}Sn NMR) displays major resonances at 14.63 ppm, $^1J(^{119}Sn-^{13}C)$ = 693 Hz ($SnCH_3$), 30.35 ppm (CH_3), and 46.74 ppm, $^1J(^{119}Sn-^{13}C)$ = 504 Hz (SnC). Additional resonances of low intensity appear in the methyl region (9.32, 11.57, 12.93, and 14.09 ppm) and in the *tert*-butyl region (29.18, 30.03, 30.35, and 30.63 ppm). The ^{13}C NMR data allow assignment of the ^{119}Sn resonance A (at −138.3 ppm) to the Me_2Sn moiety and the ^{119}Sn resonance A′ (at −145.6 ppm) to the $^tBu_2Sn$ moiety of $[^tBu_2(Cl)SnOSn(Cl)Me_2]_2$ (Figure 1).

The proton NMR spectrum (500 MHz, $CDCl_3$) of **1** displays two major resonances with a 1:3 integral ratio (δ 1.30 ppm, $^2J(^{119}Sn-^1H)$ = 82 Hz; δ 1.44 ppm, $^3J(^{119}Sn-^1H)$ = 124 Hz) which are assigned to the methyl and *tert*-butyl groups, respectively. There are additional low-intensity singlets at δ 1.00 ppm, $^2J(^{119}Sn-^1H)$ = 84 Hz, and δ 1.18, 1.34, 1.44, and 1.46 ppm. Solution NMR results for compounds **2**−**4** are similar.

The major resonances in the ^{119}Sn NMR solution spectra of **1**−**4** are assigned to the two different tin sites in the ladder

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Table 5. ^{119}Sn NMR Data for **1** + Additions of Me_2SnCl_2 ($CDCl_3$ at 25 °C)

$\delta(^{119}Sn)$, ppm	integral	$^{2}J(^{119}SnO^{117/119}Sn)$, Hz	$^{1}J(^{119}Sn-^{13}C)$, Hz	assignt[a]
1 + 1.04 equiv of Me_2SnCl_2				
54.3	46			$^{t}Bu_2SnCl_2$
−61.9	26	56 (br)	626 (370)	C
−81.9	26	58 (br)	637 (406)	B
−116.9	23	58	674 (393)	C′
−126.6	50	67	681 (394)	B′
−134.1	23	76 (br)		B″
−130.3	12	81	691 (302)	A
−145.6	11	76 (br)		A′
1 + 2.29 equiv of Me_2SnCl_2				
142.0	11			Me_2SnCl_2
54.5	88			$^{t}Bu_2SnCl_2$
−61.7	82	br	648	C
−81.9	9	br		B
−116.9	77	56	674	C′
−126.6	15	67		B′
−134.1	6	br		B″

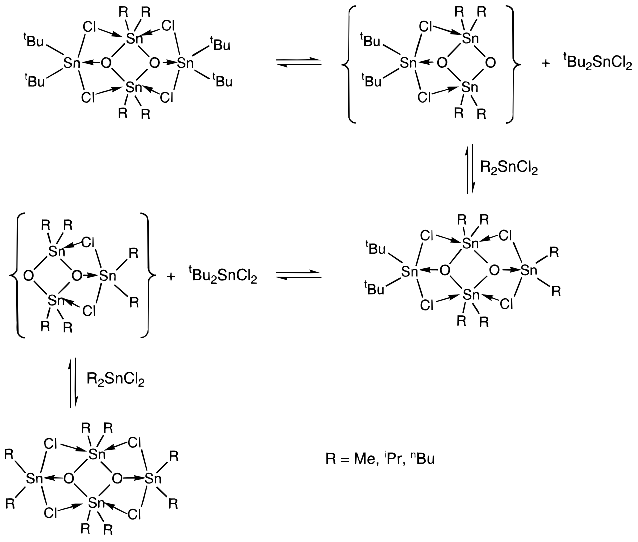
[a] A = $[(^{t}Bu_2SnCl_2)(Me_2\mathit{Sn}O)_2(^{t}Bu_2SnCl_2)]$; A′ = $[(^{t}Bu_2\mathit{Sn}Cl_2)(Me_2SnO)_2(^{t}Bu_2\mathit{Sn}Cl_2)]$; B = $[(^{t}Bu_2SnCl_2)(Me_2SnO)_2(Me_2\mathit{Sn}Cl_2)]$; B′ = $[(^{t}Bu_2SnCl_2)(Me_2\mathit{Sn}O)_2(Me_2SnCl_2)]$; B″ = $[(^{t}Bu_2\mathit{Sn}Cl_2)(Me_2SnO)_2(Me_2SnCl_2)]$; C = $[(Me_2\mathit{Sn}Cl_2)(Me_2SnO)_2(Me_2\mathit{Sn}Cl_2)]$; C′ = $[(Me_2SnCl_2)(Me_2\mathit{Sn}O)_2(Me_2SnCl_2)]$.

structure which has been confirmed in the solid state for **1** and **4**. This assignment is further supported by the similarity of the solution and solid state spectra of **1** (^{13}C) and **4** (^{119}Sn). The exocyclic ($^{t}Bu_2Sn$) tins are clearly pentacoordinate whereas the endocyclic (R_2Sn) tin sites may be considered as intermediate between penta- and hexacoordinated. The Me−Sn−Me angle for **1** in solution calculated from the equation of Lockhart and Manders[27] is 138°, close to the 144.7(2)° observed in the solid state (Table 2). The Bu−Sn−Bu angle of 136° calculated from the equation of Holecek and Lycka[28] is even closer to the value of 137.8(3)° found by X-ray analysis (Table 2).

The origin of the minor ^{119}Sn and ^{13}C NMR signals observed for solutions of **1**−**4** becomes clear from the following addition experiments. The ^{119}Sn NMR spectrum of a solution of **1** to which a 1.04 molar equivalent of Me_2SnCl_2 has been added contains only eight resonances (Table 5). There is an appreciable increase in concentration of $^{t}Bu_2SnCl_2$ and a decrease in concentration of **1** (signals A and A′). The ^{119}Sn NMR spectrum also contains resonances for the known compound[9] $[Me_2(Cl)SnOSn(Cl)Me_2]_2$, **6** (signals C and C′). The three ^{119}Sn resonances at −81.9, −126.6, and −134.1 ppm (signals B, B′, and B″; relative intensities 1:2:1) are assigned to the asymmetrical species $[(^{t}Bu_2SnCl_2)(Me_2SnO)_2(Me_2SnCl_2)]$, **7**. These results indicate that although **1** is a dimer in the solid state, there is in solution an equilibrium among $[^{t}Bu_2(Cl)SnOSn(Cl)Me_2]_2$, $[(^{t}Bu_2SnCl_2)(Me_2SnO)_2(Me_2SnCl_2)]$, $[Me_2(Cl)SnOSn(Cl)Me_2]_2$, and $^{t}Bu_2SnCl_2$. Addition of Me_2SnCl_2 favors displacement of $^{t}Bu_2SnCl_2$ from the ladder complex.

Increasing the amount of added Me_2SnCl_2 moves the equilibrium toward further displacement of exocyclic $^{t}Bu_2SnCl_2$ from ladder complexes. The ^{119}Sn NMR spectrum of a solution of **1** to which has been added 2.29 molar equiv of Me_2SnCl_2 indicates the disappearance of **1** and a significant decrease in the concentration of $[(^{t}Bu_2SnCl_2)(Me_2SnO)_2(Me_2SnCl_2)]$. The relative concentration of the species $[Me_2(Cl)SnOSn(Cl)Me_2]_2$ has increased significantly (Table 5). The ^{119}Sn NMR spectrum of a solution of **1** to which has been added 5.74 molar equiv of Me_2SnCl_2 shows that the dominant ladder species is now $[Me_2(Cl)SnOSn(Cl)Me_2]_2$ with only traces of $[(^{t}Bu_2SnCl_2)(Me_2SnO)_2(Me_2SnCl_2)]$ remaining evident. These assignments are supported by the analogous ^{13}C NMR spectra. By comparison, the ^{119}Sn NMR spectrum of a solution of **1** to which has been added 2.2 mole equiv of $^{t}Bu_2SnCl_2$ is very simple and shows only signals A and A′ and a signal for $^{t}Bu_2SnCl_2$.

Scheme 1



The ^{119}Sn NMR spectra of a solution of **3** to which various quantities of $^{i}Pr_2SnCl_2$ have been added indicate replacement of $^{t}Bu_2SnCl_2$ by $^{i}Pr_2SnCl_2$. Similarly, addition of $^{n}Bu_2SnCl_2$ to a solution made from **4** indicates replacement of $^{t}Bu_2SnCl_2$ by $^{n}Bu_2SnCl_2$.

These exchange experiments suggest that **1**−**4** can be viewed as Lewis acid−base adducts in which diorganotin oxide dimers $(R_2SnO)_2$ are stabilized by two $^{t}Bu_2SnCl_2$ units. The 1:2 adducts $(^{t}Bu_2SnCl_2)(R_2SnO)_2(^{t}Bu_2SnCl_2)$ are stable in the solid state, but in solution they undergo appreciable dissociation, which enables the exocyclic $^{t}Bu_2SnCl_2$ units to be exchanged by other R_2SnCl_2 moieties (Scheme 1).

The lability of **1**, **3**, and **4** in solution is reflected in their molecular weight determinations, which show association factors of 1.3, 0.6, and 1.2 for $[^{t}Bu_2(Cl)SnOSn(Cl)Me_2]$, $[^{t}Bu_2(Cl)SnOSn(Cl)^{i}Pr_2]$, and $[^{t}Bu_2(Cl)SnOSn(Cl)^{n}Bu_2]$, respectively, in chloroform solution. The lower Lewis acidity of the $^{t}Bu_2Sn$ moiety compared to R_2Sn (R = Me, Et, ^{i}Pr, ^{n}Bu) accounts for its facile displacement in solution. It may also account for the observation that both reactions 1 and 2 lead to the same compound **4**, in which the $^{t}Bu_2Sn$ groups are exocyclic and pentacoordinate.

The solution ^{119}Sn NMR spectrum of $[^{t}Bu_2(OH)SnOSn(Cl)^{n}Bu_2]_2$, **5**, in $CDCl_3$ is simpler than those of **1**−**3**. It shows two signals of equal intensity at −181.7 and −220.9 ppm which have two sets of $^{2}J(^{119}Sn-O-^{117}Sn)$ satellites as well as $^{1}J(^{119}Sn-^{13}C)$. The relative simplicity of the ^{119}Sn NMR spectrum of **5** indicates a higher stability of the dimeric structure because hydroxide is a better bridging group than chloride for tin.[16] The ^{119}Sn CPMAS NMR spectrum of **5** shows two resonances at −178.0 and −220.5 ppm, indicating similar structures in the solid and in solution. The molecular weight determination of **5** in chloroform shows an association factor of 1.9, which indicates negligible dissociation of the dimer in solution. Single crystals of **5** suitable for X-ray investigation could not be obtained, but the crystal structure determination

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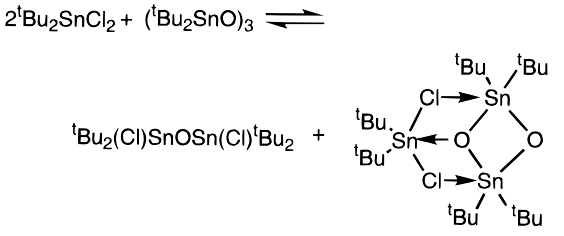
of [^{t}Bu$_2$(OH)SnOSn(Cl)(cyclohexyl)$_2$]$_2$ shows a ladder structure with exocyclic ^{t}Bu$_2$Sn units.[29]

Reaction of (^{t}Bu$_2$SnO)$_3$ with ^{t}Bu$_2$SnCl$_2$. Reaction between (^{t}Bu$_2$SnO)$_3$ and ^{t}Bu$_2$SnCl$_2$ does not appear to produce the corresponding "ladder", [^{t}Bu$_2$(Cl)SnOSn(Cl)^{t}Bu$_2$]$_2$. The room-temperature ^{119}Sn NMR spectrum of a dichloromethane solution prepared from a 1:3 molar ratio of (^{t}Bu$_2$SnO)$_3$ and ^{t}Bu$_2$SnCl$_2$ contains a very broad resonance at 57 ppm and a sharper signal at -27.3 ppm with satellites of 877 Hz. Also present is a very weak resonance at -81.7 ppm with $^2J(^{119}\mathrm{Sn{-}O{-}}^{117}\mathrm{Sn})$ coupling of 363 Hz, consistent with the presence of (^{t}Bu$_2$SnO)$_3$, and two very broad resonances at -86.2 and -215 ppm. Lowering the temperature causes the resonances to sharpen, and at -90 °C the spectrum contains a resonance of 59.5 ppm, attributed to ^{t}Bu$_2$SnCl$_2$. Also present at -90 °C is a resonance at -22.8 ppm which has $^2J(^{119}\mathrm{Sn{-}O{-}}^{117}\mathrm{Sn})$ coupling of 842 Hz. The ^{119}Sn chemical shift position of this resonance is indicative of four-coordinate tin. The large $^2J(^{119}\mathrm{Sn{-}O{-}}^{117}\mathrm{Sn})$ coupling is similar to values found for compounds with almost linear Sn−O−Sn angles (e.g., linear ^{t}Bu$_3$SnOSn^{t}Bu$_3$ has $^2J(^{119}\mathrm{Sn{-}O{-}}^{117}\mathrm{Sn}) = 900$ Hz[30,31]), and consequently this resonance is tentatively assigned to the species [^{t}Bu$_2$(Cl)SnOSn(Cl)^{t}Bu$_2$], **7**. The remaining two resonances in the ^{119}Sn NMR spectrum at -90 °C, at -82.8 and -171.7 ppm, have relative intensities of 2:1 and each has what appear to be $^{117/119}$Sn satellites of 150 Hz. These resonances are tentatively assigned to the "three-quarter" ladder species [^{t}Bu$_2$SnCl$_2$][^{t}Bu$_2$SnO]$_2$, **8**. These data are consistent with an equilibrium (eq 4) which implies at least the transient existence of the dimeric species (^{t}Bu$_2$SnO)$_2$. There are no further substantive changes in the spectrum on cooling to -100 °C.

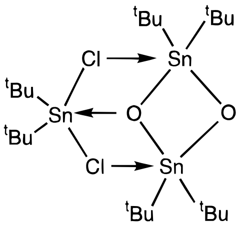


(4)

7 **8**

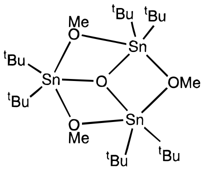
The ^{119}Sn NMR spectrum of a solution prepared from a 1:2 molar ratio (^{t}Bu$_2$SnO)$_3$ and ^{t}Bu$_2$SnCl$_2$ is identical to the above with the exception that now there is no resonance observable for ^{t}Bu$_2$SnCl$_2$. The proportion of **7** and **8** changes as a function of temperature. At room temperature, the resonance of **7** comprises about 50% of the total intensity in the ^{119}Sn NMR spectrum. At -90 °C, the relative intensity of **7** is only about 10%, with the remainder of the intensity being found in the two resonances attributed to **8**. The fact that coupling in **7** and in (^{t}Bu$_2$SnO)$_3$ is seen at room temperature in the same solution is consistent with exchange between **7** and (^{t}Bu$_2$SnO)$_3$, which is slow on the NMR time scale.

It was recently reported[32] that (^{t}Bu$_2$SnO)$_3$ reacts with BR(OH)$_2$ (R = 2,4,6-Me$_3$C$_6$H$_2$) to give the tritin species ^{t}Bu$_2$Sn(OH)$_2$[(^{t}Bu$_2$SnO)$_2$OBR], **8a**, which was characterized in the solid state. This compound exhibited ^{119}Sn NMR chemical shifts of -260.0 and -278.5 ppm (relative intensities 2:1) in solution, but no $^{117/119}$Sn−$^{117/119}$Sn coupling was reported.

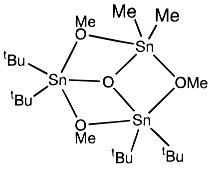


8a

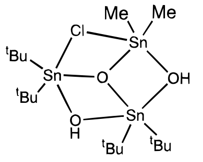
Electrospray Mass Spectrometric Data. ESMS is particularly suitable for the study of these labile organotin systems in solution, and a detailed ESMS study of these systems will be the focus of a future paper. The positive-ion spectrum of **1** dissolved in MeOH/water (50:50) is comparatively simple. The dominant fragments (*m/z* 807 (30%), 723 (100%), 699 (20%), 639 (20%), 619 (40%)) contain three tin atoms, and the assignments are shown in the following display. Fragments with *m/z* 807 are also present (100% relative abundance) in the positive spectra of solutions of **4** as well in solutions prepared from a 2:3 ratio of (^{t}Bu$_2$SnO)$_3$ and ^{t}Bu$_2$SnCl$_2$. Experimental and calculated isotopic cluster patterns are in excellent agreement.



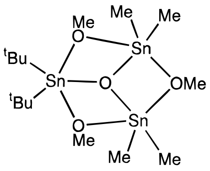
m/z 807 ($C_{27}H_{63}O_4Sn_3$)



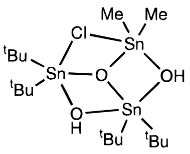
m/z 723 ($C_{21}H_{51}O_4Sn_3$)



m/z 699 ($C_{18}H_{44}O_3ClSn_3$)



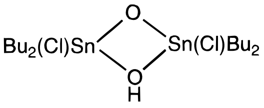
m/z 639 ($C_{15}H_{39}O_4Sn_3$)



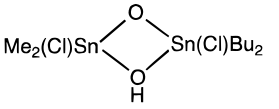
m/z 619 ($C_{21}H_{51}O_4Sn_3$)

These fragments apparently arise from reaction of **1** with the solvent system and demonstrate again the lability of ladder systems in solution. It may well be that species similar to these contribute to the very low-intensity signals observed in the ^{119}Sn NMR solution spectra of samples of **1**−**4**. Nevertheless the existence of these cationic clusters adds support for the proposed neutral 1:1 adducts of (R$_2$SnO)$_2$ in Scheme 1 and for species **8**.

The anionic spectrum of **1** contains peaks at *m/z* 485 (100%) and 569 (40%). The anionic spectrum of **4** shows a fragment peak at *m/z* 485 in 100% relative abundance. The isotope patterns associated with these peaks are totally consistent with the formulations of the two anionic species which is indirect support for existence of species such as **7**.



m/z 569 ($C_{16}H_{37}O_2Cl_2Sn_2$)



m/z 485 ($C_{10}H_{25}O_2Cl_2Sn_2$)

Conclusion. Ladder compounds containing ^{t}Bu substituents at tin may be isolated in the solid state as discrete molecular species [^{t}Bu$_2$(Cl)SnOSn(Cl)R$_2$]$_2$, which may be regarded as 1:2 adducts, [(^{t}Bu$_2$SnCl$_2$)(R$_2$SnO)$_2$(^{t}Bu$_2$SnCl$_2$)]. In solution these adducts are labile and undergo some dissociation,

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the extent of dissociation being dependent on the nature of the R group. Addition of R_2SnCl_2 to solutions of these ladders causes replacement of the exocyclic $^tBu_2SnCl_2$ groups by the added R_2SnCl_2. Attempts at formation of a ladder species, $[(^tBu_2SnCl_2)(^tBu_2SnO)_2(^tBu_2SnCl_2)]$, where all four tin atoms carry ^tBu substituents were unsuccessful. Formation of a ladder species $[(^tBu_2SnCl_2)(^tBu_2SnO)_2(^tBu_2SnCl_2)]$ would require the tin atoms in the central $(^tBu_2SnO)_2$ to be able to become six-coordinate. Apparently, the ^tBu groups reduce the Lewis acidity at tin to such an extent that six-coordination is not possible. Instead, there is evidence for the 1:1 adduct $(^tBu_2SnCl_2)(^tBu_2SnO)_2$ in which the tin atoms are all five-coordinate.

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Supporting Information Available: Listings of fractional atomic coordinates, thermal parameters, H atom parameters, and all bond distances and angles (9 pages). Ordering information is given on any current masthead page.

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