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Cohydrolysis of Organotin Chlorides with Trimethylchlorosilane. Okawara's Pioneering Work Revisited and Extended†

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The synthesis of the stannasiloxanes $\{[R_2(Me_3SiO)Sn]_2O\}_2$ (**1**, R = Me; **2**, R = Et), $[R_2(Me_3SiO)Sn]_2O$ (**8**, R = Me_3SiCH_2; **9**, R = *t*-Bu), $R_2Sn(OSiMe_3)_2$ (**3**, R = *i*-Pr; **4**, R = Me_3SiCH_2; **5**, R = *t*-Bu; **6**, R = $Cp(CO)_3W$; **7**, R = $Cp(CO)_2Fe$), and $[Cp(CO)_2Fe]_2Sn(OSiPh_3)_2$ (**7a**), the monoorganotin trichloride $Me_3SiCH_2SnCl_3$ (**13**), and the organotin oxocluster $(Me_3SiCH_2Sn)_{12}O_{14}(OH)_6Cl_2$ (**14**) is reported. Their identity was confirmed by both solution and solid state multinuclear NMR spectroscopy and in the case of **1**, **2**, **6**, **7a**, and **14** also by single-crystal X-ray analyses. A spinning sideband analysis of the ^{119}Sn MAS spectra reveals the coordination geometries of the tin atoms in the stannasiloxanes **1** and **2** to be different from those of related diorganotin oxides $(R_2SnO)_n$ (R = Me, Et). In solution, **1** and **2** exhibit an intramolecular exchange process as well as monomer−dimer equilibria. The reaction of **4** with *cyclo*-$(t\text{-}Bu_2SnO)_3$ and of *cyclo*-$[(Me_3SiCH_2)_2SnO]_3$ with *cyclo*-$(t\text{-}Bu_2SnO)_3$ provided evidence for the formation in situ of the mixed tetraorganodistannoxane $t\text{-}Bu_2(Me_3SiO)SnOSn(OSiMe_3)(CH_2SiMe_3)_2$ (**10**) and of the hexaorganotristannoxanes *cyclo*-$[(Me_3SiCH_2)_2Sn(OSn\,t\text{-}Bu_2)_2O]$ (**11**) and *cyclo*-$\{t\text{-}Bu_2Sn[OSn(CH_2SiMe_3)_2]_2O\}$ (**12**).

Introduction

During the past four decades dimeric tetraorganodistannoxanes of the type $[R_2(X)SnOSn(Y)R'_2]_2$ (X, Y = halogen, OH, OR, $OSiMe_3$, OOCR, $OSP(OR)_2$, NO_3, N_3, NCS, SH, $OReO_3$; R, R′ = alkyl, aryl) have attracted considerable attention because of their unique structural features and questions associated with this.[1−5] They are also of interest as catalysts for a variety of organic reactions such as transesterifications, acylations of alcohols, or the cleavage of silyl ethers.[6] In the solid state, these dimeric tetraorganodistannoxanes contain characteristic $Sn_4O_2X_2Y_2$ structural motifs with ladder-like or stairwise arrangements (Chart 1).[1d,3a−c] In

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[†] This work contains part of the Ph.D. theses of J. Beckmann and S. Rabe, Dortmund University, 1999, and of the intended Ph.D. thesis of U. Kaltenbrunner.

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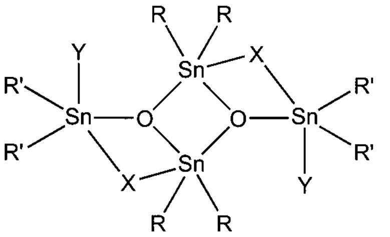
Chart 1



X, Y = Hal, OH, OR, OSiMe$_3$, OOCR, ONO$_2$,
OSP(OR)$_2$, OReO$_3$, N$_3$, NCS, SH
R, R' = alkyl, aryl

general, the tin atoms in these compounds are pentacoordinated. In concentrated solutions the dimers are preserved. However, redistribution reactions of dimeric tetraorganodistannoxanes and molecular weight measurements in diluted solutions provide evidence for their partial dissociation in solution.[1j,3k,5e,n] Moreover, for the symmetrically substituted tetrabutyldistannoxanes [Bu$_2$(X)SnOSn(X)Bu$_2$]$_2$ (X = OOCMe, OOC(2-NH$_2$-C$_6$H$_4$)) ^{119}Sn NMR spectroscopy in solution indicates monomer dimer equilibria which are slow on the NMR time scale.[3h,j] The ^{119}Sn NMR chemical shifts reported for the monomeric species Bu$_2$(X)SnOSn(Y)Bu$_2$ (X = Y= OOCMe, OOC(2-NH$_2$-C$_6$H$_4$)) of −149 and −161 ppm, respectively, suggest the tin atoms in these compounds to remain pentacoordinated. This observation can tentatively be traced to the chelating capacity of the carboxylate ligands.

The origin of the catalytic activity of tetraorganodistannoxanes is the subject of controversial discussion[6] and, according to a recent work, may be associated with the presence of monomeric tetraorganodistannoxanes.[5e] So far, only two examples of monomeric tetraorganodistannoxanes R$_2$(X)SnOSn(X)R$_2$ (R = CH(SiMe$_3$)$_2$, X = OH; R = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$, X = Cl) with tetracoordinated tin atoms are known, and these are stabilized by bulky R groups.[7] No studies concerning the catalytic activity are reported for these compounds.

In a recent series of papers we reported alkylidene-bridged double and triple ladder compounds[8] which show lower catalytic activity in acylation reactions as compared with simple [Bu$_2$(Cl)SnOSn(Cl)Bu$_2$]$_2$.[8c] This decreased activity was attributed to the higher kinetic stability of the former compounds.

In previous publications, Okawara et al. described the cohydrolysis of R$_2$SnCl$_2$ with Me$_3$SiCl, providing dimeric tetraorganodistannoxanes of the type [R$_2$(Me$_3$SiO)SnOSn(OSiMe$_3$)R$_2$]$_2$ (R = Me, Et). These compounds were only partially characterized at that time,[1a−c] and we now describe the reinvestigation of these compounds including X-ray structure analyses and both solution and solid state NMR spectroscopy. Moreover, we also describe the role of the substituents attached to tin, and we have extended the cohydrolysis method reported by Okawara et al.[1a−c] to other diorganotin dichlorides and Me$_3$SiCH$_2$SnCl$_3$ to give diorganostannasiloxanes of the type R$_2$Sn(OSiMe$_3$)$_2$ (R = *i*-Pr, CH$_2$SiMe$_3$, *t*-Bu, W(CO)$_3$Cp, Fe(CO)$_2$Cp) and the tin-oxo cluster compound (Me$_3$SiCH$_2$Sn)$_{12}$O$_{14}$(OH)$_6$Cl$_2$. To elucidate the reactivity of selected compounds, redistribution reactions were performed, the results of which are also reported.

Results and Discussion

The cohydrolysis of diorganotin dichlorides R$_2$SnCl$_2$ (R = Me, Et, *i*-Pr, CH$_2$SiMe$_3$, *t*-Bu, Cp(CO)$_3$W,[9,10] Cp(CO)$_2$Fe) with an excess of Me$_3$SiCl in aqueous ammonia/hexane was performed according to a method slightly modified from that published by Okawara et al.[1a]

The weakly basic reaction conditions give rise to in situ formation of Me$_3$SiOH, which subsequently reacts with the organotin intermediates.

Depending on the identity of R, either dimeric tetraorganodistannoxanes [R$_2$(Me$_3$SiO)SnOSn(OSiMe$_3$)R$_2$]$_2$ (**1**, R = Me; **2**, R = Et) or bis(trimethylsiloxy) diorganotin compounds R$_2$Sn(OSiMe$_3$)$_2$ (**3**, R = *i*-Pr; **4**, R = CH$_2$SiMe$_3$; **5**, R = *t*-Bu; **6**, R = Cp(CO)$_3$W; **7**, R = Cp(CO)$_2$Fe) were obtained in almost quantitative yield (Scheme 1).

Compounds **1** and **2** are colorless crystalline solids, and **6** and **7** are orange crystalline solids, whereas compounds **3**−**5** are distillable oils. Unlike comparable

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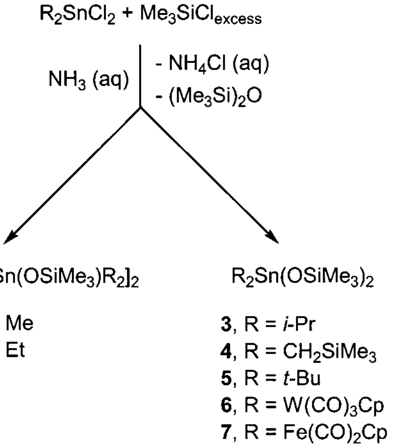
Scheme 1



diorganotin alkoxides,[11] compounds **1**−**7** are remarkably stable toward moisture. However, upon contact with moist air over several weeks, compound **2** slowly transforms to an amorphous insoluble material, which was identified by elemental analysis and IR spectroscopy as diethyltin oxide.

The molecular structures of compounds **1** and **2** are depicted in Figures 1 and 2, respectively, and crystallographic data are given in Table 1. Selected bond lengths and angles are listed in Table 2.

Both **1** and **2** are ladder-type centrosymmetric dimers with a center of inversion at 0.5, 0.5, 0.5 for **1** and at 0, 0, 0 for **2**. The Sn_4O_6 structural motif is planar to ±0.018(3) Å in **1** and to ±0.019(3) Å in **2**. Each tin atom exhibits a distorted trigonal bipyramidal geometry with the equatorial positions being occupied by two carbons (C(1), C(11) for Sn(1); C(21), C(31) for Sn(2)) and one oxygen (O(2)) and the axial positions by two oxygens (O(1), O(2a) for Sn(1); O(1), O(3) for Sn(2)). The trigonal bipyramidal configuration is more distorted at Sn(2) (geometrical goodness[12,5j,o] $\Delta\Sigma(\theta)$ 89.4 for **1**, 87.2 for **2**). The Sn(1)−O(1)−Sn(2) bridges are strongly asymmetric, with Sn(1)−O(1) and Sn(2)−O(1) distances of 2.171(5) (**1**)/2.146(4) (**2**) and 2.419(5) (**1**)/2.480(4) Å (**2**), respectively. The asymmetry of the axial Sn(2)−O(1) and Sn(2)−O(3) bonds amounts to 0.39 Å for **1** and 0.472 Å for **2**, which is greater than the asymmetries of 0.344−0.024 Å, as reported for axial Sn−Cl bonds of related tetraorganodichlorodistannoxanes.[5j] The intramolecular Sn(1)···O(3a) distances of 3.462(6) (**1**) and 3.528(4) Å (**2**) are slightly shorter than the sum of the van der Waals radii[13a] of oxygen (1.50 Å) and tin (2.20 Å), which is reflected in the opening of the C(1)−Sn(1)−C(11) bond angles of 130.3(4)° (**1**) and 128.9(2)° (**2**). The very weak but different Sn(1)···O(3a) contacts cause in turn the Sn(2)−O(3)−Si(2) bond angles in **1** and **2** to differ by 11.5°. The Si(1)−O(1) distances of 1.621(6) (**1**) and 1.630(4) Å (**2**) involving the bridging oxygens are longer than the Si(2)−O(3) distances of 1.579(6) (**1**) and 1.593(5) Å (**2**) involving nonbridging oxygens. This is a straightforward example of a Si−O bond activation by a Lewis acidic tin moiety.

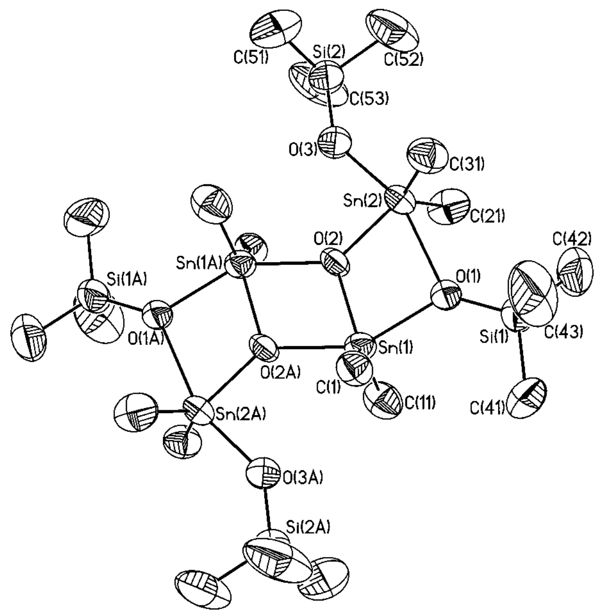


Figure 1. General view (SHELXTL) of a molecule of **1** showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: a = $-x + 1$, $-y + 1$, $-z + 1$).

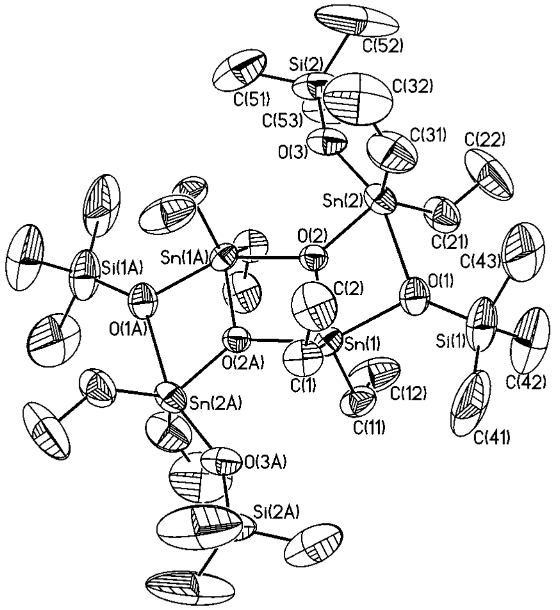


Figure 2. General view (SHELXTL) of a molecule of **2** showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: a = $-x$, $-y$, $-z$).

The molecular structure of compound **6** is shown in Figure 3. Selected bond lengths and angles are given in Table 3. The tin atom shows a distorted tetrahedral configuration with angles between 95.4(2)° (O(21)−Sn(1)−O(25)) and 126.17(2)° (W(1)−Sn(1)−W(2)). The latter angle and the Sn−W distances of 2.8267(5) and 2.7983(5) Å are comparable with the corresponding values of 125.52(5)° and 2.788(1)/2.794(1) Å, as reported for the anion $\{[(CO)_5W]_2SnOEt\}_2^{2-}$.[13b] Most remarkably, the Sn(1)−O(21) (1.891(4) Å) and Sn(1)−O(25) (1.972(4) Å) distances differ by 0.081 Å. The first one is rather short and hints at ionic bonding. The lengthening of the

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Table 1. Crystallographic Data for 1, 2, 6, 7a, and 14

	1	2	6	7a	14
formula	$C_{20}H_{60}O_6Si_4Sn_4$	$C_{28}H_{76}O_6Si_4Sn_4$	$C_{22}H_{28}O_8Si_2SnW_2$	$C_{50}H_{40}Fe_2O_6Si_2Sn$	$C_{48}H_{138}Cl_2O_{20}Si_{12}Sn_{12}\cdot 2CHCl_3$
fw	983.80	1096.01	963.01	1023.39	3345.32
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
cryst size, mm	0.20 × 0.15 × 0.10	0.30 × 0.20 × 0.20	0.20 × 0.15 × 0.15	0.10 × 0.08 × 0.08	0.40 × 0.20 × 0.20
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a, Å	7.363(1)	11.005(1)	10.383(1)	21.125(1)	15.357(1)
b, Å	24.811(1)	19.036(1)	25.716(1)	12.484(1)	16.087(1)
c, Å	11.957(1)	11.888(1)	11.125(1)	17.810(1)	16.138(1)
α, deg	90	90	90	90	96.894(1)
β, deg	101.920(1)	93.618(1)	104.601(1)	91.682(1)	114.585(1)
γ, deg	90	90	90	90	114.204(1)
V, Å^3	2137.2(4)	2485.5(3)	2874.5(4)	4694.9(5)	3097.1(3)
Z	2	2	4	4	1
ρ_{calcd}, Mg/m^3	1.529	1.464	2.225	1.448	1.794
ρ_{meas}, Mg/m^3	1.545(4)	1.485(3)	n.m.	n.m.	n.m.
μ, mm^{-1}	2.446	2.112	8.970	1.236	2.837
F(000)	968	1096	1800	2072	1620
θ range, deg	3.42−26.04	3.43−25.68	3.48−26.81	2.95−27.49	2.55−30.56
index ranges	$-7\leq h\leq 7$	$-13\leq h\leq 13$	$-13\leq h\leq 13$	$-27\leq h\leq 27$	$-21\leq h\leq 21$
	$-30\leq k\leq 30$	$-23\leq k\leq 23$	$-31\leq k\leq 31$	$-16\leq k\leq 16$	$-16\leq k\leq 16$
	$-14\leq l\leq 14$	$-14\leq l\leq 14$	$-12\leq l\leq 12$	$-22\leq l\leq 22$	$-23\leq l\leq 20$
no. of reflns collcd	28 916	33 630	40 937	59 767	39 721
completeness to θ_{max}	93.2%	99.4%	94.9%	99.3%	86.6%
no. of indep reflns/R_{int}	3920/0.03	4698/0.045	5412/0.05	10700/0.032	16435/ 0.034
no. of reflns obsd with ($I > 2\sigma(I)$)	2419	2680	3309	6080	9652
no. of refined params	163	208	324	599	497
GooF (F^2)	1.064	0.938	0.862	0.871	0.920
R1(F) ($I > 2\sigma(I)$)	0.0505	0.0370	0.0295	0.0323	0.0373
wR2(F^2) (all data)	0.1417	0.0927	0.0585	0.0668	0.0825
$(\Delta/\sigma)_{max}$	0.001	0.001	<0.001	0.001	0.001
largest diff peak/hole, e/Å^3	2.361/−0.806	0.439/−0.629	0.666/−1.074	0.479/−0.401	0.638/−0.794

second bond distance seems to be the result of a weak intramolecular O(25)···H−C(7) hydrogen bridge of 3.242(9) Å. This is also reflected by the smaller Si(2)−O(25)−Sn(1) angle of 140.2(3)° as compared with the Si(1)−O(21)−Sn(1) angle of 154.9(3)°.

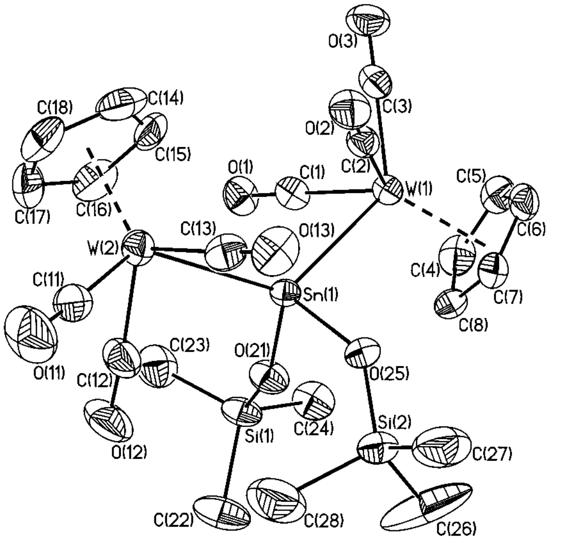

Figure 3. General view (SHELXTL) of a molecule of **6** showing 30% probability displacement ellipsoids and the atom numbering.

No single crystals suitable for X-ray diffraction could be obtained from the iron-substituted stannasiloxane **7**, but were obtained from its Si−Ph-substituted analogue $[Cp(CO)_2Fe]_2Sn(OSiPh_3)_2$ (**7a**), which was prepared from $[Cp(CO)_2Fe]_2SnCl_2$ and Ph_3SiOH. The molecular structure of compound **7a** is shown in Figure 4. Selected bond lengths and bond angles are given in Table 3. The tin atom shows again a distorted tetrahedral configuration with angles between 95.8(1)° (O(1)−Sn(1)−O(2)) and 125.88(2)° (Fe(1)−Sn(1)−Fe(2)). The latter angle and the Sn−Fe distances of 2.5482(4) and 2.5385(4) Å are comparable with the corresponding values of 126.3(2)° and 2.563(1) Å as reported for $[Cp(CO)_2Fe]_2Sn(ONO)_2$[13c], the only other crystallographically characterized tetracoordinated tin compound with an Fe_2SnO_2 substituent pattern. Both Sn−O as well as both Si−O bond lengths are equal within experimental errors and do not show any particularities.

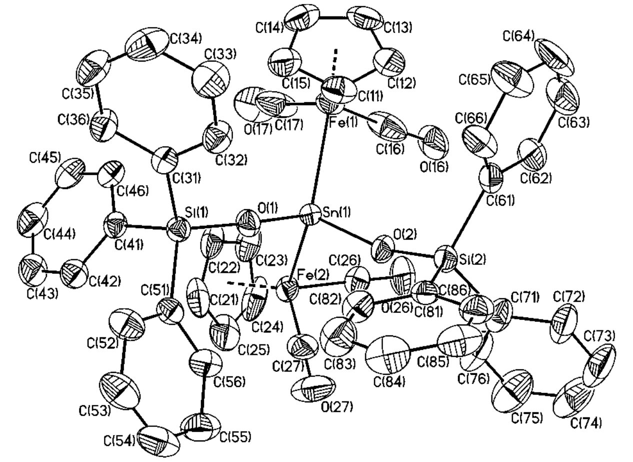

Figure 4. General view (SHELXTL) of a molecule of **7a** showing 30% probability displacement ellipsoids and the atom numbering.

Compounds **6**, **7**, and **7a** can be regarded as simple molecular models for surface complexes between transi-

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 1 and 2[a]

	1	**2**
Sn(1)−O(1)	2.171(5)	2.146(4)
Sn(1)−O(2)	2.006(5)	2.013(3)
Sn(1)−O(2a)	2.143(5)	2.184(3)
Sn(1)−O(3a)	3.462(6)	3.528(4)
Sn(1)−C(1)	2.107(8)	2.098(5)
Sn(1)−C(11)	2.093(10)	2.090(5)
Sn(2)−O(1)	2.419(5)	2.480(4)
Sn(2)−O(2)	1.990(5)	1.977(3)
Sn(2)−O(3)	2.029(6)	2.008(4)
Sn(2)−C(21)	2.113(8)	2.141(6)
Sn(2)−C(31)	2.103(9)	2.095(8)
Si(1)−O(1)	1.621(6)	1.630(4)
Si(2)−O(3)	1.579(6)	1.593(5)
O(1)−Sn(1)−O(2)	76.48(19)	76.72(14)
O(1)−Sn(1)−O(2a)	148.97(19)	149.91(13)
O(2)−Sn(1)−O(2a)	72.5(2)	73.20(13)
O(1)−Sn(1)−C(1)	97.0(3)	98.3(2)
O(1)−Sn(1)−C(11)	97.0(3)	97.5(2)
O(2)−Sn(1)−C(1)	115.3(3)	115.49(19)
O(2)−Sn(1)−C(11)	114.3(4)	115.37(19)
O(2a)−Sn(1)−C(1)	95.6(3)	95.1(2)
O(2a)−Sn(1)−C(11)	96.2(4)	94.8(2)
C(1)−Sn(1)−C(11)	130.3(4)	128.9(2)
O(1)−Sn(2)−O(2)	71.13(19)	69.81(12)
O(1)−Sn(2)−O(3)	158.2(2)	159.18(15)
O(2)−Sn(2)−O(3)	87.1(2)	89.37(15)
O(1)−Sn(2)−C(21)	89.5(3)	88.5(2)
O(1)−Sn(2)−C(31)	89.3(3)	89.7(3)
O(2)−Sn(2)−C(21)	114.1(3)	113.8(2)
O(2)−Sn(2)−C(31)	114.8(3)	112.5(3)
O(3)−Sn(2)−C(21)	101.2(3)	100.2(2)
O(3)−Sn(2)−C(31)	98.7(3)	98.9(3)
C(21)−Sn(2)−C(31)	127.7(5)	129.7(4)
Sn(1)−O(1)−Sn(2)	95.58(19)	95.24(13)
Sn(1)−O(1)−Si(1)	131.1(3)	129.3(3)
Sn(2)−O(1)−Si(1)	133.1(3)	135.2(2)
Sn(1)−O(2)−Sn(1a)	107.5(2)	106.80(13)
Sn(1)−O(2)−Sn(2)	116.8(2)	118.21(15)
Sn(1a)−O(2)−Sn(2)	135.7(3)	134.96(16)
Sn(2)−O(3)−Si(2)	141.3(4)	152.8(3)

[a] Symmetry transformations used to generate equivalent atoms: a = $-x + 1, -y + 1, -z + 1$ (**1**). a = $-x, -y, -z$ (**2**)

tion metals grafted on silica and organotin species. Such surface complexes find increasing interest as tailor-made heterogeneous catalysts for a variety of organic reactions.[14] The solid-state structures of **1** and **2** are confirmed by ^{119}Sn MAS, ^{29}Si MAS, and ^{13}C MAS NMR spectroscopy. The ^{119}Sn MAS spectra of **1** and **2** each display two signals (−137.9 and −156.9 ppm, and −162.3 and −185.5 ppm) which reflect the two crystallographically independent tin sites in each compound. The chemical shifts are in the range of pentacoordinated diorganotin compounds,[3k] but the signals could not be assigned unambiguously to exo- and endocyclic tin atoms.[3g,h,4e,5j,l,n] The ^{29}Si MAS spectra of **1** and **2** each show two signals (−0.6, 3.4 ppm; −1.1, 2.0 ppm). The ^{13}C MAS NMR spectrum of **1** shows two signals at 5.4 and 5.6 ppm for the trimethylsiloxy ligands and four signals at 6.5, 7.6, 8.2, and 8.5 ppm for the dimethyltin groups. The ^{13}C MAS NMR of **2** shows two signals at 5.6 and 6.1 ppm for the trimethylsiloxy ligands and four signals at 11.6, 12.4, 18.5, and 20.7 ppm for the ethyl groups. The latter seem to be superimposed, as the X-ray structure of **2** requires eight distinct carbon resonances for these groups.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for 6 and 7a

	6, X(1) = O(21), X(2) = O(25), M = W	**7a**, X(1) = O(1), X(2) = O(2), M = Fe
Sn(1)−X(1)	1.891(4)	1.999(2)
Sn(1)−X(2)	1.972(4)	1.994(2)
Si(1)−X(1)	1.545(5)	1.597(2)
Si(2)−X(2)	1.617(4)	1.605(2)
Sn(1)−M(1)	2.8267(5)	2.5482(4)
Sn(1)−M(2)	2.7983(5)	2.5385(4)
X(1)−Sn(1)−X(2)	95.4(2)	95.87(7)
Sn(1)−X(1)−Si(1)	154.9(3)	158.7(1)
Sn(1)−X(2)−Si(2)	140.2(3)	164.1(1)
X(1)−Sn(1)−M(1)	106.42(2)	108.47(5)
X(1)−Sn(1)−M(2)	111.51(2)	109.04(5)
X(2)−Sn(1)−M(1)	101.15(2)	107.91(5)
X(2)−Sn(1)−M(2)	111.44(2)	105.56(5)
M(1)−Sn(1)−M(2)	126.17(2)	125.88(2)

Table 4. Selected ^{119}Sn MAS NMR Data for 1, $(Me_2SnO)_n$, 2, and $(Et_2SnO)_n$

	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	$\Delta\sigma$	η
1	266.1	−94.9	−584.9	−137.9	−670.5	0.81
	286.7	−96.1	−659.5	−156.9	−754.8	0.76
$(Me_2SnO)_n$	251.3	−139.3	−567.1	−151.8	−623.1	0.94
2	178.9	−88.2	−577.6	−162.3	−623.0	0.64
	209.7	−112.3	−653.9	−185.5	−702.6	0.69
$(Et_2SnO)_n$	207.0	−145.2	−561.7	−166.6	−592.6	0.89

To compare the geometry of the tin atoms in **1** and **2** with those of polymeric $(Me_2SnO)_n$ and $(Et_2SnO)_n$, for all of these compounds spinning sideband analyses of the ^{119}Sn MAS spectra were performed using the method of Herzfeld and Berger.[15] The three independent parameters obtained are expressed in terms of the generally accepted tensor notation and the more suitable Haeberlein notation, respectively (Table 4). The diorganotin oxides $(Me_2SnO)_n$ and $(Et_2SnO)_n$ show a single ^{119}Sn NMR resonance at −151.8[16] and −166.6 ppm, respectively, being close to one of the resonances of **1** (−156.9 ppm) and **2** (−162.3), respectively. Therefore it appears likely that the tin atoms within these compounds are all pentacoordinated. However, a comparison of the anisotopy and asymmetry parameters of compounds having the same R groups, i.e., $(Me_2SnO)_n$ with **1**, and $(Et_2SnO)_n$ with **2**, suggests different tin geometries within the same R group pair. Hence, the structures of the dimeric tetraorganodistannoxanes **1** and **2** are not related to those of the polymeric diorganotin oxides $(Me_2SnO)_n$ and $(Et_2SnO)_n$.[16]

^{119}Sn NMR spectroscopy (toluene-d_8) shows that the dimeric structure of the tetraorganodistannoxanes **1** and **2** is retained in solution.[3g,h,k,4e,k] For compounds **1** and **2**, two signals in the pentacoordinated range are observed at −136.3 and −155.8 ppm, and at −166.8 and −183.8 ppm, respectively, which is in the pentacoordinated range observed in the ^{119}Sn MAS NMR.[2b]

However, the ^{29}Si NMR spectrum of **1** (toluene-d_8) shows only a single resonance at 1.8 ppm ($W_{1/2}$ = 25 Hz), which is in contrast with the solid state, where two resonances were observed. The ^{13}C NMR spectrum of **1** exhibits two distinct signals at 6.1 and 6.6 ppm for the exo- and endocyclic methyltin groups, whereas only one

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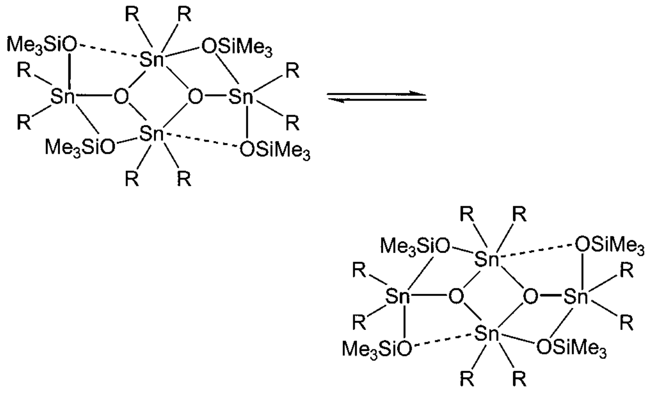
(14) (a) Humblot, F.; Didillon, D.; Lepeltier, F.; Candy, J. P.; Croker, J.; Clause, O.; Bayard, F.; Basset, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 137, and references therein.

(15) (a) Herzfeld, J.; Chen, X. *Encyclopedia of Nuclear Magnetic Resonance*; John Wiley & Sons Ltd.: New York, 1996; Vol. 7, p 4362. (b) Eichle, K.; Wasylishen, R. E. *Wsolids1, HBA 1.2, Simulation and fitting programs*; Dalhousie University: Halifax, Canada, 1996.

(16) Harris, R. K.; Sebald, A. *J. Organomet. Chem.* **1987**, *331*, C9.

Scheme 2



1, R = Me
2, R = Et

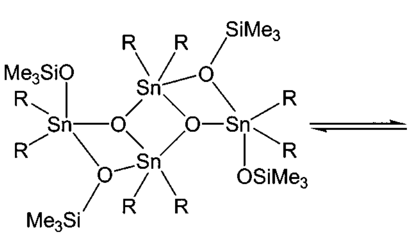
signal is observed at 3.8 ppm for the trimethylsiloxy ligands. Given the high resolution of ^{13}C NMR spectroscopy, it appears likely that the trimethylsiloxy groups are magnetically equivalent rather than the signals being superimposed. This assumption is further supported by the ^{1}H NMR spectrum of **1**, which exhibits two signals for the dimethyltin groups at 0.59 and 0.79 ppm with $^2J(^1H-C-^{119}Sn)$ couplings of 77 and 81 Hz, respectively, and only one signal at 0.11 ppm for the trimethylsiloxy ligand. These results indicate that the trimethylsiloxy ligands are equivalent in solution. Similar observations hold for compound **2**, as well (see Experimental Section). The most likely explanation is the assumption of a dynamic process (a kind of wagging) occurring in solution which is fast on the ^{1}H, ^{13}C, and ^{29}Si NMR time scales (Scheme 2). Similar observations have already been reported for other symmetrically substituted dimeric tetraorganodistannoxanes $[R_2(X)SnOSn(X)R_2]_2$ (X = OOCR, F; R = alkyl).[5a,h,n,0,q] Attempts to slow the exchange process on the NMR time scale failed because of the poor solubility of **1** and **2** at lower temperatures.

To investigate the dissociation of dimeric tetraorganodistannoxanes, ^{119}Sn NMR spectra (c = 50 mM, toluene) of **1** and **2** were recorded at 20, 40, and 80 °C.

No significant change of the ^{119}Sn NMR spectrum was observed for $[Me_2(Me_3SiO)SnOSn(OSiMe_3)Me_2]_2$ (**1**) at 40°; however at 80 °C an additional signal at −7.4 ppm (integral 6%) appeared, which is tentatively assigned to the monomeric tetraorganodistannoxane $Me_2(Me_3SiO)SnOSn(OSiMe_3)Me_2$ (**1a**) (eq 1). The chemical shift clearly indicates the tin atoms in **1a** to be tetracoordinated.

The coexistence at higher temperatures of separate signals belonging to **1** and **1a** suggests a monomer−dimer equilibrium (i) that is slow on the ^{119}Sn NMR time scale and (ii) the position of which is temperature dependent. Upon cooling to room temperature, the resonance at −7.4 ppm disappears and the original spectrum of **1** is observed.

High-temperature ^{1}H NMR (60 MHz) studies on **1** as previously reported by Considine et al. led the authors to the conclusion that a monomer−dimer equilibrium exists which is fast on the ^{1}H NMR time scale.[1g] However, considering our high-temperature ^{119}Sn NMR studies on one hand and the low resolution of the 60 MHz NMR spectrometer used for the high-temperature ^{1}H NMR measurements on the other hand, it appears likely that Considine et al. observed a superposition of signals rather than coalescense.[1g]



1, R = Me
2, R = Et

$$2\ R_2(Me_3SiO)SnOSn(OSiMe_3)R_2 \quad (1)$$

1a, R = Me
2a, R = Et

Similar observations hold for $[Et_2(Me_3SiO)SnOSn(OSiMe_3)Et_2]_2$ (**2**), although here the dissociation is more pronounced at lower temperatures (eq 1). The ^{119}Sn NMR spectrum at 40 °C already shows a new signal at −47.4 ppm (integral 4%) that increases at 80 °C (integral 14%) and which is assigned to the monomeric tetraorganodistannoxane $Et_2(Me_3SiO)SnOSn(OSiMe_3)Et_2$ (**2a**) (Figure 5).

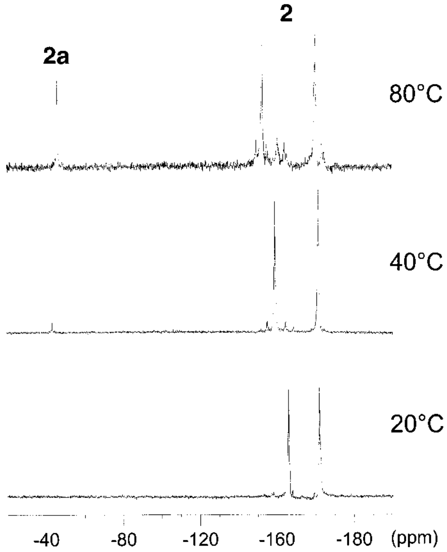


Figure 5. ^{119}Sn NMR spectra (in toluene) of **2** at temperatures of 20, 40, and 80 °C.

For both cases **1** and **2**, along with the presence of the signals due to the monomeric tetraorganodistannoxanes **1a** and **2a**, new signals of minor intensity appeared in the pentacoordinate region at −130.8, −152.6, −153.6, and −155.8 ppm (**1**, total integral 10%) and at −152.7, −155.6, −161.4, −165.1, −181.8, and −184.3 ppm (**2**, total integral 20%), but these were not assigned. However, these signals point out the presence of further species being in equilibrium with **1** and **1a**, as well as **2** and **2a**.

It has been reported that tributyltin alkoxides n-Bu_3SnOR (R = Et, n-Bu) react with CCl_4 to give n-Bu_3SnCl, $CHCl_3$, and aldehyde.[17a]

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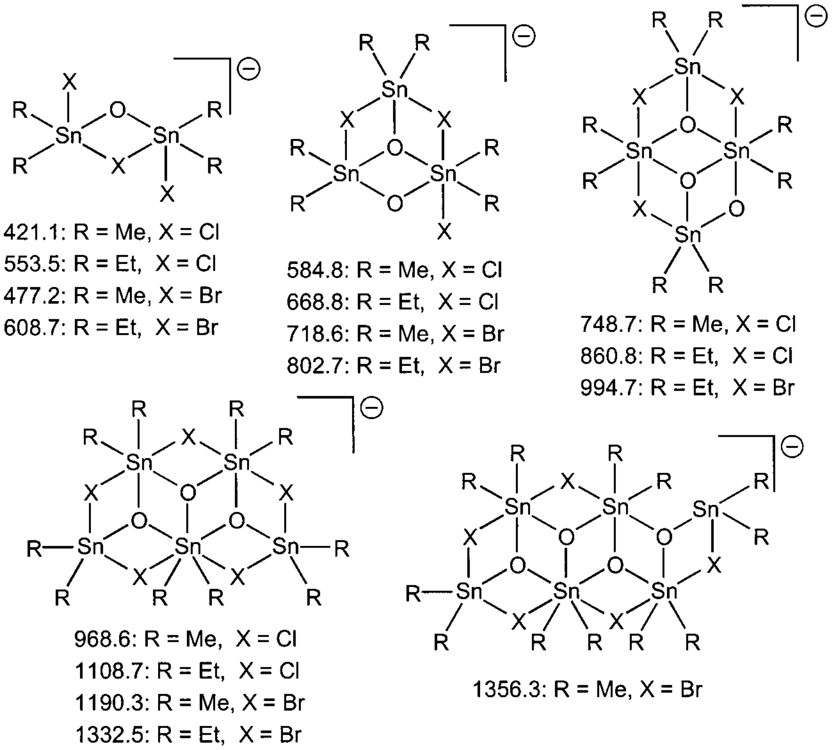
(17) (a) Blunden, S. J.; Hill, R. *Appl. Organomet. Chem.* **1988**, *2*, 83. (b) Alcock, N. W.; Pennington, M.; Willey, G. R. *J. Chem. Soc., Dalton. Trans.* **1985**, 2683.

Chart 2



421.1: R = Me, X = Cl
553.5: R = Et, X = Cl
477.2: R = Me, X = Br
608.7: R = Et, X = Br

584.8: R = Me, X = Cl
668.8: R = Et, X = Cl
718.6: R = Me, X = Br
802.7: R = Et, X = Br

748.7: R = Me, X = Cl
860.8: R = Et, X = Cl
994.7: R = Et, X = Br

968.6: R = Me, X = Cl
1108.7: R = Et, X = Cl
1190.3: R = Me, X = Br
1332.5: R = Et, X = Br

1356.3: R = Me, X = Br

Similarly, a sample of **2** in deuterated tetrachloroethane (sealed under argon) that had originally been prepared for the purpose of high-temperature ^{119}Sn NMR studies changed with time. In the beginning, the ^{119}Sn NMR spectrum showed two signals at −160.8 and −182.8 ppm (ratio 1:1), which are very close to the chemical shifts in toluene as reported above. After 6 months two new major signals appeared at −143.3 and −169.1 ppm (ratio 1:1, integral 78%), which both show a $^{2}J(^{119}\mathrm{Sn{-}O{-}}^{117/119}\mathrm{Sn})$ coupling of 200 Hz. We assign these signals to the asymmetrically substituted dimeric tetraorganodistannoxane $[\mathrm{Et_2(Me_3SiO)SnOSn(Cl)Et_2}]_2$, which was formed upon reaction of **2** with the solvent. In addition, four minor signals appeared at −118.2, −146.4, −172.2, and −180.1 ppm (total integral 22%), which are tentatively assigned to the mono- or trisiloxy-substituted species $\{[\mathrm{Et_2(Me_3SiO)SnOSn(Cl)Et_2}][\mathrm{Et_2(Cl)SnOSn(Cl)Et_2}]\}$ and $\{[\mathrm{Et_2(Me_3SiO)SnOSn(Cl)Et_2}][\mathrm{Et_2(Me_3SiO)SnOSn(OSiMe_3)Et_2}]\}$, respectively, which are formed by association of the corresponding tetraorganodistannoxane units. In analogy with related derivatives reported by Gross,[3k] these compounds appear to be stable toward redistribution to symmetrical dimers, at least on the ^{119}Sn NMR time scale.

The assumption that **1** and **2** can react with halogenated solvents is further supported by electrospray mass spectrometry.

To detect mass clusters of ionic species being related to their parent compounds, mass spectra of **1** and **2** were measured in acetonitrile, acetonitrile/dichloromethane, and acetonitrile/dibromomethane, respectively. No mass clusters in pure acetonitrile could be detected. In acetonitrile/dichloromethane and acetonitrile/dibromomethane, respectively, mass clusters containing chlorine and bromine, respectively, were observed in the negative ion detection mode. Proposed structures of these clusters are depicted in Chart 2. The same mass clusters are present in spectra of acetonitrile solutions of $\mathrm{Me_2SnCl_2}$ and $\mathrm{Et_2SnCl_2}$.

These anionic species can be regarded as hydrolysis products of $\mathrm{Me_2SnCl_2}$ and $\mathrm{Et_2SnCl_2}$, respectively, and the proposed structures are closely related to the structural motif of dimeric tetraorganodistannoxanes. Notably, the anion $\mathrm{(Me_2Sn)_5O_3Cl_5}^-$ (mass cluster: 1108.7 g·mol^{-1}) has been isolated as a diethylammonium salt from the reaction of $\mathrm{Me_2SnCl_2}$, toluene-3,4-dithiol, triethylamine, and traces of water.[17b]

To further explore the synthetic possibilities, NMR scale reactions of bis(trimethylsiloxy)diorganotin species $\mathrm{R_2Sn(OSiMe_3)_2}$ (**4**, R = $\mathrm{CH_2SiMe_3}$; **5**, R = *t*-Bu) with the diorganotin oxides $\mathrm{(R_2SnO)_3}$ (R = $\mathrm{CH_2SiMe_3}$, *t*-Bu) were investigated.

The ^{119}Sn NMR spectrum (toluene) of a mixture of $\mathrm{(Me_3SiCH_2)_2Sn(OSiMe_3)_2}$ (**4**) with $[\mathrm{(Me_3SiCH_2)_2SnO}]_3$ showed in addition to the two signals of the starting compounds at −16.5 and 44.5 ppm (integral 32% each) a signal at 8.9 ppm (integral 36%) with $^{2}J(^{119}\mathrm{Sn{-}O{-}}^{117}\mathrm{Sn}) = 501$ Hz, which is assigned to the monomeric tetraorganodistannoxane $\mathrm{(Me_3SiCH_2)_2(Me_3SiO)SnOSn(OSiMe_3)(CH_2SiMe_3)_2}$ (**8**). Obviously, **8** is in equilibrium with the starting compounds (eq 2).

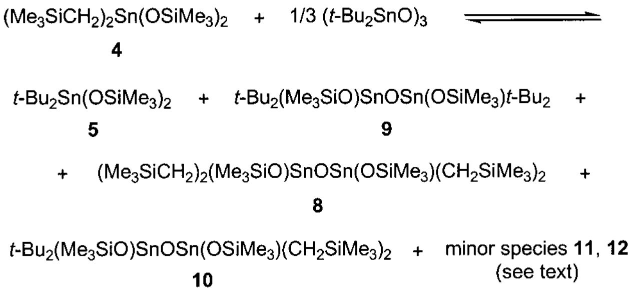
$$\mathrm{R_2Sn(OSiMe_3)_2} + 1/3\ \mathrm{(R_2SnO)_3} \rightleftharpoons \mathrm{R_2(Me_3SiO)SnOSn(OSiMe_3)R_2} \qquad (2)$$

8, R = $\mathrm{CH_2SiMe_3}$
9, R = *t*-Bu

There was no indication of the presence of dimeric tetraorganodistannoxanes in this reaction. The ^{119}Sn NMR spectrum of the same sample at −80 °C remained unchanged.

Similar observations hold for the reaction of **5** with *cyclo*-$(t\text{-}\mathrm{Bu_2SnO})_3$. The ^{119}Sn spectrum (toluene) showed

Scheme 3

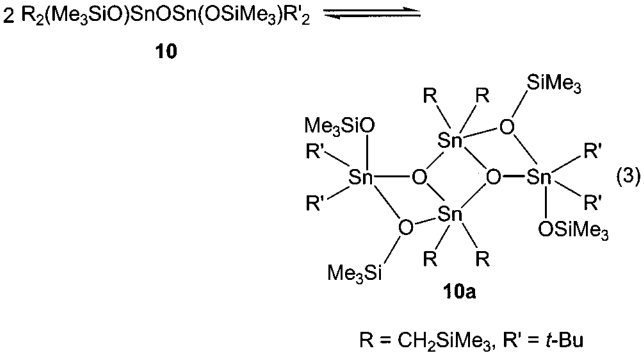


$(Me_3SiCH_2)_2Sn(OSiMe_3)_2$ (**4**) + 1/3 $(t\text{-}Bu_2SnO)_3$ $\rightleftharpoons$ $t\text{-}Bu_2Sn(OSiMe_3)_2$ (**5**) + $t\text{-}Bu_2(Me_3SiO)SnOSn(OSiMe_3)t\text{-}Bu_2$ (**9**) + $(Me_3SiCH_2)_2(Me_3SiO)SnOSn(OSiMe_3)(CH_2SiMe_3)_2$ (**8**) + $t\text{-}Bu_2(Me_3SiO)SnOSn(OSiMe_3)(CH_2SiMe_3)_2$ (**10**) + minor species **11**, **12** (see text)

two signals at −148.7 and −84.3 ppm (integral 32% each) for the starting compounds and a signal for the monomeric tetraorganodistannoxane t-Bu$_2$(Me$_3$SiO)SnOSn(OSiMe$_3$)t-Bu$_2$ (**9**) at −127.3 ppm (integral 36%) with a $^2J(^{119}Sn{-}O{-}^{117}Sn)$ coupling of 870 Hz (eq 2).

The identity of **8** and **9**, respectively, follows unambiguously from the ^{119}Sn NMR chemical shifts, which are in the range of tetracoordinated diorganotin compounds, and from the magnitude of the $^2J(^{119}Sn{-}O{-}^{117}Sn)$ couplings, which are comparable with those of hexaorganodistannoxanes containing almost linear SnOSn angles.[18]

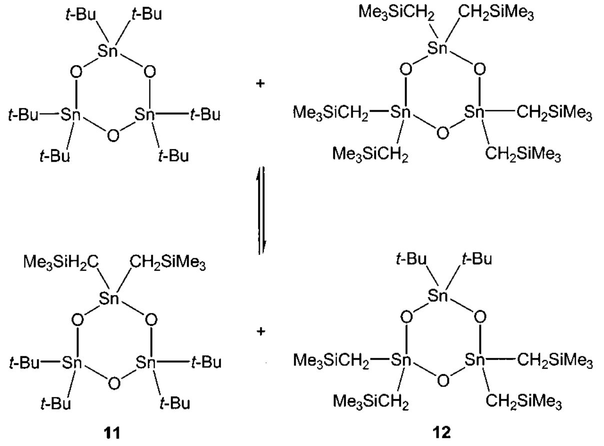
The reaction between (Me$_3$SiCH$_2$)$_2$Sn(OSiMe$_3$)$_2$ (**4**) and *cyclo*-(t-Bu$_2$SnO)$_3$ is more complex (Scheme 3). The ^{119}Sn NMR spectrum (toluene) of the reaction mixture according to Scheme 3 showed six major signals at −148.8 (**5**, integral 35%), −127.4 (**9**, integral 10%), −16.3 (**4**, integral 13%), 43.4 (*cyclo*-[(Me$_3$SiCH$_2$)$_2$SnO]$_3$, integral 8%), −116.1 (integral 8%), and 5.6 ppm (integral 8%). The two latter signals, which both exhibit a $^2J(^{119}Sn{-}O{-}^{117/119}Sn)$ coupling of 652 Hz, are assigned to the monomeric tetraorganodistannoxane t-Bu$_2$(Me$_3$SiO)SnOSn(OSiMe$_3$)(CH$_2$SiMe$_3$)$_2$ (**10**) (eq 3). In addition to the major signals, five minor signals were observed at 9.0 (**8**, integral 3%), 43.4 (integral 6%), 41.2 (integral 2%), −72.2 (integral 3%), and −77.1 ppm (integral 4%). The latter four signals are assigned to the hexaorganotristannoxanes **11** and **12** (Scheme 3, eq 4).



10 **10a** (3)

R = CH$_2$SiMe$_3$, R′ = t-Bu

At −80 °C the ^{119}Sn NMR spectrum of the same sample principally shows the same picture. However, two new signals are observed at −153.6 (integral 10%) and −173.3 (integral 10%), which are assigned to the dimeric tetraorganodistannoxane [t-Bu$_2$(Me$_3$SiO)SnOSn(OSiMe$_3$)(CH$_2$SiMe$_3$)$_2$]$_2$ (**10a**), which is formed upon dimerization of **10** (eq 3).



(4)

11 **12**

This assignment is supported by isolation and complete characterization of [t-Bu$_2$(HO)SnOSn(OH)(CH$_2$SiMe$_3$)$_2$]$_2$, which was formed by adding water to the reaction mixture.[19]

To prove the formation of the hexaorganotristannoxanes **11** and **12** in the reaction according to Scheme 3, a redistribution reaction was performed between *cyclo*-(t-Bu$_2$SnO)$_3$ and *cyclo*-[(Me$_3$SiCH$_2$)$_2$SnO]$_3$. The ^{119}Sn NMR spectrum (benzene) of an equimolar mixture of both reactants showed three signals in the range between 46 and 40 ppm (assigned to (Me$_3$SiCH$_2$)$_2$Sn(O−)$_2$ containing species) and three signal in the range between −70 and −85 ppm (assigned to t-Bu$_2$Sn(O−)$_2$ containing species).

The starting compounds *cyclo*-[(Me$_3$SiCH$_2$)$_2$SnO]$_3$ and *cyclo*-(t-Bu$_2$SnO)$_3$ show signals at 45.6 ($^2J(^{119}Sn{-}O{-}^{117}Sn) = 347$ Hz, integral 11%) and −83.5 ppm ($^2J(^{119}Sn{-}O{-}^{117}Sn) = 385$ Hz, integral 8%), respectively, whereas the new species *cyclo*-(Me$_3$SiCH$_2$)$_2$Sn(OSnt-Bu$_2$)$_2$O (**11**) and *cyclo*-{t-Bu$_2$Sn[OSn(CH$_2$SiMe$_3$)]$_2$O} (**12**) show two signals each at 41.9 ($^2J(^{119}Sn{-}O{-}^{117/119}Sn) = 378$ Hz, integral 15%) and −76.4 ppm ($^2J(^{119}Sn{-}O{-}^{117/119}Sn) = 378$ Hz, integral 30%), as well as 44.2 ($^2J(^{119}Sn{-}O{-}^{117/119}Sn) = 305$ Hz, integral 24%) and −71.3 ppm ($^2J(^{119}Sn{-}O{-}^{117/119}Sn) = 369$ Hz, integral 12%), respectively (eq 4). To the best of our knowledge, **11** and **12** are the first mixed molecular diorganotin oxides. Notably, mixed molecular triorganotin oxides[20a] as well as mixed molecular diorganotin sulfides and selenides[20b,c] are known from the literature.

Cohydrolysis of Me$_3$SiCH$_2$SnCl$_3$ with Me$_3$SiCl. The treatment of Me$_3$SiCH$_2$SnPh$_3$ with gaseous hydrogen chloride provided Me$_3$SiCH$_2$SnCl$_3$ (**13**) as colorless oil in almost quantitative yield (eq 5).

$$Me_3SiCH_2SnPh_3 \xrightarrow[-\,3\ PhH]{3\ HCl} \underset{\mathbf{13}}{Me_3SiCH_2SnCl_3} \qquad (5)$$

The cohydrolysis of Me$_3$SiCH$_2$SnCl$_3$ (**13**) with trimethylchlorosilane, under the same reaction conditions as mentioned above, did not provide Me$_3$SiCH$_2$Sn(OSiMe$_3$)$_3$ or related trimethylsiloxy-containing species, as anticipated, but did form the organotinoxo cluster

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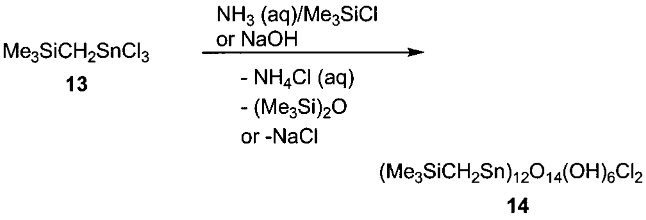
Scheme 4



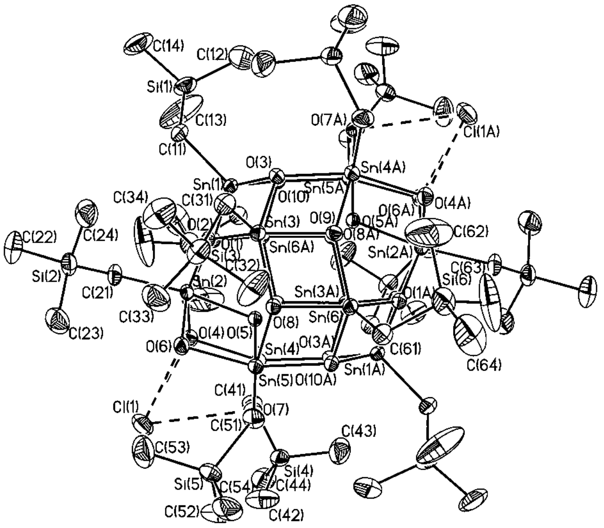


Figure 6. General view (SHELXTL) of a molecule of **14** showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: a = $-x + 1$, $-y + 1$, $-z$).

$(Me_3SiCH_2Sn)_{12}O_{14}(OH)_6Cl_2$ (**14**) (Scheme 4). The same compound was prepared by hydrolysis of $Me_3SiCH_2SnCl_3$ (**13**) with sodium hydroxide in aqueous solution according to a procedure published for $(BuSn)_{12}O_{14}(OH)_6Cl_2$.[21a]

Compound **14** was obtained as a microcrystalline colorless solid, which is readily soluble in solvents such as chloroform or toluene. However, upon storage at air for a few days, the microcrystalline solid slowly turns into an amorphous solid along with an extreme decrease of the solubility. The solubility can be regained by heating the amorphous solid at 100 °C in vacuo. Compound **14** was characterized by single-crystal X-ray diffraction analysis. Its molecular structure is shown in Figure 6. The crystallographic data are given in Table 1. Selected bond lengths and angles are listed in Table 5. The structure of compound **14** resembles those of $(BuSn)_{12}O_{14}(OH)_6X_2$ (X = Cl,[21a] OH,[22a] 4-$CH_3C_6H_4$-SO_3[22b]) and $(i\text{-}PrSn)_{12}O_{14}(OH)_6Cl_2$.[21b] Thus, the molecule is situated about a crystallographic center of inversion. The cluster consists of a $[(Me_3SiCH_2Sn)_{12}O_{14}(OH)_6]^{2+}$ dication and two chloride anions, which are held together by O(4)−H···Cl(1), O(6)−H···Cl(1), and O(7)−H···Cl(1) hydrogen bridges of 3.085(3), 3.175(3), and 3.203(3) Å, respectively. The cation contains six five-coordinate tin atoms with distorted square pyramidal configurations (Sn(1/1a), Sn(3/3a), Sn(6/6a)) and six octahedrally configurated tins (Sn(2/2a), Sn(4/4a), Sn(5/5a)), which are connected via oxygen bridges. The Sn−O distances are between 2.032(2) and 2.148(3) Å.

The different coordination numbers of the tin atoms in the organotin oxocluster **14** are also reflected by its Mössbauer spectrum, which displays two isomer shifts/quadrupole splittings at IS 0.50/QS 1.80 and IS 0.86/QS 1.40 mm/s.

The ^{119}Sn NMR spectrum ($CDCl_3$) of **14** is fully consistent with the solid state structure. It displays two equally intense signals at −269.6 ($^2J(^{119}Sn_{sp}-O-^{117/119}Sn_{oct})$ = 434 Hz, $^2J(^{119}Sn_{sp}-O-^{117}Sn_{sp})$ = 183 Hz, Sn_{sp}) and −460.5 ppm ($^2J(^{119}Sn_{oct}-O-^{117/119}Sn_{sp})$ = 434 Hz, ($^2J(^{119}Sn_{oct}-O-^{117}Sn_{oct})$ = 191 Hz; Sn_{oct}), which are attributed to the penta- and hexacoordinated tin atoms, respectively.[21a,22]

Conclusions

The cohydrolysis of diorganotin dichlorides with trimethylchlorosilanes is a convenient method for the synthesis of stannasiloxanes. However, the products of this reaction depend on the identity of the tin-bonded substituents, which in turn control the Lewis acidity of the tin center. Thus, small organic groups such as methyl and ethyl provide under partial hydrolysis trimethylsiloxy-substituted tetraorganodistannoxanes, whereas more bulky substituents such as isopropyl, trimethylsilylmethyl, and *tert*-butyl, or transition metal fragments such as $Cp(CO)_3W$ and $Cp(CO)_2Fe$, give the corresponding bis(trimethylsiloxy)tin derivatives.

Under the same reaction conditions, the more Lewis acidic monoorganotin trichloride $Me_3SiCH_2SnCl_3$ undergoes complete hydrolysis to give the organotin oxocluster $(Me_3SiCH_2Sn)_{12}O_{14}(OH)_6Cl_2$.

Experimental Section

General Data. All solvents were dried according to standard procedures and freshly distilled prior to use. Diorganotin dichlorides R_2SnCl_2 (R = Me,[23a] Et,[23a] *i*-Pr,[23b] CH_2SiMe_3,[23c] *t*-Bu,[23d] $W(CO)_3Cp$,[9,10] $Fe(CO)_2Cp$),[23e] diorganotin oxides $(R_2SnO)_3$ (R = CH_2SiMe_3,[23c] *t*-Bu[23f]), and $Me_3SiCH_2SnPh_3$[23g] were synthesized according to literature methods. Me_3SiCl was delivered by Fluka and used as supplied. Solution ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$, and $^{119}Sn\{^1H\}$ NMR spectra were recorded on a Bruker DRX 400 instrument at 400.13 (^1H), 100.31 (^{13}C), 79.49 (^{29}Si), and 149.20 MHz (^{119}Sn) and were referenced to $SiMe_4$ (^1H, ^{13}C, ^{29}Si) or $SnMe_4$ (^{119}Sn). High-temperature $^{119}Sn\{^1H\}$ NMR spectra were recorded on a JEOL GX 270 spectrometer. $^{119}Sn\{^1H\}$ MAS NMR spectra were obtained from a Bruker MSL 400 spectrometer using cross polarization and high-power proton decoupling. Tetracyclohexyltin was used as a second reference (δ −97.35 ppm against $SnMe_4$). $^{13}C\{^1H\}$ MAS and $^{29}Si\{^1H\}$ MAS NMR spectra were recorded on a UNITYplus 300 spectrometer using cross polarization and high-power proton decoupling. Adamantane and tetrakis(trimethylsilyl)silan were used as second references.

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Table 5. Selected Bond Lengths [Å] and Angles [deg] for 14[a]

Sn(1)−O(10)	2.032(3)	Sn(3)−O(8)	2.037(3)	Sn(5)−O(5)	2.084(3)
Sn(1)−O(3)	2.033(3)	Sn(3)−O(2)	2.038(3)	Sn(5)−O(8)	2.107(3)
Sn(1)−O(1)	2.070(3)	Sn(3)−O(9)	2.084(3)	Sn(5)−O(10a)	2.115(3)
Sn(1)−O(2)	2.102(3)	Sn(3)−O(3)	2.100(3)	Sn(5)−O(7)	2.116(3)
Sn(1)−C(11)	2.106(5)	Sn(3)−C(31)	2.102(4)	Sn(5)−C(51)	2.131(4)
Sn(2)−O(5)	2.097(3)	Sn(4)−O(5)	2.083(3)	Sn(5)−O(6)	2.141(3)
Sn(2)−O(2)	2.102(3)	Sn(4)−O(3a)	2.100(3)	Sn(6)−O(9)	2.036(3)
Sn(2)−O(1)	2.111(3)	Sn(4)−O(9a)	2.113(3)	Sn(6)−O(1a)	2.037(3)
Sn(2)−O(4)	2.130(3)	Sn(4)−C(41)	2.116(4)	Sn(6)−O(8)	2.091(3)
Sn(2)−C(21)	2.138(4)	Sn(4)−O(4)	2.129(3)	Sn(6)−O(10a)	2.097(3)
Sn(2)−O(6)	2.143(3)	Sn(4)−O(7)	2.148(3)	Sn(6)−C(61)	2.110(4)
O(10)−Sn(1)−O(3)	96.0(1)	O(9)−Sn(3)−C(31)	111.5(2)	O(9)−Sn(6)−O(8)	77.6(1)
O(10)−Sn(1)−O(1)	77.8(1)	O(3)−Sn(3)−C(31)	110.1(2)	O(1a)−Sn(6)−O(8)	134.8(1)
O(3)−Sn(1)−O(1)	135.8(1)	O(5)−Sn(4)−O(3a)	87.7(1)	O(9)−Sn(6)−O(10a)	135.6(1)
O(10)−Sn(1)−O(2)	136.1(1)	O(5)−Sn(4)−O(9a)	87.9(1)	O(1a)−Sn(6)−O(10a)	77.0(1)
O(3)−Sn(1)−O(2)	78.1(1)	O(3a)−Sn(4)−O(9a)	76.6(1)	O(8)−Sn(6)−O(10a)	77.3(1)
O(1)−Sn(1)−O(2)	77.3(1)	O(5)−Sn(4)−C(41)	170.6(2)	O(9)−Sn(6)−C(61)	111.7(2)
O(10)−Sn(1)−C(11)	115.4(2)	O(3a)−Sn(4)−C(41)	100.7(2)	O(1a)−Sn(6)−C(61)	112.9(2)
O(3)−Sn(1)−C(11)	109.6(2)	O(9a)−Sn(4)−C(41)	98.2(2)	O(8)−Sn(6)−C(61)	110.9(2)
O(1)−Sn(1)−C(11)	113.0(2)	O(5)−Sn(4)−O(4)	76.8(1)	O(10a)−Sn(6)−C(61)	111.2(2)
O(2)−Sn(1)−C(11)	107.4(2)	O(3a)−Sn(4)−O(4)	159.8(1)	Sn(6a)−O(1)−Sn(1)	102.9(1)
O(5)−Sn(2)−O(2)	87.7(1)	O(9a)−Sn(4)−O(4)	89.9(1)	Sn(6a)−O(1)−Sn(2)	135.6(1)
O(5)−Sn(2)−O(1)	87.3(1)	C(41)−Sn(4)−O(4)	95.9(2)	Sn(1)−O(1)−Sn(2)	103.4(1)
O(2)−Sn(2)−O(1)	76.4(1)	O(5)−Sn(4)−O(7)	76.2(1)	Sn(3)−O(2)−Sn(1)	101.7(1)
O(5)−Sn(2)−O(4)	76.4(1)	O(3a)−Sn(4)−O(7)	91.9(1)	Sn(3)−O(2)−Sn(2)	136.1(1)
O(2)−Sn(2)−O(4)	159.7(1)	O(9a)−Sn(4)−O(7)	160.8(1)	Sn(1)−O(2)−Sn(2)	102.7(1)
O(1)−Sn(2)−O(4)	90.2(1)	C(41)−Sn(4)−O(7)	99.0(2)	Sn(1)−O(3)−Sn(3)	102.0(1)
O(5)−Sn(2)−C(21)	171.1(2)	O(4)−Sn(4)−O(7)	96.7(1)	Sn(1)−O(3)−Sn(4a)	135.4(1)
O(2)−Sn(2)−C(21)	101.1(2)	O(5)−Sn(5)−O(8)	87.4(1)	Sn(3)−O(3)−Sn(4a)	103.0(1)
O(1)−Sn(2)−C(21)	96.3(2)	O(5)−Sn(5)−O(10a)	87.3(1)	Sn(4)−O(4)−Sn(2)	102.0(1)
O(4)−Sn(2)−C(21)	95.4(2)	O(8)−Sn(5)−O(10a)	76.5(1)	Sn(4)−O(5)−Sn(5)	104.9(1)
O(5)−Sn(2)−O(6)	76.9(1)	O(5)−Sn(5)−O(7)	76.9(1)	Sn(4)−O(5)−Sn(2)	104.6(1)
O(2)−Sn(2)−O(6)	92.3(1)	O(8)−Sn(5)−O(7)	160.9(1)	Sn(5)−O(5)−Sn(2)	104.4(1)
O(1)−Sn(2)−O(6)	161.0(1)	O(10a)−Sn(5)−O(7)	91.6(1)	Sn(5)−O(6)−Sn(2)	100.9(1)
O(4)−Sn(2)−O(6)	96.2(1)	O(5)−Sn(5)−C(51)	178.0(2)	Sn(5)−O(7)−Sn(4)	101.5(1)
C(21)−Sn(2)−O(6)	100.9(2)	O(8)−Sn(5)−C(51)	93.3(2)	Sn(3)−O(8)−Sn(6)	102.1(1)
O(8)−Sn(3)−O(2)	95.2(1)	O(10a)−Sn(5)−C(51)	94.7(2)	Sn(3)−O(8)−Sn(5)	136.0(1)
O(8)−Sn(3)−O(9)	77.8(1)	O(7)−Sn(5)−C(51)	102.7(2)	Sn(6)−O(8)−Sn(5)	103.3(1)
O(2)−Sn(3)−O(9)	135.5(1)	O(5)−Sn(5)−O(6)	77.2(1)	Sn(6)−O(9)−Sn(3)	102.4(1)
O(8)−Sn(3)−O(3)	135.2(1)	O(8)−Sn(5)−O(6)	92.6(1)	Sn(6)−O(9)−Sn(4a)	135.3(1)
O(2)−Sn(3)−O(3)	78.0(1)	O(10a)−Sn(5)−O(6)	161.5(1)	Sn(3)−O(9)−Sn(4a)	103.1(1)
O(9)−Sn(3)−O(3)	77.2(1)	O(7)−Sn(5)−O(6)	94.5(1)	Sn(1)−O(10)−Sn(6a)	102.1(1)
O(8)−Sn(3)−C(31)	113.5(2)	C(51)−Sn(5)−O(6)	101.0(2)	Sn(1)−O(10)−Sn(5a)	135.5(1)
O(2)−Sn(3)−C(31)	111.5(2)	O(9)−Sn(6)−O(1a)	96.2(1)	Sn(6a)−O(10)−Sn(5a)	102.8(1)

[a] Symmetry transformations used to generate equivalent atoms: a = $-x + 1$, $-y + 1$, $-z$.

Mass spectra were obtained on a Finnigan MAT 8230 spectrometer. Electrospray mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) using an acetonitrile mobile phase. Solutions (1 mmol·L^{-1}), respectively, of the compounds were injected directly into the spectrometer via a Rheodyne injector equipped with a 50 μL loop. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 10 μL·min^{-1}. Nitrogen was used as both a drying gas and for nebulization with flow rates of approximately 200 and 20 mL·min^{-1}, respectively. Pressure in the mass analyzer region was usually about 4 × 10^{-5} mbar. Typically 10 signal-averaged spectra were collected. Ions showed the expected isotopic pattern. The elemental analyses were performed on an instrument from Carlo Erba Strumentazione (model 1106). The density of the single crystals were determined using a Micromeritics Accu Pyc 11330.

General Procedure for the Cohydrolysis of Diorganotin Dichlorides with Trimethylchlorosilane. To ice-cooled hexane (200 mL) and aqueous ammonia (200 mL) a mixture of R_2SnCl_2 (20 mmol: 4.39 g (R = Me), 4.95 g (R = Et), 5.52 g (R = *i*-Pr), 6.08 g (R = *t*-Bu) 7.28 g (R = Me_3SiCH_2), 10.87 g (R = $Fe(CO)_2Cp$), 17.07 g (R = $W(CO)_3Cp$)) and Me_3SiCl (0.10 mol) in benzene (150 mL) was added dropwise. After stirring for 1 h the ice bath was removed and H_2O (200 mL) was added. The organic phase was separated, washed with 50 mL of H_2O, and dried with Na_2SO_4. Evaporation of the solvent resulted in colorless solids (**1**, 4.55 g, 4.62 mmol, 93%, mp 167 °C; **2**, 4.83 g, 4.41 mmol, 92%, mp 128−132 °C), orange solids (**6**, 10.21 g, 10.6 mmol, 53%, mp 126−135 °C; **7**, 11.20 g, 17.2 mmol, 86%, mp 124−128 °C), or colorless oils, respectively (**3**, 7.16 g, 18.68 mmol, 94%, bp 190 °C at 10^{-2} Torr; **4**, 8.13 g, 17.24 mmol, 88%, bp 215 °C at 10^{-2} Torr; **5**, 7.93 g, 19.28 mmol, 96%, bp 21 °C at 10^{-2} Torr). The solids were purified by recrystallization from hexane/toluene, whereas the oils were purified by Kugelrohr distillation in vacuo.

Bis[bis(trimethylsiloxydimethyldistannoxane)] (1). ^{1}H NMR (toluene-d_8) δ: 0.79 (12H, s, $^2J(^{119}Sn-C-^1H)$ = 81 Hz; Sn*Me*$_2$), 0.59 (12H, s, $^2J(^{119}Sn-C-^1H)$ = 77 Hz; Sn*Me*$_2$), 0.11 (36H, s, OSi*Me*$_3$). $^{13}C\{^1H\}$ NMR (toluene-d_8) δ: 6.6, 6.0 (Sn*Me*$_2$), 3.8 (OSi*Me*$_3$). $^{29}Si\{^1H\}$ NMR (toluene-d_8) δ: 1.8. $^{119}Sn\{^1H\}$ NMR (toluene-d_8) δ: −136.3 ($^2J(^{119}Sn-^{117/119}Sn)$ = 102 Hz), −155.8 ($^2J(^{119}Sn-^{117/119}Sn)$ = 102 Hz). $^{13}C\{^1H\}$ MAS NMR δ: 8.51, 8.17, 7.64, 6.47 (Sn*Me*$_2$), 6.64, 5.41 (OSi*Me*$_3$). $^{29}Si\{^1H\}$ MAS NMR δ: −0.64, 3.35. $^{119}Sn\{^1H\}$ MAS NMR $\Delta\delta$: −137.9 (δ_{11}: 260.1, δ_{22}: −94.9 δ_{33}: −584.9; $\Delta\sigma$: −670.5, η: 0.81), −156.3, (δ_{11}: 286.7, δ_{22}: −96.1 δ_{33}: −659.5; $\Delta\sigma$: −754.8, η: 0.76). Molecular weight measurement (19.37 mg·ml^{-1}, $CHCl_3$): 992 g·mol^{-1}. MS *m*/*z* (%): 894 (4) [$M^+ - C_3H_9OSi$], 641 (25) [$M^+ - C_9H_{27}O_2Si_2Sn$], 567 (20) [$M^+ - C_{12}H_{36}O_2Si_3Sn$], 479 (5) [$M^+ - C_{15}H_{45}O_3Si_4Sn$]. Anal. Calcd for $C_{20}H_{60}O_6Si_4Sn_4$ (983.97): C, 24.41; H, 6.15. Found: C, 24.51; H, 6.30.

Bis[bis(trimethylsiloxydiethyldistannoxane)] (2). ^{1}H

NMR (toluene-d_8) δ: 0.23 (OSiMe_3). ^{13}C{^{1}H} NMR (toluene-d_8) δ: 3.5 (OSiMe_3), 9.43, 9.59 (SnCH$_2$CH$_3$), 17.21, 17.74 (SnCH_2CH$_3$). ^{29}Si{^{1}H} NMR (toluene-d_8): no signal observed, (CH$_2$Cl$_2$/D$_2$Oext.) δ 0.5. ^{119}Sn{^{1}H} NMR (toluene-d_8) δ: −166.8, −183.8 ($W_{1/2}$ = 120 Hz), ^{13}C{^{1}H} MAS NMR δ: 5.75, 6.14 (OSiMe_3), 11.75, 12.35, 18.46, 20.67 (SnEt_2). ^{29}Si{^{1}H} MAS NMR δ: −1.08, 2.02. ^{119}Sn{^{1}H} MAS NMR δ: −162.3 (δ_{11}: 178.9, δ_{22}: −88.2 δ_{33}: −577.6; $\Delta\sigma$: −623.0, η: 0.64), −185.5 (δ_{11}: 209.7, δ_{22}: −112.3, δ_{33}: −653.9; $\Delta\sigma$: −702.6, η: 0.69). Molecular weight measurement (21.23 mg·ml^{-1}, CHCl$_3$): 1043 g·mol^{-1}. MS m/z (%): 341 (61) [1/2M$^+$ − C$_8$H$_{23}$O$_2$Si$_2$], 326 (12) [1/2M$^+$ − C$_9$H$_{26}$O$_2$Si$_2$], 281 (29) [1/2M$^+$ − C$_{12}$H$_{34}$O$_2$Si$_2$]. Anal. Calcd for C$_{28}$H$_{76}$O$_6$Si$_4$Sn$_4$ (1096.19): C, 30.68; H, 6.99. Found: C, 30.70; H, 7.11.

Bis(trimethylsiloxy)diisopropyltin (3). ^{1}H NMR (CDCl$_3$) δ: 0.00 (18H, s; SiMe_3), 1.28 (12H, d, ^3J(^{1}H−^{1}H) = 7.5 Hz, ^3J(^{1}H−^{119}Sn) = 108 Hz; SnCHMe_2), 1.68 (2H, sept, ^3J(^{1}H−^{1}H) = 7.5, SnCHMe$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$) δ: 3.49 (OSiMe_3), 20.3 (SnCHMe_2), 25.5 (^1J(^{13}C−^{119}Sn) = 524 Hz; SnCHMe$_2$). ^{29}Si{^{1}H} NMR (CDCl$_3$) δ: 7.81 (^2J(^{29}Si−O−$^{117/119}$Sn) = 44 Hz). ^{119}Sn{^{1}H} NMR (CDCl$_3$) δ: −95.9 (^2J(^{119}Sn−O−^{29}Si) = 43 Hz). Anal. Calcd for C$_{12}$H$_{32}$O$_2$Si$_2$Sn (383.29): C, 37.60; H, 8.42. Found: C, 37.09; H, 8.09.

Bis(trimethylsiloxy)bis(trimethylsilylmethyl)tin (4). ^{1}H NMR (CDCl$_3$) δ: 0.16 (4H, s; CH_2SiMe$_3$), 0.06 (18H, s; CH$_2$-SiMe_3), 0.00 (18H, s OSiMe_3). ^{13}C{^{1}H} NMR δ: 0.00 (OSiMe$_3$), 29.8 (SnC(CH$_3$)$_3$), 38.0 ((^1J(^{119}Sn−^{13}C) = 524 Hz) (SnC(CH$_3$)$_3$). ^{29}Si{^{1}H} NMR (CDCl$_3$) δ 1.85 (^2J(^{29}Si−^{119}Sn) = 51 Hz, CH$_2$-SiMe$_3$), 8.30 (^2J(^{29}Si−^{119}Sn) = 58 Hz, OSiMe$_3$). ^{119}Sn{^{1}H} NMR (CDCl$_3$) δ: −15.4 (^2J(^{119}Sn−O−^{29}Si) = 58 Hz). Anal. Calcd for C$_{14}$H$_{40}$O$_2$Si$_4$Sn (464.11): C, 35.66; H, 8.55. Found: C, 35.68; H, 8.80.

Bis(trimethylsiloxy)di-*tert*-butyltin (5). ^{1}H NMR (CDCl$_3$) δ: 0.00 (18H, s), 1.23 (18H, s, ^3J(^{1}H−^{119}Sn) = 99 Hz; SnCMe_3). ^{13}C{^{1}H} NMR (CDCl$_3$) δ: 38.0 (^1J(^{13}C−^{119}Sn) = 524 Hz; SnCMe$_3$), 29.8 (SnCMe_3)), 3.63 (OSiMe_3). ^{29}Si{^{1}H} NMR (CDCl$_3$) δ: 6.63 (^2J(^{29}Sn−O−^{119}Sn) = 57 Hz). ^{119}Sn{^{1}H} NMR (CDCl$_3$) δ: −148.8 (^2J(^{119}Sn−O−^{29}Si) = 58 Hz). Anal. Calcd for C$_{16}$H$_{40}$O$_2$Si$_4$Sn (495.57): C, 38.76; H, 8.14. Found: C, 41.10; H, 9.10.

Bis(trimethylsiloxy)bis(η^5-cyclopentadienyltricarbonyltungsten)tin (6). ^{1}H NMR (CDCl$_3$) δ: 5.52 (s, 10 H, Cp); 0.05 (s, 18 H, SiMe_3). ^{13}C{^{1}H} NMR (CDCl$_3$) δ: 218,0, 214.7 (CO), 89.6 (^2J(^{13}C−W−^{119}Sn) = 172 Hz; Cp), 3.1 (^1J(^{13}C−^{29}Si) = 58 Hz; SiMe_3). ^{29}Si{^{1}H} NMR (CDCl$_3$) δ: 2.30 (^2J(^{29}Si−O−^{119}Sn) = 73 Hz). ^{119}Sn{^{1}H} NMR (CDCl$_3$) δ: −44.1 (^1J(^{119}Sn−^{183}W) = 419 Hz, ^2J(^{119}Sn−O−^{29}Si) = 72 Hz). IR (KBr) νCO: 2012, 1984, 1926, 1911, 1874 cm^{-1}. Anal. Calcd for C$_{24}$H$_{28}$O$_8$Si$_2$SnW$_2$ (963.02): C, 27.43; H, 3.01; Found: C, 28.19; H, 3.20.

Bis(trimethylsiloxy)bis(η^5-cyclopentadienyldicarbonyliron)tin (7). ^{1}H NMR (CDCl$_3$) δ: 4.87 (10 H, s; Cp), 0.06 (18 H, s; SiMe_3). ^{13}C{^{1}H} NMR (CDCl$_3$) δ: 212.2 (^2J(^{13}C−Fe−^{119}Sn) = 162 Hz; CO), 81.7 (Cp), 2.29 (SiMe_3). ^{29}Si{^{1}H} NMR (CDCl$_3$) δ: 1.92 (^2J(^{29}Si−O−$^{117/119}$Sn) = 70 Hz). ^{119}Sn{^{1}H} NMR (CDCl$_3$) δ: 242.7 (^2J(^{119}Sn−O−^{29}Si) = 71 Hz, (^2J(^{119}Sn−Fe−^{13}C) =160 Hz). IR (KBr) ν_{CO}: 2006, 1989,1950, 1933 cm^{-1}. Anal. Calcd for C$_{20}$H$_{28}$O$_6$Fe$_2$Si$_2$Sn (651.04): C, 36.90; H, 4.34. Found: C, 36.95; H, 4.40.

Bis(triphenylsiloxy)bis(η^5-cyclopentadienyldicarbonyliron)tin (7a). A suspension of Ph$_3$SiOLi (0.410 g, 1.45 mmol) in 50 mL of toluene was added dropwise into a solution of [Fe(CO)$_2$Cp]$_2$Sn(OSiPh$_3$)$_2$ (0.395 g, 0.73 mmol) in 25 mL of toluene. The reaction mixture was stirred for 2 weeks at room temperature. LiCl was filtered, leaving an orange solution. The solvent was removed to a few milliliters under reduced pressure. The solution was kept at −18 °C to precipitate [Fe(CO)$_2$Cp]$_2$Sn(OSiPh$_3$)$_2$ as an orange crystalline solid (0.11 g, 0.1 mmol, 14%, mp 180−183 °C). ^{1}H NMR (CDCl$_3$) δ: 7.70−7.25,(36 H, m, Ph), 4.36 (10 H, s, C$_p$). ^{13}C{^{1}H} NMR (CDCl$_3$) δ: 212.9 (CO), 139.0 (C$_i$), 135.2 (C$_o$), 128.9 (C$_p$), 127.4 (C$_m$), 82.7 (Cp). ^{29}Si{^{1}H} NMR (CDCl$_3$) δ: −24.5 (^2J(^{29}Si−O−$^{117/119}$Sn) = 88 Hz). ^{119}Sn{^{1}H} NMR (CDCl$_3$) δ: 260.0 (^2J(^{119}Sn−O−^{29}Si) = 90 Hz). IR (KBr): ν_{CO} 2008, 1983, 1954, 1941 cm^{-1}. Anal. Calcd for C$_{50}$H$_{46}$O$_6$Fe$_2$Si$_2$Sn (1023.39): C, 58.68; H, 4.53. Found: C, 58.24; H, 4.04.

Reactions of Bis(trimethylsiloxyl)diorganotin Compounds with Diorganotin Oxides. (i) R$_2$Sn(OSiMe$_3$)$_2$ (0.25 mmol, 117.8 mg (**4**), 102.8 mg (**5**)) and (R$_2$SnO)$_3$ (0.25 mmol, 77.28 mg (R = CH$_2$SiMe$_3$), 62.22 mg (R = t-Bu)) were dissolved in toluene-d_8 (300μL) and heated in a sealed NMR tube to 50 °C for 6 h. (ii) (Me$_3$SiCH$_2$)$_2$Sn(OSiMe$_3$)$_2$ (117.8 mg, 0.25 mmol) and (t-Bu$_2$SnO)$_3$ (0.25 mmol, 62.22 mg) were disolved in toluene-d_8 (300 μL) and heated in a sealed NMR tube to 50 °C for 6 h.

Reaction of *cyclo*-(t-Bu$_2$SnO)$_3$ with *cyclo*-[(Me$_3$SiCH$_2$)$_2$SnO]$_3$. *Cyclo*-(t-Bu$_2$SnO)$_3$ (87.11 mg, 0.35 mmol) and *cyclo*-[(Me$_3$SiCH$_2$)$_2$SnO]$_3$ (108.2 mg, 0.35 mmol) in C$_6$D$_6$ (300μL) were heated in a sealed NMR tube to 45 °C for 12 h.

Synthesis of Trimethylsilylmethyltin Trichloride (13). Dried hydrogen chloride gas was bubbled into an ice-cooled solution of Me$_3$SiCH$_2$SnPh$_3$ (43.9 g, 100 mmol) in toluene (150 mL). The cooling bath was removed after 2 h, and after 48 h the reaction was finished. The progress of the reaction was monitored by ^{119}Sn NMR spectroscopy. Removing the solvent and distillation in vacuo resulted in Me$_3$SiCH$_2$SnCl$_3$ (29.7 g, 95.0 mmol, 95%) as a colorless oil, which changed its color to brown after a few days. ^{1}H NMR (400.13 MHz, CDCl$_3$) δ: 1.47 (^1J(^{1}H−^{119}Sn) = 143 Hz; CH_2Sn), 0.33 (SiMe_3). ^{13}C{^{1}H} NMR (100.62 MHz, CDCl$_3$) δ: 17.6 (^1J(^{13}C−^{119}Sn) = 465 Hz; CH$_2$-Sn), 0.6 (SiMe_3). ^{29}Si{^{1}H} NMR (79.49 MHz, CDCl$_3$) δ: 3.5 (^2J(^{29}Si−C−$^{119/117}$Sn) = 60 Hz). ^{119}Sn{^{1}H} NMR (149.20 MHz, CDCl$_3$) δ: 18.9. Anal. Calcd for C$_4$H$_{11}$Cl$_3$SiSn (312.32): C, 15.38; H, 3.55. Found: C, 16.60; H, 3.90.

Synthesis of (Me$_3$SiCH$_2$Sn)$_{12}$O$_{14}$(OH)$_6$Cl$_2$ (14). Method 1. A mixture of trimethylsilyltin trichloride (9.64 g, 30 mmol) and trimethylchlorosilane (21.72 g, 200 mmol) was slowly added to an ice-cooled two-layer mixture of toluene (400 mL) and aqueous ammonia (200 mL, 15%). Approximately 3.5 g of product that immediately precipitated was filtered. The organic layer was separated, dried over Na$_2$SO$_4$, and distilled in vacuo, providing another 3.5 g of product. The combined precipitates were washed twice with water and hexane and dried at 100 °C in vacuo to give **14** as an amorphous powder (6.7 g, 2.33 mmol, 93%, mp > 250 °C (dec)).

Method 2. To a stirred solution of Me$_3$SiCH$_2$SnCl$_3$ (5.0 g, 16.0 mmol) in 100 mL of distilled water was slowly added a 1 M aqueous KOH solution until the pH was stable at 4.0. The colorless precipitate was filtered and washed with 500 mL of distilled water. After drying at 80 °C and 1.5 Torr overnight, the material was crystallized from chloroform to give a microcrystalline solid (3.3 g, 85%, mp > 250 °C (dec)). ^{1}H NMR (400.13 MHz, CDCl$_3$) δ: 0.14 (9H; SiMe_3), 0.21 (9H, SiMe_3), 0.34 (2H, (^2J(^{1}H−^{119}Sn$_{oct}$) = 172 Hz; CH_2Sn), 0.56 (2H, ^2J (^{1}H−^{119}Sn$_{sp}$) = 141 Hz; CH_2Sn). ^{13}C{^{1}H} NMR (100.62 MHz, CDCl$_3$) δ: 1.4 (^3J(^{13}C−^{119}Sn$_{sp}$) = 34 Hz; SiMe_3), 1.8 (^3J(^{13}C−$^{117/119}$Sn$_{oct}$) = 43 Hz; SiMe_3), 7.9 (^1J(^{13}C−^{119}Sn$_{sp}$) = 667 Hz; CH$_2$Sn), 15.1 (^1J(^{13}C−^{119}Sn$_{oct}$) = 965 Hz; CH$_2$Sn). ^{29}Si{^{1}H} NMR (79.49 MHz, CDCl$_3$) δ: 0.6, 2.4. ^{119}Sn{^{1}H} NMR (149.20 MHz, CDCl$_3$) δ: −269.6 (^2J(^{119}Sn$_{sp}$−O−$^{117/119}$Sn$_{oct}$) = 434 Hz, (^2J(^{119}Sn$_{sp}$−O−^{117}Sn$_{sp}$) = 183 Hz), −460.5 (^2J(^{119}Sn$_{oct}$−O−$^{117/119}$Sn$_{sp}$) = 434 Hz, (^2J(^{119}Sn$_{oct}$−O−^{117}Sn$_{oct}$) = 191 Hz; Sn$_{oct}$). Mössbauer spectroscopy: IS 0.50, QS 1.80; IS 0.86, QS 1.40. IR (KBr) ν_{OH}: 3645 cm^{-1}. Anal. Calcd for C$_{48}$H$_{138}$Cl$_2$O$_{10}$Si$_{12}$Sn$_{12}$ (2868.35): C, 20.10; H, 4.85; Cl, 2.47. Found: C, 20.10; H, 5.00; Cl, 2.20.

Crystallography. Intensity data for the colorless (**1**, **2**, **14**) and orange (**6**, **7a**) crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα (0.71069 Å) radiation at 291 K. The data collection covered almost the whole sphere of reciprocal space with 360 frames via ω-rotation (Δ/ω = 1°) at two times 5 s (**2**), 10 s (**6**, **14**), 30 s (**7a**), and 40 s (**1**) per frame. The crystal-to-detector distance was 2.7 cm (**1**, **6**, **14**), 2.8 cm (**2**), and 3.0 cm with a detector-θ-offset of 5° (**7a**). Crystal decay was monitored by repeating the initial frames at the end of data collection. The data were not corrected for absorption effects. Analyzing the duplicate reflections, there was no indication for any decay. The structure was solved by direct methods using SHELXS97[24a] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods with SHELXL97.[24b]

The H atoms were placed in geometrically calculated positions using a riding model ($C-H_{prim.}$ 0.96 Å, $C-H_{sec.}$ 0.97 Å; H_{aryl} C−H 0.93). The H atoms isotropic temperature factors of **1** and **2** are constrained to be 1.2 times those of the carrier atom, and those of **6**, **7a**, and **14** are refined with common isotropic temperature factors for H_{aryl} (0.080(8) (**6**), 0.095(2) (**7a**) Å^2) and for H_{alkyl} (U_{iso} 0.16(1) (**6**); 0.134(3) (**14**) Å^2).

Disordered trimethylsilyl (**1**, **2**), ethyl (**2**), and carbonyl (**7a**) groups were found with occupancies of 0.4 (C(51′)) and 0.6 (C(51)) in **1** and of 0.5 (C(32), C(43), C(32′), C(43′)) in **2** and (O(16), O(17), O(16′), O(17′)) in **7a**. Disordered phenyl rings in **7a** were refined as constrained regular hexagons with occupancies of 0.7 (C(61) > C(66)) and 0.3 (C(61′) > C(66′)).

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from International Tables for X-ray Crystallography.[24c] The figures were created by SHELXTL.[24d] Crystallographic data are given in Table 1.

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Supporting Information Available: Tables of all coordinates, anisotropic displacement parameters, and geometric data for compounds **1**, **2**, **6**, **7a**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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