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Articles

Condensation of Diphenylsilane Diol through Organostannoxane Catalysis: A Case Study[†]

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Small amounts of $[Ph_2(OH)Sn]_2CH_2$ effectively catalyze the condensation of $Ph_2Si(OH)_2$ to give *cyclo*-$(Ph_2SiO)_4$ in good yield. The reaction proceeds under remarkably mild conditions. In contrast, the reaction of $[Ph_2(OH)Sn]_2CH_2$ with $Ph_2Si(OH)_2$ in a stoichiometric ratio quantitatively gives the six-membered stannasiloxane ring *cyclo*-$Ph_2Si(OSnPh_2)_2CH_2$ (**1**). Compound **1** reacts slowly and irreversibly with $Ph_2Si(OH)_2$ to provide the eight-membered stannasiloxane ring *cyclo*-$O(Ph_2SiOSnPh_2)_2CH_2$ (**2**) and $[Ph_2(OH)Sn]_2CH_2$. The driving force for this reaction is attributed to the release of ring strain in **1**. Condensation of $[Ph_2(OH)Sn]_2CH_2$ with diphenylsiloxanols $HO(Ph_2SiO)_nH$ ($n = 2-4$), *t*-$Bu_2Si(OH)_2$, and *t*-$Bu_2Ge(OH)_2$, respectively, provides the metallastannoxane rings *cyclo*-$O(Ph_2SiOSnPh_2)_2CH_2$ (**2**), *cyclo*-$Ph_2Si(OSiPh_2OSnPh_2)_2CH_2$ (**3**), *cyclo*-$O(Ph_2SiOPh_2SiOSnPh_2)_2CH_2$ (**4**), *cyclo*-*t*-$Bu_2Si(OSnPh_2)_2CH_2$ (**5**), and *cyclo*-*t*-$Bu_2Ge(OSnPh_2)_2CH_2$ (**6**). The molecular structures of **2** and **5** were determined by X-ray diffraction.

Introduction

Among various industrial applications, organotin compounds serve as catalysts for the curing of silicone elastomers.[1] The benefits of organotin catalysts, namely, diorganotin dicarboxylates, are their high efficiency under virtually neutral and mild conditions and their low cost and comparatively low toxicity. Despite the importance of the curing process, little attention has been paid to the role of the catalysts. We are aware of only two publications dealing with kinetic studies on model curing reactions.[2] Although stannasiloxanes were assumed to be intermediates in these reactions, so far there is no experimental proof for this assumption. More recent works were focused on the preparation of latent organotin catalysts for instant mixtures with long pot-lives in which the catalysts are activated by heat prior to use.[3]

During the course of our studies on polystannasiloxanes,[4] we found that small amounts of $[Ph_2(OH)Sn]_2CH_2$ catalyze the condensation of $Ph_2Si(OH)_2$ to give *cyclo*-$(Ph_2SiO)_4$. Further investigations on this reaction revealed the involvement of stannasiloxanes along the reaction pathway.

The reactions described within this work can be regarded as a case study on the condensation of organosilanols catalyzed by organostannoxanes, which, in general, is relevant for the industrial curing of silicone elastomers.

Results and Discussion

The reaction in acetone of $Ph_2Si(OH)_2$ with catalytic amounts of $[Ph_2(OH)Sn]_2CH_2$ (10 mol % at 60 °C for 20 h) provided *cyclo*-$(Ph_2SiO)_4$ as a colorless precipitate in good yield (eq 1).

The identity of *cyclo*-$(Ph_2SiO)_4$ was established by its ^{29}Si NMR chemical shift ($CDCl_3$) of −42.7 ppm and by

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[†] This work contains part of the Ph.D. thesis of S. Rabe, Dortmund University, 1999.

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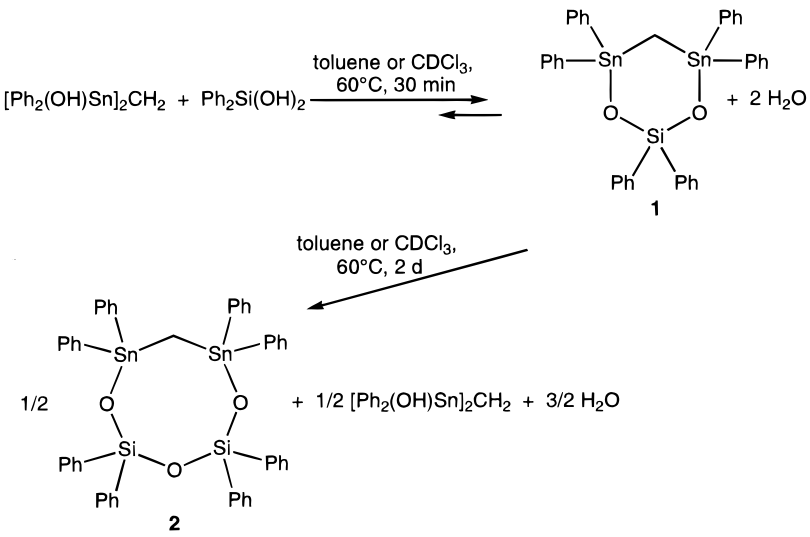
Scheme 1



$$4\ Ph_2Si(OH)_2 \xrightarrow[-\ 4\ H_2O]{\text{acetone, 60°C, 20 h,}\ 10\ \text{mol \%}\ [Ph_2(OH)Sn]_2CH_2} cyclo\text{-}(Ph_2SiO)_4 \tag{1}$$

addition of an authentic sample of *cyclo*-$(Ph_2SiO)_4$. Trace amounts of *cyclo*-$(Ph_2SiO)_3$ were identified (δ ^{29}Si 33.5 ppm, $CDCl_3$) as byproduct in the mother liquor from which *cyclo*-$(Ph_2SiO)_4$ had been filtered off. In the absence of $[Ph_2(OH)Sn]_2CH_2$, a solution of $Ph_2Si(OH)_2$ treated under the same conditions remained unchanged. It is worth mentioning that the hydrolysis of Ph_2SiCl_2 affords mixtures of diphenylsil(ox)anediols $HO(SiPh_2O)_nH$ ($n = 1, 2, 3$) and diphenylsiloxanes *cyclo*-$(Ph_2SiO)_m$ ($m = 3, 4$).[5]

Obviously, the condensation of $Ph_2Si(OH)_2$ is a multistep reaction, which makes kinetic investigations concerning the mechanistic pathway difficult. However, the following experiments allow us to suggest certain intermediate species likely to be involved in the condensation reaction.

The reaction in $CDCl_3$ or toluene at 60 °C for 30 min of equimolar quantities of $Ph_2Si(OH)_2$ and $[Ph_2(OH)Sn]_2CH_2$ gave a clear solution, the ^{29}Si and ^{119}Sn NMR spectra of which displayed single resonances at −34.0 ($^2J(^{29}Si{-}O{-}^{117/119}Sn) = 25$ Hz) and −34.7 ppm (($^2J(^{119}Sn{-}C{-}^{117}Sn) = 512$ Hz), respectively. The ^{29}Si chemical shift, the $^2J(^{29}Si{-}O{-}^{117/119}Sn)$ coupling, and the signal-to-satellite integral ratio of the latter support the exclusive presence of the six-membered stannasiloxane ring, *cyclo*-$Ph_2Si(OSnPh_2)_2CH_2$ (**1**). In a previous paper we have shown that these NMR data are very sensitive to the ring size of *cyclo*-stannasiloxanes.[4d] Within several days at room temperature or 2 days at 60 °C, or upon evaporation of this solution even in vacuo, the six-membered stannasiloxane ring **1** is converted into $[Ph_2(OH)Sn]_2CH_2$ and the eight-membered stannasiloxane ring, *cyclo*-$O(Ph_2SiOSnPh_2)_2CH_2$ (**2**) (Scheme 1). The latter was isolated as a colorless crystalline solid and has been completely characterized by NMR spectroscopy and X-ray analysis (Figure 1).

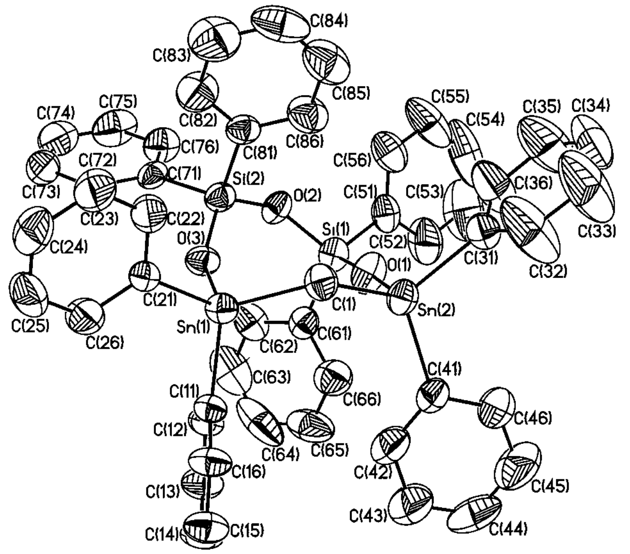


Figure 1. General view (SHELXTL-PLUS) of a molecule of **2a** showing 30% probability displacement ellipsoids and the atom numbering. The other conformer **2b**, being slightly different from **2a**, is not shown.

The formation of **2** can be explained by a combination of kinetically and thermodynamically controlled reactions. Although the six-membered stannasiloxane ring **1** is rapidly formed, it is still in equilibrium with the starting compounds; that is, even in the presence of traces of moisture there is a steady state concentration of $Ph_2Si(OH)_2$, which slowly reacts with the six-membered stannasiloxane ring **1** to give compound **2**, $[Ph_2(OH)Sn]_2CH_2$, and water (Scheme 1).

Although no kinetic studies were performed, the rapid formation of the six-membered stannasiloxane ring **1** suggests the presence of the same compound in the condensation of $Ph_2Si(OH)_2$ catalyzed by $[Ph_2(OH)Sn]_2CH_2$.

Compound **2** was also obtained in good yield by the reaction of $[Ph_2(OH)Sn]_2CH_2$ with $O(Ph_2SiOH)_2$ (Scheme 2).

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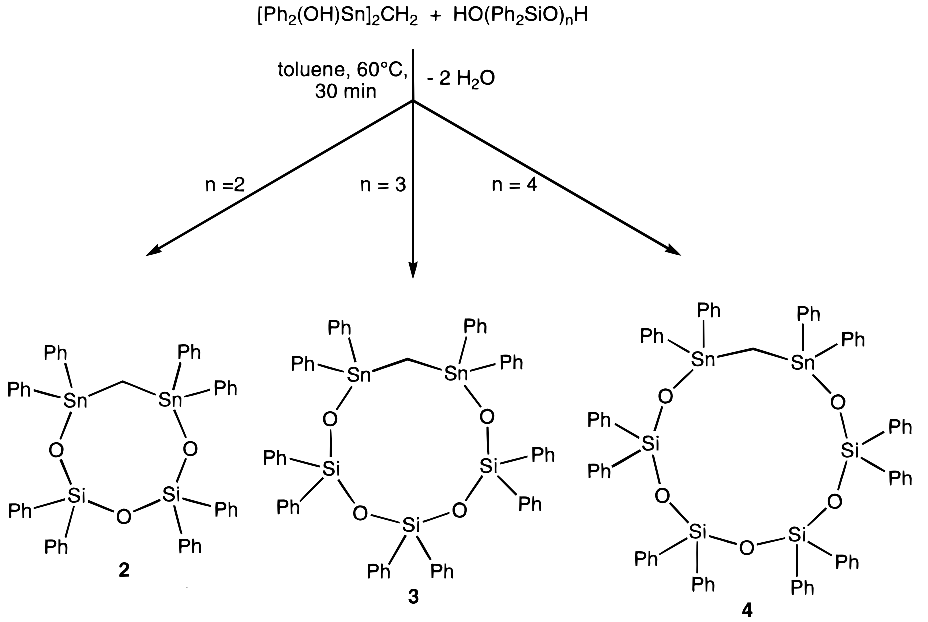
[5] (a) Kipping, F. S. *J. Chem. Soc.* **1912**, *101*, 2125. (b) Kipping, F. S.; Robinson, R. *J. Chem. Soc.* **1914**, *105*, 484. (c) Kipping, F. S. *J. Chem. Soc.* **1927**, 2728. (d) Burkhard, C. A. *J. Am. Chem. Soc.* **1945**, *67*, 2173. (e) Hyde, J. F.; Frevel, L. K.; Nutting, H. S.; Petrie, P. S.; Purcel, M. A. *J. Am. Chem. Soc.* **1947**, *69*, 488. (f) Young, C. W.; Servais, P. C.; Currie, C. C.; Hunter, M. *J. Am. Chem. Soc.* **1948**, *70*, 3758. (g) Behbehani, H.; Brisdon, B. J.; Mahon, M. F.; Molloy, K. C. *J. Organomet. Chem.* **1993**, *463*, 41.

Scheme 2



The molecular structure of **2** is shown in Figure 1, and selected geometrical data are given in Table 1. The unit cell of **2** contains two individual molecules, **2a** and **2b**, which differ only slightly in their bond lengths and bond angles. The two tin atoms in each of these conformers are nonequivalent, as also reflected in the ^{119}Sn MAS NMR spectrum of **2**, which contains four resonances (δ −18.8, −25.5, −30.7, and −31.8 ppm). The Si−O, Si−C, Sn−O, and Sn−C bond lengths are as expected and comparable with those of other *cyclo*-stannasiloxanes.[4]

The eight-membered stannasiloxane ring **2** can formally be regarded as derived from *cyclo*-($Ph_2SiO)_4$, in which one ($Ph_2SiOSiPh_2$) unit has been replaced by a ($Ph_2SnCH_2SnPh_2$) fragment. Thus, the C−Si−C, C−Si−O, and O−Si−O bond angles of **2** are very close to the values reported for the parent compound, whereas the Si−O−Si bond angles of 138.3(2)° (**2a**) and 140.4(2)° (**2b**) are significantly smaller than the average Si−O−Si bond angle of 160.4(4)° reported for *cyclo*-($Ph_2SiO)_4$.[6] The high flexibility of the Si−O−Sn bond angles is demonstrated by the chemically equivalent Si(1)−O−Sn(2) and Si(2)−O−Sn(1) bond angles in **2a** and **2b**, which differ by 30.8(2)° and 24.8(2)°, respectively. The Sn−C−Sn bond angles in **2a** of 120.4(2)° and **2b** of 118.0(2)° can be best compared with the corresponding angles of 116.8(6)° and 117.9(7)° measured for the *cyclo*-1,3,5,7-tetrastannaoctane derivative, *cyclo*-($Me_2SnCH_2)_4$.[7] According to a classification scheme recently introduced for the conformations of eight-membered germasiloxane rings[8] and extended for stannasiloxane rings,[4d] both conformers **2a** and **2b** adopt G-type conformations (Figure 3).

The condensation of $[Ph_2(OH)Sn]_2CH_2$ with diphenylsiloxanediols $HO(Ph_2SiO)_nH$ ($n = 3-4$) provided the 10- and 12-membered stannasiloxane rings **3** and **4** (Scheme 2). Unlike the six-membered ring **1**, these larger rings show no tendency to rearrange in toluene at 60 °C and are stable against moisture. We attribute the higher stability of **2**−**4** to the reduced ring strain as compared to the six-membered stannasiloxane ring **1**. In addition to elemental analysis, NMR spectroscopy, and mass spectrometry (see Experimental Section) the identity of the 12-membered stannasiloxane ring **4** was also established by single-crystal X-ray diffraction. However, the structure could not be satisfactorily refined because of disorder of the silicon and tin atoms.

If the *cyclo*-stannasiloxanes **2**−**4** are involved in the $[Ph_2(OH)Sn]_2CH_2$-catalyzed condensation of $Ph_2Si(OH)_2$ to give *cyclo*-($Ph_2SiO)_4$ as the major product, then compounds **2**, **3**, and **4**, respectively, should react with $Ph_2Si(OH)_2$, which is present in large excess in the condensation reaction described above.

The corresponding reactions described below were monitored by ^{29}Si and ^{119}Sn NMR spectroscopy, and integration of the ^{119}Sn resonances are given. The reaction of *cyclo*-O($Ph_2SiOSnPh_2)_2CH_2$ (**2**) with $Ph_2Si(OH)_2$ in $CDCl_3$ (60 °C, 20 h) gave the 10-membered stannasiloxane ring **3** (integral 41), unreacted eight-membered stannasiloxane ring **2** (integral 48), and small amounts of the six- and 12-membered stannasiloxane rings **1** (integral 4.5) and **4** (integral 5.7), respectively. The diphenylsiloxanediols $Ph_2Si(OSiPh_2OH)_2$ and $O(SiPh_2OSiPh_2OH)_2$ as well as trace amounts of *cyclo*-($Ph_2SiO)_3$ were also formed. The identity of the three latter compounds was unambiguously established by addition of authentic samples to the reaction mixture. In addition there are unassigned signals of very low intensity at δ ^{29}Si −37.1, −45.6 (approximately 2% of the major signals).

The reaction mixture of the 10-membered stannasiloxane ring *cyclo*-O($Ph_2SiOPh_2SiOSnPh_2)_2CH_2$ (**3**) with $Ph_2Si(OH)_2$ in $CDCl_3$ (60 °C, 20 h) showed the presence of the 12-membered stannasiloxane ring **4** (integral 47) as well as unreacted 10-membered stannasiloxane ring **3** (integral 42), eight-membered stannasiloxane ring **2** (integral 4), and six-membered stannasiloxane ring **1** (integral 7). In addition, the ^{29}Si NMR spectrum indicated the presence of $O(SiPh_2OSiPh_2OH)_2$ (δ ^{29}Si −36.9, −45.4).

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(6) Braga, D., Zanotti, G. *Acta Crystallogr.* **1980**, *B36*, 950.

Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 2a, 2b, and 5

	2a	**2b**	**5**
Sn(1)−O(2)			1.983(6)
Sn(1)−O(3)	1.978(3)	1.983(3)	
Sn(1)−C(1)	2.126(4)	2.124(4)	2.135(8)
Sn(1)−C(11)	2.107(5)	2.105(6)	2.140(7)
Sn(1)−C(21)	2.108(5)	2.103(5)	2.146(7)
Sn(2)−O(1)	1.942(3)	1.952(3)	1.975(6)
Sn(2)−C(1)	2.130(4)	2.115(5)	2.136(9)
Sn(2)−C(31)	2.101(6)	2.090(7)	2.145(8)
Sn(2)−C(41)	2.107(6)	2.115(5)	2.138(8)
Si(1)−O(1)	1.585(3)	1.600(3)	1.627(6)
Si(1)−O(2)	1.631(3)	1.631(3)	1.605(6)
Si(1)−C(51)	1.842(7)	1.850(5)	1.910(9)
Si(1)−C(61)	1.844(6)	1.860(5)	1.909(8)
Si(2)−O(2)	1.612(3)	1.619(3)	
Si(2)−O(3)	1.596(3)	1.596(3)	
Si(2)−C(71)	1.853(5)	1.859(5)	
Si(2)−C(81)		1.850(5)	
O(2)−Sn(1)−C(1)			105.7(3)
O(2)−Sn(1)−C(11)			109.0(3)
O(2)−Sn(1)−C(21)			101.4(3)
O(3)−Sn(1)−C(1)	110.21(16)	109.62(15)	
O(3)−Sn(1)−C(11)	102.28(18)	104.16(17)	
O(3)−Sn(1)−C(21)	105.48(16)	101.12(19)	
C(1)−Sn(1)−C(11)	114.81(19)	109.2(2)	112.8(3)
C(1)−Sn(1)−C(21)	110.6(2)	114.04(19)	113.7(3)
C(11)−Sn(1)−C(21)	112.7(2)	117.6(3)	113.2(3)
O(1)−Sn(2)−C(1)	106.04(16)	103.29(14)	106.3(3)
O(1)−Sn(2)−C(31)	102.3(2)	103.0(2)	106.1(3)
O(1)−Sn(2)−C(41)	102.54(18)	106.91(17)	104.5(3)
C(1)−Sn(2)−C(31)	114.6(2)	115.2(3)	111.0(4)
C(1)−Sn(2)−C(41)	116.5(3)	112.35(18)	113.5(3)
C(31)−Sn(2)−C(41)	112.7(3)	114.6(3)	114.6(3)
O(1)−Si(1)−O(2)	110.77(18)	111.58(17)	113.2(3)
O(1)−Si(1)−C(51)	109.2(2)	108.8(2)	107.7(4)
O(1)−Si(61)−C(61)	109.9(3)	110.1(2)	105.7(3)
O(2)−Si(1)−C(51)	105.9(3)	107.8(2)	106.4(4)
O(2)−Si(1)−C(61)	108.8(3)	106.8(2)	107.8(4)
C(51)−Si(1)−C(61)	112.3(3)	111.8(2)	116.3(4)
O(3)−Si(2)−O(2)	112.52(19)	113.44(17)	
O(2)−Si(2)−C(71)	106.2(2)	107.5(2)	
O(2)−Si(2)−C(81)	107.6(3)	107.8(2)	
O(3)−Si(2)−C(71)	108.9(3)	107.6(2)	
O(3)−Si(2)−C(81)	110.5(2)	109.5(2)	
C(71)−Si(2)−C(81)	111.2(3)	111.1(2)	
Sn(2)−O(1)−Si(1)	171.5(2)	163.1(2)	134.6(4)
Sn(1)−O(2)−Si(1)			136.4(3)
Si(1)−O(2)−Si(2)	138.3(2)	140.4(2)	
Sn(1)−O(3)−Si(2)	140.71(19)	138.82(17)	
Sn(1)−C(1)−Sn(2)	120.4(2)	118.0(2)	113.9(4)
O(1)−Sn(2)−C(1)−Sn(1)	39.6(3)	41.0(3)	−32.1(5)
C(1)−Sn(2)−O(1)−Si(1)	−10.5(17)	77.4(7)	14.8(6)
O(2)−Si(1)−O(1)−Sn(2)	35.8(18)	−64.6(7)	9.9(6)
O(1)−Si(1)−O(2)−Si(2)	−40.3(4)	−20.5(4)	
O(1)−Si(1)−O(2)−Sn(1)			−18.0(6)
O(3)−Si(2)−O(2)−Si(1)	−21.0(4)	−26.8(4)	
O(2)−Si(2)−O(3)−Sn(1)	94.0(3)	90.9(3)	
C(1)−Sn(1)−O(3)−Si(2)	−28.7(4)	−23.5(3)	
O(3)−Sn(1)−C(1)−Sn(2)	−57.1(3)	−65.1(3)	
Si(1)−O(2)−Sn(1)−C(1)			−1.8(6)
O(2)−Sn(1)−C(1)−Sn(2)			27.5(5)

Interestingly, neither the 14-membered stannasiloxane ring *cyclo*-$Ph_2Si(OSiPh_2OSiPh_2OSnPh_2)_2CH_2$ nor open-chain stannasiloxanes were formed in these reactions.

From these results, one possible reaction sequence for the $[Ph_2(OH)Sn]_2CH_2$-catalyzed condensation of $Ph_2Si(OH)_2$ is proposed in Scheme 3. In a kind of growth reaction, the initially formed six-membered stannasiloxane ring **1** reacts with $Ph_2Si(OH)_2$ to give the eight-membered stannasiloxane ring **2**, which in turn reacts with further $Ph_2Si(OH)_2$ to give the 10-membered stannasiloxane ring **3**. The latter, however, reacts with $Ph_2Si(OH)_2$ to give the 12-membered ring **4** as well as the six-membered ring **1** and the organosiloxanol $Ph_2Si(OSiPh_2OH)_2$. Further ring enlargment seems to be not possible, and consequently the catalytic cycle is closed by reaction of the 12-membered stannasiloxane ring **4** with $Ph_2Si(OH)_2$ to give six-membered stannasiloxane **1** and the organosiloxanol $O(SiPh_2OSiPh_2OH)_2$. The organosiloxanols generated in steps III and IV (Scheme 3) are then transformed into *cyclo*-$(Ph_2SiO)_3$ and *cyclo*-$(Ph_2SiO)_4$, respectively.

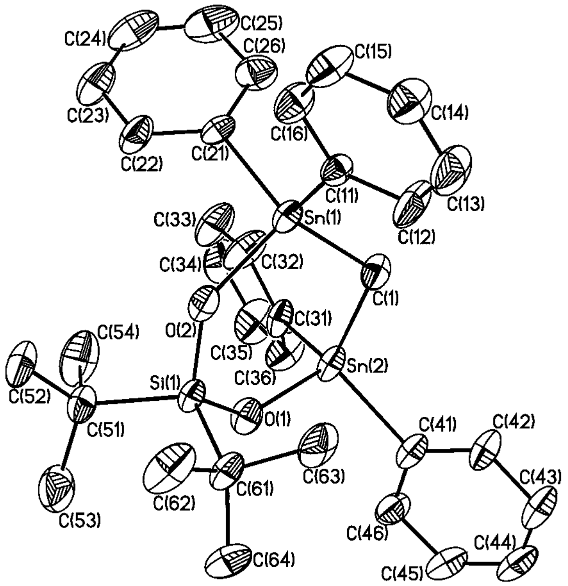
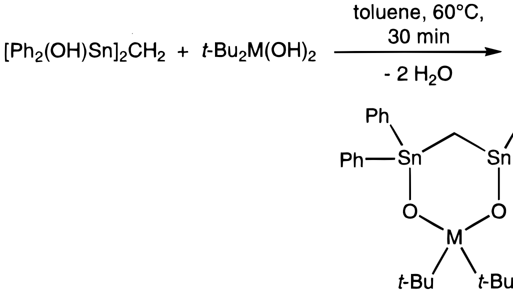


Figure 2. General view (SHELXTL-PLUS) of a molecule of **5** showing 30% probability displacement ellipsoids and the atom numbering.

In analogy with compound **1**, the synthesis of the six-membered metallastannoxane rings, *cyclo*-*t*-$Bu_2Si(OSnPh_2)_2CH_2$ (**5**) and *cyclo*-*t*-$Bu_2Ge(OSnPh_2)_2CH_2$ (**6**), was achieved by condensation of $[Ph_2(OH)Sn]_2CH_2$ with *t*-$Bu_2Si(OH)_2$ and *t*-$Bu_2Ge(OH)_2$, respectively (eq 2). Compounds **5** and **6** show no tendency to rearrange to give larger rings, which is to be expected when considering the stability toward self-condensation of *t*-$Bu_2Si(OH)_2$ and *t*-$Bu_2Ge(OH)_2$.[9]



(2)

5, M = Si
6, M = Ge

The molecular structure of **5** is shown in Figure 2, and selected geometrical data are given in Table 1. The two tin atoms in **5** are nonequivalent, which is also

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(7) (a) Kühn, S. Ph.D. Thesis, Dortmund University, 1997. (b) Kühn, S.; Hummeltenberg, R.; Schürmann, M.; Jurkschat, K. *Phosphorus, Sulfur, Relat. Elem.* **1999**, 150−151, 333.

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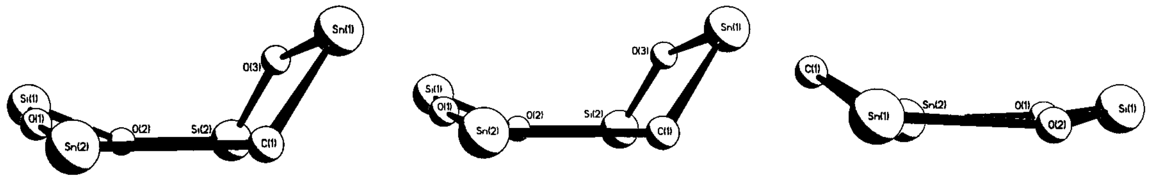
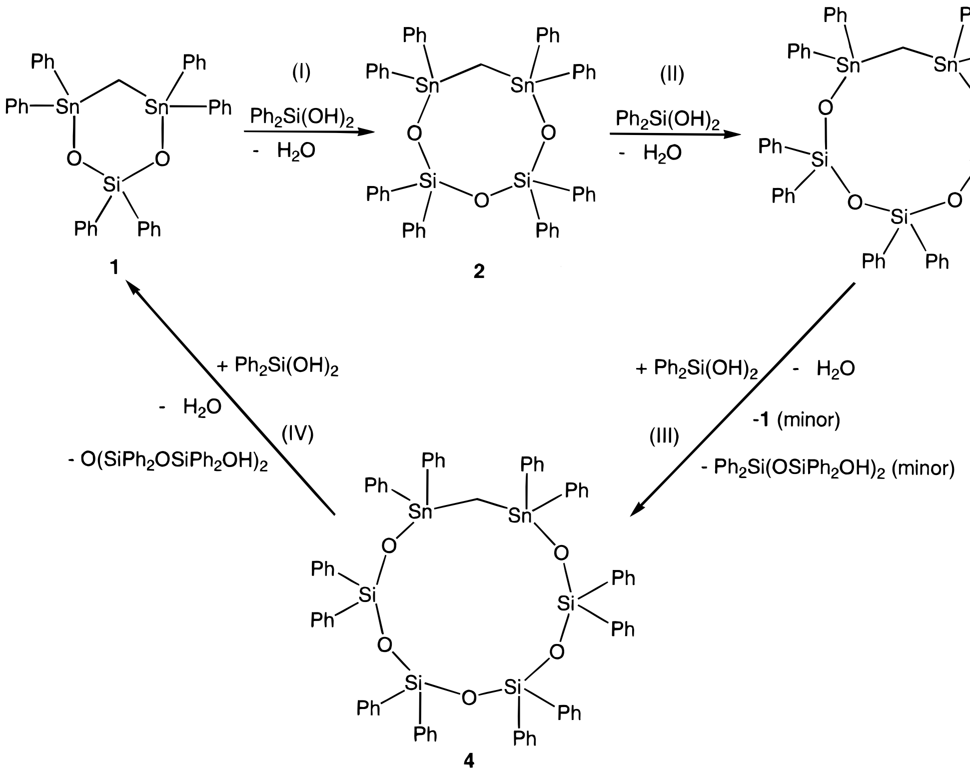


2a **2b** **5**

Figure 3. Ring conformations (SHELXTL-PLUS) of *cyclo*-stannasiloxanes **2a**, **2b**, and **5**.

Scheme 3



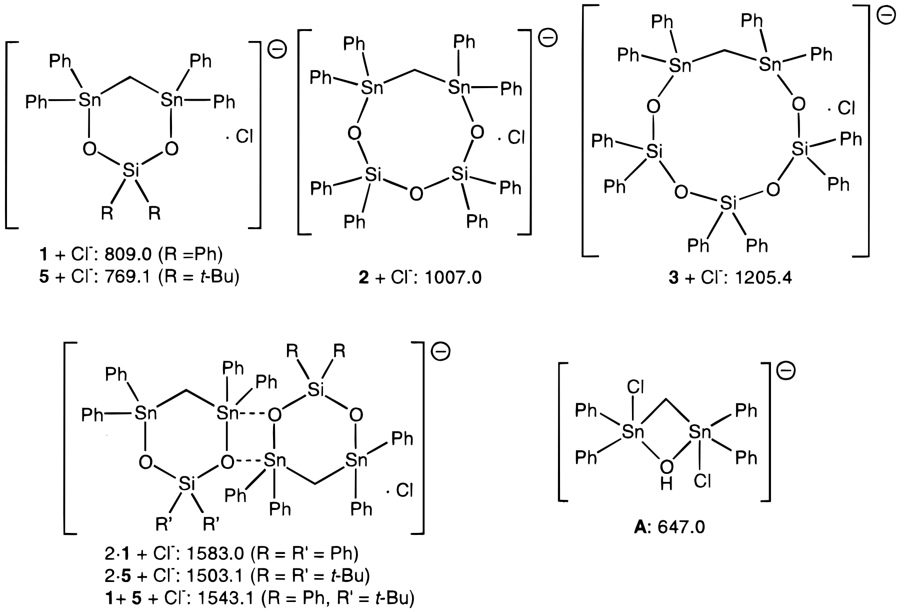
reflected by two ^{119}Sn MAS NMR resonances (−34.2 and −35.2 ppm).

The six-membered stannasiloxane ring **5** can formally be regarded as derived from *cyclo*-(t-Bu_2SiO)$_3$[10] in which one (t-$Bu_2SiOSi$$t$-$Bu_2$) unit is replaced by a (Ph_2SnCH_2-$SnPh_2$) fragment. As a consequence of the six-membered ring structure of **5**, the Si(1)−O(1)−Sn(2), Si(1)−O(2)−Sn(1), and Sn(1)−C(1)−Sn(2) bond angles of 134.6(4)°, 136.4(3)°, and 113.9(4)°, respectively, are smaller than the corresponding angles of the eight-membered stannasiloxane ring **2** (Table 1). The ring conformation of **5** (Figure 3) is almost planar, with C(1) showing the largest deviation from the plane (−0.622(9) Å).

The ^{1}H and ^{13}C NMR spectra (Experimental Section) of compounds **2**−**6** are fully consistent with their proposed structures in solution. The ^{29}Si NMR chemical shifts of the stannasiloxane rings **1**−**5** exhibit the expected dependence on the ring size (Table 3).[4d] Surprisingly the ^{119}Sn NMR chemical shifts show a reverse dependence on the ring size. Usually, the ^{119}Sn chemical shifts of smaller rings appear at higher frequency than those of larger rings.[4d] Here, the ^{119}Sn NMR signals of the six-membered *cyclo*-stannasiloxanes **1** and **5** at −34.7 and −42.8 ppm, respectively, are more low-frequency shifted than the signals at −29.8, −26.1, and −26.9 ppm of the eight-, 10-, and 12-membered *cyclo*-stannasiloxanes **2**, **3**, and **4**, respectively (Table 3). One possible explanation for this reversed trend is the assumption of monomer−dimer equilibria in solutions of **1** and **5**, the population of dimers being sufficient to influence the ^{119}Sn chemical shift. Upon dimerization, the coordination number at tin becomes 5, which usually causes considerable high-field shifts in ^{119}Sn NMR spectroscopy.[4d] These equilibria are fast on the ^{119}Sn NMR time scale. Given the ring strain in the six-membered *cyclo*-stannasiloxanes **1** and **5**, their endocyclic C−Sn−O bond angles are smaller than those of the larger rings **2**−**4**, and thus the tin atoms are more affected by the dimerization. A comparison of the solid state and solution ^{119}Sn NMR spectra of the eight-membered stannasiloxane ring **2** (low strain) and six-membered stannasiloxane ring **5** (high strain) shows that the signals in the solid state are high-frequency shifted by 3.1 and 8.1 ppm, respectively. The observed $^2J(^{119}Sn{-}O{-}^{117}Sn)$ and $^2J(^{29}Si{-}O{-}^{119}Sn)$ couplings in the *cyclo*-stannasiloxanes **1**−**5** show no systematic trend related to the ring size, which is in sharp contrast to other *cyclo*-stannasiloxanes.[4d]

The presence of monomer−dimer equilibria is further supported by electrospray mass spectroscopy. To identify ionic species related to the parent compounds, we measured electrospray mass spectra (negative mode) of

Chart 1



1 + Cl^-: 809.0 (R = Ph)
5 + Cl^-: 769.1 (R = *t*-Bu)

2 + Cl^-: 1007.0

3 + Cl^-: 1205.4

2·1 + Cl^-: 1583.0 (R = R' = Ph)
2·5 + Cl^-: 1503.1 (R = R' = *t*-Bu)
1+ **5** + Cl^-: 1543.1 (R = Ph, R' = *t*-Bu)

A: 647.0

Table 2. Crystallographic Data for 2 and 5

	2	5
formula	$C_{49}H_{42}O_3Si_2Sn_2$	$C_{33}H_{40}O_2SiSn_2$
fw	972.39	734.12
cryst syst	triclinic	triclinic
cryst size, mm	0.15 × 0.10 × 0.10	0.26 × 0.16 × 0.06
space group	$P\bar{1}$	$P\bar{1}$
a, Å	10.434(1)	10.713(4)
b, Å	15.493(1)	12.7321(9)
c, Å	29.220(1)	13.387(2)
α, deg	95.570(1)	102.225(4)
β, deg	91.011(1)	107.37(2)
γ, deg	106.169(1)	100.61(1)
V, $Å^3$	4510.3(5)	1642.2(7)
Z	4	2
ρ_{calcd}, Mg/m^3	1.432	1.485
ρ_{meas}, Mg/m^3	1.4388(4)	1.5537(8)
μ, mm^{-1}	1.200	12.638
F(000)	1952	736
θ range, deg	2.56−23.22	3.61−74.77
index ranges	$-10 \le h \le 10$ $-17 \le k \le 16$ $-32 \le l \le 32$	$-12 \le h \le 13$ $-15 \le k \le 15$ $-16 \le l \le 0$
no. of reflns collcd	48 237	7033
completeness to θ_{max}	94.6	99.7
no. of indep reflns/R_{int}	12 208/0.041	6731/0.1026
no. of reflns obsd with ($I > 2\sigma(I)$)	5831	5465
abs corr	n.m.	ψ-scan
T_{max}/T_{min}		1.000/0.655
no. of refined params	1010	352
GooF (F^2)	0.761	1.059
$R1(F)$ ($I > 2\sigma(I)$)	0.0331	0.0649
$wR2(F^2)$ (all data)	0.0564	0.1998
$(\Delta/\sigma)_{max}$	<0.001	<0.001
largest diff peak/hole, e/$Å^3$	0.244/−0.223	1.750/−2.729

Table 3. Selected ^{119}Sn and ^{29}Si NMR Parameter for 1−6 in $CDCl_3$

	$\delta(^{119}Sn)$	$^2J(^{119}Sn{-}C{-}^{117}Sn)$	$\delta(^{29}Si)$	$^2J(^{29}Si{-}O{-}^{117/119}Sn)$
1	−34.7	512	−34.0	25
2	−29.8	535	−41.0	36
3	−26.1	474	−42.2, −46.8	33
4	−26.9	551	−42.1, −47.5	33
5	−42.8	508	−13.5	39
6	−38.3	508		

acetonitrile/dichloromethane solutions (1:1) of **1**−**3** and **5**, respectively, and of a mixture of **1** and **5**. The solution of **1** was prepared in situ by reacting $[Ph_2(OH)Sn]_2CH_2$ with $Ph_2Si(OH)_2$. The mass clusters and the proposed structures are depicted in Chart 1. For all compounds the mass peak plus chloride was detected. In addition, compounds **1** and **5** exhibit a dimer mass peak plus chloride. An equimolar mixture of **1** and **5** shows the presence of both the homodimers plus chloride and the heterodimer plus chloride. In all solutions a mass cluster consistent with the anionic four-membered stannoxane **A** was observed.

Conclusion

The $[Ph_2(OH)Sn]_2CH_2$-catalyzed condensation of $Ph_2Si(OH)_2$ to give *cyclo*-$(Ph_2SiO)_4$ appears to be initiated by the formation of the six-membered *cyclo*-stannasiloxane $Ph_2Si(OSnPh_2)_2CH_2$ (**1**). Very likely, the eight-, 10-, and 12-membered stannasiloxane rings **2**−**4** are also involved in the condensation pathway.

Unlike these three latter stannasiloxane rings, the six-membered *cyclo*-stannasiloxane **1** is unstable in solution and reacts with water present in the reaction mixture to give the eight-membered *cyclo*-stannasiloxane **2** and $[Ph_2(OH)Sn]_2CH_2$.

Experimental Section

The starting compounds *t*-$Bu_2Si(OH)_2$,[11a] *t*-$Bu_2Ge(OH)_2$,[8c] $[Ph_2(OH)Si]_2O$,[5g] $[Ph_2(OH)SiO]_2SiPh_2$,[5g] $[Ph_2(OH)SiOSiPh_2]_2O$,[4f] and $[Ph_2(OH)Sn]_2CH_2$[11b] were prepared according to literature methods. $Ph_2Si(OH)_2$ was supplied by Fluka and used as received. Solution state NMR spectra were recorded in $CDCl_3$ on a Bruker DRX 400 spectrometer at 400.13 MHz (^{1}H), 100.62 MHz ($^{13}C\{^1H\}$), 79.49 MHz ($^{29}Si\{^1H\}$), and 149.21 MHz ($^{119}Sn\{^1H\}$) using Me_4Si and Me_4Sn as external references. Solid state $^{119}Sn\{^1H\}$ NMR spectra were recorded on a Bruker MSL 400 spectrometer at 149.21 MHz using cross polarization (CP) and magic angle spinning techniques (MAS) (recycle delay 4.0 s, 90° pulse 5.0 μs, contact time 3.5 ms) at spinning frequencies of 8 and 10 kHz, respectively. Tetracyclohexyltin was used as

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(10) Clegg, W. *Acta Crystallogr.* **1982**, *B38*, 1648.

(11) (a) Weidenbruch, M.; Pesel, H.; Hieu, D. V. *Z. Naturforsch.* **1980**, *35b*, 31. (b) Gielen, M.; Jurkschat, K. *J. Organomet. Chem.* **1984**, *273*, 303.

a second reference (−97.35 ppm against Me_4Sn) and to optimize Hartmann−Hahn matching conditions. Mass spectra were measured on a Finnigan MAT 8230 spectrometer. Electrospray mass spectra were obtained with a Micromass Platform II single quadrupole mass spectrometer using an acetonitrile mobile phase. Acetonitrile/dichloromethane solutions (1:1; $c = 1 \times 10^{-3}$ mol L^{-1}) 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 both as 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. Elemental analyses were performed on an instrument from Carlo Erba Strumentazione (model 1106). The density of single crystals was determined using a Micromeritics Accu Pyc 1330.

Catalytic Condensation of Diphenylsilandiol. A mixture of $[Ph_2(OH)Sn]_2CH_2$ (1.19 g, 2.00 mmol) and $Ph_2Si(OH)_2$ (4.32 g, 20.0 mmol) in acetone (50 mL) was heated at 60 °C. After 20 h a colorless precipitate of *cyclo*-$(Ph_2SiO)_4$ was filtered (2.53 g, 3.19 mmol, 64%). $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: −42.7. Anal. Calcd for $C_{48}H_{40}O_4Si_4$ (793.19): C, 72.69; H, 5.08. Found: 72.6; H, 5.1.

In Situ Synthesis of 1,1,3,3,5,5-Hexaphenyl-4,6-dioxa-1,3-distanna-5-silacyclohexane (1). A mixture of $[Ph_2(OH)Sn]_2CH_2$ (29.7 mg, 0.05 mmol) and $Ph_2Si(OH)_2$ (10.8 mg, 0.05 mmol) in $CDCl_3$ (300 μL) was heated at 60 °C for 30 min, resulting in a clear solution. ^{119}Sn and ^{29}Si NMR spectroscopy showed the exclusive formation of **1**. $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: −34.0 ($^2J(^{29}Si{-}O{-}^{117/119}Sn) = 25$ Hz. $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ: −34.7 ($^2J(^{119}Sn{-}C{-}^{117}Sn) = 512$ Hz, $^2J(^{119}Sn{-}O{-}^{29}Si) = 25$ Hz). Then the mixture was heated again at 60 °C for 2 days. During this period the solution was investigated by ^{119}Sn and ^{29}Si NMR spectroscopy, which revealed increasing amounts of **2**. After a short time a colorless precipitate was observed, which was not filtered.

The above reaction was repeated on a preparative scale using $[Ph_2(OH)Sn]_2CH_2$ (1.48 g, 2.50 mmol) and $Ph_2Si(OH)_2$ (0.54 g, 2.50 mmol) in toluene (25 mL): The precipitate was filtered. It consisted exclusively of $[Ph_2(OH)Sn]_2CH_2$, which was identified by elemental analysis and by comparison of its IR spectrum with that of an authentic sample. The filtrate was evaporated in vacuo ,and the solid residue was crystallized from hexane/dichloromethane, affording **2** (0.86 g, 0.88 mmol, 35%, mp 110 °C).

Synthesis of the *cyclo*-Metallastannoxanes 2−6. A mixture of $[Ph_2(OH)Sn]_2CH_2$ (1.49 g, 2.5 mmol) and 2.5 mmol of the corresponding silanol (1.04 g $[Ph_2(OH)Si]_2O$ for **2**, 1.53 g $[Ph_2(OH)SiO]_2SiPh_2$ for **3**, 2.03 g $[Ph_2(OH)SiOSiPh_2]_2O$ for **4**, and 0.44 g t-$Bu_2Si(OH)_2$ for **5**) or germane diol (0.55 g t-$Bu_2Ge(OH)_2$ for **6**), respectively, in toluene (25 mL) was heated at 60 °C in an open flask, resulting in a clear solution. The solvent was removed in vacuo, and the solid residue was crystallized from hexane/dichloromethane (1:1) to give the *cyclo*-metallastannoxanes **2**−**6**.

1,1,3,3,5,5,7,7-Octaphenyl-4,6,8-trioxa-1,3-distanna-5,7-disilacyclooctane (2). Yield: 1.96 g, 2.02 mmol, 81%; mp 110 °C. ^1H NMR ($CDCl_3$) δ: 7.7−7.1 (40H, m; *Ph*), 0.87 (2H, s, $^2J(^1H\text{-}^{119}Sn) = 55$ Hz; $SnCH_2Sn$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 139.9 (SnC_i), 138.2 (SiC_i), 135.8 (SnC_o), 134.4 (SiC_o), 129.7, (SnC_p), 129.0 (SiC_p), 128.6, (SnC_m), 127.3 (SiC_m), −5.22 ($SnCH_2Sn$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: −41.0 ($^2J(^{29}Si{-}O{-}^{117/119}Sn) = 36$ Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ: −29.8 ($^2J(^{119}Sn{-}C{-}^{117}Sn) = 535$ Hz, $^2J(^{119}Sn{-}O{-}^{29}Si) = 36$ Hz). $^{119}Sn\{^1H\}$ MAS NMR δ: −18.8, −25.5, −30.7, −31.8. MS m/z (%): 816 (14) $[M^+ - C_{12}H_{10}]$, 697 (12) $[M^+ - C_{25}H_{22}SiSn]$, 637 (12) $[M^+ - C_{18}H_{15}O_3Si_3]$, 594 (26) $[M^+ - C_{25}H_{22}OSn_2]$. Anal. Calcd for $C_{49}H_{42}O_3Si_2Sn_2$ (972.51): C, 60.52; H, 4.35. Found: C, 60.5; H, 4.4.

1,1,3,3,5,5,7,7,9,9-Decaphenyl-4,6,8,10-tetraoxa-1,3-distanna-5,7,9-trisilacyclodecane (3). Yield: 2.32 g, 1.98 mmol, 79%; mp 115 °C. ^1H NMR ($CDCl_3$) δ: 7.7−7.1 (50 H, m; *Ph*), 0.95 (2H, s, $^2J(^{119}Sn\text{-}^1H) = 59$ Hz; $SnCH_2Sn$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 139.9 ($SnPhC_i$), 137.6 ($(SiO)_2SiPhC_i$), 135.9 ($SnOSiPhC_i$), 135.8 ($SnPhC_o$), 134.7 ($(SiO)_2SiPhC_o$), 134.5 ($SnOSiPhC_o$), 129.6 ($SnPhC_p$), 129.4 ($(SiO)_2SiPhC_p$), 129.1 ($SnOSiPhC_p$), 128.5 ($SnPhC_m$), 127.3 ($(SiO)_2SiPhC_m$), 127.2 ($SnOSiPhC_m$), −5.91 ($SnCH_2Sn$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: −42.2 ($^2J(^{29}Si{-}O{-}^{117/119}Sn) = 33$ Hz; $SnOSi$), −46.8 ($(SiO)_2Si$). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ: −26.1 ($^2J(^{119}Sn{-}C{-}^{117}Sn) = 474$ Hz, $^2J(^{119}Sn{-}O{-}^{29}Si) = 33$ Hz). MS m/z (%): 896 (8) $[M^+ - C_{12}H_{10}Sn]$, 696 (4) $[M^+ - C_{25}H_{22}SiSn]$, 636 (13) $[M^+ - C_{30}H_{20}O_3Si_3]$, 594 (32) $[M^+ - C_{25}H_{22}OSn_2]$. Anal. Calcd for $C_{61}H_{52}O_4Si_3Sn_2$ (1170.81): C, 62.58; H, 4.48. Found: C, 62.6; H, 4.5.

1,1,3,3,5,5,7,7,9,9,11,11-Dodecaphenyl-4,6,8,10,12-pentaoxa-1,3-distanna-5,7,9,11-tetrasilacyclododecane (4). Yield: 2.51 g, 1.85 mmol, 74%; mp 182 °C. ^1H NMR ($CDCl_3$) δ: 7.7−7.1 (60H, m; *Ph*). 0.94 (2H, s; $^2J(^{119}Sn{-}^1H) = 63$ Hz; $SnCH_2Sn$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 141.2 ($SiPhC_i$), 139.5 ($SiPhC_i$), 137.1 ($SiPhC_i$), 137.8 ($SnPhC_o$), 136.7 ($SiPhC_o$), 136.6 ($SiPhC_o$), 131.7 ($SiPhC_p$), 131.6 ($SiPhC_p$), 131.2 ($SnPhC_p$), 130.5 5 ($SnPhC_m$), 129.5 ($SiPhC_m$), 129.4 ($SiPhC_m$), −2.04 ($SnCH_2Sn$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: −42.1 ($^2J(^{29}Sn{-}O{-}^{117/119}Sn) = 33$ Hz; $SnOSi$), −47.5 ($(SiO)_2Si$). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ: −26.9 ($^2J(^{119}Sn{-}C{-}^{117}Sn) = 551$ Hz, $^2J(^{119}Sn{-}O{-}^{29}Si) = 33$ Hz). MS m/z (%): 890 (16) $[M^+ - C_{18}H_{15}OSi]$, 813 (7) $[M^+ - C_{24}H_{20}OSi]$, 637 (48) $[M^+ - C_{42}H_{35}O_5Si_4)$, 558 (28) $[M^+ - C_{48}H_{40}O_5Si_4]$. Anal. Calcd for $C_{73}H_{62}O_5Si_4Sn_2$ (1357.10): C, 63.72; H, 4.60. Found: C, 64.2; H, 4.6.

1,1,3,3-Tetraphenyl-5,5-di-*tert*-butyl-4,6-dioxa-1,3-distanna-5-silacyclohexane (5). Yield: 1.75 g, 2.38 mmol, 95%; mp 148 °C. ^1H NMR ($CDCl_3$) δ: 7.6−7.20 (20H, m; Ph), 0.96 (2H, s, $^2J(^1H\text{-}^{119}Sn) = 53$ Hz; $SnCH_2Sn$), 0.85 (18H, s; $SiCMe_3$). 13C$\{^1H\}$ NMR ($CDCl_3$) δ: 140.1 ($SnPhC_i$), 135.4 ($SnPhC_o$), 129.4 ($SnPhC_p$), 128.2 ($SnPhC_m$), 27.8 ($SiCMe_3$), 21.0 ($SiCMe_3$), −8.1 ($SnCH_2Sn$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: −13.5 ($^2J(^{29}Si{-}O{-}^{117/119}Sn) = 39$ Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ: −42.8 ($^2J(^{119}Sn{-}C{-}^{117}Sn) = 551$ Hz, $^2J(^{119}Sn{-}O{-}^{29}Si) = 39$ Hz). $^{119}Sn\{^1H\}$ MAS NMR δ: −34.2, −35.2. MS m/z (%): 676 (100) $[M^+ - C_4H_9]$, 634 (30) $[M^+ - C_5H_{12}]$, 556 (27) $[M^+ - C_{10}H_{17}]$. Anal. Calcd for $C_{33}H_{40}O_2SiSn_2$ (734.24): C, 53.98; H, 5.49. Found: C, 54.0; H, 5.9.

1,1,3,3-Tetraphenyl-5,5-di-*tert*-butyl-4,6-dioxa-1,3-distanna-5-germacyclohexane (6). Yield: 1.60 g; 2.05 mmol, 82%; mp 117 °C. ^1H NMR ($CDCl_3$) δ: 7.7−7.2 (20H, m; *Ph*), 1.05 (2H, s, $SnCH_2Sn$), 1.13 (18H, s, $SiCMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 141.6 ($SnPhC_i$), 135.8 ($SnPhC_o$), 129.5 ($SnPhC_p$), 128.7 ($SnPhC_m$), 30.1 ($GeCMe_3$), 28.1 ($GeCMe_3$), −7.0 ($SnCH_2Sn$). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ: −38.3 ($^2J(^{119}Sn{-}C{-}^{117}Sn) = 508$ Hz). $^{119}Sn\{^1H\}$ MAS NMR δ: −30.2, −33.7, −37.4, −40.8. MS m/z (%): 721 (92) $[M^+ - C_4H_9]$, 664 (10) $[M^+ - C_8H_{18}]$, 577 (45) $[M^+ - C_8H_{18}Ge]$, 499 (10) $[M^+ - C_{14}H_{23}Ge]$, 421 (8) $[M^+ - C_{20}H_{28}Ge]$. Anal. Calcd for $C_{33}H_{40}O_2GeSn_2$ (778.78): C, 50.90; H, 5.18. Found: C, 50.9; H, 5.2.

In Situ Reaction of *cyclo*-$O(Ph_2SiOSnPh_2)_2CH_2$ (2) and *cyclo*-$Ph_2Si(OPh_2SiOSnPh_2)_2CH_2$ (3) with $Ph_2Si(OH)_2$. Equimolar quantities of $Ph_2Si(OH)_2$ (19 mg, 0.088 mmol) and *cyclo*-$O(Ph_2SiOSnPh_2)_2CH_2$ (**2**) (85.6 mg, 0.088 mmol) (case A) or *cyclo*-$Ph_2Si(OPh_2SiOSnPh_2)_2CH_2$ (**3**) (103 mg, 0.088 mmol) (case B) were dissolved in $CDCl_3$ to give clear solutions. From these solutions, ^{29}Si and ^{119}Sn NMR spectra were recorded, the results of which are given below.

Case A: **3** (δ ^{119}Sn −26.1, $^2J(^{119}Sn{-}C{-}^{117}Sn)$ 474 Hz, integral 41; δ ^{29}Si −42.2, $^2J(^{29}Si{-}O\text{-}^{117/119}Sn)$ 33 Hz, δ ^{29}Si −46.8), **2** (δ ^{119}Sn −29.8, $^2J(^{119}Sn{-}C{-}^{117}Sn)$ 535 Hz, integral 48; δ ^{29}Si −41.0, $^2J(^{29}Si{-}O{-}^{117/119}Sn)$ 36 Hz), **1** (δ ^{119}Sn −34.7, integral 4.5; δ ^{29}Si −34.0, $^2J(^{29}Si{-}O{-}^{117/119}Sn)$ 25 Hz), **4** (δ ^{119}Sn −26.9, integral 5.7; $\delta^{29}Si$ −42.1 $^2J(^{29}Si{-}O{-}^{117/119}Sn)$ 33 Hz, δ ^{29}Si −47.5), $Ph_2Si(OSiPh_2OH)_2$ (δ ^{29}Si −36.1, −44.2), $O(SiPh_2$-

$OSiPh_2OH)_2$ (δ ^{29}Si −36.9, −45.3), *cyclo*-$(Ph_2SiO)_3$ (δ ^{29}Si −33.6), unidentified signals at δ ^{29}Si −37.1, −45.6.[12]

Case B: **4** (δ ^{119}Sn −26.9, integral 47; δ^{29}Si −42.1 $^2J(^{29}Si{-}O{-}^{117/119}Sn)$ 33 Hz, δ^{29}Si −47.5), **3** (δ ^{119}Sn −26.1, $^2J(^{119}Sn{-}C{-}^{117}Sn)$ 474 Hz, integral 42; δ ^{29}Si −42.2, $^2J(^{29}Si{-}O{-}^{117/119}Sn)$ 33 Hz, δ ^{29}Si −46.8), **2** (δ ^{119}Sn −29.8, integral 4; δ ^{29}Si −41.0, $^2J(^{29}Si{-}O{-}^{117/119}Sn)$ 36 Hz), **1** (δ ^{119}Sn −34.7, integral 7), $O(SiPh_2OSiPh_2OH)_2$ (δ ^{29}Si −36.9, −45.4).

Crystallography. Intensity data for the colorless crystals were collected on a Nonius CAD4 (**5**) and KappaCCD (**2**) diffractometer with graphite-monochromated Cu Kα (**5**) and Mo Kα (**2**) radiation at 291 K. Three standard reflections were recorded every 60 min (**5**), and an anisotropic intensity loss up to 10.0% (**5**) was detected during X-ray exposure. The data collections for **2** covered the sphere of reciprocal space with 360 frames via ω-rotation ($\Delta/\omega = 1°$) at two times 30 s per frame. The crystal-to-detector distance was 2.9 cm (**2**). Crystal decay was monitored by repeating the initial frames at the end of data collection. Analyzing the duplicate reflections showed there was no indication of any decay (**2**). The structures were solved by direct methods using SHELXS97[12a] and successive difference Fourier syntheses. Refinements applied full-matrix least-squares methods, SHELXL97.[12b] The H atoms were placed in geometrically calculated positions using a riding model and refined with common isotropic temperature factors for different C−H types ($C{-}H_{prim.}$ 0.96 Å, $C{-}H_{sec.}$ 0.97 Å, U_{iso} 0.114(11) Å^2; $C{-}H_{aryl}$ 0.93 Å, U_{iso} 0.112(11) Å^2 (**5**); U_{iso} 0.123(3) Å^2 (**2**).

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from *International Tables for X-ray Crystallography*.[12c] The figures were created by SHELXTL-Plus.[12d] Crystallographic data are given in Table 2; selected bond lengths, angles, and torsion angles are listed in Table 1.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, Wacker Chemie GmbH, and the Australian Research Council (ARC) for financial support.

Supporting Information Available: Tables of all coordinates, anisotropic displacement parameters, and geometric data for compounds **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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