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-(Ph₂SiO)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-Ph₂Si(OSnPh₂)₂CH₂ (1). Compound 1 reacts slowly and irreversibly with Ph₂Si(OH)₂ to provide the eight-membered stannasiloxane ring cyclo-O(Ph₂SiOSnPh₂)₂CH₂ (2) and [Ph₂(OH)Sn]₂CH₂. The driving force for this reaction is attributed to the release of ring strain in 1. Condensation of $[Ph_2(OH)Sn]_2$ -CH₂ with diphenylsiloxanols HO(Ph₂SiO)_nH (n = 2-4), t-Bu₂Si(OH)₂, and t-Bu₂Ge(OH)₂, respectively, provides the metallastannoxane rings cvclo-O(Ph₂SiOSnPh₂)₂CH₂ (2), cvclo-Ph₂Si(OSiPh₂OSnPh₂)₂CH₂ (**3**), cyclo-O(Ph₂SiOPh₂SiOSnPh₂)₂CH₂ (**4**), cyclo-t-Bu₂Si(OSnPh₂)₂- CH_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 potlives 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 $[Ph_2(OH)Sn]_2$ -CH₂ catalyze the condensation of Ph₂Si(OH)₂ to give cyclo-(Ph₂SiO)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 Ph₂Si(OH)₂ with catalytic amounts of [Ph₂(OH)Sn]₂CH₂ (10 mol % at 60 °C for 20 h) provided cyclo-(Ph₂SiO)₄ as a colorless precipitate in good yield (eq 1).

The identity of cyclo-(Ph₂SiO)₄ was established by its ²⁹Si NMR chemical shift (CDCl₃) of -42.7 ppm and by

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

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4 Ph₂Si(OH)₂

Scheme 1



addition of an authentic sample of *cyclo*-(Ph₂SiO)₄. Trace amounts of *cyclo*-(Ph₂SiO)₃ were identified (δ^{29} Si 33.5 ppm, CDCl₃) as byproduct in the mother liquor from which *cyclo*-(Ph₂SiO)₄ had been filtered off. In the absence of [Ph₂(OH)Sn]₂CH₂, a solution of Ph₂Si(OH)₂ treated under the same conditions remained unchanged. It is worth mentioning that the hydrolysis of Ph₂SiCl₂ affords mixtures of diphenylsil(ox)anediols HO(SiPh₂O)_nH (n = 1, 2, 3) and diphenylsiloxanes *cyclo*-(Ph₂SiO)_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 CDCl₃ or toluene at 60 °C for 30 min of equimolar quantities of Ph₂Si(OH)₂ and [Ph₂(OH)Sn]₂-CH₂ gave a clear solution, the ²⁹Si and ¹¹⁹Sn NMR spectra of which displayed single resonances at -34.0 $(^{2}J(^{29}\text{Si}-\text{O}-^{117/119}\text{Sn}) = 25 \text{ Hz})$ and -34.7 ppm (($^{2}J(^{119} Sn-C-^{117}Sn$ = 512 Hz), respectively. The ²⁹Si chemical shift, the ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{117/119}\text{Sn})$ coupling, and the signalto-satellite integral ratio of the latter support the exclusive presence of the six-membered stannasiloxane ring, cyclo-Ph₂Si(OSnPh₂)₂CH₂ (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 [Ph₂(OH)Sn]₂CH₂ and the eight-membered stannasiloxane ring, cyclo-O(Ph₂SiOSnPh₂)₂CH₂ (2) (Scheme 1). The



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.

latter was isolated as a colorless crystalline solid and has been completely characterized by NMR spectroscopy and X-ray analysis (Figure 1).

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 sixmembered 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 $[Ph_2(OH)Sn]_2$ -CH₂.

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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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 ¹¹⁹Sn 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-(Ph₂SiO)₄, in which one (Ph₂SiOSiPh₂) unit has been replaced by a (Ph₂SnCH₂SnPh₂) 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-(Ph₂SiO)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-1,3,5,7tetrastannaoctane derivative, cyclo-(Me₂SnCH₂)₄.7 According to a classification scheme recently introduced for the conformations of eight-membered germasiloxane rings⁸ 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 10and 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 ²⁹Si and ¹¹⁹Sn NMR spectroscopy, and integration of the ¹¹⁹Sn resonances are given. The reaction of cyclo-O(Ph₂SiOSnPh₂)₂CH₂ (2) with Ph₂Si-(OH)₂ in CDCl₃ (60 °C, 20 h) gave the 10-membered stannasiloxane ring 3 (integral 41), unreacted eightmembered 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 Ph₂Si(OSiPh₂-OH)2 and O(SiPh2OSiPh2OH)2 as well as trace amounts of cyclo-(Ph₂SiO)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 ²⁹Si -37.1, -45.6 (approximately 2% of the major signals).

The reaction mixture of the 10-membered stannasiloxane ring *cyclo*-O(Ph₂SiOPh₂SiOSnPh₂)₂CH₂ (**3**) with Ph₂Si(OH)₂ in CDCl₃ (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 ²⁹Si NMR spectrum indicated the presence of O(SiPh₂OSiPh₂OH)₂ (δ ²⁹Si - 36.9, -45.4).

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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)	1.000(0)
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) Si(1) - C(61)	1.842(7)	1.850(5)	1.910(9)
$S_1(1) = C_1(01)$ $S_2(2) = O_2(2)$	1.044(0)	1.600(3)	1.909(8)
$S_1(2) = O(2)$ $S_2(2) = O(3)$	1.012(3) 1.506(3)	1.019(3)	
Si(2) = C(71)	1.853(5)	1.859(5)	
Si(2) - C(81)	1.000(0)	1.850(5)	
O(2) - Sn(1) - C(1)		1.000(0)	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) 115.9(2)	104.5(3)
C(1) = Sn(2) = C(31) C(1) = Sn(2) = C(41)	114.0(2) 116.5(2)	113.2(3) 119.25(10)	111.0(4) 112.5(2)
C(1) = SII(2) = C(41) C(31) = Sp(2) = C(41)	110.3(3)	112.33(10) 114.6(3)	113.3(3)
O(1) - Si(1) - O(2)	112.7(3) 110 77(18)	114.0(3) 111 58(17)	1132(3)
O(1) - Si(1) - C(51)	109 2(2)	108 8(2)	107.2(0)
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) - S1(2) - C(81)	111.2(3)	111.1(2)	104.0(4)
Sn(2) = O(1) = S1(1) Sn(1) = O(2) = Si(1)	171.5(2)	163.1(2)	134.6(4)
SII(1) = O(2) = SI(1) Si(1) = O(2) = Si(2)	128 2(2)	140 4(9)	130.4(3)
$S_{n}(1) = O(2) = S_{1}(2)$ $S_{n}(1) = O(2) = S_{1}(2)$	130.3(2) 140.71(10)	140.4(2) 120 02(17)	
Sn(1) = C(1) - Sn(2)	140.71(13) 120 $1(2)$	138.02(17) 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)	1.0(0)
$S_1(1) - U(2) - S_1(1) - U(1)$			-1.8(6)
O(2) - Sn(1) - C(1) - Sn(2)			27.5(5)

Interestingly, neither the 14-membered stannasiloxane ring *cyclo*-Ph₂Si(OSiPh₂OSiPh₂OSnPh₂)₂CH₂ nor open-chain stannasiloxanes were formed in these reactions.

From these results, one possible reaction sequence for the [Ph₂(OH)Sn]₂CH₂-catalyzed condensation of Ph₂Si-(OH)₂ is proposed in Scheme 3. In a kind of growth reaction, the initially formed six-membered stannasiloxane ring **1** reacts with Ph₂Si(OH)₂ to give the eightmembered stannasiloxane ring **2**, which in turn reacts with further Ph₂Si(OH)₂ to give the 10-membered stannasiloxane ring **3**. The latter, however, reacts with Ph₂-Si(OH)₂ to give the 12-membered ring **4** as well as the six-membered ring **1** and the organosiloxanol Ph₂Si-(OSiPh₂OH)₂. Further ring enlargment seems to be not



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

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.

In analogy with compound **1**, the synthesis of the sixmembered metallastannoxane rings, *cyclo-t*-Bu₂Si-(OSnPh₂)₂CH₂ (**5**) and *cyclo-t*-Bu₂Ge(OSnPh₂)₂CH₂ (**6**), was achieved by condensation of $[Ph_2(OH)Sn]_2CH_2$ with *t*-Bu₂Si(OH)₂ and *t*-Bu₂Ge(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*-Bu₂Si-(OH)₂ and *t*-Bu₂Ge(OH)₂.⁹



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



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*-Bu₂SiO)₃¹⁰ in which one (*t*-Bu₂SiOSi*t*-Bu₂) unit is replaced by a (Ph₂SnCH₂-SnPh₂) 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 ¹H and ¹³C NMR spectra (Experimental Section) of compounds **2–6** are fully consistent with their proposed structures in solution. The ²⁹Si NMR chemical shifts of the stannasiloxane rings **1–5** exhibit the expected dependence on the ring size (Table 3).^{4d} Surprisingly the ¹¹⁹Sn NMR chemical shifts show a reverse dependence on the ring size. Usually, the ¹¹⁹Sn chemical shifts of smaller rings appear at higher frequency than those of larger rings.^{4d} Here, the ¹¹⁹Sn 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 ¹¹⁹Sn chemical shift. Upon dimerization, the coordination number at tin becomes 5, which usually causes considerable high-field shifts in ¹¹⁹Sn NMR spectroscopy.^{4d} These equilibria are fast on the ¹¹⁹Sn NMR time scale. Given the ring strain in the sixmembered 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 ¹¹⁹Sn NMR spectra of the eightmembered stannasiloxane ring 2 (low strain) and sixmembered 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 $^{2}J(^{119}\text{Sn}-\text{O}-^{117}\text{Sn})$ and $^{2}J(^{29}\text{Si}-\text{O}-^{119}\text{Sn})$ 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



Table 2. Crystallographic Data for 2 and 5

	z	5
formula	C49H42O3Si2Sn2	C33H40O2SiSn2
fw	972.39	734.12
cryst syst	triclinic	triclinic
cryst size, mm	$0.15 \times 0.10 \times 0.10$	$0.26\times0.16\times0.06$
space group	$P\bar{1}$	$P\bar{1}$
a, Å	10.434(1)	10.713(4)
<i>b</i> , Å	15.493(1)	12.7321(9)
<i>c</i> , 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)
<i>V</i> , Å ³	4510.3(5)	1642.2(7)
Z	4	2
$ ho_{ m calcd}$, Mg/m ³	1.432	1.485
$ ho_{ m meas}$, Mg/m ³	1.4388(4)	1.5537(8)
μ , mm ⁻¹	1.200	12.638
<i>F</i> (000)	1952	736
θ range, deg	2.56 - 23.22	3.61 - 74.77
index ranges	$-10 \le h \le 10$	$-12 \le h \le 13$
	$-17 \leq k \leq 16$	$-15 \le k \le 15$
	$-32 \leq l \leq 32$	$-16 \leq l \leq 0$
no. of reflns collcd	48 237	7033
completeness to θ_{max}	94.6	99.7
no. of indep reflns/ <i>R</i> _{int}	12 208/0.041	6731/0.1026
no. of reflns obsd with	5831	5465
$(I > 2\sigma(I))$		
abs corr	n.m.	ψ -scan
$T_{\rm max}/T_{\rm min}$		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
$(\Delta/\sigma)_{\rm max}$	< 0.001	< 0.001
largest diff peak/hole, e/A ³	0.244/-0.223	1.750/-2.729

Table 3. Selected ¹¹⁹Sn and ²⁹Si NMR Parameterfor 1-6 in CDCl3

		-				
	δ (¹¹⁹ Sn)	$^{2}J(^{119}Sn-C-^{117}Sn)$	δ (²⁹ Si)	$^{2}J(^{29}\text{Si}-\text{O}-^{117/119}\text{Sn})$		
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_2 -Si(OH)₂ to give *cyclo*- $(Ph_2SiO)_4$ appears to be initiated by the formation of the six-membered *cyclo*-stannasi-loxane $Ph_2Si(OSnPh_2)_2CH_2$ (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*-Bu₂Si(OH)₂,^{11a} *t*-Bu₂Ge(OH)₂,^{8c} [Ph₂(OH)Si]₂O,^{5g} [Ph₂(OH)SiO]₂SiPh₂,^{5g} [Ph₂(OH)SiOSiPh₂]₂O,^{4f} and [Ph₂(OH)Sn]₂CH₂^{11b} were prepared according to literature methods. Ph₂Si(OH)₂ was supplied by Fluka and used as received. Solution state NMR spectra were recorded in CDCl₃ on a Bruker DRX 400 spectrometer at 400.13 MHz (¹H), 100.62 MHz (¹³C{¹H}), 79.49 MHz (²⁹Si{¹H}), and 149.21 MHz (¹¹⁹Sn{¹H}) using Me₄Si and Me₄Sn as external references. Solid state ¹¹⁹Sn{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 μ s, contact time 3.5 ms) at spinning frequencies of 8 and 10 kHz, respectively. Tetracyclohexyltin was used as

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a second reference (-97.35 ppm against Me₄Sn) 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 μ L loop. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 10 μ L 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%). ²⁹Si{¹H} NMR (CDCl₃) δ : -42.7. Anal. Calcd for C₄₈H₄₀O₄Si₄ (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 [Ph₂(OH)-Sn]₂CH₂ (29.7 mg, 0.05 mmol) and Ph₂Si(OH)₂ (10.8 mg, 0.05 mmol) in CDCl₃ (300 μ L) was heated at 60 °C for 30 min, resulting in a clear solution. ¹¹⁹Sn and ²⁹Si NMR spectroscopy showed the exclusive formation of 1. ²⁹Si{¹H} NMR (CDCl₃) δ : -34.0 (²J(²⁹Si-O-^{117/119}Sn) = 25 Hz. ¹¹⁹Sn{¹H} NMR (CDCl₃) δ : -34.7 (²J(¹¹⁹Sn-C-¹¹⁷Sn) = 512 Hz, ²J(¹¹⁹Sn-O-²⁹Si) = 25 Hz). Then the mixture was heated again at 60 °C for 2 days. During this period the solution was investigated by ¹¹⁹Sn and ²⁹Si 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*-Bu₂Si(OH)₂ for 5) or germane diol (0.55 g *t*-Bu₂-Ge(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*-metal-lastannoxanes **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 (CDCl₃) δ : 7.7–7.1 (40H, m; *Ph*), 0.87 (2H, s, ²*J*(¹H-¹¹⁹Sn) = 55 Hz; SnC*H*₂Sn). ¹³C{¹H} NMR (CDCl₃) δ : 139.9 (Sn*C*_i), 138.2 (Si*C*_i), 135.8 (Sn*C*_o), 134.4 (Si*C*_o), 129.7, (Sn*C*_p), 129.0 (Si*C*_p), 128.6, (Sn*C*_m), 127.3 (Si*C*_m), -5.22 (Sn*C*H₂-Sn). ²⁹Si{¹H} NMR (CDCl₃) δ : -41.0 (²*J*(²⁹Si–O–^{117/119}Sn) = 36 Hz). ¹¹⁹Sn{¹H} NMR (CDCl₃) δ : -29.8 (²*J*(¹¹⁹Sn–C–¹¹⁷Sn) = 535 Hz, ²*J*(¹¹⁹Sn–O–²⁹Si) = 36 Hz). ¹¹⁹Sn{¹H} MAS NMR δ : -18.8, -25.5, -30.7, -31.8. MS *m*/*z* (%): 816 (14) [M⁺ - C₁₂H₁₀], 697 (12) [M⁺ - C₂₅H₂₂OSn₂]. Anal. Calcd for C₄₉H₄₂O₃-Si₂Sn₂ (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 (CDCl₃) δ : 7.7–7.1 (50 H, m; *Ph*), 0.95 (2H, s, ²J(¹¹⁹Sn-¹H) = 59 Hz; SnCH₂Sn). ¹³C{¹H} NMR (CDCl₃) δ : 139.9 (SnPh*C*_{*i*}), 137.6 ((SiO)₂SiPh*C*_{*i*}), 135.9 (SnO-SiPh*C*_{*i*}), 135.8 (SnPh*C*_{*o*}), 134.7 ((SiO)₂SiPh*C*_{*i*}), 134.5 (SnO-SiPh*C*_{*i*}), 129.6 (SnPh*C*_{*p*}), 129.4 ((SiO)₂SiPh*C*_{*i*}), 129.1 (SnO-SiPh*C*_{*i*}), -5.91 (SnCH₂Sn). ²⁹Si{¹H} NMR (CDCl₃) δ : -42.2 (²J(²⁹Si-O-^{117/119}Sn) = 33 Hz; SnO*Si*), -46.8 ((SiO)₂*Si*). ¹¹⁹Sn{¹H} NMR (CDCl₃) δ : -26.1 (²J(¹¹⁹Sn-C-¹¹⁷Sn) = 474 Hz, ²J(¹¹⁹Sn-O-²⁹Si) = 33 Hz). MS *m*/*z* (%): 896 (8) [M⁺ - C₁₂H₁₀-Sn], 696 (4) [M⁺ - C₂₅H₂₂SiSn], 636 (13) [M⁺ - C₃₀H₂₀O₃Si₃], 594 (32) [M⁺ - C₂₅H₂₂OSn₂]. Anal. Calcd for C₆₁H₅₂O₄Si₃Sn₂ (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 (CDCl₃) δ : 7.7–7.1 (60H, m; *Ph*). 0.94 (2H, s; ²J(¹¹⁹Sn–¹H) = 63 Hz; SnC*H*₂Sn). ¹³C{¹H} NMR (CDCl₃) δ : 141.2 (SiPh*C*_{*i*}), 139.5 (SiPh*C*_{*i*}), 137.1 (SiPh*C*_{*j*}), 137.8 (SnPh*C*_{*o*}), 136.7 (SiPh*C*_{*o*}), 136.6 (SiPh*C*_{*o*}), 131.7 (SiPh*C*_{*p*}), 131.6 (SiPh*C*_{*o*}), 136.7 (SiPh*C*_{*o*}), 130.5 5 (SnPh*C*_{*m*}), 129.5 (SiPh*C*_{*m*}), 129.4 (SiPh*C*_{*m*}), -2.04 (Sn*C*H₂-Sn). ²⁹Si{¹H} NMR (CDCl₃) δ : -42.1 (²J(²⁹Sn–O–^{117/119}Sn) = 33 Hz; SnO*Si*), -47.5 ((SiO)₂*Si*). ¹¹⁹Sn{¹H} NMR (CDCl₃) δ : -26.9 (²J(¹¹⁹Sn–C–¹¹⁷Sn) = 551 Hz, ²J(¹¹⁹Sn–O–²⁹Si) = 33 Hz). MS *m*/*z* (%): 890 (16) [M⁺ – C₁₈H₁₅OSi], 813 (7) [M⁺ – C₂₄H₂₀OSi], 637 (48) [M⁺ – C₄₂H₃₅O₅Si₄), 558 (28) [M⁺ – C₄₈H₄₀O₅Si₄]. Anal. Calcd for C₇₃H₆₂O₅Si₄Sn₂ (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-dis-tanna-5-silacyclohexane (5).** Yield: 1.75 g, 2.38 mmol, 95%; mp 148 °C. ¹H NMR (CDCl₃) δ : 7.6–7.20 (20H, m; Ph), 0.96 (2H, s, ²J(¹H-¹¹⁹Sn) = 53 Hz; SnCH₂Sn), 0.85 (18H, s; SiCMe₃). 13C{¹H} NMR (CDCl₃) δ : 140.1 (SnPhC_i), 135.4 (SnPhC_o), 129.4 (SnPhC_p), 128.2 (SnPhC_m), 27.8 (SiCMe₃), 21.0 (SiCMe₃), -8.1 (SnCH₂Sn). ²⁹Si{¹H} NMR (CDCl₃) δ : -13.5 (²J(²⁹Si–O–^{117/119}Sn) = 39 Hz). ¹¹⁹Sn{¹H} NMR (CDCl₃) δ : -42.8 (²J(¹¹⁹Sn–C-¹¹⁷Sn) = 551 Hz, ²J(¹¹⁹Sn–O-²⁹Si) = 39 Hz). ¹¹⁹Sn{¹H} MAS NMR δ : -34.2, -35.2. MS *m*/*z* (%): 676 (100) [M⁺ – C₄H₉], 634 (30) [M⁺ – C₅H₁₂], 556 (27) [M⁺ – C₁₀H₁₇]. Anal. Calcd for C₃₃H₄₀O₂SiSn₂ (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-dis-tanna-5-germacyclohexane (6).** Yield: 1.60 g; 2.05 mmol, 82%; mp 117 °C. ¹H NMR (CDCl₃) δ : 7.7–7.2 (20H, m; *Ph*), 1.05 (2H, s, SnC*H*₂Sn), 1.13 (18H, s, SiC*Me*₃). ¹³C{¹H} NMR (CDCl₃) δ : 141.6 (SnPh*C*_{*i*}), 135.8 (SnPh*C*₀), 129.5 (SnPh*C*_{*p*}), 128.7 (SnPh*C*_{*m*}), 30.1 (Ge*C*Me₃), 28.1 (Ge*C*Me₃), -7.0 (Sn*C*H₂-Sn). ¹¹⁹Sn{¹H} NMR (CDCl₃) δ : -38.3 (²*J*(¹¹⁹Sn–C⁻¹¹⁷Sn) = 508 Hz). ¹¹⁹Sn{¹H} MAS NMR δ : -30.2, -33.7, -37.4, -40.8. MS *m/z* (%): 721 (92) [M⁺ - C₄H₉], 664 (10) [M⁺ - C₈H₁₈], 577 (45) [M⁺ - C₈H₁₈Ge], 499 (10) [M⁺ - C₁₄H₂₃Ge], 421 (8) [M⁺ - C₂₀H₂₈Ge]. Anal. Calcd for C₃₃H₄₀O₂GeSn₂ (778.78): C, 50.90; H, 5.18. Found: C, 50.9; H, 5.2.

In Situ Reaction of *cyclo*-O(Ph₂SiOSnPh₂)₂CH₂ (2) and *cyclo*-Ph₂Si(OPh₂SiOSnPh₂)₂CH₂ (3) with Ph₂Si(OH)₂. Equimolar quantities of Ph₂Si(OH)₂ (19 mg, 0.088 mmol) and *cyclo*-O(Ph₂SiOSnPh₂)₂CH₂ (2) (85.6 mg, 0.088 mmol) (case A) or *cyclo*-Ph₂Si(OPh₂SiOSnPh₂)₂CH₂ (3) (103 mg, 0.088 mmol) (case B) were dissolved in CDCl₃ to give clear solutions. From these solutions, ²⁹Si and ¹¹⁹Sn NMR spectra were recorded, the results of which are given below.

Case A: **3** (δ ¹¹⁹Sn -26.1, ²*J*(¹¹⁹Sn-C-¹¹⁷Sn) 474 Hz, integral 41; δ ²⁹Si -42.2, ²*J*(²⁹Si-O-^{117/119}Sn) 33 Hz, δ ²⁹Si -46.8), **2** (δ ¹¹⁹Sn -29.8, ²*J*(¹¹⁹Sn-C-¹¹⁷Sn) 535 Hz, integral 48; δ ²⁹Si -41.0, ²*J*(²⁹Si-O-^{117/119}Sn) 36 Hz), **1** (δ ¹¹⁹Sn -34.7, integral 4.5; δ ²⁹Si -34.0, ²*J*(²⁹Si-O-^{117/119}Sn) 25 Hz), **4** (δ ¹¹⁹Sn -26.9, integral 5.7; δ ²⁹Si -42.1 ²*J*(²⁹Si-O-^{117/119}Sn) 33 Hz, δ ²⁹Si -47.5), Ph₂Si(OSiPh₂OH)₂ (δ ²⁹Si -36.1, -44.2), O(SiPh₂- Case B: **4** (δ^{119} Sn -26.9, integral 47; δ^{29} Si -42.1 ${}^{2}J({}^{29}$ Si - 0^{-117/119}Sn) 33 Hz, δ^{29} Si -47.5), **3** (δ^{119} Sn -26.1, ${}^{2}J({}^{119}$ Sn - C⁻¹¹⁷Sn) 474 Hz, integral 42; δ^{29} Si -42.2, ${}^{2}J({}^{29}$ Si -0^{-117/119}Sn) 33 Hz, δ^{29} Si -46.8), **2** (δ^{119} Sn -29.8, integral 4; δ^{29} Si -41.0, ${}^{2}J({}^{29}$ Si -0^{-117/119}Sn) 36 Hz), **1** (δ^{119} Sn -34.7, integral 7), O(SiPh₂OSiPh₂OH)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 K α (5) and Mo K α (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 ($\Delta/\omega = 1^\circ$) 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 fullmatrix 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) Å²; C–H_{aryl} 0.93 Å, U_{iso} 0.112(11) Å² (**5**); U_{iso} 0.123-(3) Å² (**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.

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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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