Articles

Strained Metallastannoxanes−Ring-Opening Polymerization versus Retention of Six-Membered-Ring Structure[†]

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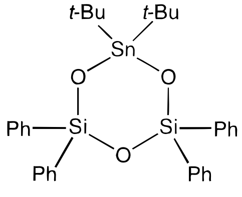
The synthesis is reported of the novel stannasiloxanes *cyclo*-$M(OSiPh_2)_2O$ (**1**, M = $Sn[(CH_2)_3NMe_2]_2$; **2**, M = $Sn[(CH_2)_3N(Me)CH_2]_2$; **4**, M = $Sn[Cp(CO)_2Fe]_2$; **5**, M = $Sn[Cp(CO)_3W]_2$; **6**, M = $Sn(t\text{-}Bu)[Cp(CO)_3W]$) and *cyclo*-$(Ph_2SiOSnR_2O)_2$ (**3**, R = $(CH_2)_3NMe_2$), and of the stannagermoxane *cyclo*-*t*-$Bu_2Sn(OGePh_2)_2O$ (**7**). The molecular structures are described of **1**−**4**, **6**, and **7**. The compounds exhibit reduced ring strain as a result of either intramolecular Sn−N coordination (**1**, **2**) or electronic influence of the transition-metal fragments (**4**−**6**), and consequently they are six-membered rings in solution as well as in the solid state, whereas compound **3** is an eight-membered ring.

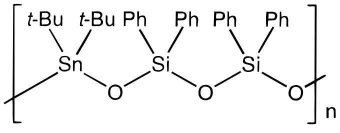
Introduction

In the past decade inorganic polymers have received increasing interest, and the controlled synthesis of such well-defined materials still remains a challenge.[1a,b]

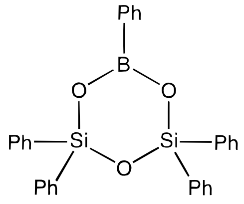
One requirement is the synthesis of appropriate monomeric precursors which can be polymerized under mild conditions. Among different strategies, the thermally or catalytically induced ring-opening polymerization (ROP) of small strained rings is a well-established method for making inorganic polymers.[1a,b] An important example is the base-catalyzed conversion of the six- or eight-membered *cyclo*-$(Me_2SiO)_n$ (n = 3, 4) to poly(dimethylsiloxanes).[1c−e]



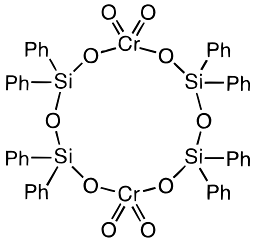
(**A**)



(**A′**)



(**B**)



(**C**)

For some time we have been interested in stannasiloxanes.[2] Recently we reported *cyclo*-*t*-$Bu_2Sn(OSiPh_2)_2O$, which contains a six-membered ring (**A**) in solution but is the first well-defined polystannasiloxane (**A′**) in the solid state.[2a] In fact, *cyclo*-*t*-$Bu_2Sn(OSiPh_2)_2O$ represents a unique subject for the study of the interplay between the kinetic lability of the Sn−O bond, entropy-favored six-membered-ring formation and enthalpically ring strain favored polymerization. In contrast to the above-mentioned *cyclo*-stannasiloxane, the closely related borasiloxane *cyclo*-$PhB(OSiPh_2)_2O$[3a−c] (**B**) is a six-membered-ring species both in solution and in the solid state, although, as a result of the much smaller radius of boron in comparison with tin, the ring strain and hence the driving force for polymerization should be higher in the boron compound. It seems likely that the strong B−O bond in **B** prevents polymerization.

[†] This work contains parts of the Ph.D. thesis of N. Pieper, Dortmund University, 1998, and of the intended Ph.D. theses of J. Beckmann and U. Kaltenbrunner.

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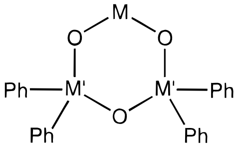
Recently, the crystal structure of *cyclo*-[$O_2Cr(OSiPh_2)_2O]_2$, which is a 12-membered ring (**C**) in the solid state, has been reported.[4] No information was given concerning its structure in solution, but on the basis of our systematic study of six- and eight-membered *cyclo*-stannasiloxanes,[2d] especially the ^{29}Si NMR chemical shift of 31.9 ppm of this compound suggests that $O_2Cr(OSiPh_2)_2O$ is present as a six-membered-ring species in solution.

Compounds of the types **A**−**C** can formally be derived from *cyclo*-$(Ph_2SiO)_3$ by replacement of one Ph_2Si unit by a metal oxo or organometal fragment. It seems that certain of these compounds differ in their solution and solid-state structures.

In a recent paper we reported the synthesis and structures of a number of eight-membered *cyclo*-stannasiloxanes[2d] which exhibit no or little ring strain and hence show no tendency to undergo polymerization. On the other hand, the stannasiloxane *cyclo*-[(*t*-BuFSi)$_2$O-(*t*-Bu_2SnO)] is a 10-membered ring in the solid state but a 5-membered ring in solution.[2c]

In this paper we report first the results of a systematic study on the influence of the metals M and their substituents on the structure of *cyclo*-metallastannoxanes of type **D**.



(**D**)

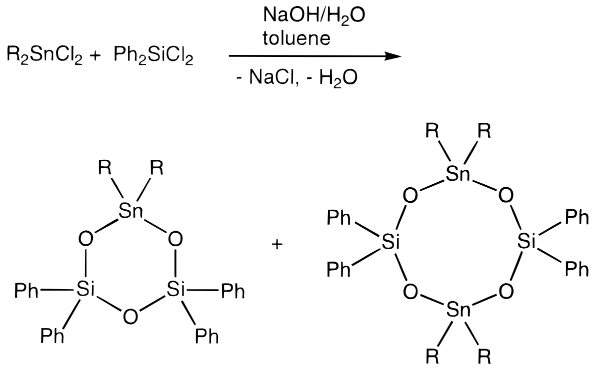
1, M = $Sn[(CH_2)_3NMe_2]_2$; M' = Si
2, M = $Sn[(CH_2)_3N(Me)(CH_2]_2$; M' = Si
4, M = $Sn[Cp(CO)_2Fe]_2$; M' = Si
5, M = $Sn[Cp(CO)_3W]_2$; M' = Si
6, M = Sn(*t*-Bu)$[Cp(CO)_3W]$; M' = Si
7, M = Sn(*t*-Bu)$_2$; M' = Ge

In compounds **1** and **2** potentially intramolecularly coordinating 3-aminopropyl ligands[5,6] were used in order to change the angles at tin from tetrahedral to octahedral. Compounds **4**−**6** represent the first examples of transition-metal-substituted stannasiloxane rings.

Results and Discussion

Synthetic Aspects and Solution NMR Studies. The cohydrolysis of bis(3-(dimethylamino)propyl)dichlorostannane[5a] and diphenyldichlorosilane was performed in the molar ratios 1:1.6 (case A) and 2:1 (case B) and provided the six-membered stannasiloxane ring *cyclo*-1,1-bis(3-(dimethylamino)propyl)-3,3,5,5-tetraphenyl-2,4,6-trioxa-3,5-disila-1-stannacyclohexane (**1**) and the eight-membered stannasiloxane ring *cyclo*-1,1,5,5-tetrakis(3-(dimethylamino)propyl)-3,3,7,7-tetraphenyl-2,4,6,8-tetraoxa-3,7-disila-1,5-distannacyclooctane (**3**) (Scheme 1) which were separated by fractional crystallization.

Scheme 1

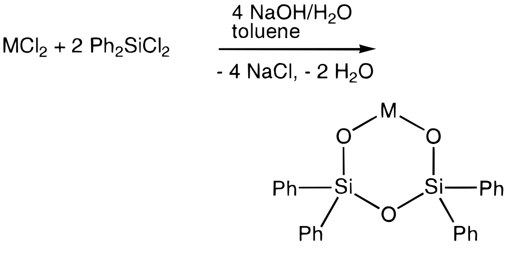


1, R = $(CH_2)_3NMe_2$ **3**, R = $(CH_2)_3NMe_2$

The ^{119}Sn NMR spectrum of the crude reaction mixture revealed for case A the six-membered stannasiloxane **1** to be the major product (δ −254.6 ppm, integral 9.5) and the eight-membered stannasiloxane ring **3** (δ −225.5 ppm, integral 0.5) to be the minor product. The ^{29}Si NMR spectrum of the same solution showed a major resonance at −39.2 ppm ($^2J(^{29}Si{-}O{-}^{117/119}Sn) = 32$ Hz) assigned to compound **1** and two low but equally intense signals at −45.2 and −45.7 ppm for which no assignment was made. From this reaction mixture the six-membered stannasiloxane ring **1** was isolated.

The ^{119}Sn NMR spectrum of the crude reaction mixture according to case B showed signals at −255.5 ppm (integral 3.7) assigned to the eight-membered stannasiloxane ring **3**, at −256 ppm (integral 0.2) assigned to the six-membered stannasiloxane ring **1**, at −184 ppm (integral 0.9) assigned to $[Me_2N(CH_2)_3]_2SnCl_2$,[5a] and at −155 ppm (integral 2.4) and −280 ppm (integral 1.5) for which no assignment was made. The ^{29}Si NMR spectrum of the same solution revealed the presence of compounds **1** (δ −39.7 ppm) and **3** (δ −46.9 ppm, $^2J(^{29}Si{-}O{-}^{117/119}Sn) = 54$ Hz) as the only silicon-containing species. From this reaction mixture the eight-membered stannasiloxane ring **3** was isolated.

The stannasiloxane *cyclo*-1,4-dimethyl-10,12-tetraphenyl-1,4-diaza-9,11,13-trioxa-10,12-disila-8-stannatetracyclo[3.2.3.5]decane (**2**) was prepared by cohydrolysis of the corresponding diorganotin dichloride[5b] and diphenyldichlorosilane in the ratio 1:2 (eq 1).



(1)

2, M = $Sn[(CH_2)_3N(Me)CH_2]_2$

The ^{119}Sn NMR spectrum of the crude reaction mixture (eq 1) showed in addition to the major signal at −274 ppm (integral 7) belonging to compound **2** two signals of almost equal intensity at −279 and −290 ppm (total integral 3) which were not assigned. The ^{29}Si NMR spectrum of the same solution displayed a resonance at −41.0 ppm ($^2J(^{29}Si{-}O{-}^{117/119}Sn) = 29$ Hz) belonging to compound **2** and two signals at −47.2 and −47.6 ppm which were not assigned.

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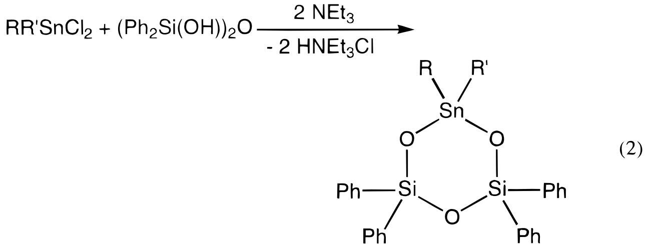
Remarkably, the *cyclo*-diphenylsiloxanes *cyclo*-($Ph_2SiO)_n$ ($n = 3$, $\delta(^{29}Si)$ −33.0[3c]/−33.3[3d] ppm; $n = 4$, $\delta(^{29}Si)$ −42.4 ppm[3c]) were detected neither in the reactions according to Scheme 1 nor in the reaction according to eq 1.

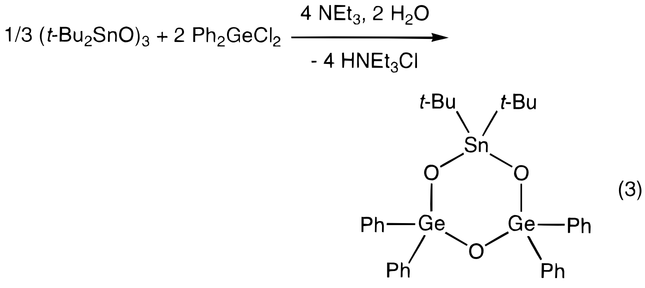
The transition-metal-substituted stannasiloxane rings *cyclo*-1,1-bis((η^5-cyclopentadienyl)dicarbonyliron)-3,3,5,5-tetraphenyl-1,4,5-trioxa-3,5-disila-1-stannacyclohexane (**4**), *cyclo*-1,1-bis((η^5-cyclopentadienyl)tricarbonyltungsten)-3,3,5,5-tetraphenyl-1,4,5-trioxa-3,5-disila-1-stannacyclohexane (**5**), and *cyclo*-1-*tert*-butyl-1-((η^5-cyclopentadienyl)tricarbonyltungsten)-3,3,5,5-tetraphenyl-1,4,5-trioxa-3,5-disila-1-stannacyclohexane (**6**) were obtained in good yields by the reaction of 1,3-tetraphenyldisiloxanediol with the corresponding diorganodichlorostannanes[7a,c] in the presence of triethylamine (eq 2).



4, R = R' = Cp(CO)$_2$Fe
5, R = R' = Cp(CO)$_3$W
6, R = *t*-Bu, R' = Cp(CO)$_3$W

No byproducts were detected by the ^{29}Si as well as the ^{119}Sn NMR spectra of the crude reaction mixtures according to eq 2.

The reaction of *cyclo*-(t-$Bu_2SnO)_3$[8] with Ph_2GeCl_2 in the presence of water and triethylamine gave the stannagermoxane *cyclo*-1,1-di-*tert*-butyl-3,3,5,5-tetraphenyl-1,4,5-trioxa-3,5-digerma-1-stannacyclohexane (**7**) as the only isolated product (eq 3). However, the ^{119}Sn NMR spectrum of the crude reaction mixture showed in addition to the signal at −96.4 ppm (integral 62), assigned to the six-membered stannagermoxane ring **7**, resonances at −87.6 ppm (integral 16), −89.1 ppm (integral 9), −91.4 ppm (integral 5), and −104.4 ppm (integral 8), which were not assigned.



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The compounds **1**−**7** are crystalline solids which are stable toward moist air and which are readily soluble in common organic solvents such as dichloromethane and acetone.

Osmometric molecular weight determinations showed compounds **1**, **2**, and **4**−**7** to be six-membered rings in solution, while compound **3** was found to be an eight-membered ring. These conclusions are strongly supported by NMR spectroscopy. For the *cyclo*-stannasiloxanes **1**, **2**, and **4**−**6** containing the ($-OPh_2Si)_2O-$ fragment the ^{29}Si NMR chemical shifts between −39.0 and −41.0 ppm as well as the $^2J(^{29}Si-O-^{119}Sn)$ coupling constants of 29−43 Hz are close to those reported for related six-membered *cyclo*-stannasiloxanes[2d] t-$Bu_2Sn(OSiPh_2)_2O$ ($\delta(^{29}Si) = -35.9$ ppm, $^2J(^{29}Si-O-^{119}Sn) = 34$ Hz), $Ph_2Si(OSn$-t-$Bu_2)_2O$ ($\delta(^{29}Si) = -38.3$, $^2J(^{29}Si-O-^{119}Sn) = 36$ Hz), and $Ph_2Si(OSn$-t-$Bu_2)_2S$ ($\delta(^{29}Si) = -39.9$, $^2J(^{29}Si-O-^{119}Sn) = 41$ Hz) as well as for the parent compound *cyclo*-$(Ph_2SiO)_3$ ($\delta(^{29}Si) = -33.3$ ppm).[3c] The ^{29}Si NMR chemical shift and $^2J(^{29}Si-O-^{119}Sn)$ coupling of eight-membered *cyclo*-stannasiloxane **3** ($\delta(^{29}Si) = -46.8$ ppm, $^2J(^{29}Si-O-^{119}Sn) = 53$ Hz) is close to the value reported for the eight-membered *cyclo*-stannasiloxane $(Ph_2SiOSn$-t-$Bu_2O)_2$ ($\delta(^{29}Si) = -45.3$ ppm, $^2J(^{29}Si-O-^{119}Sn) = 66$ Hz).

The ^{119}Sn NMR chemical shifts for compounds **1**−**3** of −255.0, −273.5, and −225 ppm indicate the tin atoms to be hexacoordinated[5] by an intramolecular Sn−N Lewis acid−Lewis base interaction. The low-frequency shift of the ^{119}Sn MAS NMR signals at −290.8 ppm (**1**), −290.2 ppm (**2**), and −252 ppm (**3**) is indicative of stronger Sn−N coordinations in the solid state than in solution. This effect is more pronounced for **1**, in which the nitrogen atoms in solution can more easily dissociate from tin than can the nitrogens in **2**. A similar effect was observed for the related organotin sulfides $\{[CH_2(Me)N(CH_2)_3]SnS\}_2$[6] and $\{[Me_2N(CH_2)_3]_2SnS\}_2$.[5c] Both the solution and the solid-state ^{119}Sn chemical shifts indicate the weakest intramolecular Sn−N coordination to occur in the eight-membered *cyclo*-stannasiloxane **3**.

The ^{119}Sn NMR chemical shift in $CDCl_3$ (δ −92.4 ppm) and the ^{119}Sn MAS NMR chemical shift (δ −92.3 ppm) of the *cyclo*-stannagermoxane **7** are identical within experimental error and very close to the values of −83.5[8] and −84.3 ppm[2b] reported for *cyclo*-(t-$Bu_2SnO)_3$. In contrast to its related stannasiloxane *cyclo*-t-$Bu_2Sn(OSiPh_2)_2O$[2a,d] the stannagermoxane **7** does not react with di-*tert*-butyltin oxide to give the corresponding eight-membered stannagermoxane ring *cyclo*-[(t-$Bu_2SnO)_2(Ph_2GeO)_2$] (**7a**). One possible explanation is that compound **7** exhibits less ring strain than *cyclo*-t-$Bu_2Sn(OSiPh_2)_2O$.

Solid-State Structures of Compounds 1−4, 6, and 7. The molecular structures of **1**−**4**, **6**, and **7** are shown in Figures 1−6. Crystallographic data are given in Table 1, and selected bond lengths and bond angles are given in Tables 2 and 3. The conclusions drawn from NMR spectroscopy and molecular weight determinations concerning the ring size and Si−O−Sn connectivities in solution are confirmed by X-ray analysis. Compounds **1**, **2**, **4**, and **6** are six-membered rings which

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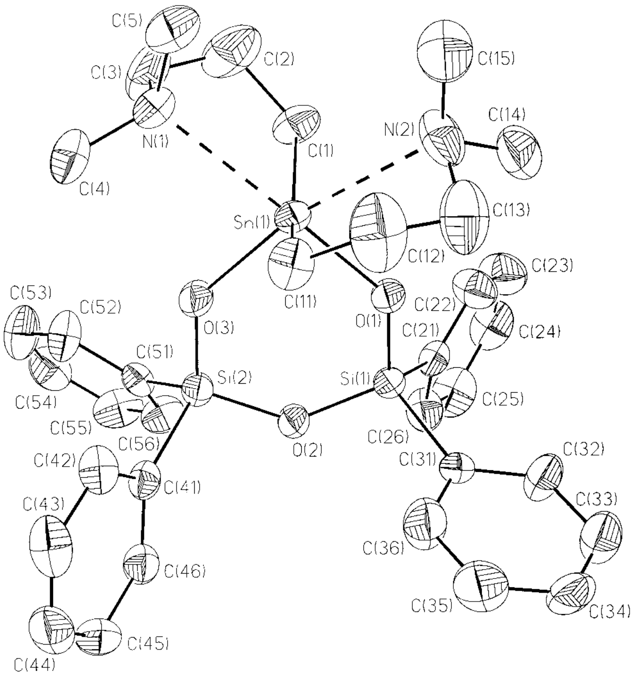

Figure 1. General view (SHELXTL-PLUS) of a molecule of **1** showing 30% probability displacement ellipsoids and the atom-numbering scheme.

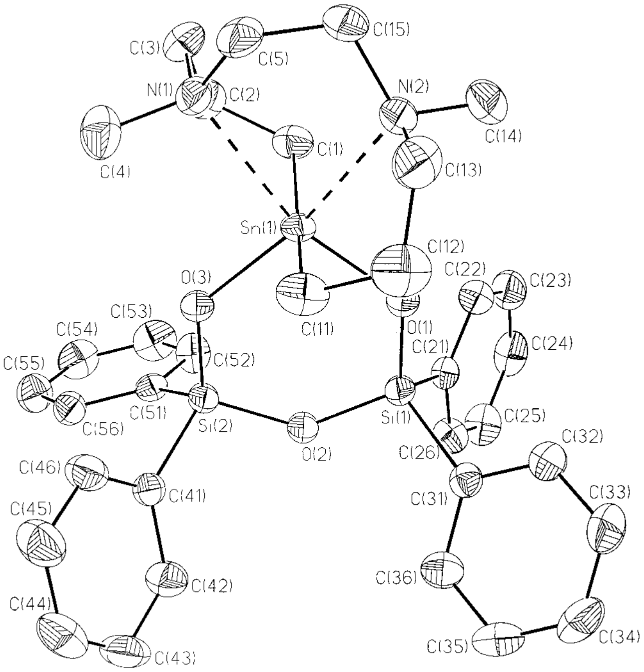

Figure 2. General view (SHELXTL-PLUS) of a molecule of **2** showing 30% probability displacement ellipsoids and the atom-numbering scheme.

can be regarded as formal derivatives of *cyclo*-$(Ph_2SiO)_3$[9a] in which one Ph_2Si unit is replaced by $Sn[(CH_2)_3NMe_2]_2$, $Sn[(CH_2)_3N(Me)CH_2]_2$, $Sn[Cp(CO)_2Fe]_2$, and Sn(*t*-Bu)-[Cp(CO)$_3$W], respectively. Eight-membered *cyclo*-stannasiloxane **3** is a formal derivative of *cyclo*-$(Ph_2SiO)_4$[9b] with two Ph_2Si units being replaced by $Sn[(CH_2)_3NMe_2]$.

The Si−O bond lengths in **1**−**4** and **6** of 1.583(3)−1.647(4) Å are as expected and are comparable with

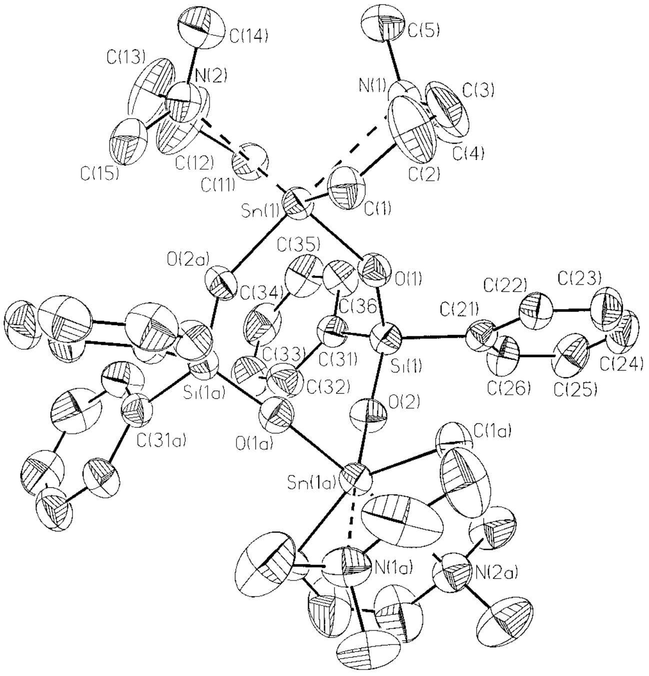

Figure 3. General view (SHELXTL-PLUS) of a molecule of **3** showing 30% probability displacement ellipsoids and the atom-numbering scheme. Symmetry transformation used to generate equivalent atoms: (a) $-x + 1$, y, $-z + 1.5$.

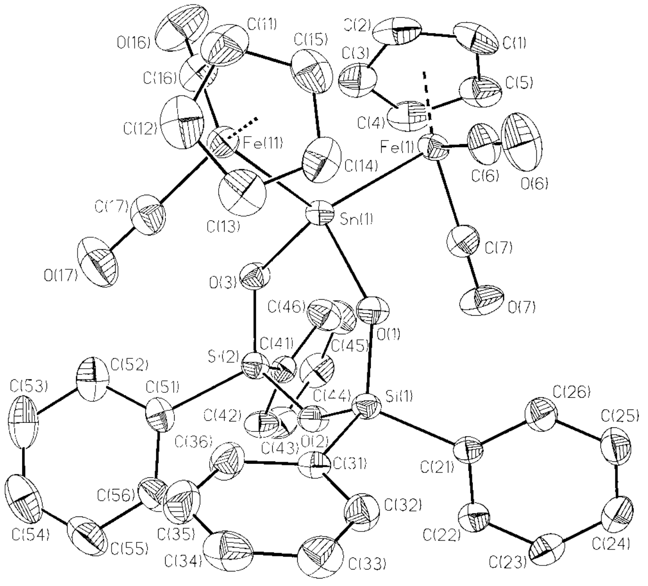

Figure 4. General view (SHELXTL-PLUS) of a molecule of **4** showing 30% probability displacement ellipsoids and the atom-numbering scheme.

those in *cyclo*-$(Ph_2SiO)_n$ ($n = 3$,[9a] $n = 4$[9b]) and in the eight-membered stannasiloxane *cyclo*-(Ph$_2$SiOSn-*t*-Bu$_2$O)$_2$.[2d]

As a result of the different substituent patterns and coordination numbers at tin the Sn−O distances in **1**−**4**, **6**, and **7** vary between 2.052(2) Å (**2**) and 1.968(2) Å (**7**), with the latter value being close to those in related *cyclo*-stannasiloxanes.[2]

In compounds **1**−**3** the tin atoms are each hexacoordinated by 2C, 2N, and 2O and adopt a distorted-octahedral configuration with the carbon atoms in mutually trans and the nitrogen and oxygen atoms in

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[9] (a) Tomlins, P. E.; Lydon, J. E.; Akrigg, D.; Sheldrick, B. *Acta Crystallogr.* **1985**, *C41*, 292. (b) Braga, D.; Zanotti, G. *Acta Crystallogr.* **1980**, *B36*, 950.

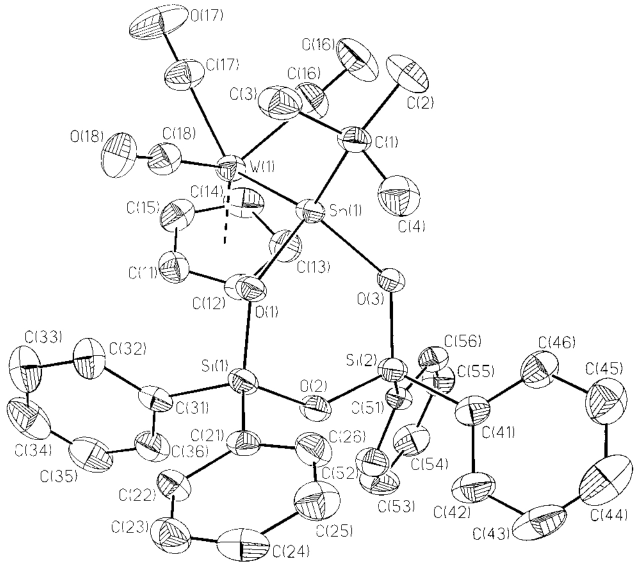

Figure 5. General view (SHELXTL-PLUS) of a molecule of **6a** showing 30% probability displacement ellipsoids and the atom-numbering scheme. The same numbering scheme applies for **6b**, the drawing of which is not shown.

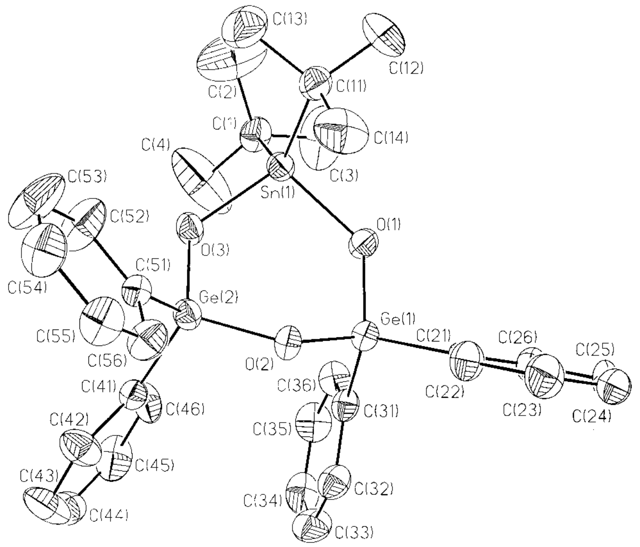

Figure 6. General view (SHELXTL-PLUS) of a molecule of **7** showing 30% probability displacement ellipsoids and the atom-numbering scheme.

cis positions. The distortions from the ideal configuration are illustrated by the deviation from 180° of the trans angles C(1)−Sn(1)−C(11) (**1**, 155.9(2)°; **2**, 167.4(1)°; **3**, 151.5(2)°), O(1)−Sn(1)−N(1) or O(2a)−Sn(1)−N(1) (**1**, 170.3(1)°; **2**, 163.65(8)°; **3**, 175.3(1)°), and O(3)−Sn(1)−N(2) or O(1)−Sn(1)−N(2) (**1**, 167.5(2)°; **2**, 164.68(8)°; **3**, 175.3(1)°). The configuration of the tin atom in **1** is very close to that of the tin atom in $[Me_2N(CH_2)_3]_2Sn(OPh)_2$.[5e] The geometry at tin in compound **2** can be best compared with those found in $[CH_2(Me)N(CH_2)_3]_2SnBr_2$[5e] and $\{[CH_2(Me)N(CH_2)_3]_2SnS\}_2$.[6]

The Sn−N distances vary between 2.508(2) Å for the six-membered *cyclo*-stannasiloxane **2** and 2.811(4) Å for the eight-membered *cyclo*-stannasiloxane **3**. They are shorter than in *cyclo*-$\{[OSn(C(Me_2)(CH_2)_3NMe_2)_2][OSiMe_2]_2\}$ (2.869(3), 2.959(4) Å).[2e]

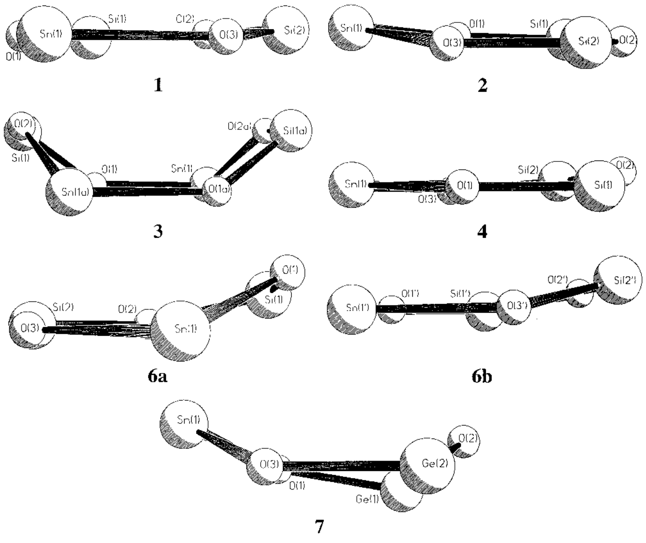

Figure 7. Side-on view of six- (**1**, **2**, **4**, **6**, **7**) and eight-membered (**3**) metallastannoxane rings.

The tin atom in **4** shows a strongly distorted tetrahedral configuration with an Fe−Sn−Fe angle of 124.57(2)° and a O−Sn−O angle of 95.8(1)°. These angles are comparable with those reported for $[Cp(CO)_2Fe]_2SnCl_2$ (128.6(3), 94.1(6)° for Cl−Sn−Cl).[7f] The deviation of the Fe−Sn−Fe angle from tetrahedral is even greater for $[Cp(CO)_2Fe]_2SnF_2{\cdot}BF_3$ (135.7(1)°).[7f] A detailed discussion on the bonding in $[Cp(CO)_2Fe]_2SnR_2$ compounds has been given.[7d,e]

The unit cell of **6** contains two independent molecules, **6a** and **6b**, which differ especially in their bond angles. As for the iron-substituted derivative **4** the configuration at tin in **6a** and **6b**, respectively, is strongly distorted, as is evidenced by the C(1)−Sn−W(1) angles of 129.0(2)° (**6a**) and 127.1(2)° (**6b**). The Sn−W distance amounts to 2.7790(5) Å (**6a**) and 2.7614(5) Å (**6b**), respectively, and fits into the range of Sn−W distances between 2.706(1)[10a] and 2.897 Å[10b] given in the Cambridge Structural Data Base for 28 entries.

In comparison with *cyclo*-t-$Bu_2Sn(OSiPh_2)_2O$, the O(1)−Sn(1)−O(3) angles in **1**, **2**, **4**, and **6** of 92.4(1), 98.27(7), 95.8(1), and 96.7(2)/97.0(2)° reduce the ring strain in these derivatives and, consequently, six-membered rings are favored over spontaneous polymerization.

Species containing the $(-OPh_2Si)_2O$ fragment are known to show a great variation of the Si−O−Si bond angle (Table 3) which in the case of cyclic derivatives can be taken as a measure for the ring strain. For the parent compounds *cyclo*-$(Ph_2SiO)_n$ ($n = 3$, 4) this angle is 132.4° ($n = 3$,[9a] average) and 160.4° ($n = 4$,[9b] average). In the strain-free open-chain stannasiloxane $(Ph_3SnOSiPh_2)_2O$[13a] this angle is 165.4°. So far, the smallest Si−O−Si angle of 127.1(1)° has been reported for *cyclo*-$PhB(OSiPh_2)_2O$.[3] To some extent it is surprising that

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Table 1. Crystallographic Data for 1−4, 6, and 7

	1	**2**	**3**	**4**	**6**	**7**
formula	$C_{34}H_{44}N_2O_3Si_2Sn$	$C_{34}H_{42}N_2O_3Si_2Sn$	$C_{44}H_{68}O_4Si_2Sn_2$	$C_{38}H_{30}Fe_2O_7Si_2Sn \cdot CH_2Cl_2$	$C_{36}H_{34}O_6Si_2SnW$	$C_{32}H_{38}Ge_2O_3Sn$
fw	703.58	701.57	1010.58	970.12	921.35	734.49
cryst syst	triclinic	triclinic	monoclinic	triclinic	triclinic	orthorhombic
cryst size, mm	0.4 × 0.18 × 0.15	0.2 × 0.15 × 0.15	0.4 × 0.2 × 0.20	0.4 × 0.2 × 0.18	0.3 × 0.2 × 0.2	0.25 × 0.15 × 0.15
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$Pbca$
a, Å	9.633(1)	9.691(1)	22.411(1)	11.188(1)	13.633(1)	16.372(1)
b, Å	10.864(1)	10.925(1)	10.459(1)	11.227(1)	16.661(1)	12.804(1)
c, Å	18.563(1)	17.895(1)	21.335(1)	18.430(1)	18.588(1)	31.140(1)
α, deg	95.515(1)	91.431(1)	90	107.957(1)	108.996(1)	90
β, deg	100.448(1)	105.624(1)	100.242(1)	92.982(1)	89.613(1)	90
γ, deg	110.634(1)	110.377(1)	90	111.412(1)	112.874(1)	90
V, Å^3	1760.7(3)	1695.6(3)	4921.2(6)	2014.5(3)	3643.3(4)	6527.8 (7)
Z	2	2	4	2	4	8
ρ_{calcd}, Mg/m^3	1.327	1.374	1.364	1.599	1.680	1.495
ρ_{measd}, Mg/m^3	1.385(5)	1.390(1)	1.406(3)	1.557(8)	1.691(2)	1.563(2)
μ, mm^{-1}	0.828	0.859	1.105	1.565	3.948	2.618
$F(000)$	728	724	2080	972	1800	2944
θ range, deg	3.20−24.72	3.49−25.74	2.79−25.64	4.17−25.68	3.42−25.75	2.81−27.87
index ranges	$-11 \le h \le 11$ $-11 \le k \le 11$ $-21 \le l \le 21$	$-11 \le h \le 11$ $-11 \le k \le 11$ $-21 \le l \le 20$	$-27 \le h \le 27$ $-11 \le k \le 11$ $-25 \le l \le 25$	$-11 \le h \le 11$ $-13 \le k \le 12$ $-22 \le l \le 22$	$-16 \le h \le 16$ $-20 \le k \le 18$ $-22 \le l \le 22$	$-21 \le h \le 21$ $-16 \le k \le 16$ $-38 \le l \le 38$
no. of rflns collcd	15 492	22 995	21 943	27 683	42 099	60 346
completeness to θ_{max}	86.1	92.5	95.8	92.7	92.3	97.9
no. of indep rflns/R_{int}	5176/0.050	6004/0.031	4441/0.047	7123/0.037	12873/0.046	7626/0.057
no. of rflns obsd with $I > 2\sigma(I)$	3130	4514	2316	5159	7780	3153
no. of refined params	385	383	259	479	831	351
GOF(F^2)	0.871	1.018	0.841	1.027	0.903	0.758
R1(F) ($I > 2\sigma(I)$)	0.0402	0.0307	0.0392	0.0394	0.0382	0.0355
wR2(F^2) (all data)	0.0811	0.0714	0.0892	0.0975	0.0794	0.0530
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001	< 0.001	0.001	0.001
largest diff peak/hole, e/Å^3	0.265/−0.347	1.156/−1.433	0.642/−0.391	0.667/−0.820	1.905 (near W(1))/−1.138	0.428/−0.296

the replacement of one Ph_2Si unit in *cyclo*-$(Ph_2SiO)_3$ by an R_2Sn unit in **1, 2**, **4**, and **6** causes the Si−O−Si angle in **2**, **4**, and **6** to increase by only 4.1, 3.0, and 2.9/3.7°, respectively, and in **1** even to decrease by 0.2°.

The stannagermoxane **7** can formally be regarded as derived from either *cyclo*-$(Ph_2GeO)_3$[11a] or *cyclo*-(*t*-$Bu_2SnO)_3$.[8] Consequently, the average Ge−O and Sn−O bond lengths in **7** of 1.765(2) and 1.973(2) Å are close to the corresponding values reported for *cyclo*-$(Ph_2GeO)_3$[12a] and *cyclo*-(*t*-$Bu_2SnO)_3$.[8] The tin atom in **7** shows a distorted-tetrahedral configuration with C(1)−Sn−C(11) and O(1)−Sn−O(3) angles of 123.6(2) and 103.43(8)°, respectively. The latter angle is smaller as compared to the corresponding angle in *cyclo*-(*t*-$Bu_2SnO)_3$.[8] The Ge(1)−O(2)−Ge(2) angle of 127.1(1)° is almost identical with the Ge−O−Ge angle in *cyclo*-$(Ph_2GeO)_3$.[11a] It seems that Ge−O−Ge angles in general are smaller than Si−O−Si angles of comparable compounds, and hence, the *cyclo*-stannagermoxane **7** is likely to have less ring strain than its stannasiloxane analogue *cyclo*-*t*-$Bu_2Sn(OSiPh_2)_2O$. This conclusion is supported by the lack of reactivity of **7** toward *cyclo*-(*t*-$Bu_2SnO)_3$.

It is worth mentioning that the compound HO-$(Ph_2GeO)_nH$ is thought to be a polymer.[11b]

The crystal structure of $Ph_3SnOGePh_3$[12] has previously been reported, but because of disorder of the metal positions only averaged bond lengths and bond angles could be given.

The SnO_3Si_2 six-membered rings in the *cyclo*-stannasiloxanes **1**, **2**, and **4** are almost planar (Figure 7) and comparable with *cyclo*-$(R_2SiO)_3$ (R = Ph,[9a] *t*-Bu[9c]) and *cyclo*-(*t*-$Bu_2SnO)_3$.[8] The maximal displacement of 0.16 Å from the ideal plane is observed for O(2) in compound **4**.

In contrast, the *cyclo*-stannasiloxane **6** as well as the *cyclo*-stannagermoxane **7** exhibit strong deviations from planarity (Figure 7), as is illustrated by the maximal displacement of O(1) by 0.612(6) Å (**6a**), of Si(2′) by 0.352(6) Å (**6b**), and of Sn(1) by 0.543(3) Å (**7**) from the planes defined by Sn(1)O(2)Si(2)O(3), Sn(1′)O(2′)Si(2′)O(3′), and O(1)O(3)Ge(2), respectively.

According to a classification scheme recently introduced[13c] and applied[2d] for eight-membered rings, compound **3** is a G-type structure.

On the basis of a sideband analysis[14] of its ^{119}Sn MAS NMR spectrum, we recently proposed that in *cyclo*-(*t*-$Bu_2SnO)_3$ an intramolecular rotation takes place in the solid state.[2b]

Because of symmetry considerations, in general, the existence of axial symmetric tensors ($\eta = 0$) can be excluded for A_2B_2-substituted tetrahedra. However, if there is such a tensor, the pseudosymmetry associated with it is a hint for mobility in general and here in particular for a rotation about the vertical molecular axis. Such a rotation is fast on the ^{119}Sn MAS NMR time scale.

To check the possibility for an intramolecular rotation in crystalline *cyclo*-stannagermoxane **7**, we recorded a

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(14) (a) The procedure of sideband analysis is made possible by a group theoretical connectivity[14b] of the local symmetry at the tin atom with the anisotropy of the chemical shift, which is expressed by the three principal tensor components δ_{11}, δ_{22}, and δ_{33} or even better by the parameters isotropic chemical shift (δ_{iso}), anisotropy ($\Delta\delta$), and asymmetry (η).[14c,d] (b) Buckingham, A. D.; Malm, S. M. *Mol. Phys.* **1971**, *22*, 1127. (c) Harris, R. K.; Lawrence, S. E.; Oh, S. W. *J. Mol. Struct.* **1995**, *347*, 309. (d) Herzfeld, J.; Chen, X. *Encyclopedia of Nuclear Magnetic Resonance*; Wiley: London, 1996; Vol. 7, p 4362, and references cited therein. (e) Eichele, K.; Wasylishen, R. E. Wsolids1, HBA 1.2, Simulation and Fitting Programs; Dalhousie University, Halifax, Canada, 1997.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 1−4, 6, and 7

	1 (E = C, M = Si, *X* = 3)	**2** (E = C, M = Si, *X* = 3)	**3** (E = C, M = Si, *X* = 2a)	**4** (E = Fe, M = Si, *X* = 3)	**6a** (M = Si, *X* = 3, E(1) = C(1), E(11) = W(1))	**6b** (M = Si, *X* = 3, E(1) = C(1), E(11) = W(1))	**7** (E = C, M = Ge, *X* = 3)
Sn(1)−O(1)	2.022(3)	2.051(2)	2.010(3)	2.024(3)	1.997(3)	1.996(4)	1.977(2)
Sn(1)−O(*X*)	2.032(3)	2.052(2)	2.011(3)	2.028(3)	2.001(4)	2.000(4)	1.968(2)
Sn(1)−E(1)	2.112(5)	2.136(3)	2.128(4)	2.5186(7)	2.188(6)	2.171(7)	2.139(4)
Sn(1)−E(11)	2.127(5)	2.137(3)	2.135(4)	2.5180(7)	2.7790(5)	2.7614(5)	2.157(4)
Sn(1)−N(1)	2.621(4)	2.518(2)	2.721(4)				
Sn(1)−N(2)	2.638(5)	2.508(2)	2.811(4)				
M(1)−O(1)	1.598(3)	1.597(2)	1.583(3)	1.601(3)	1.618(4)	1.599(4)	1.755(2)
M(1)−O(2)	1.641(3)	1.636(2)	1.601(3)	1.645(3)	1.647(4)	1.635(4)	1.776(2)
M(1)−C(21)	1.866(5)	1.863(3)	1.888(5)	1.867(4)	1.878(6)	1.872(7)	1.931(4)
M(1)−C(31)	1.854(5)	1.863(3)	1.879(4)	1.876(4)	1.849(7)	1.859(7)	1.929(4)
M(2)−O(2)	1.642(3)	1.642(2)		1.632(3)	1.633(4)	1.631(4)	1.769(2)
M(2)−O(*X*)	1.599(3)	1.595(2)		1.607(3)	1.614(4)	1.610(4)	1.760(2)
M(2)−C(41)	1.849(5)	1.863(3)		1.874(4)	1.836(7)	1.856(7)	1.935(4)
M(2)−C(51)	1.861(5)	1.873(3)		1.870(5)	1.855(6)	1.860(7)	1.914(4)
O(1)−Sn(1)−O(*X*)	92.4(1)	98.27(7)	97.4(1)	95.8(1)	96.7(2)	97.0(2)	103.43(8)
O(1)−Sn(1)−E(1)	96.1(27)	94.4(1)	98.4(2)	102.88(8)	97.4(2)	104.7(2)	107.8(1)
O(*X*)−Sn(1)−E(1)	100.6(2)	92.7(1)	99.6(2)	113.14(8)	108.5(2)	102.4(2)	103.7(1)
O(1)−Sn(1)−E(11)	99.8(2)	94.0(1)	101.5(2)	107.99(8)	110.2(1)	109.5(1)	105.3(1)
O(X)−Sn(1)−E(11)	96.7(2)	95.4(1)	98.0(2)	108.19(8)	109.7(1)	111.8(1)	111.3(1)
E(1)−Sn(1)−E(11)	155.9(2)	167.4(1)	151.5(2)	124.57(2)	129.0(2)	127.1(2)	123.6(2)
O(1)−Sn(1)−N(1)	170.3(1)	163.65(8)	82.5(1)				
O(X)−Sn(1)−N(1)	82.7(1)	95.19(8)	175.3(1)				
C(1)−Sn(1)−N(1)	76.7(2)	75.7(1)	75.8(2)				
C(11)−Sn(1)−N(1)	89.1(2)	93.9(1)	86.6(2)				
O(1)−Sn(1)−N(2)	79.1(2)	95.10(8)	175.3(1)				
O(X)−Sn(1)−N(2)	167.4(2)	164.68(8)	83.8(1)				
C(1)−Sn(1)−N(2)	89.6(2)	93.8(1)	86.0(2)				
C(11)−Sn(1)−N(2)	75.9(2)	76.2(1)	73.8(2)				
N(1)−Sn(1)−N(2)	107.0(2)	73.01(9)	96.8(2)				
O(1)−M(1)−O(2)	111.9(2)	113.2(1)	115.7(2)	111.1(1)	109.1(2)	111.1(2)	108.3(1)
O(2)−M(2)−O(3)	113.2(2)	112.4(1)		111.6(1)	112.1(2)	110.5(2)	107.70(9)
Sn(1)−O(1)−M(1)	135.9(2)	129.3(1)	144.3(2)	132.6(2)	130.1(2)	131.6(2)	125.5(1)
Sn(1)−O(3)−M(2)	134.2(2)	129.9(1)		131.9(2)	129.1(2)	130.8(2)	126.6(1)
M(1)−O(2)−M(2)	132.2(2)	136.5(1)		135.4(2)	135.3(3)	136.1(3)	127.1(1)
M(1)−O(2)−Sn(1a)			145.9(2)				
O(*X*)−Sn(1)−O(1)−M(1)	−0.2(3)	−5.6(2)	38.0(3)	3.5(2)	−30.2(3)	2.0(4)	−20.6(2)
Sn(1)−O(1)−M(1)−O(2)	−2.0(3)	2.0(2)	−74.5(4)	5.7(3)	21.0(4)	−10.9(4)	−12.6(2)
O(1)−M(1)−O(2)−Sn(1a)			−21.2(4)				
M(1)−O(2)−Sn(1a)−O(1a)			55.0(3)				
O(1)−M(1)−O(2)−M(2)	0.4(3)	1.2(2)		−14.9(3)	9.5(5)	7.1(5)	49.4(2)
M(1)−O(2)−M(2)−O(3)	3.5(3)	1.4(2)		9.8(3)	−19.7(5)	6.9(5)	−38.7(2)
O(2)−M(2)−O(3)−Sn(1)	−7.0(3)	−7.4(2)		5.4(3)	1.1(4)	−19.7(4)	−9.3(2)
M(2)−O(3)−Sn(1)−O(1)	5.3(3)	8.7(2)		−9.9(2)	17.2(3)	15.5(3)	33.6(2)

^{119}Sn MAS NMR spectrum and performed a sideband analysis according to the method of Herzfeld and Berger.[14c−e] The experimental and iteratively fitted spectra are shown in Figure 8. The asymmetry η amounts to 0.08 and differs slightly from an axial symmetric tensor. This makes likely an intramolecular rotation about the vertical axis, but unlike the one observed for *cyclo*-(t-Bu$_2$SnO)$_3$,[2b] this rotation seems to be distorted. We trace this observation to the nonplanarity of the *cyclo*-stannagermoxane **7** (Figure 7).

Conclusion

The results presented here demonstrate that the tendency to undergo spontaneous polymerization of six-membered *cyclo*-stannasiloxanes, as was observed for *cyclo*-t-Bu$_2$Sn(OSiPh$_2$)$_2$O,[2a] is controlled by the O−Sn−O angle which can be tuned by (i) electronic effects (introduction of transition-metal fragments) or (ii) by change of the coordination geometry at tin (intramolecular Sn−N coordination). Furthermore, the replacement of silicon in *cyclo*-t-Bu$_2$Sn(OSiPh$_2$)$_2$O by germanium to give *cyclo*-t-Bu$_2$Sn(OGePh$_2$)$_2$O reduces the ring strain in the latter compound and, consequently, no spontaneous polymerization of this derivative is observed.

Experimental Section

R$_2$SnCl$_2$ (R = (CH$_2$)$_3$NMe$_2$,[5b] (CH$_2$)$_3$N(Me)CH$_2$,[5a] Cp(CO)$_2$Fe,[7a] Cp(CO)$_3$W[7c]) (t-Bu$_2$SnO)$_3$,[8] and (Ph$_2$SiOH)$_2$O[15] were prepared according to literature procedures. Ph$_2$SiCl$_2$ and Ph$_2$GeCl$_2$ were purchased from Gelest. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures and were distilled prior to use.

Solution NMR spectra were recorded on a Bruker DRX 400 instrument and were referenced against SiMe$_4$ (^{1}H, ^{13}C, ^{29}Si) or SnMe$_4$ (^{119}Sn). ^{119}Sn MAS NMR spectra were obtained using a Bruker MSL 400 spectrometer using cross-polarization and high-power proton decoupling. Tetracyclohexyltin, (c-C$_6$H$_{11}$)$_4$Sn, was used as a second reference (δ −97.35 ppm) and to optimize Hartmann−Hahn CP matching conditions. To obtain sufficient signal-to-noise ratios for spinning sideband analysis, several thousand transients were accumulated (conditions:

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[15] (a) Behbehani, H.; Brisdon, B. J.; Mahon, M. F.; Molloy, K. C.; Mazhar, M. *J. Organomet. Chem.* **1993**, *463*, 41. (b) Braunstein, P.; Bender, R.; Jud, J. *Inorg. Synth.* **1989**, *26*, 341.

Table 3. Selected Bond Angles (deg) of Compounds Containing the Sequence −O−MPh$_2$−O−MPh$_2$−O−

	M−O−M	structure	ref
	M = Si		
PhB(OSiPh$_2$)$_2$O	127.1(1)	6-membered ring	3a−c
1	132.2(2)	6-membered ring	this work
(Ph$_2$SiO)$_3$ (triclinic)	131.9(3), 132.6(3), 132.8(3)	6-membered ring	9a
4	135.4(2)	6-membered ring	this work
6	135.3(3), 136.1(3)	6-membered ring	this work
2	136.5(1)	6-membered ring	this work
(Ph$_2$SiO)$_3$(PhBO)	144.74(19), 149.12(20)	8-membered ring	3c
(Ph$_2$SiO)$_3$(*t*-Bu$_2$SnO)	145.66(14), 150.6(2)	8-membered ring	2d
(Ph$_2$SiO)$_2$(*t*-Bu$_2$SnO)$_2$	150.6(2)	8-membered ring	2d
(Ph$_2$SiO)$_4$	152.8(4), 153.7(4), 167.1(5), 167.8(5)	8-membered ring	9b
(Ph$_2$SiO)$_2$(Ph$_2$Ge)$_2$O	157.9(2)	7-membered ring	13b
(Ph$_2$SiO)$_2$(Ph$_3$Sn)$_2$O	165.4	linear chain	13a
[O$_2$Cr(OSiPh$_2$)$_2$O]$_2$	169.3(1)	12-membered ring	4
[*t*-Bu$_2$Sn(OSiPh$_2$)$_2$O]$_n$	180.0	linear polymer	2a
	M = Ge		
7	127.1(1)	6-membered ring	this work
(Ph$_2$GeO)$_3$	127.7(2), 127.9(2), 130.3(2)	6-membered ring	11a
(Ph$_2$GeO)$_4$ (monoclinic)	131.2(4), 134.1(4), 136.9(4), 136.7(4)	8-membered ring	11b

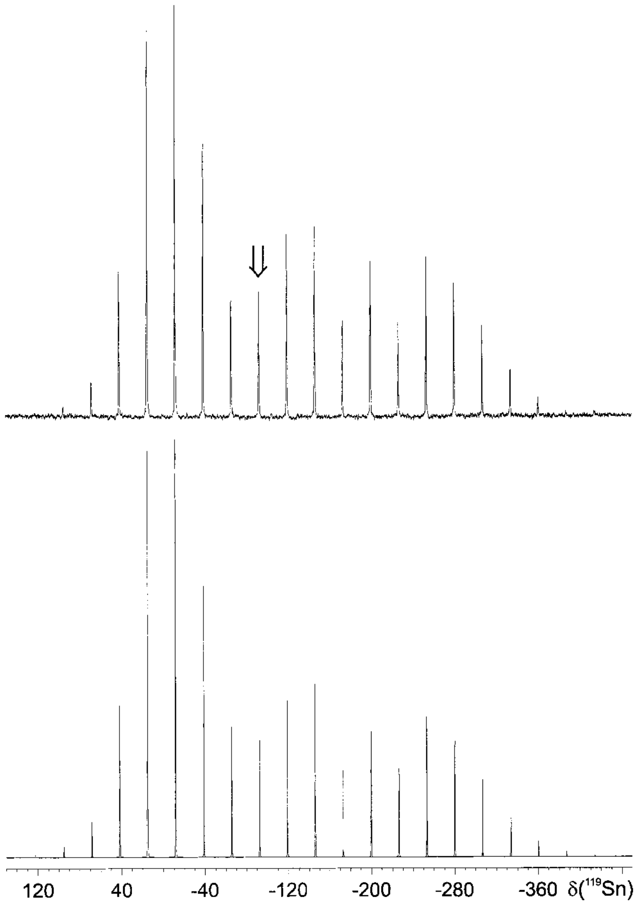

Figure 8. Experimental (above) and iteratively fitted (below) ^{119}Sn MAS NMR spectra of **7** (MAS frequency 4 kHz). The center band is indicated by an arrow.

recycle delay 4.0 s, 90° pulse 5.0 μs, contact time 3.5 ms). MAS frequencies were estimated for about 15 intensive sidebands suitable for Herzfeld−Berger analysis. The mass spectra were obtained on a Finnigan MAT 8230 spectrometer. The ions showed the expected isotopic pattern. Only tin-containing fragments are given. The IR spectra were recorded on a Bruker FTIR IFS 113v spectrometer. The density of single crystals of **1**−**4**, **6**, and **7** was determined using a Micromeritics Accu Pyc 1330.

Synthesis of *cyclo*-1,1-Bis(3-(dimethylamino)propyl)-3,3,5,5-tetraphenyl-2,4,6-trioxa-3,5-disila-1-stannacyclohexane (1). Bis(3-(dimethylamino)propyl)dichlorostannane (1.0 g, 2.76 mmol) and diphenyldichlorosilane (1.11 g, 4.38 mmol) were heated at reflux in toluene (50 mL) followed by dropwise addition of aqueous sodium hydroxide (0.87 g, 0.022 mol, 5 mL). The reaction mixture was heated at reflux for 45 min. The organic layer was separated and dried over Na$_2$SO$_4$. The solvent was evaporated in vacuo, and the residue was recrystallized from hexane to yield 0.93 g of **1** (60%) as colorless crystals, mp 158 °C.

^{1}H NMR (CDCl$_3$): δ 7.7−7.1 (m, 20H; Ph), 2.10 (t, 4H; NCH$_2$), 1.96 (s, 12H; NMe$_3$), 1.65 (q, 4H; CCH$_2$), 0.99 (t, 4H; SnCH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 140.6 (C$_i$), 134.7 (C$_o$), 134.3 (C$_m$), 127.1 (C$_p$), 59.9 (N*C*H$_2$), 45.5 (N*Me$_3$*), 21.9 (*C*H$_2$), 20.7 (Sn*C*H$_2$). ^{29}Si{^{1}H} NMR (CDCl$_3$): δ −39.2 (^2J (^{29}Si−O−$^{117/119}$Sn) = 32 Hz). ^{119}Sn{^{1}H} NMR (CDCl$_3$): δ −255.0. ^{119}Sn MAS NMR: δ_{iso} −290.8. MS: *m*/*z* (%) 703 (5) [C$_{34}$H$_{43}$N$_2$O$_3$Si$_2$Sn$^+$], 618 (23) [C$_{29}$H$_{32}$NO$_3$Si$_2$Sn$^+$], 455 (10) [C$_{18}$H$_{15}$O$_3$Si$_2$Sn$^+$], 377 (5) [C$_{12}$H$_{10}$O$_3$Si$_2$Sn$^+$], 206 (6) [C$_5$H$_{12}$NSn$^+$]. Anal. Calcd for C$_{34}$H$_{44}$N$_2$O$_3$Si$_2$Sn (703.64): C, 58.04; H, 6.30; N, 3.98. Found: C, 58.54; H, 7.20; N, 3.93. MW (10 mg mL^{-1} of CHCl$_3$): 718.

Synthesis of *cyclo*-1,4-Dimethyl-10,12-tetraphenyl-1,4-diaza-9,11,13-trioxa-10,12-disila-8-stannatetracyclo[3.2.3.5]-tridecane (2). 1,4-Dimethyl-8,8-dibromo-1,4-diaza-8-stannatricyclo[3.2.3]undecane (820 mg, 1.827 mmol) and diphenyldichlorosilane (1.15 g, 3.690 mmol) were heated in refluxing toluene (80 mL). Aqueous NaOH (450 mg, 0.011 mol, 5 mL) was added dropwise, and the mixture was magnetically stirred for 45 min. After separation of the layers the organic phase was dried over Na$_2$SO$_4$ and the solvent was evaporated in vacuo. The precipitate was recrystallized from *n*-hexane to afford 745 mg of **2** (58%) as colorless crystals, mp 210 °C.

^{1}H NMR (CDCl$_3$): δ 7.6−7.2 (m, 20H, Ph), 2.74 (m, 2H; NCH$_2$), 2.57 (m, 2H; NCH$_2$), 2.53 (s, 12H; NCH$_3$), 2.43 (m, 2H; NCH$_2$C), 2.25 (m, 2H; NCH$_2$C), 1.93 (m, 2H; CCH$_2$), 1.73 (m, 2H; CCH$_2$), 1.08 (m, 2H; SnCH$_2$), 0.88 (m, 2H; SnCH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 140.6 (C$_i$), 134.5 (C$_o$), 134.4 (C$_m$), 127.1 (C$_p$), 57.4 (N*C*H$_2$), 55.3 (NCH$_2$*C*), 45.3 (N*C*H$_3$), 22.7 (C*C*H$_2$), 21.73 (Sn*C*H$_2$). ^{29}Si{^{1}H} NMR (CDCl$_3$): δ −41.0 (^2J (^{29}Si−O−$^{117/119}$Sn) = 29 Hz). ^{119}Sn{^{1}H} NMR (CDCl$_3$): δ −273.5. ^{119}Sn MAS NMR: δ_{iso} −290.2. MS: *m*/*z* (%) 701 (1) [*M*$^+$], 687 (1) [C$_{33}$H$_{39}$N$_2$O$_3$Si$_2$Sn$^+$], 532 (2) [C$_{24}$H$_{20}$O$_3$Si$_2$Sn$^+$], 455 (10) [C$_{16}$H$_{27}$N$_2$O$_2$Si$_2$Sn$^+$]. Anal. Calcd for C$_{34}$H$_{42}$N$_2$O$_3$Si$_2$Sn (701.63): C, 58.20; H, 6.03; N, 3.99. Found: C, 58.20; H, 6.27; N, 4.09. MW (10 mg mL^{-1} of CHCl$_3$): 646.

Synthesis of *cyclo*-1,1,5,5-Tetrakis(3-(dimethylamino)-propyl)-3,3,7,7-tetraphenyl-2,4,6,8-tetraoxa-3,7-disila-1,5-distannacyclooctane (3). Aqueous NaOH (0.54 g, 0.014 mol, 5 mL) was added dropwise to a refluxing solution of bis(3-(dimethylamino)propyl)dichlorostannane (1.18 g, 3.26 mmol) and diphenyldichlorosilane (0.41 g, 1.62 mmol) in toluene (50 mL). After 45 min of heating at reflux, the organic layer was separated and dried over Na_2SO_4. After evaporation of the solvent the residue was recrystallized from *n*-hexane to afford 0.67 g of **3** (82% with respect to Ph_2SiCl_2) as colorless crystals, mp 137 °C.

^{1}H NMR ($CDCl_3$): δ 7.1−7.6 (m, 20H; Ph), 2.11 (t, 8H; NC*H*$_2$), 1.96 (s, 24H; NC*H*$_3$), 1.65 (q, 8H; CC*H*$_2$), 0.99 (t, 8H; SnC*H*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.7 (C_i), 135.1 (C_o), 127.5 (C_m), 126.6 (C_p), 60.7 (N*C*H$_2$), 45.7 (N*C*H$_3$), 22.1 (C*C*H$_2$), 19.7 (Sn*C*H$_2$). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −224 ($^2J(^{119}Sn-O-^{29}Si)$ = 53 Hz). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −47 ($^2J(^{29}Si-O-^{117/119}Sn)$ = 53 Hz). ^{119}Sn MAS NMR: δ_{iso} −252.5. MS: *m*/*z* (%) 641 (3) [$C_{24}H_{20}O_4SiSn_2^+$], 618 (6) [$C_{15}H_{36}N_3O_4Si_2Sn_2^+$], 507 (21) [$C_{22}H_{34}N_2O_2SiSn^+$], 455 (5) [$C_{18}H_{15}O_3Si_2Sn^+$], 206 (7) [$C_5H_{12}NSn^+$]. Anal. Calcd for ($C_{44}H_{68}N_4O_4Si_2Sn_2$): C, 52.03; H, 6.84; N, 5.52. Found: C, 52.60; H, 7.21; N, 5.61. MW (10 mg mL^{-1} of $CHCl_3$): 867.

Synthesis of *cyclo*-1,1-Bis((η^5-cyclopentadienyl)dicarbonyliron)-3,3,5,5-tetraphenyl-1,4,5-trioxa-3,5-disila-1-stannacyclohexane (4). To a stirred solution of $(Ph_2SiOH)_2O$ (365 mg, 0.88 mmol) and NEt_3 (0.25 mL, 1.76 mmol) in Et_2O (50 mL) was added a solution of $[Cp(CO)_2Fe]_2SnCl_2$ (478 mg, 0.88 mmol) in Et_2O (50 mL) slowly through a dropping funnel. After a few minutes, precipitation of $[HNEt_3]Cl$ was observed. The reaction mixture was stirred overnight at room temperature. $[HNEt_3]Cl$ was filtered, leaving a yellow solution. The solvent was removed under reduced pressure to afford **4** as orange-brown crystals (710 mg, 0.80 mmol, 91%), mp 169−173 °C.

^{1}H NMR (C_6D_6): δ 8.1−7.1 (m, Ph; 20H), 4.2 (s, Cp; 10H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 212.5 (*C*O); 138.8 (C_i), 134.4 (C_o), 129.1 (C_p), 127.4 (C_m), 82.7 (*Cp*). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −39.7 (^2J ($^{29}Si-O-^{119}Sn$) = 39.6 Hz). $^{119}Sn\{^1H\}$ NMR (C_6D_6): δ 359.6. IR (KBr): ν_{CO} 2007, 1982, 1958, 1935 cm^{-1}. MS: *m*/*z* (%) 652 (95) [$M^+ - C_9H_5FeO_4$], 904 (21) [$M^+ - C_6H_7C_{l2}$], 850 (21) [$M^+ - C_8H_5Cl_2O_2$]. Anal. Calcd for $C_{38}H_{30}O_7Fe_2Si_2Sn$ (885.26): C, 51.56; H, 3.42. Found: C, 51.55; H, 3.60. MW (10 mg mL^{-1} of C_6H_6): 924.

Synthesis of *cyclo*-1,1-Bis((η-cyclopentadienyl)tricarbonyltungsten)-3,3,5,5-tetraphenyl-1,4,5-trioxa-3,5-disila-1-stannacyclohexane (5). To a stirred solution of $(Ph_2SiOH)_2O$ (339 mg, 0.82 mmol) and NEt_3 (0.23 mL, 1.64 mmol) in Et_2O (50 mL) was added a solution of $[Cp(CO)_3W]_2SnCl_2$ (700 mg, 0.82 mmol) in Et_2O (50 mL) slowly through a dropping funnel. After a few minutes precipitation of $[HNEt_3]Cl$ was observed. The reaction mixture was stirred overnight at room temperature. $[HNEt_3]Cl$ was filtered, giving an orange solution. The solvent was removed under reduced pressure to afford an orange solid (940 mg, 0.78 mmol, 95%), mp 194−197 °C.

^{1}H NMR (C_6D_6): δ 7.8−7.3 (m, 20H; Ph), 5.1 (s, 10H; Cp). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 216.7 (*C*O), 214.2 (*C*O), 138.9 (C_i), 134.3 (C_o), 129.3 (C_p), 127.6 (C_m), 89.8 (*Cp*). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −40.1 (^2J ($^{29}Si-O-^{117/119}Sn$) = 43 Hz). $^{119}Sn\{^1H\}$ NMR (C_6D_6): δ 114.8 ($^1J(^{119}Sn-^{183}W)$ = 428 Hz). IR (KBr): ν_{CO} 2018, 1995, 1914 cm^{-1}. MS: *m*/*z* (%) 864 (4) [$M^+ - C_9H_5O_3W$], 853 (14) [$M^+ - C_{22}H_{20}O_2Si$], 825 (15) [$M^+ - C_{23}H_{20}O_3Si$], 797 (22) [$M^+ - C_{24}H_{20}O_4Si$], 780 (7) [$M^+ - C_{12}H_5O_6W$]. Anal. Calcd for $C_{40}H_{30}O_9Si_2SnW_2$ (1197.27): C, 40.13; H, 2.53. Found: C, 40.02; H, 2.41. MW (10 mg mL^{-1} of C_6H_6): 1241.

Synthesis of 1-*tert*-Butyl-1-((η^5-cyclopentadienyl)tricarbonyltungsten)diphenyltin, (*t*-Bu)[Cp(CO)$_3$W]SnPh$_2$. To a stirred solution of Na[W(CO)$_3$Cp]·2DME [15b] (5.0 g, 9.32 mmol) in thf (100 mL) was added a solution of Ph_2Sn(*t*-Bu)I (4.26 g, 9.32 mmol) in thf (20 mL) through a dropping funnel at −78 °C. The reaction mixture was warmed to room temperature and was stirred overnight. From the clear yellow solution the thf was removed at reduced pressure, and toluene (50 mL) was added to the residue. The reaction mixture was stirred for 1 h. After filtration of NaI 90% of the solvent was removed under reduced pressure. *n*-Hexane (5 mL) was added, and the solution was kept in a refrigerator to give a yellow crystalline solid (5.14 g, 7.75 mmol, 83%), mp 163−165 °C.

^{1}H NMR (C_6D_6): δ 7.6−7.2 (m, 10H; Ph), 5.2 (s, 5H; Cp), 1.3 (s, 9H, *t*-Bu) ($^3J(^1H-^{117/119}Sn)$ = 80 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 218.6 ($^1J(^{13}C-^{183}W)$ = 149 Hz, $^2J(^{13}C-^{117/119}Sn)$ = 24 Hz, *C*O), 215.2 ($^1J(^{13}C-^{183}W)$ = 154 Hz, $^2J(^{13}C-^{117/119}Sn)$ = 120/125 Hz, *C*O), 144.1 ($^1J(^{13}C-^{117/119}Sn)$ = 286/299 Hz, C_i), 137.6 ($^2J(^{13}C-^{117/119}Sn)$ = 31 Hz, C_o), 128.8 (C_p), 128.6 ($^3J(^{13}C-^{117/119}Sn)$ = 39 Hz, C_m), 89.0 (Cp), 33.0 ($^1J(^{13}C-^{117/119}Sn)$ = 379/395 Hz, *C*Me$_3$), 32.7 ($^2J(^{13}C-^{117/119}Sn)$ = 31 Hz, C*Me*$_3$). $^{119}Sn\{^1H\}$ NMR (C_6D_6): δ −11.2 ($^1J(^{119}Sn-^{183}W)$ = 214 Hz). IR (KBr): ν_{CO} 1983, 1871 cm^{-1}. Anal. Calcd for $C_{24}H_{24}O_3SnW$ (663.05) C, 43.48; H, 3.65. Found: C, 43.21; H, 3.52.

Synthesis of 1-*tert*-Butyl-1-((η^5-cyclopentadienyl)tricarbonyltungsten)tin Dichloride, (t-Bu)[Cp(CO)$_3$W]SnCl$_2$. (Cp(CO)$_3$W)(*t*-Bu)SnPh$_2$ (2.5 g, 3.7 mmol) was dissolved in CH_2Cl_2 (30 mL). Dry HCl gas was bubbled through the reaction mixture for 90 min. The insoluble precipitate was filtered. The solvent was removed under reduced pressure, and the remaining yellow oil was dissolved in CH_2Cl_2/hexane (20 mL, 1/1). The solution was kept in a refrigerator to give a yellow crystalline solid (1.7 g, 2.93 mmol, 77%), mp 107−109 °C.

^{1}H NMR (C_6D_6): δ 5.7 (s, 5H, Cp), 1.4 (s, 9H, *t*-Bu) ($^3J(^1H-^{117/119}Sn)$ = 123/129 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 215.1 ($^1J(^{13}C-^{183}W)$ = 141 Hz, $^2J(^{13}C-^{117/119}Sn)$ = 40 Hz, *C*O), 212.4 ($^1J(^{13}C-^{183}W)$ = 146 Hz, $^2J(^{13}C-^{117/119}Sn)$ = 164/172 Hz, *C*O), 89.5 (*Cp*), 48.3 ($^1J(^{13}C-^{117/119}Sn)$ = 404/385 Hz, *C*Me$_3$), 28.1 (C*Me*$_3$). $^{119}Sn\{^1H\}$ NMR (C_6D_6): δ 211.8 ($^1J(^{119}Sn-^{183}W)$ = 492 Hz). IR (KBr): ν_{CO} 2017, 1944, 1918 cm^{-1}. MS: *m*/*z* (%) 579 (4) [M^+], 522 (8) [$M^+ - C_4H_9$]. Anal. Calcd for $C_{12}H_{14}O_3Cl_2SnW$ (579.73): C, 24.86; H, 2.43. Found: C, 24.54; H, 2.41.

The identity of (*t*-Bu)[Cp(CO)$_3$W]SnCl$_2$ was further confirmed by an X-ray analysis.[16]

Synthesis of *cyclo*-1-*tert*-Butyl-1-((η^5-cyclopentadienyl)-tricarbonyltungsten)-3,3,5,5-tetraphenyl-1,4,5-trioxa-3,5-disila-1-stannacyclohexane (6). To a stirred solution of $(Ph_2SiOH)_2O$ (500 mg, 1.21 mmol) and NEt_3 (0.34 mL, 2.42 mmol) in Et_2O (100 mL) was added a solution of [Cp(CO)$_3$W](*t*-Bu)SnCl$_2$ (700 mg, 1.21 mmol) in Et_2O (50 mL) slowly through a dropping funnel. After a few minutes precipitation of $[HNEt_3]Cl$ was observed. The reaction mixture was stirred overnight at room temperature. $[HNEt_3]Cl$ was filtered, giving a pale orange solution. The solvent was removed under reduced pressure to afford a pale orange solid (990 mg, 1.07 mmol, 91%), mp 183−189 °C.

^{1}H NMR (C_6D_6): δ 7.8−7.2 (m, 20H; Ph), 5.0 (s, 5H; Cp), 1.2 (s, $^3J(^1H-^{117/119}Sn)$ = 110/115 Hz, 9H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 215.7 ($^1J(^{13}C-^{183}W)$ = 143 Hz, $^2J(^{13}C-^{117/119}Sn)$ = 39 Hz, *C*O), 212.7 ($^1J(^{13}C-^{183}W)$ = 147 Hz, $^2J(^{13}C-^{117/119}Sn)$ = 179/188 Hz, *C*O), 138.7 ($^1J(^{13}C-^{29}Si)$ = 94 Hz, C_i), 138.0 $^1J(^{13}C-^{29}Si)$ = 96 Hz, C_i), 134.2 (C_o), 129.4 (C_p), 129.3 (C_p), 127.6, 127.4 (C_m), 88.8 (*Cp*), 46.0, (*C*Me$_3$), 28.5 (C*Me*$_3$). $^{29}Si\{^1H\}$ NMR ($CH_2Cl_2/D_2O_{capillary}$): δ −39.0 (^2J ($^{29}Si-O-^{117/119}Sn$) = 38 Hz, $^1J(^{29}Si-^{13}C_i)$ = 94.5 Hz). $^{119}Sn\{^1H\}$ NMR ($CH_2Cl_2/D_2O_{capillary}$): δ 71.5 ($^1J(^{119}Sn-^{183}W)$ = 451 Hz, $^2J(^{119}Sn\text{-}^{29}Si)$ = 38 Hz, $^2J(^{119}Sn-^{13}CO)$ = 188 Hz). IR (KBr): ν_{CO} 2009, 1946, 1934, 1919, 1899 cm^{-1}. MS: *m*/*z* (%) 863 (96) [$M^+ - C_4H_9$], 779 (99) [$M^+ - C_7H_{10}O_3$], 703 (14, $M^+ - C_{13}H_{15}O_3$]). Anal. Calcd for $C_{36}H_{34}O_6Si_2SnW$ (921.41): C, 46.93; H, 3.72. Found: C, 47.10; H, 4.10. MW (24 mg mL^{-1} of C_6H_6): 918.

Synthesis of *cyclo*-1,1-Di-*tert*-butyl-3,3,5,5-tetraphenyl-1,4,5-trioxa-3,5-digerma-1-stannacyclohexane (7). To a mixture of *cyclo*-(*t*-Bu$_2$SnO)$_3$ (747 mg, 1.0 mmol), NEt_3 (1.22 g, 12.0 mmol), and H_2O (108 mg, 6.0 mmol) in toluene (50 mL) was added dropwise with magnetic stirring a solution of Ph_2GeCl_2 (1.79 g, 6.0 mmol) in toluene (10 mL). Immediate precipitation of $[HNEt_3]Cl$ took place. After 15 h the latter was filtered and the solvent was evaporated in vacuo. The solid

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[16] Kaltenbrunner, U.; Schürmann, M.; Jurkschat, K. Submitted for publication in *Z. Kristallogr.*

residue was recrystallized form hexane to afford colorless crystals (1.39 g, 1.89 mmol, 63%), mp 126 °C.

^{1}H NMR (CDCl$_3$): δ 7.7−7.2 (m, 20H, Ph), 1.31 (s, $^3J(^1\text{H}-\text{CC}-^{119}\text{Sn}) = 98.1$ Hz, 18H; *t*-Bu). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 137.8 (C_i), 133.6 (C_o), 129.9 (C_m), 127.9 (C_p), 39.7 (s, $^1J(^{13}\text{C}-^{119}\text{Sn}) = 476$ Hz; *C*Me$_3$), 30.1 (s, C*Me$_3$*). ^{119}Sn{^{1}H} NMR (CDCl$_3$): δ −92.4. ^{119}Sn MAS NMR: δ_{iso} −92.3 (δ_{11}, 42.4; δ_{22}, 22.1; δ_{33}, −342.5; $\Delta\delta$, −374.8; η, 0.08). MS: *m*/*z* (%) 676 (22) [$M^+ - C_4H_{10}$], 620 (90) [$M^+ - C_8H_{18}$], 542 (65) [$M^+ - C_{14}H_{25}$]. Anal. Calcd for $C_{32}H_{38}Ge_2O_3Sn$ (734.65): C, 52.32; H, 5.21. Found: C, 52.40; H, 5.40. MW (10 mg mL^{-1} of CHCl$_3$): 776.

NMR Scale Reaction of 7 with *cyclo*-(*t*-Bu$_2$SnO)$_3$. A mixture of **7** (73.5 mg, 0.1 mmol) and *cyclo*-(*t*-Bu$_2$SnO)$_3$ (24.9 mg, 0.033 mmol) in CDCl$_3$ (300 μL) was heated to 60 °C for 2 days to give a clear solution. ^{119}Sn NMR spectroscopy showed that no reaction had occurred.

Crystallography. Intensity data for the colorless crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα (0.710 69 Å) radiation at 291 K. The data collection covered the whole sphere of reciprocal space with 360 frames via ω-rotation ($\Delta/\omega = 1°$) at two times 5 s (**4**, **6**), 10 s (**3**, **7**), 20 s (**1**), and 25 s (**2**) per frame. The crystal-to-detector distance was 2.7 cm (**1**−**4**, **6**, **7**). Crystal decay was monitored by repeating the initial frames at the end of data collection. The data were not corrected for absorption effects. From an analysis of the duplicate reflections, there was no indication for any decay. The structure was solved by direct methods (SHELXS97[17a]) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (SHELXL97[17b]).

The H atoms were placed in geometrically calculated positions and refined with common isotropic temperature factors for different C−H types (C−H$_{\text{prim}}$ = 0.96 Å, C−H$_{\text{sec}}$ = 0.97 Å, $U_{\text{iso}} = 0.128(5)$ (**1**), 0.088(3) (**2**), 0.201(7) (**3**), 0.141(8) (**6**), 0.152(5) Å^2 (**7**); H$_{\text{aryl}}$ C−H = 0.93 Å, $U_{\text{iso}} = 0.090(4)$ (**1**), 0.085(3) (**2**), 0.088(5) (**3**), 0.077(3) (**4**), 0.083(3) (**6**), 0.081(3) Å^2 (**7**)). For the solvent molecule CH$_2$Cl$_2$ (**4**) the atomic displacement parameters were fixed to 1.5 times those of the C atoms.

Disordered atoms were found for **1**: C(13) (sof 0.7), C(13′) (sof 0.3), and C(15) and C(15′) (sof 0.5). Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 17c. The figures were created by SHELXTL-Plus.[17d] Crystallographic data are given in Table 1 and selected bond distances and angles for **1**−**4**, **6**, and **7** in Table 2.

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Supporting Information Available: Tables giving atomic coordinates, thermal parameters, bond distances and angles, and least-squares planes for **1**−**4**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980790+

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