328 *Organometallics* **2003,** *22,* 328−336

Novel 10- and 20-Membered Tin- and Silicon-Containing Rings: Synthesis, Complexation Behavior, and Conversion into a Lewis Acidic Polymer[†,‡]

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Received September 9, 2002

Reaction of the dimethylsilylmethyl-substituted tetraorganotin derivative $CH_2[CH_2Sn(Ph_2)CH_2Si(H)Me_2]_2$ (**1**) and $CH_2[CH_2Sn(Ph_2)CH_2Si(i\text{-}PrO)Me_2]_2$ (**3**), respectively, with mercuric chloride afforded the novel silicon- and tin-containing 10- and 20-membered rings *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**4**) and *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)CH_2]_2CH_2$ (**5**). Both compounds **4** and **5** can be converted into the soluble Lewis acidic polymer poly-$[Si(Me_2)CH_2Sn(Cl_2)(CH_2)_3Sn(Cl_2)CH_2Si(Me_2)O]$ (**8**). ^{119}Sn NMR studies indicate that **4** acts as a bidentate Lewis acid toward chloride ions, exclusively forming the 1:1 complex [*cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O{\cdot}Cl]^-[(Ph_3P)_2N]^+$ (**7**). The molecular structures as determined by single-crystal X-ray diffraction analysis of **4** and **7** are reported.

Introduction

The selective complexation of anions and neutral donor molecules by molecular hosts has become a subject of growing interest, and the results achieved so far have been extensively reviewed.[1] One concept for the design of tailor-made receptors is the synthesis of bi-, tri-, or multidentate Lewis acids containing elements such as B,[2] Al,[3a,b] Ga,[3c] In,[4] Si,[5] Ge,[6] Sn,[7] and Hg.[8]

Our interest in this area has mainly focused on the synthesis and complexation studies of open-chain and

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[†] Dedicated to Prof. H.-P. Abicht on the occasion of his 60th birthday.

[‡] This paper contains part of the Ph.D. thesis of M. Schulte, Universität Dortmund, 2000. Part of this work was first presented at the Xth International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin, and Lead, July 8-12, 2001, Bordeaux, France, Book of Abstracts IL9, and at the 222nd ACS National Meeting, Chicago, Il, August 26−30, 2001, Division of Inorg. Chem., Book of Abstracts 504.

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10.1021/om020740b CCC: $25.00 © 2003 American Chemical Society
Publication on Web 12/14/2002

cyclic organotin-based[7d,e,k−r,v] Lewis acids, and, more recently, tin- as well as silicon-containing rings[7s−u] have been included in these studies. An interesting aspect of our investigations is the observation[7o,v] that bis(phenyldichlorostannyl)methane, $CH_2[Sn(Cl_2)Ph]_2$,[9] when incorporated into a polyethylene matrix, exhibits a remarkably high selectivity toward dihydrogen phosphate. However, the ion-sensitive electrode based on this organotin compound showed a rather short lifetime, due to leaching of the carrier from the membrane. One possible strategy to overcome this shortcoming is the incorporation of the $Sn(Cl_2)CH_2Sn(Cl_2)$ fragment into a polymer. In earlier work we synthesized the eight-membered rings *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$[7u] and *cyclo*-$CH_2[Sn(Ph_2)CH_2Si(Me_2)]_2O$[7u] but failed to achieve their ring-opening polymerization. In continuation of this earlier work we now report the synthesis of the 10- and 20-membered rings *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ and *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)CH_2]_2CH_2$, respectively, and explore their potential to undergo ring-opening polymerization.

Results and Discussion

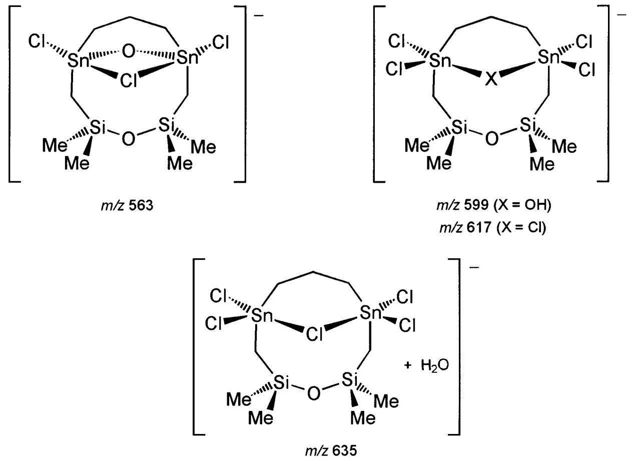
The reaction of 1,3-bis(diphenylfluorostannyl)propane,[10] $CH_2[CH_2Sn(F)Ph_2]_2$, and bis(diphenylfluorostannyl)methane,[7p] $CH_2[Sn(F)Ph_2]_2$, with 2 molar equiv of the Grignard reagent $Me_2(H)SiCH_2MgCl$[11] provided the organosilylmethyl-substituted organotin compounds $CH_2[CH_2Sn(Ph_2)CH_2Si(H)Me_2]_2$ (**1**) and $CH_2[Sn(Ph_2)CH_2Si(H)Me_2]_2$ (**2**), respectively (eq 1). The reaction of $CH_2[CH_2Sn(F)Ph_2]_2$ with 2 molar equiv of the Grignard reagent $Me_2(i\text{-PrO})SiCH_2MgCl$[12] gave the corresponding organotin derivative $CH_2[CH_2Sn(Ph_2)CH_2Si(i\text{-PrO})Me_2]_2$ (**3**) (eq 1). Compounds **1**−**3** are colorless oils that were obtained in almost quantitative yield.

$$Ph_2FSn(CH_2)_nSnFPh_2 \xrightarrow[-2\ \text{"MgClF"}]{2\ RMgCl} Ph_2RSn(CH_2)_nSnRPh_2 \qquad (1)$$

1, R = $Me_2(H)SiCH_2$, $n = 3$
2, R = $Me_2(H)SiCH_2$, $n = 1$
3, R = $Me_2(i\text{-PrO})SiCH_2$, $n = 3$

Treatment of $CH_2[CH_2Sn(Ph_2)CH_2Si(H)Me_2]_2$ (**1**) with 4 molar equiv of mercuric chloride in acetone gave a crude reaction product, the ^{119}Sn NMR spectrum ($CDCl_3$) of which showed two major signals at δ 115.9 (signal a) and 110.2 (signal b) with an integral ratio of about 1:1 and four minor resonances at δ 118.2, 114.8, 107.5, and 81.9 (total integral approximately 15% of the major signals). The ^{29}Si NMR spectrum of the same sample displayed signals at δ 12.3 ($^2J(^{29}Si-^{117/119}Sn) = 36$ Hz) (signal c), 10.4 ($^2J(^{29}Si-^{117/119}Sn) = 31$ Hz) (signal d), 9.2, 8.6, 8.3, and −3.2. On the basis of coupling data, the signals (a) and (c) are assigned to the 10-membered ring *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**4**) and the signals (b) and (d) to the 20-membered ring *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)CH_2]_2CH_2$ (**5**). No assignment was made for the other minor intense signals.

Chart 1



m/z 563

m/z 599 (X = OH)
m/z 617 (X = Cl)

m/z 635

Compounds **4** and **5** were isolated from the reaction mixture in moderate yield by combination of fractional crystallization and size exclusion chromatography. The 10-membered ring **4** is a colorless crystalline solid that is soluble in dichloromethane, chloroform, diethyl ether, and thf, but almost insoluble in *n*-hexane. The 20-membered ring **5** is a colorless amorphous solid that is soluble in acetone, less soluble in dichloromethane and chloroform, and almost insoluble in diethyl ether and *n*-hexane.

Both the 10- and 20-membered rings **4** and **5** have been characterized by standard analytical methods such as elemental analysis, multinuclear NMR spectroscopy (see Experimental Section), and single-crystal X-ray analysis (compound **4**, see below). The identity of the 10- and 20-membered ring structures in solution has been further confirmed by molecular weight measurements (see Experimental Section) and electrospray mass spectrometry (ESMS). Thus, the negative ion electrospray mass spectrum of a solution of compound **4** in acetonitrile exhibits the four major isotopic cluster patterns shown in Chart 1, and the spectrum taken from compound **5** under the same conditions shows an isotopic cluster pattern centered at $m/z = 1199$, which corresponds to $[\mathbf{5}\cdot Cl]^-$.

Notably, the ESMS spectrum of the 10-membered ring *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**4**) also shows isotopic cluster patterns corresponding to ionized dimers and trimers of **4**, a possible hint at the ability of **4** to undergo ring-opening polymerization (see below).

Although no detailed studies concerning the mechanism for the formation of compounds **4** and **5** have been performed, the following reaction sequence appears plausible. In the first step, mercuric chloride cleaves the tin−phenyl bonds to give the diorganotin dichloro

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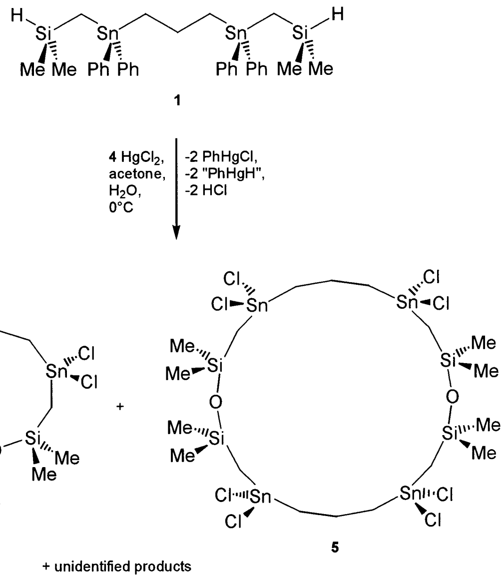
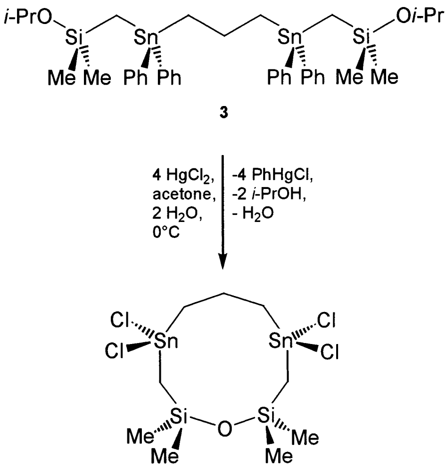
(12) Dow Corning Corp., US Patent, 1959.

Scheme 1



derivative $CH_2[CH_2Sn(Cl_2)CH_2Si(H)Me_2]_2$ (**1a**) and phenylmercury chloride, PhHgCl. Half of the latter reacts with the silane fuctionalities of **1a** to give PhHgH, which decomposes into benzene and mercury, and $CH_2[CH_2Sn(Cl_2)CH_2Si(Cl)Me_2]_2$ (**1b**), which, in the presence of water and remaining PhHgCl, hydrolyzes and condenses to form the siloxane bridge-containing compounds **4** and **5**. This view is supported by the observation (i) that only $HgCl_2$ and not PhHgCl cleaves two phenyl groups from a diphenyldiorganostannane and that no tin−phenyl bond was left in the reaction shown in Scheme 1, (ii) that PhHgCl is able to cleave the Si−H bond in a triorganosilane, and (iii) that formation of mercury was indicated by the gray color of the reaction mixture, and (iv) that only half of the amount of PhHgCl to be expected from the first reaction step has been isolated.

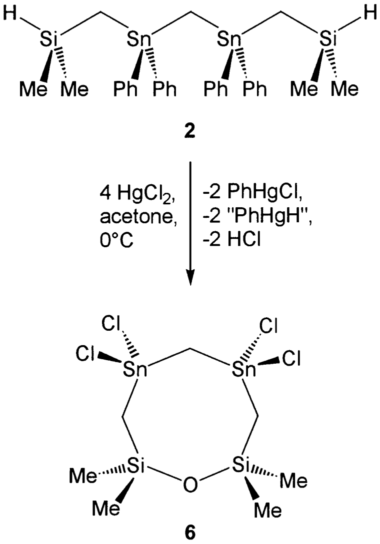
Alternatively and similar to the synthesis of the eight-membered ring *cyclo*-$CH_2[Sn(Cl_2)CH_2SiMe_2]_2O$ (**6**),[7u] the 10-membered ring *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**4**) has also been prepared by reaction of the dimethylisopropoxysilylmethyl-substituted tetraorganostannane derivative **3** with mercuric chloride (eq 2).



(2)

In this reaction no mercury is formed and the first reaction step involves cleavage of the tin−phenyl bonds to give the diorganotin dichloro derivative $CH_2[CH_2Sn(Cl_2)CH_2Si(i\text{-}PrO)Me_2]_2$ (**3a**), which subsequently undergoes diorganotin dichloride-catalyzed hydrolysis of the isopropoxysilyl groups and condensation of the resulting silanol functionalities to give *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**4**). In addition to the signals assigned to compound **4**, the ^{29}Si and ^{119}Sn NMR spectra (CH_2Cl_2) of the crude reaction mixture according to eq 2 showed further resonances in the regions δ 10−7 and 111−105, which are likely to belong to the 20-membered ring **5** and higher oligomers. No attempts were made to isolate the 20-membered ring **5** from this reaction mixture.

Furthermore, the previously reported eight-membered ring *cyclo*-$CH_2[Sn(Cl_2)CH_2SiMe_2]_2O$ (**6**)[7u] has also been prepared by reaction of compound **2** with 4 molar equiv of mercuric chloride (eq 3).



(3)

The reactions shown in eqs 1−3 and Scheme 1 illustrate the generality of both dimethylsilylmethyl- and dimethylisopropoxysilylmethyl-substituted organotin derivatives to serve as synthons for convenient one-pot syntheses of siloxane as well as organotin moiety-containing rings.

Molecular Structure of *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (4). The molecular structure of compound **4** is illustrated in Figure 1. Unit cell data, refinement details, and selected interatomic parameters are listed in Tables 1−3.

The unit cell of *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**4**) contains two centrosymmetric dimers with the dimerization realized by unsymmetrical intermolecular Sn(1)−Cl(2)···Sn(1a)/Sn(1)···Cl(2a)−Sn(1a) bridges. The coordination geometry at Sn(1) can be best described as bicapped tetrahedron ([4+2] coordination); that is, in addition to the Sn(1)−C(1), Sn(1)−C(9), Sn(1)−Cl(1), and Sn(1)−Cl(2) bonds with lengths of 2.137(4), 2.105(4), 2.351(1), and 2.381(1) Å being in the typical range for such bonds there are intramolecular Sn(1)···O(1) and intermolecular Sn(1)···Cl(2a) contacts of 3.312(2) and 3.441(1) Å, respectively. The two latter distances are shorter than the sums of the van der Waals radii[13]

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[13] Huheey, J. E.; Keiter, E. A.; Keiter, R. L. In *Inorganic Chemistry−Principles of Structure and Reactivity*, 4th ed.; Harper Collins College Publishers: New York, 1993.

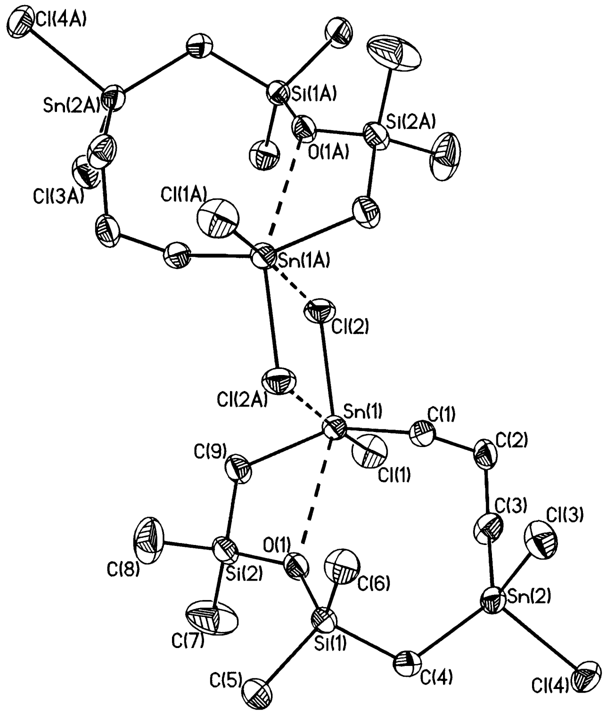

Figure 1. General view (SHELXTL) of a dimer of molecules of **4** showing 30% probability displacement ellipsoids and the atom-numbering scheme (symmetry transformations used to generate equivalent atoms: $-x$, $-y + 1$, $-z + 1$).

Table 1. Crystallographic Data for 4 and 7

	4	**7**
formula	$C_9H_{22}Cl_4OSi_2Sn_2$	$C_{45}H_{52}Cl_5NOP_2Si_2Sn_2$
fw, g/mol	581.63	1155.63
cryst syst	monoclinic	monoclinic
cryst size, mm	0.30 × 0.15 × 0.15	0.30 × 0.25 × 0.25
space group	$P2_1/c$	$P2_1/c$
a, Å	9.202(1)	9.645(1)
b, Å	18.570(1)	17.596(1)
c, Å	12.760(1)	30.846(1)
β, deg	109.197(1)	96.270(1)
V, Å^3	2059.2(3)	5203.7(6)
Z	4	4
ρ_{calcd}, Mg/m^3	1.876	1.475
ρ_{meas}, Mg/m^3	1.864(2)	1.486(9)
μ, mm^{-1}	3.050	1.357
F(000)	1120	2320
θ range, deg	4.39 to 25.69	4.09 to 26.37
index ranges	$-11 \leq h \leq 11$ $-22 \leq k \leq 22$ $-13 \leq l \leq 13$	$-11 \leq h \leq 11$ $-21 \leq k \leq 21$ $-38 \leq l \leq 38$
no. of reflns collcd	27 698	63 868
completeness to θ_{max}	92.9	94.2
no. of indep reflns/ R_{int}	3639/0.029	10008/0.059
no. of reflns obsd with ($I > 2\sigma(I)$)	2976	4312
no. of refined params	168	529
GooF (F^2)	1.035	0.780
R1(F) ($I > 2\sigma(I)$) wR2(F^2) (all data)	0.0283 0.0770	0.0363 0.0732
$(\Delta/\sigma)_{max}$	0.001	0.001
largest diff peak/ hole, e/Å^3	0.419/−0.873	0.503/−0.511

of tin (2.20 Å) and oxygen (1.50 Å) and of tin and chlorine (1.70 Å), respectively. In the related eight-membered ring *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**6**),[7u] which crystallizes with two different conformers, intramolecular Sn···O distances below the sum of the van der Waals radii of these atoms to both tin atoms occur with one being longer (3.559(2) Å) and three being shorter (3.061(2), 3.074(2), 3.184(2) Å) than the Sn(1)···O(1) distance in *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**4**). Although a number of organotin compounds exhibiting intramolecular Sn···O distances between 2.38(4) and 3.067(2) Å have been reported,[14] *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**6**)[7u] and *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**4**) are the only ones reported so far with the oxygen donor site bound to silicon. Associated with this intramolecular Sn(1)···O(1) distance in the 10-membered ring **4** is the Si(1)−O(1)−Si(2) angle of 138.0(2)°, which

Table 2. Selected Interatomic Bond Distances (Å) for 4 and 7

	4	**7**
Sn(1)−C(9)	2.105(4)	2.120(4)
Sn(1)−C(1)	2.137(4)	2.118(5)
Sn(1)−Cl(1)	2.351(1)	2.453(2)
Sn(1)−Cl(2)	2.381(1)	2.362(2)
Sn(1)−O(1)	3.312(2)	3.428(3)
Sn(1)−Cl(2a)	3.441(1)	
Sn(1)−Cl(5)		2.812(1)
Sn(2)−C(4)	2.105(4)	2.108(4)
Sn(2)−C(3)	2.138(4)	2.132(4)
Sn(2)−Cl(3)	2.355(1)	2.359(1)
Sn(2)−Cl(4)	2.341(1)	2.505(1)
Sn(2)−Cl(5)		2.686(1)
Si(1)−O(1)	1.646(3)	1.627(3)
Si(2)−O(1)	1.642(3)	1.622(3)

Table 3. Selected Bond Angles (deg) for 4 and 7

	4	7
C(9)−Sn(1)−C(1)	134.4(2)	138.2(2)
C(9)−Sn(1)−Cl(1)	103.5(1)	95.1(1)
C(1)−Sn(1)−Cl(1)	106.4(1)	93.5(2)
C(9)−Sn(1)−Cl(2)	106.0(1)	108.5(1)
C(1)−Sn(1)−Cl(2)	102.4(1)	111.6(2)
Cl(1)−Sn(1)−Cl(2)	99.05(5)	94.20(7)
C(9)−Sn(1)−O(1)	57.5(1)	54.5(1)
C(1)−Sn(1)−O(1)	78.9(1)	84.4(2)
Cl(1)−Sn(1)−O(1)	114.35(6)	111.02(7)
Cl(2)−Sn(1)−O(1)	144.96(5)	149.64(8)
C(9)−Sn(1)−Cl(2a)	78.1(1)	
C(1)−Sn(1)−Cl(2a)	73.3(1)	
Cl(1)−Sn(1)−Cl(2a)	177.59(4)	
Cl(2)−Sn(1)−Cl(2a)	78.76(4)	
O(1)−Sn(1)−Cl(2a)	67.99(5)	
C(9)−Sn(1)−Cl(5)		86.9(1)
C(1)−Sn(1)−Cl(5)		85.8(1)
Cl(1)−Sn(1)−Cl(5)		177.66(5)
Cl(2)−Sn(1)−Cl(5)		84.00(5)
Cl(5)−Sn(1)−O(1)		71.15(6)
C(4)−Sn(2)−C(3)	124.0(2)	138.0(2)
C(4)−Sn(2)−Cl(3)	108.4(1)	110.1(1)
C(3)−Sn(2)−Cl(3)	108.0(1)	111.7(1)
C(4)−Sn(2)−Cl(4)	107.0(1)	94.0(1)
C(3)−Sn(2)−Cl(4)	106.7(1)	89.4(1)
Cl(3)−Sn(2)−Cl(4)	100.19(5)	90.45(5)
C(4)−Sn(2)−Cl(5)		87.4(1)
C(3)−Sn(2)−Cl(5)		90.7(1)
Cl(3)−Sn(2)−Cl(5)		87.40(5)
Cl(4)−Sn(2)−Cl(5)		177.74(4)
Sn(1)−Cl(5)−Sn(2)		109.62(4)
Si(1)−O(1)−Si(2)	138.0(2)	150.0(2)
Si(1)−C(4)−Sn(2)	119.7(2)	118.5(2)
Si(2)−C(9)−Sn(1)	117.0(2)	114.8(2)

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[14] (a) Willem, R.; Delmotte, A.; Borger, I. D.; Biesemans, M.; Gielen, M.; Kayser, F.; Tiekink, E. R. T. *J. Organomet. Chem.* **1994**, *480*, 255. (b) Kayser, F.; Biesemans, M.; Delmotte, A.; Verbruggen, I.; Borger, I. D.; Gielen, M.; Willem, R.; Tiekink, E. R. T. *Organometallics* **1994**, *13*, 4026. (c) Kolb, U.; Dräger, M.; Jousseaume, B. *Organometallics* **1991**, *10*, 2737. (d) Kolb, U.; Beuter, M.; Dräger, M. *Inorg. Chem.* **1994**, *33*, 4522.

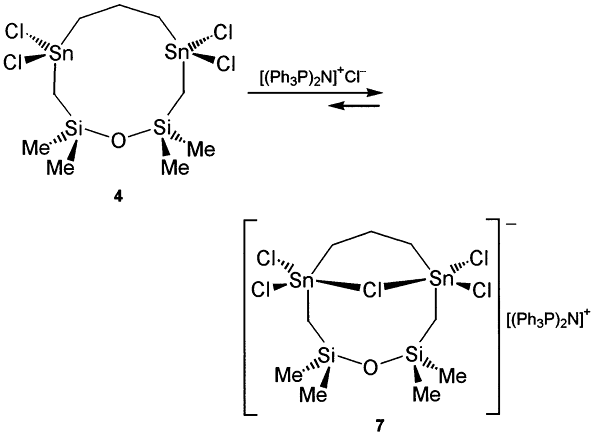
is rather small when compared with the corresponding angles of 144.7(2)−169.3(1)° found in eight-, 10-, and 12-membered metallasiloxanes showing no such intramolecular contacts[15a] or with the eight-membered ring **6** (Si−O−Si 144.9(1)°, 145.5(2)°).[7u] The same angle might also be indicative for weak or medium ring strain present in **4**. In comparison, the highly strained *cyclo*-$(Me_2SiO)_3$ and the practically strain-free *cyclo*-$(Me_2SiO)_4$ reveal gas-phase Si−O−Si angles of 131.6(4)° and 144(1)°, respectively.[15b] Similar to compound **6**,[7u] the Si(1)−O(1) and Si(2)−O(1) bond distances in compound **4** of 1.646(3) and 1.642(3) Å, respectively, are close to standard Si−O bond lengths[16] and are not affected by the intramolecular Sn···O coordination, a hint at the ionic character of the latter.

The Sn(2) atom exhibits a distorted tetrahedral configuration (mean angle 109.04°). The intramolecular Sn(2)···O(1) distance amounts to 3.836(3) Å and exceeds the sum of the van der Waals radii of oxygen and tin. The Sn−Cl bond lengths are 2.341(1) Å for Sn(2)−Cl(4) and 2.355(1) Å for Sn(2)−Cl(3) and are comparable with Sn−Cl distances reported for diorganotin dichlorides.[17]

The nonequivalence in the solid state of the two tin atoms in compound **4** as established by single-crystal X-ray diffraction analysis is reflected by observation of two ^{119}Sn CP MAS resonances at δ 98 and 158. Upon dissolution in CD_2Cl_2, the nonequivalence is lost on the ^{119}Sn NMR time scale; that is, only a single resonance is observed at room temperature (δ 120.9) as well as at −85 °C (δ 118.8). These chemical shifts are slightly low-frequency shifted with respect to $CH_2[CH_2Sn(Cl_2)CH_2SiMe_3]_2$ (δ ^{119}Sn 132.8[18]) and indicate that the weak intramolecular Sn···O coordination in compound **4** persists in solution.

No single crystals suitable for X-ray diffraction analysis could be obtained so far for the 20-membered ring *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)CH_2]_2CH_2$ (**5**). Its ^{119}Sn CP MAS NMR spectrum displays two resonances at δ 58 and 119, indicating two different tin sites with, at least for the former one, a coordination number higher than four. In $CDCl_3$ solution, however, the tin atoms are again equivalent on the ^{119}Sn NMR time scale, and a single resonance is observed at δ 110.2.

Complexation Behavior in Solution of *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (4) toward Chloride Ions. The ^{119}Sn NMR chemical shifts in $CDCl_3$ of **4** to which various amounts of $[(Ph_3P)_2N]^+Cl^-$ had been added (eq 4) indicate quantitative formation of the 1:1 complex with the chloride ion, $[$*cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O\cdot Cl]^-[(Ph_3P)_2N]^+$ (**7**).



(4)

Interestingly, even though adduct formation appears to be almost quantitative, the observation of a single resonance during the course of the titration indicates rapid intermolecular exchange of chlorides between **4** and **7**.

The negative ion ESMS spectrum of a mixture of **4** and $[(Ph_3P)_2N]^+Cl^-$ confirms the results obtained from ^{119}Sn NMR spectroscopy; that is, only the isotopic cluster patterns shown in Chart 1 were found, with no indication for the existence of a 1:2 complex $[\mathbf{4}\cdot 2Cl]^{2-}\cdot 2\text{-}[(Ph_3P)_2N]^+$.

The pentachlorodistannate derivative **7** was isolated as a colorless crystalline solid.

The molecular structure of compound **7** is shown in Figure 2. Unit cell data, refinement details, and selected interatomic parameters are listed in Tables 1−3. The lattice of **7** comprises discrete $[$*cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O\cdot Cl]^-$ anions and $[(Ph_3P)_2N]^+$ cations showing no significant interionic contacts. Both tin atoms in the anionic part of **7** exhibit a distorted trigonal bipyramidal geometry ($\Sigma\vartheta_{eq} - \Sigma\vartheta_{ax}{}^{14d} = 75.5°$ for Sn(1) and 85.9° for Sn(2)) with the axial positions being occupied by Cl(1), Cl(5) for Sn(1) and Cl(4), Cl(5) for Sn(2). The remaining chlorine atoms Cl(2) for Sn(1) and Cl(3) for Sn(2) and the carbon atoms C(1), C(9) for Sn(1) and C(3), C(4) for Sn(2) define the equatorial planes from which the Sn(1) and Sn(2) atoms are displaced in direction of Cl(1) and Cl(4) by 0.162(3) and 0.052(2) Å, respectively. The bigger distortion from the ideal trigonal bipyramidal configuration for Sn(1) is the result of an additional intramolecular O(1)···Sn(1) contact of 3.428(3) Å being shorter than the sum of the van der Waals radii[13] of oxygen and tin and making Sn(1) a typical example for a [5+1] coordination. The Sn−Cl(equatorial) bond lengths (Sn(1)−Cl(2) 2.362(2), Sn(2)−Cl(3) 2.359(1) Å) are shorter than the Sn−Cl(axial) ones (Sn(1)−Cl(1) 2.453(2), Sn(2)−Cl(4) 2.505(1) Å). The Sn(1)−Cl(5)−Sn(2) bridge is unsymmetric with Sn(1)−Cl(5) 2.812(1) Å and Sn(2)−Cl(5) 2.686(1) Å. A similar asymmetry was reported for the Sn−Cl−Sn bridge in the chloride complex of 1,1,5,5,9,9-hexachloro-1,5,9-tristannacyclododecane.[7d] The Si(1)−O(1)−Si(2) bond angle of 150.0(2)° is bigger than that observed for compound **4** and in line with a longer intramolecular O(1)···Sn(1) distance mentioned above.

In $CDCl_3$ solution of **7**, both tin atoms are pentacoordinated as evidenced by (i) the ^{119}Sn NMR chemical shift of δ −55.7 ppm being low-frequency shifted with respect to tetracoordinated compound **4** (δ 117.8) and (ii) the observation of increased $^1J(^{117/119}Sn-^{13}C)$ and $^2J(^{117/119}Sn-^1H)$ couplings of 407/426, 125/130 Hz for

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[15] (a) Beckmann, J.; Jurkschat, K. *Coord. Chem. Rev.* **2001**, *215*, 267. (b) Oberhammer, H.; Zeil, W.; Fogarasi, G. *J. Mol. Struct.* **1973**, *18*, 309.

[16] (a) Barrow, M. J.; Ebsworth, E. A. V.; Harding, M. M. *Acta Crystallogr. Sect. B* **1979**, *35*, 2093. (b) Tomlins, P. E.; Lydon, J. E.; Akrigg, D.; Sheldrick, B. *Acta Crystallogr. Sect. C* **1985**, *41*, 292. (c) Karle, I. L.; Karle, J. M.; Nielsen, C. J. *Acta Crystallogr. Sect. C* **1986**, *42*, 64.

[17] Kolb, U.; Dräger, M.; Jousseaume, B. *Organometallics* **1991**, *10*, 2737.

[18] Dakternieks, D.; Jurkschat, K.; Schollmeyer, D.; Wu, H. *Organometallics* **1994**, *13*, 4121.

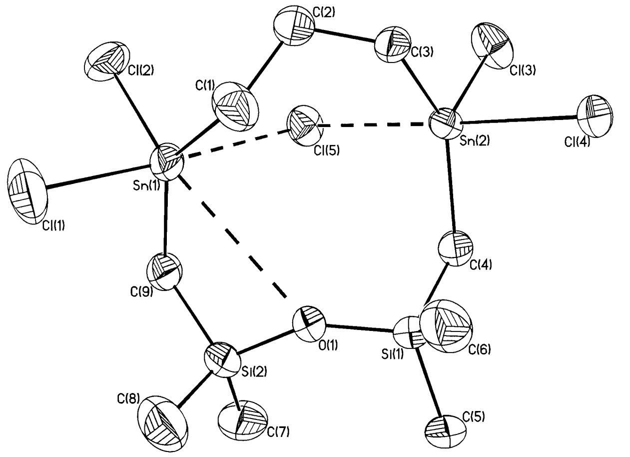


Figure 2. General view (SHELXTL) of the anion in **7** showing 30% probability displacement ellipsoids and the atom-numbering scheme. The cation $(Ph_3P)_2N^+$ is omitted for clarity.

Si*CH*$_2$Sn and 635/669, 77/81 Hz for CH_2*CH*$_2$Sn, respectively, in comparison with the corresponding couplings measured for compound **4** (261/273, 101/106 Hz for Si*CH*$_2$Sn; 482/504, 67 Hz for CH_2*CH*$_2$Sn). At room temperature, the chloride bridge in **7** is symmetric on the ^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR time scales; that is, the methyl groups and methylene groups as well as the silicon and tin atoms are equivalent. The equivalence of the methyl groups in the ^1H and ^{13}C NMR spectra indicates the chloride complex **7** to be kinetically labile.

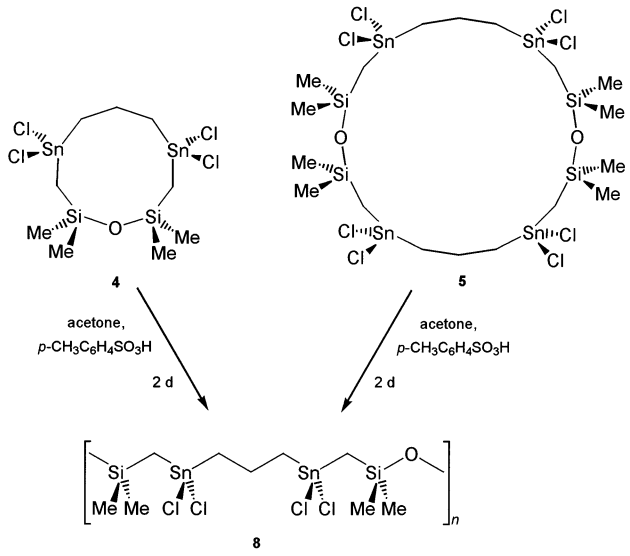
The 20-membered ring **5** was insufficiently soluble in $CDCl_3$ to allow a similar ^{119}Sn NMR investigation.

The complexation behavior in solution of *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**4**) toward fluoride ions has also been studied, but none of the compounds identified by NMR spectroscopy were isolated (see Supporting Information).

Ring-Opening Polymerization of *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (4) and of *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)CH_2]_2CH_2$ (5). No oligo- or polymerization was observed after three weeks at room temperature of the 10-membered ring **4** which had been dissolved in toluene. However, upon standing for several days in CH_2Cl_2 solution at ambient temperature and as monitored by ^{29}Si NMR spectroscopy, the 10-membered ring **4** is converted almost quantitatively into the 20-membered ring **5**, the latter being poorly soluble in this solvent, and precipitates analytically pure from the solution. In the more polar solvent acetone, the 20-membered ring **5** is more soluble, and a solution of compound **4** in this solvent is converted into a mixture of higher oligomers after several hours already. By heating at reflux and addition of catalytic amounts of *p*-toluenesulfonic acid, solutions of both the 10- and 20-membered rings **4** and **5**, respectively, are quantitatively converted into solutions of the polymer poly-$[Si(Me_2)CH_2Sn(Cl_2)(CH_2)_3Sn(Cl_2)CH_2Si(Me_2)O]$ (**8**) (Scheme 2).

Compound **8** is a waxlike solid, which melts in the range 93−105 °C. It is soluble in CH_2Cl_2, $CHCl_3$, thf, acetone and acetonitrile but almost insoluble in *n*-hexane. The polymerization of the six-membered ring *cyclo*-$Cl_2Sn[CH_2Si(Me_2)]_2O$ was achieved in a similar manner.[19a] Elemental analysis as well as ^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectroscopy (see Experimental Section) confirmed the purity of the polymer **8**. However, obtaining information on the molecular weight distribution using MALDI-MS and gel-permeation chromatography failed. The negative ion ESMS spectrum (see Supporting Information) of a solution of compound **8** in acetonitrile showed a large number of overlapping cluster patterns between $m/z = 1000$ and 2500, corresponding to negative charge uptakes of 0.6 to 0.25 per monomeric unit. No molecular weight distribution could be estimated from this spectrum.

Scheme 2



Conclusion. Diorganohydridosilylmethyl- as well as diorganoisopropoxysilyl-functionalized spacer-bridged ditin compounds of the general type $Me_2(R)SiCH_2(Ph_2)Sn(CH_2)_nSn(Ph_2)CH_2Si(R)Me_2$ ($R = H$, *i*-PrO; $n = 1, 3$) are easily accessible synthons for the convenient one-pot synthesis of both silicon- and tin-containing rings *cyclo*-$(CH_2)_n[Sn(Cl_2)CH_2Si(Me_2)]_2O$ ($n = 1, 3$). Apparently, the ability to undergo acid-catalyzed ring-opening polymerization is higher for $n = 3$ than for $n = 1$. The reason for this is not quite clear but might be related to the greater intramolecular Sn···O distance (weaker bond) in the 10-membered ring **4**, facilitating protonation of the oxygen atom in the latter. Along the polymerization pathways, oligomers such as the 20-membered ring *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)CH_2]_2CH_2$ appear as intermediates and can be isolated.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry argon. The solvents were purified by distillation from appropriate drying agents under argon. Mercuric chloride and bis(triphenylphosphoranylidene)ammonium chloride were commercial products. Bis(diphenylfluorostannyl)methane,[7p] bis(diphenylfluorostannyl)propane,[10] (chloromethyl)dimethylsilane,[13] and (chloromethyl)dimethylisopropoxysilane[19b] were synthesized according to literature methods. The density of the crystals was measured using

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[19] (a) Mironov, V. F.; Shiryaev, V. I.; Stepina, É. M.; Makhalkina, L. V.; Lapina, A. I.; Bochkarev, V. N.; Nechaeva, A. I. *J. Gen. Chem. USSR* **1976**, *46*, 1039. (b) Andrianov, K. A.; Golubenko, A. *J. Gen. Chem. USSR* **1975**, *45*, 2614.

a Micromeritics Accu Pyc 1330. Elemental analyses were performed on a LECO-CHNS-932 analyzer. Molecular weights were measured osmometrically using a Knauer osmometer.

NMR Spectroscopy. NMR spectra in solution were recorded on Bruker DRX400 and Bruker DPX 300 FT NMR spectrometers with broadband decoupling of ^{13}C at 100.63 MHz, ^{19}F at 282.41 MHz, ^{29}Si at 79.49 MHz, ^{31}P at 161.98 MHz, and ^{119}Sn at 149.21 MHz using an internal deuterium lock. ^{1}H, ^{13}C, ^{19}F, ^{29}Si, ^{31}P, and ^{119}Sn NMR chemical shifts δ are given in ppm and referenced to external Me_4Si (^{1}H,^{13}C, ^{29}Si), $CFCl_3$ (^{19}F), 85% aqueous H_3PO_4 (^{31}P), and Me_4Sn (^{119}Sn), respectively. Temperatures were maintained using a Bruker control system. The NMR spectra were recorded at room temperature if not otherwise stated. The complexes for NMR investigations were generally prepared in situ, and the concentration of the compounds **4** and **5** was about 0.1 M. $^{119}Sn\{^{1}H\}$ MAS NMR spectra were recorded on a Bruker MSL 400 spectrometer using cross polarization and high-power proton decoupling (contact time 3.5 ms, MAS speeds 4500, 6000, 8000 Hz). Tetracyclohexyltin was used as a second reference (δ −97.35 ppm against $SnMe_4$).

Crystallography. Crystals of *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**4**) and $[cyclo\text{-}CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O\cdot Cl]^-[(Ph_3P)_2N]^+$ (**7**) were grown from hexane and CH_2Cl_2/hexane solutions, respectively, by slow evaporation of the solvents. Intensity data for the colorless crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation. The data collection covered almost the whole sphere of reciprocal space with 360 frames via ω-rotation ($\Delta\Delta/\omega = 1°$) at two times 10 s for **4** and two times 5 s for **7** per frame. The crystal-to-detector distance was 2.7 cm (**4**) and 2.8 cm (**7**) with a detector−θ-offset of 5°. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analyzing the duplicate reflections there was no indication for any decay. The structures were solved by direct methods using SHELXS97[20] and successive difference Fourier syntheses. Refinement involved applying full-matrix least-squares methods using SHELXL97.[21]

The H atoms were placed in geometrically calculated positions using a riding model and refined with a common isotropic temperature factor for different C−H types (C−$H_{prim.}$ 0.96 Å, C−$H_{sec.}$ 0.97 Å, U_{iso} 0.104(4) Å^2 (**4**), 0.112(4) Å^2 (**7**), C_{aryl}−H 0.93 Å (**7**), U_{iso} 0.083(4) Å^2 (**7**)).

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from the literature.[22] The figures were created by SHELXTL.[23] Crystallographic data are given in Table 1, selected bond distances (Å) in Table 2, and bond angles (deg) in Table 3.

Electrospray Mass Spectrometry. Electrospray mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) using an acetonitrile mobile phase. Approximately 1 mg of each compound was placed in 1 mL of acetonitrile and sonicated for 10 min. The solutions were injected directly into the spectrometer via a Rheodyne injector equipped with a 100 μL loop. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 20 μL min^{-1}. Nitrogen was used as both a drying gas and for nebulization with flow rates of approximately 200 and 15 mL min^{-1}, respectively. Pressure in the mass analyzer region was usually about 3 × 10^{-5} mbar. Typically 10 signal-averaged spectra were collected.

Synthesis of 1,3-Bis{[(dimethylsilyl)methyl]diphenylstannyl}propane, $CH_2[CH_2Sn(Ph_2)CH_2Si(H)Me_2]_2$ (1). To a suspension of 1,3-bis(diphenylfluorostannyl)propane (11.26 g, 18.0 mmol) in thf (60 mL) was added dropwise at 0 °C a 0.545 M solution of $Me_2(H)SiCH_2MgCl$ (66.0 mL, 36.0 mmol) in thf that was prepared from $Me_2(H)SiCH_2Cl$ (4.87 g, 45.0 mmol) and magnesium turnings (1.46 g, 60.0 mmol). The reaction mixture was stirred at room temperature for 16 h before removing the solvent in vacuo. Hexane (100 mL) was added to the residue, and after stirring thoroughly the mixture was filtered, the procedure being repeated two times. The solvent was removed in vacuo to give 12.95 g (17.6 mmol, 98%) of $CH_2[CH_2Sn(Ph_2)CH_2Si(H)Me_2]_2$ (**1**) as a colorless oil. ^{1}H NMR (C_6D_6): δ 0.14 (d, 12H, $^{1}J(^{13}C-^{1}H) = 120$ Hz, $^{2}J(^{29}Si-^{1}H) = 6$ Hz, $^{3}J(^{1}H-^{1}H) = 4$ Hz, CH_3), 0.21 (d, 4H, $^{1}J(^{13}C-^{1}H) = 120$ Hz, $^{2}J(^{29}Si-^{1}H) = 7$ Hz, $^{3}J(^{1}H-^{1}H) = 4$ Hz, $SiCH_2Sn$), 1.51 (t, 4H, $^{1}J(^{13}C-^{1}H) = 112$ Hz, $^{2}J(^{117/119}Sn-^{1}H) = 52$ Hz, $^{3}J(^{1}H-^{1}H) = 8$ Hz, $CH_2\mathit{CH_2}Sn$), 2.17 (quint, 2H, $^{1}J(^{13}C-^{1}H) = 117$ Hz, $^{3}J(^{117/119}Sn-^{1}H) = 65/68$ Hz, $^{3}J(^{1}H-^{1}H) = 8$ Hz, $\mathit{CH_2}CH_2Sn$), 4.48 (m, 2H, $^{1}J(^{29}Si-^{1}H) = 183$ Hz, $^{3}J(^{1}H-^{1}H)$ 4 Hz, SiH), 7.30 (m, 12H, H_m/H_p), 7.61 (dd, 8H, $^{3}J(^{117/119}Sn-^{1}H) = 46$ Hz, $^{3}J(^{1}H-^{1}H) = 8$ Hz, $^{4}J(^{1}H-^{1}H) = 2$ Hz, H_o). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ −8.49 (s, $^{1}J(^{117/119}Sn-^{13}C) = 231/243$ Hz, $^{1}J(^{29}Si-^{13}C) = 48$ Hz, CH_2Si), −0.94 (s, $^{1}J(^{29}Si-^{13}C) = 51$ Hz, $^{3}J(^{117/119}Sn-^{13}C) = 17$ Hz, CH_3), 17.03 (s, $^{1}J(^{117/119}Sn-^{13}C) = 353/370$ Hz, $^{3}J(^{117/119}Sn-^{13}C) = 65$ Hz, $CH_2\mathit{CH_2}Sn$), 24.74 (s, $^{2}J(^{117/119}Sn-^{13}C) = 21$ Hz, $\mathit{CH_2}CH_2Sn$), 128.65 (s, $^{3}J(^{117/119}Sn-^{13}C) = 46$ Hz, C_m), 128.86 (s, $^{4}J(^{117/119}Sn-^{13}C) = 10$ Hz, C_p), 137.00 (s, $^{2}J(^{117/119}Sn-^{13}C) = 35$ Hz, C_o), 140.52 (s, $^{1}J(^{117/119}Sn-^{13}C) = 442/462$ Hz, C_i). $^{29}Si\{^{1}H\}$ NMR (C_6D_6): δ −13.1 (s, $^{1}J(^{13}CH_3-^{29}Si) = 51$ Hz, $^{1}J(^{13}CH_2-^{29}Si) = 49$ Hz, $^{2}J(^{117/119}Sn-^{29}Si) = 26$ Hz). $^{119}Sn\{^{1}H\}$ NMR (C_6D_6): δ −64.0 (s, $^{1}J(^{13}C_i-^{119}Sn) = 462$ Hz, $^{1}J(CH_2{}^{13}CH_2-^{119}Sn) = 370$ Hz, $^{1}J(Si^{13}CH_2-^{119}Sn) = 244$ Hz, $^{2}J(^{13}C_o-^{119}Sn) = 36$ Hz, $^{2}J(^{29}Si-^{119}Sn) = 26$ Hz, $^{3}J(^{13}C_m-^{119}Sn) = 47$ Hz). Anal. Calcd for $C_{33}H_{44}Si_2Sn_2$ (734.30): C, 54.0; H, 6.0. Found: C, 54.1; H, 6.2.

Synthesis of Bis{[(dimethylsilyl)methyl]diphenylstannyl}methane, $CH_2[Sn(Ph_2)CH_2Si(H)Me_2]_2$ (2). To a suspension of bis(diphenylfluorostannyl)methane (10.00 g, 16.7 mmol) in thf (70 mL) was added dropwise at 0 °C a 0.493 M solution of $Me_2(H)SiCH_2MgCl$ (70.0 mL, 33.5 mmol) in thf that was prepared from $Me_2(H)SiCH_2Cl$ (3.80 g, 35.0 mmol) and magnesium turnings (1.22 g, 50.0 mmol). The reaction mixture was stirred at room temperature for 15 h before removing the solvent in vacuo. Hexane (100 mL) was added to the residue, and after stirring thoroughly the mixture was filtered, the procedure being repeated two times. The solvent was removed in vacuo to give 11.34 g (16.1 mmol, 96%) of $CH_2[Sn(Ph_2)CH_2Si(H)Me_2]_2$ (**2**) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.00 (d, 12H, $^{1}J(^{13}C-^{1}H) = 121$ Hz, $^{2}J(^{29}Si-^{1}H) = 7$ Hz, $^{3}J(^{1}H-^{1}H) = 4$ Hz, CH_3), 0.08 (d, 4H, $^{1}J(^{13}C-^{1}H) = 119$ Hz, $^{2}J(^{117/119}Sn-^{1}H) = 71/75$ Hz, $^{3}J(^{1}H-^{1}H) = 4$ Hz, $SiCH_2Sn$), 0.72 (s, 2H, $^{1}J(^{13}C-^{1}H) = 126$ Hz, $^{2}J(^{117/119}Sn-^{1}H) = 59/62$ Hz, $SnCH_2Sn$), 4.11 (m, 2H, $^{1}J(^{29}Si-^{1}H) = 182$ Hz, $^{3}J(^{1}H-^{1}H) = 4$ Hz, SiH), 7.31 (m, 12H, H_m/H_p), 7.43 (m, 8H, $^{3}J(^{117/119}Sn-^{1}H) = 47$ Hz, H_o). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ −14.73 (s, $^{1}J(^{117/119}Sn-^{13}C) = 269/281$ Hz, $SnCH_2Sn$), −7.02 (s, $^{1}J(^{117/119}Sn-^{13}C) = 253/264$ Hz, $^{1}J(^{29}Si-^{13}C) = 47$ Hz, $SiCH_2Sn$), −1.20 (s, $^{1}J(^{29}Si-^{13}C) = 50$ Hz, $^{3}J(^{117/119}Sn-^{13}C) = 19$ Hz, CH_3), 128.17 (s, $^{3}J(^{117/119}Sn-^{13}C) = 49$ Hz, C_m), 128.53 (s, $^{4}J(^{117/119}Sn-^{13}C) = 11$ Hz, C_p), 136.48 (s, $^{2}J(^{117/119}Sn-^{13}C) = 38$ Hz, C_o), 140.94 (s, $^{1}J(^{117/119}Sn-^{13}C) = 465/487$ Hz, $^{3}J(^{117/119}Sn-^{13}C) = 11$ Hz, C_i). $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ −13.8 (s, $^{1}J(^{13}CH_3/^{13}CH_2-^{29}Si) = 49$ Hz, $^{2}J(^{117/119}Sn-^{29}Si) = 26$ Hz). $^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$): δ −37.6 (s, $^{1}J(^{13}C_{i-Ph}-^{119}Sn) = 492$ Hz, $^{1}J(Sn^{13}CH_2-^{119}Sn) = 280$ Hz, $^{1}J(Si^{13}CH_2-^{119}Sn) = 262$ Hz, $^{2}J(^{117}Sn-^{119}Sn) = 243$ Hz, $^{2}J(^{29}Si-^{119}Sn) = 25$ Hz). Anal. Calcd for $C_{31}H_{40}Sn_2Si_2$ (706.25): C, 52.7; H, 5.7. Found: C, 52.7; H, 5.8.

Synthesis of 1,1,5,5-Tetrachloro-7,7,9,9-tetramethyl-7,9-disila-1,5-distanna-8-oxacyclodecane, *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (4), and 1,1,5,5,11,11,15,15-Octachloro-7,7,9,9,17,17,19,19-octamethyl-8,18-dioxa-7,9,17,19-tetrasila-1,5,11,15-tetrastannacycloeicosane, *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)$-

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$CH_2]_2CH_2$ (5). Method A. To a solution of 1,3-bis{[(dimethylsilyl)methyl]diphenylstannyl}propane (**1**) (5.00 g, 6.81 mmol) in acetone (40 mL) at 0 °C was added dropwise a solution of $HgCl_2$ (7.39 g, 27.2 mmol) in acetone (40 mL). The resulting suspension was stirred overnight at room temperature before removing the PhHgCl by filtration. After removing the solvent in vacuo the residue was suspended in 30 mL of CH_2Cl_2 and the suspension was filtered. The filtrate was allowed to stand overnight at 5 °C, giving 0.54 g (0.46 mmol, 14%) of *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)CH_2]_2CH_2$ (**5**) as a colorless solid, mp 181−184 °C. After filtration from compound **5** the solvent was removed in vacuo and the residue was suspended in 50 mL of hot hexane. The suspension was filtered, the filtrate collected, and the procedure repeated with another 50 mL of hot hexane. The combined filtrates were allowed to stand overnight at 5 °C, giving 0.59 g (1.01 mmol, 15%) of *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**4**) as a colorless crystalline solid, mp 96−98 °C. The filtrate was dissolved in 10 mL of CH_2Cl_2 and another 0.77 g (1.13 mmol, 17%) of *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**4**) isolated by size exclusion chromatography (100 g Sephadex LH20, CH_2Cl_2).

Spectroscopic Data for 4. ^1H NMR ($CDCl_3$): δ 0.31 (s, 12H, $^1J(^{13}C-^1H) = 119$ Hz, $^2J(^{29}Si-^1H) = 7$ Hz, CH_3), 1.06 (s, 4H, $^1J(^{13}C-^1H) = 125$ Hz, $^2J(^{117/119}Sn-^1H) = 101/106$ Hz, $^2J(^{29}Si-^1H) = 6$ Hz, $SiCH_2Sn$), 1.97 (t, 4H, $^1J(^{13}C-^1H) = 134$ Hz, $^2J(^{117/119}Sn-^1H) = 67$ Hz, $^3J(^1H-^1H) = 7$ Hz, $CH_2\mathit{CH_2}Sn$), 2.49 (quint, 2H, $^1J(^{13}C-^1H) = 133$ Hz, $^3J(^{117/119}Sn-^1H) = 160/168$ Hz, $^3J(^1H-^1H) = 7$ Hz, $\mathit{CH_2}CH_2Sn$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 2.98 (s, $^1J(^{29}Si-^{13}C) = 60$ Hz, $^3J(^{117/119}Sn-^{13}C) = 26$ Hz, CH_3), 14.62 (s, $^1J(^{117/119}Sn-^{13}C) = 261/273$ Hz, $^1J(^{29}Si-^{13}C) = 54$ Hz, $SiCH_2Sn$), 20.51 (s, $^2J(^{117/119}Sn-^{13}C) = 29$ Hz, $\mathit{CH_2}CH_2Sn$), 31.14 (s, $^1J(^{117/119}Sn-^{13}C) = 482/504$ Hz, $^3J(^{117/119}Sn-^{13}C) = 53$ Hz, $CH_2\mathit{CH_2}Sn$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 12.2 (s, $^1J(^{13}CH_2-^{29}Si) = 55$ Hz, $^1J(^{13}CH_3-^{29}Si) = 60$ Hz, $^2J(^{117/119}Sn-^{29}Si) = 36$ Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ 117.8 (s, $^1J(CH_2{}^{13}CH_2-^{119}Sn) = 499$ Hz, $^1J(Si^{13}CH_2-^{119}Sn) = 278$ Hz). $^{119}Sn\{^1H\}$ CP-MAS NMR: δ 98, 158. Anal. Calcd for $C_9H_{22}Cl_4OSi_2Sn_2$ (581.68): C, 18.6; H, 3.8; Cl, 24.4. Found: C, 18.9; H, 3.9; Cl, 24.0. Mol wt: (VPO, C_6H_6): 673 (calcd 582).

Spectroscopic Data for 5. ^1H NMR (acetone-d_6): δ 0.31 (s, 24H, $^1J(^{13}C-^1H) = 119$ Hz, $^2J(^{29}Si-^1H) = 7$ Hz, CH_3), 1.15 (s, 8H, $^1J(^{13}C-^1H) = 124$ Hz, $^2J(^{117/119}Sn-^1H) = 100/104$ Hz, $^2J(^{29}Si-^1H) = 6$ Hz, $SiCH_2Sn$), 2.03 (t, 8H, $^1J(^{13}C-^1H) = 137$ Hz, $^2J(^{117/119}Sn-^1H) = 67$ Hz, $^3J(^1H-^1H) = 8$ Hz, $CH_2\mathit{CH_2}Sn$), 2.35 (quint, 4H, $^3J(^{117/119}Sn-^1H) = 90/95$ Hz, $^3J(^1H-^1H) = 8$ Hz, $\mathit{CH_2}CH_2Sn$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 3.27 (s, $^1J(^{29}Si-^{13}C) = 60$ Hz, $^3J(^{117/119}Sn-^{13}C) = 20$ Hz, CH_3), 16.71 (s, $^1J(^{117/119}Sn-^{13}C) = 343/360$ Hz, $^1J(^{29}Si-^{13}C) = 55$ Hz, $SiCH_2Sn$), 22.01 (s, $^2J(^{117/119}Sn-^{13}C) = 35$ Hz, $\mathit{CH_2}CH_2Sn$), 33.36 (s, $^1J(^{117/119}Sn-^{13}C) = 527/551$ Hz, $^3J(^{117/119}Sn-^{13}C) = 120/125$ Hz, $CH_2\mathit{CH_2}Sn$). $^{29}Si\{^1H\}$ NMR (acetone-d_6): δ 9.4 (s, $^1J(^{13}CH_2-^{29}Si) = 56$ Hz, $^1J(^{13}CH_3-^{29}Si) = 60$ Hz, $^2J(^{117/119}Sn-^{29}Si) = 32$ Hz). $^{119}Sn\{^1H\}$ NMR (acetone-d_6): δ 43.9 (s, $^4J(^{119}Sn-^{117}Sn) = 328$ Hz). $^{119}Sn\{^1H\}$ CP-MAS NMR: δ 58, 119. Anal. Calcd for $C_{18}H_{44}Cl_8O_2Si_4Sn_4$ (1163.35): C, 18.6; H, 3.8. Found: C, 18.7; H, 3.9. Mol wt: (VPO, acetone): 1205 (calcd 1163).

Method B (for the synthesis of **4**). To a suspension of 1,3-bis(diphenylfluorostannyl)propane (8.83 g, 14.1 mmol) in thf (50 mL) was added dropwise at 0 °C a solution of $Me_2(i\text{-}PrO)SiCH_2MgCl$ (28.2 mmol) in thf (70 mL), which had been prepared from (chloromethyl)dimethylisopropoxysilane and magnesium turnings. The reaction mixture was stirred at room temperature for 15 h before removing the solvent in vacuo. Hexane (100 mL) was added to the residue, and after stirring thoroughly the mixture was filtered, the procedure being repeated two times. The solvent was removed in vacuo to give 11.48 g (13.5 mmol, 96%) of $CH_2[CH_2Sn(Ph_2)CH_2Si(i\text{-}PrO)Me_2]_2$ (**3**) as a colorless oil of sufficient purity. ^1H NMR ($CDCl_3$): δ 0.12 (s, 12H, $^1J(^{13}C-^1H) = 120$ Hz, $SiCH_3$), 0.36 (s, 4H, $^1J(^{13}C-^1H) = 118$ Hz, $^2J(^{117/119}Sn-^1H) = 73$ Hz, $SiCH_2Sn$), 1.17 (d, 12H, $^1J(^{13}C-^1H) = 127$ Hz, $^3J(^1H-^1H) = 6$ Hz, $CH(\mathit{CH_3})_2$), 1.53 (t, 4H, $^1J(^{13}C-^1H) = 135$ Hz, $^2J(^{117/119}Sn-^1H) = 54$ Hz, $^3J(^1H-^1H) = 8$ Hz, $CH_2\mathit{CH_2}Sn$), 2.08 (m, 2H, $^3J(^1H-^1H) = 8$ Hz, $C\mathit{H_2}CH_2Sn$), 4.03 (sept, 2H, $^1J(^{13}C-^1H) = 129$ Hz, $^3J(^1H-^1H) = 6$ Hz, $C\mathit{H}(CH_3)_2$), 7.40 (m, 12H, $H_{m,p}$), 7.57 (m, 8H, $^3J(^{117/119}Sn-^1H) = 45$ Hz, H_o). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −4.84 (s, $^1J(^{117/119}Sn-^{13}C) = 227/239$ Hz, $^1J(^{29}Si-^{13}C) = 58$ Hz, $SiCH_2Sn$), 1.18 (s, $^1J(^{29}Si-^{13}C) = 58$ Hz, $^3J(^{117/119}Sn-^{13}C) = 10$ Hz, $SiCH_3$), 17.26 (s, $^1J(^{117/119}Sn-^{13}C) = 360/375$ Hz, $^3J(^{117/119}Sn-^{13}C) = 68$ Hz, $CH_2\mathit{C}H_2Sn$), 24.32 (s, $^2J(^{117/119}Sn-^{13}C) = 20$ Hz, $\mathit{C}H_2CH_2Sn$), 25.77 (s, $^3J(^{29}Si-^{13}C) = 21$ Hz, $CH(\mathit{C}H_3)_2$), 64.66 (s, OCH), 128.05 (s, $^3J(^{117/119}Sn-^{13}C) = 46$ Hz, C_m), 128.28 (s, $^4J(^{117/119}Sn-^{13}C) = 10$ Hz, C_p), 136.67 (s, $^2J(^{117/119}Sn-^{13}C) = 36$ Hz, C_o), 140.77 (s, $^1J(^{117/119}Sn-^{13}C) = 439/458$ Hz, C_i). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 14.9 (s, $^1J(^{13}CH_2/^{13}CH_3-^{29}Si) = 58$ Hz, $^2J(^{117/119}Sn-^{29}Si) = 19$ Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −65.4 (s, $^1J(^{13}C_i-^{119}Sn) = 459$ Hz, $^1J(CH_2{}^{13}CH_2-^{119}Sn) = 376$ Hz, $^1J(Si^{13}CH_2-^{119}Sn) = 239$ Hz, $^3J(^{13}C_m-^{119}Sn) = 47$ Hz, $^4J(^{117}Sn-^{119}Sn) = 71$ Hz).

A solution of $HgCl_2$ (9.54 g, 35.1 mmol) in acetone (60 mL) was added dropwise at 0 °C over a period of 1 h to a solution of 1,3-bis{[(dimethylisopropoxysilyl)methyl]diphenylstannyl}propane (**3**) (7.47 g, 8.78 mmol) in acetone (60 mL). The reaction mixture was stirred for 14 h at room temperature before removing the PhHgCl by filtration. The solvent was removed in vacuo and the residue extracted two times with 100 mL of hot *n*-hexane. The combined extracts were kept overnight at −25 °C, giving a precipitate. The latter was filtered and dried to give 2.10 g (3.61 mmol, 41%) of *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**4**) as a colorless crystalline solid.

Synthesis of 1,1,3,3-Tetrachloro-5,5,7,7-tetramethyl-1,7-distanna-3,5-disila-4-oxacyclooctane, *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ (6). To a solution of bis{[(dimethylsilyl)methyl]diphenylstannyl}methane (**2**) (11.00 g, 15.6 mmol) in acetone (80 mL) at 0 °C was added dropwise a solution of $HgCl_2$ (16.92 g, 62.3 mmol) in acetone (80 mL). The resulting suspension was stirred at room temperature for 14 h before removing the PhHgCl by filtration. After removing the solvent in vacuo the residue was suspended in 100 mL of hot hexane. The suspension was filtered, the filtrate collected, and the procedure repeated with another 100 mL of hot hexane. The combined filtrates were allowed to stand overnight at 5 °C, giving 2.93 g (5.30 mmol, 34%) of *cyclo*-$O[Si(Me_2)CH_2Sn(Cl_2)]_2CH_2$ (**6**) as a colorless crystalline solid, mp 107−109 °C. ^1H NMR ($CDCl_3$): δ 0.31 (s, 12H, $^1J(^{13}C-^1H) = 120$ Hz, $^2J(^{29}Si-^1H) = 7$ Hz, CH_3), 1.21 (s, 4H, $^1J(^{13}C-^1H) = 127$ Hz, $^2J(^{117/119}Sn-^1H) = 115/121$ Hz, $SiCH_2Sn$), 1.70 (s, 2H, $^1J(^{13}C-^1H) = 137$ Hz, $^2J(^{117/119}Sn-^1H) = 76/80$ Hz, $SnCH_2Sn$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 2.67 (s, $^1J(^{29}Si-^{13}C) = 61$ Hz, $^3J(^{117/119}Sn-^{13}C) = 22$ Hz, CH_3), 13.89 (s, $^1J(^{117/119}Sn-^{13}C) = 335/351$ Hz, $^1J(^{29}Si-^{13}C) = 55$ Hz, $SiCH_2Sn$), 16.91 (s, $^1J(^{117/119}Sn-^{13}C) = 370/387$ Hz, $SnCH_2Sn$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 14.2 (s, $^2J(^{117/119}Sn-^{29}Si) = 56/59$ Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ 109.0 (s, $^2J(^{117}Sn-^{119}Sn) = 419$ Hz). $^{119}Sn\{^1H\}$ CP-MAS NMR: δ 87, 114. Anal. Calcd for $C_7H_{18}Cl_4OSn_2Si_2$ (553.62): C, 15.2; H, 3.3. Found: C, 15.2; H, 3.3. Mass spectrum: *m/e* (%) 59 (11.83, $[CH_3SiO]^+$), 117 (11.59, $[C_3H_9Si_2O]^+$), 131 (52.65, $[C_4H_{11}OSi_2]^+$), 539 (100.00, $[M-CH_3]^+$, $^{35}Cl_3{}^{37}Cl^{118}Sn^{120}Sn$). Mol wt: (VPO, CH_2Cl_2) 547 (calcd 554).

Synthesis of Bis(triphenylphosphoranylidene)ammonium-1,1,5,5-tetrachloro-7,7,9,9-tetramethyl-7,9-disila-1,5-distanna-8-oxacyclodecane chloride, [*cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O\cdot Cl]^-[(Ph_3P)_2N]^+$ (7). To a solution of 1,1,5,5-tetrachloro-7,7,9,9-tetramethyl-7,9-disila-1,5-distanna-8-oxacyclodecane (**4**) (200 mg, 0.34 mmol) in CH_2Cl_2 (10 mL) was added bis(triphenylphosphoranylidene)ammonium chloride (197 mg, 0.34 mmol). The mixture was stirred at room temperature for 10 min and the solvent removed in vacuo to give 397 mg (0.34 mmol, 100%) of [*cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O\cdot Cl]^-[(Ph_3P)_2N]^+$ (**7**) as a colorless crystalline solid, mp 176−178 °C. ^1H NMR ($CDCl_3$): δ 0.24 (s, 12H, $^1J(^{13}C-^1H)$

= 118 Hz, $^{2}J(^{29}\text{Si}-^{1}\text{H})$ = 7 Hz, CH_3), 1.19 (s, 4H, $^{1}J(^{13}\text{C}-^{1}\text{H})$ = 128 Hz, $^{2}J(^{117/119}\text{Sn}-^{1}\text{H})$ = 125/130 Hz, $^{2}J(^{29}\text{Si}-^{1}\text{H})$ = 6 Hz, $SiCH_2Sn$), 2.01 (t, 4H, $^{1}J(^{13}\text{C}-^{1}\text{H})$ = 120 Hz, $^{2}J(^{117/119}\text{Sn}-^{1}\text{H})$ = 77/81 Hz, $^{3}J(^{1}\text{H}-^{1}\text{H})$ = 6 Hz, $CH_2\mathit{CH_2}Sn$), 2.49 (quint, 2H, $^{1}J(^{13}\text{C}-^{1}\text{H})$ = 130 Hz, $^{3}J(^{117/119}\text{Sn}-^{1}\text{H})$ = 200/209 Hz, $^{3}J(^{1}\text{H}-^{1}\text{H})$ = 6 Hz, $\mathit{CH_2}CH_2Sn$), 7.40−7.67 (m, 30H, PhP). $^{13}\text{C}\{^{1}\text{H}\}$ NMR ($CDCl_3$): δ 3.26 (s, $^{1}J(^{29}\text{Si}-^{13}\text{C})$ = 61 Hz, $^{3}J(^{117/119}\text{Sn}-^{13}\text{C})$ = 35 Hz, CH_3), 20.84 (s, $^{2}J(^{117/119}\text{Sn}-^{13}\text{C})$ = 38 Hz, $\mathit{CH_2}$-CH_2Sn), 23.77 (s, $^{1}J(^{117/119}\text{Sn}-^{13}\text{C})$ = 407/426 Hz, $^{1}J(^{29}\text{Si}-^{13}\text{C})$ = 59 Hz, $SiCH_2Sn$), 38.12 (s, $^{1}J(^{117/119}\text{Sn}-^{13}\text{C})$ = 635/669 Hz, $^{3}J(^{117/119}\text{Sn}-^{13}\text{C})$ = 39 Hz, $CH_2\mathit{CH_2}Sn$), 126.78−133.82 (4 signals with ^{31}P-couplings, PhP). $^{29}\text{Si}\{^{1}\text{H}\}$ NMR ($CDCl_3$): δ 9.2 (s, $^{1}J(^{13}\text{CH}_2-^{29}\text{Si})$ = 65 Hz, $^{1}J(^{13}\text{CH}_3-^{29}\text{Si})$ = 60 Hz, $^{2}J(^{117/119}\text{Sn}-^{29}\text{Si})$ = 44 Hz). $^{31}\text{P}\{^{1}\text{H}\}$ NMR ($CDCl_3$): δ 21.8 (s, $^{1}J(^{13}\text{C}_i-^{31}\text{P})$ = 108 Hz). $^{119}\text{Sn}\{^{1}\text{H}\}$ NMR ($CDCl_3$): δ −55.7 (s, $^{1}J(\text{CH}_2{}^{13}\text{CH}_2-^{119}\text{Sn})$ = 671 Hz, $^{1}J(\text{Si}^{13}\text{CH}_2-^{119}\text{Sn})$ = 425 Hz, $^{2}J(^{29}\text{Si}-^{119}\text{Sn})$ = 43 Hz). Anal. Calcd for $C_{45}H_{52}Cl_5NOP_2Si_2Sn_2$ (1155.72): C, 46.8; H, 4.5; N, 1.2; Cl, 15.3. Found: C, 47.2; H, 4.7; N, 1.2; Cl, 14.9.

Synthesis of poly-[Si(Me$_2$)CH$_2$Sn(Cl$_2$)(CH$_2$)$_3$Sn(Cl$_2$)-CH$_2$Si(Me$_2$)O] (8). A solution of 1,1,5,5,11,11,15,15-octachloro-7,7,9,9,17,17,19,19-octamethyl-8,18-dioxa-7,9,17,19-tetrasila-1,5,11,15-tetrastannacycloeicosane (**5**) (0.15 g, 0.13 mmol) and a trace amount of *para*-toluenesulfonic acid in 5 mL of acetone was heated to reflux for 2 days. The solvent was removed in vacuo, giving 0.15 g (100%) of poly-[OSi(Me$_2$)CH$_2$Sn(Cl$_2$)(CH$_2$)$_3$-Sn(Cl$_2$)CH$_2$Si(Me$_2$)] (**8**) as a colorless waxy solid, mp 93−105°C. ^{1}H NMR ($CDCl_3$): δ 0.29 (s, 12H, $^{1}J(^{13}\text{C}-^{1}\text{H})$ = 119 Hz, CH_3), 1.01 (s, 4H, $^{1}J(^{13}\text{C}-^{1}\text{H})$ = 118 Hz, $^{2}J(^{117/119}\text{Sn}-^{1}\text{H})$ = 88/92 Hz, $SiCH_2Sn$), 1.89 (t, 4H, $^{1}J(^{13}\text{C}-^{1}\text{H})$ = 150 Hz, $^{2}J(^{117/119}\text{Sn}-^{1}\text{H})$ = 50/53 Hz, $^{3}J(^{1}\text{H}-^{1}\text{H})$ = 8 Hz, $CH_2\mathit{CH_2}Sn$), 2.31 (quint, 2H, $^{3}J(^{117/119}\text{Sn}-^{1}\text{H})$ = 88/92 Hz, $^{3}J(^{1}\text{H}-^{1}\text{H})$ = 8 Hz, $\mathit{CH_2}CH_2Sn$). $^{13}\text{C}\{^{1}\text{H}\}$ NMR (acetone-d_6): δ 3.27 (s, $^{1}J(^{29}\text{Si}-^{13}\text{C})$ = 61 Hz, $^{3}J(^{117/119}\text{Sn}-^{13}\text{C})$ = 15 Hz, CH_3), 16.63 (s, $^{1}J(^{117/119}\text{Sn}-^{13}\text{C})$ = 346/362 Hz, $^{1}J(^{29}\text{Si}-^{13}\text{C})$ = 54 Hz, $SiCH_2Sn$), 21.87 (s, $^{2}J(^{117/119}\text{Sn}-^{13}\text{C})$ = 38 Hz, $\mathit{CH_2}CH_2Sn$), 32.96 (s, $^{1}J(^{117/119}\text{Sn}-^{13}\text{C})$ = 530/555 Hz, $^{3}J(^{117/119}\text{Sn}-^{13}\text{C})$ = 124/129 Hz, $CH_2\mathit{CH_2}$-Sn). $^{29}\text{Si}\{^{1}\text{H}\}$ NMR (acetone-d_6): δ 7.7 (s, $^{1}J(^{13}\text{CH}_2-^{29}\text{Si})$ = 54 Hz, $^{1}J(^{13}\text{CH}_3-^{29}\text{Si})$ = 61 Hz, $^{2}J(^{117/119}\text{Sn}-^{29}\text{Si})$ = 20 Hz). $^{119}\text{Sn}\{^{1}\text{H}\}$ NMR (acetone-d_6): δ 42.1 (s, $^{4}J(^{119}\text{Sn}-^{117}\text{Sn})$ = 346 Hz). Anal. Calcd for $1/n(C_9H_{22}Cl_4OSi_2Sn_2)_n\cdot 1/n(581.68)_n$: C, 18.6; H, 3.8. Found: C, 18.9; H, 3.8.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Australian Research Council for financial support. A.D. thanks the Freundesgesellschaft der Universität Dortmund for supporting a three month stay at Dortmund University.

Supporting Information Available: Tables of all coordinates, anisotropic displacement parameters, and geometric data for compounds **4** and **7**. The discussion of the complexation behavior of compound **4** toward fluoride ions and the ESMS spectrum of compound **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020740B