$Ph_{(3-n)}X_nSnCH_2$-16-crown-5 (X = F, Cl, Br, I, SCN; *n* = 1, 2): Intramolecular O → Sn Coordination versus Ditopic Complexation of Sodium Thiocyanate†

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The synthesis of the organotin-substituted crown ethers $Ph_{(3-n)}X_nSn$-CH_2-16-crown-5 (**1**, *n* = 0; **2**, *n* = 1, X = I; **3**, *n* = 1, X = Br; **4**, *n* = 1, X = Cl; **5**, *n* = 1, X = F; **6**, *n* = 1, X = SCN; **7**, *n* = 2, X = Cl; **8**, *n* = 2, X = I) is reported. The compounds are characterized by elemental analyses and ^{1}H, ^{13}C, ^{19}F, ^{23}Na, and ^{119}Sn NMR spectroscopy and in the case of compound **4** also by ^{119}Sn MAS NMR spectroscopy. Single-crystal X-ray diffraction analyses reveal for compounds **2**−**5** trigonal-bipyramidally configurated tin atoms with intramolecular Sn−O distances ranging between 2.530(2) (**5**) and 2.571(1) Å (**4**), whereas the tin atom in compound **1** shows a distorted tetrahedral configuration. The tin atoms in compounds **7** and **8** are hexacoordinated with intramolecular Sn−O distances ranging between 2.473(1) (**7**) and 2.522(1) Å (**7**). NMR spectroscopy reveals the ability of compound **4** to form, in competition with intramolecular O → Sn coordination, a ditopic complex with NaSCN.

Introduction

The design of molecular hosts for selective recognition of anions has become a rather popular topic of contemporary chemical research, and this is manifested by a plethora of publications. The progress made in this field has been regularly reviewed over the years.[1−23] These studies complement in an ideal manner the rich chemistry of selective cation receptors, which got started almost simultaneously in the late 1960s, with that of anion recognition but which developed much faster to the extent that the Nobel Prize was awarded in 1987 to their front leaders Pedersen, Lehn, and Cram.

One challenge for chemists that originates as a logical consequence from the two subdisciplines of ion recognition is the combination of both cation and anion binding sites in one molecule in order to create a heteroditopic receptor, which, for instance, should make possible the selective recognition and/or extraction of particular salts. This concept was shown to be successful, and a variety of heteroditopic hosts for salts have been reported to date.[24−29]

Among these, only a few organoelement species are known such as the boron- and organotin-substituted crown ethers **A**,[30,31] **B**,[32] and **C**,[33] respectively (Chart 1). The former binds potassium fluoride, KF, as an associated ion pair, whereas compound **B** is a straightforward example of a host molecule that binds sodium thiocyanate, NaSCN, as separate ions. This ability of compound **B** is remarkable because ion separation requires energy to

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Chart 1

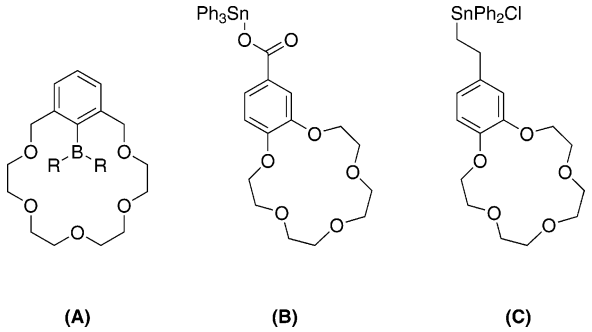
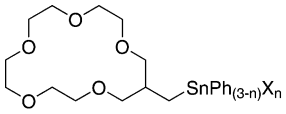


Chart 2



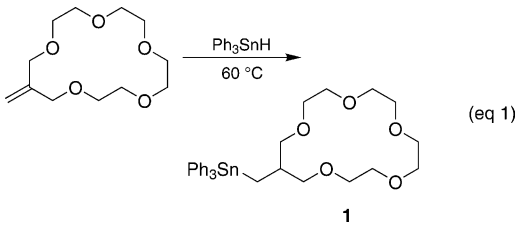
(D), n = 1, 2; X = F, Cl, Br, I, SCN

overcome the Coulomb forces. However, both compounds **A** and **B** are unstable under noninert conditions, which limits their potential applications. With this in mind we have synthesized the more robust organotin-substituted crown ether **C**, in which the organotin moiety is linked to the crown ether via a dimethylene spacer. As it was demonstrated by a U-tube experiment, compound **C** is able to transport sodium thiocyanate from aqueous solution through a dichloromethane phase into an aqueous phase.

In continuation of our systematic studies on organotin-substituted crown ethers[33] we report here compounds of type **D** (Chart 2) and investigate the complexation behavior of one representative ($n = 1$, X = Cl) toward $[(Ph_3P)_2N]^+Cl^-$, *n*-Bu_4NSCN, $NaBPh_4$, NaI, NaCl, and NaSCN.

Results and Discussion

Synthetic Aspects and Molecular Structures in the Solid State. The reaction of 15-methylene-1,4,7,10,13-pentaoxacyclohexadecane[34] with triphenyltin hydride provided the triphenytin-substituted crown ether **1** (eq 1). The molecular structure



(eq 1)

1

of compound **1** is shown in Figure 1, and selected bond distances and bond angles are listed in Table 1.

The tin atom in the tetraorganotin compound **1** adopts a monocapped-tetrahedral configuration with the O(5) atom being the capping atom. The latter approaches the tin atom via the tetrahedral face defined by C(1), C(13), and C(21) at a Sn(1)···O(5) distance of 3.206(1) Å, shorter than the sum of the van der Waals radii[35] of oxygen (1.50 Å) and tin (2.20 Å). The Sn(1) atom is displaced by 0.5593(9) Å out of this plane in the direction of C(7).

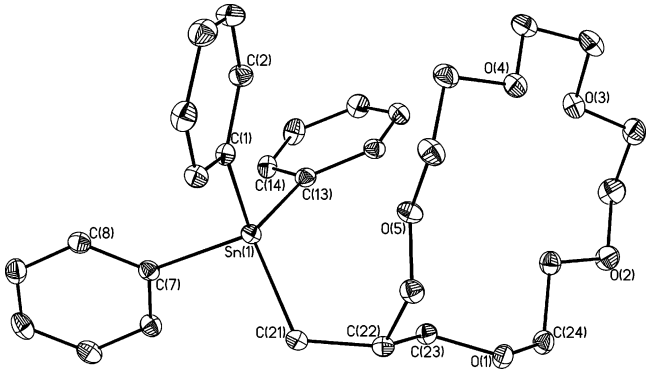


Figure 1. Molecular structure of **1** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

Table 1. Selected Bond Distances (Å) for Compounds 1−5

	1	**2**	**3**	**4**	**5**
	X = C(13)	X = I(1)	X = Br(1)	X = Cl(1)	X = F(1)
Sn(1)−C(1)	2.132(2)	2.149(3)	2.140(2)	2.131(2)	2.136(3)
Sn(1)−C(7)	2.158(2)	2.136(3)	2.146(2)	2.144(2)	2.142(3)
Sn(1)−X	2.153(2)	2.8220(3)	2.6088(4)	2.4541(5)	2.0147(15)
Sn(1)−C21	2.161(2)	2.128(3)	2.129(2)	2.131(2)	2.136(2)
Sn1−O1	4.990(1)	2.554(2)	2.564(2)	2.571(1)	2.5301(18)
Sn1−O5	3.206(1)				

Reaction in CH_2Cl_2 under ice cooling of the tetraorganostannane **1** with 1 molar equiv of iodine and bromine almost quantitatively gave the corresponding triorganotin iodide **2** and the triorganotin bromide **3**, respectively. Treatment of **2** with an excess of AgCl in CH_3CN afforded the triorganotin chloride **4**, whereas reaction with *n*-$Bu_4NF{\cdot}3H_2O$ in CH_2Cl_2 provided the triorganotin fluoride **5**. Finally, reaction of the triorganotin iodide with AgSCN gave the triorganotin thiocyanate **6** (Scheme 1).

Compounds **1**−**6** are colorless to slightly yellow (**2**) crystalline solids, which are well soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, and thf.

As a representative of the triorganotin halides **2**−**5** the molecular structure of the triorganotin chloride **4** is shown in Figure 2. The structures of compounds **2**, **3**, and **5** are rather similar, and they are given in the Supporting Information (Figures S1−S3). Selected geometrical parameters of compounds **2**−**5** are collected in Tables 1 and 2.

The tin atoms in compounds **2**−**5** show distorted trigonal bipyramidal configurations (geometrical goodness $\Delta\Sigma(\vartheta)$[36] 63° (**2**), 64° (**3**, **4**, and **5**)) with the carbon atoms C(1), C(7), and C(21) occupying the equatorial and the halogen atoms (I(1) (**2**), Br(1) (**3**), Cl(1) (**4**), F(1) (**5**)) and the oxygen atom O(1) occupying the axial positions. The Sn(1) atom is displaced by 0.152(2) (**2**), 0.588(1) (**3**), 0.269(1) (**4**), and 0.266(2) (**5**) Å from the plane defined by C(1), C(7), and C(21) in the direction of the corresponding halogen atom. The intramolecular Sn(1)−O(1) distances differ only slightly and fall in the range between 2.530(2) (**5**) and 2.571(1) (**4**) Å. They are comparable with Sn−O distances found in other intramolecularly coordinated triorganotin halides containing five-membered chelates.[37−40] As

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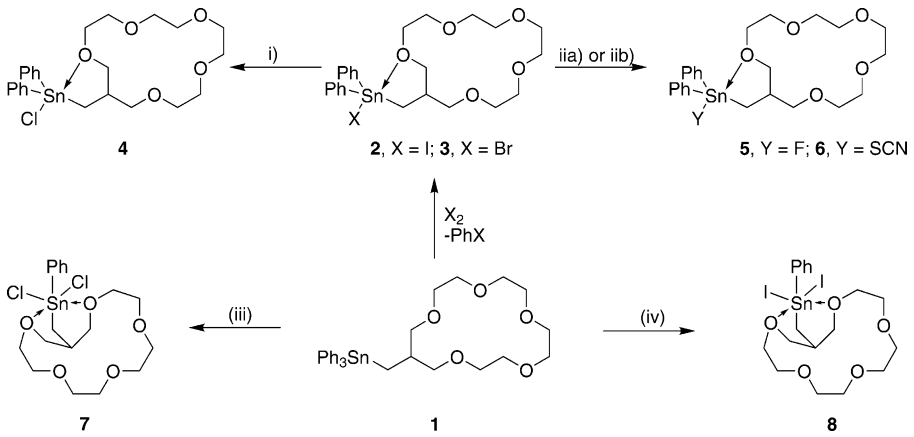
Scheme 1 [a]



[a] Conditions: (i) AgCl (excess), CH_3CN, −AgI; (iia) for Y = F: *n*-Bu_4NF (excess), CH_2Cl_2, −*n*-Bu_4NI; (iib) for Y = SCN: AgSCN, −AgI; (iii) HCl(g), CH_2Cl_2, −78 °C, −C_6H_6; (iv) 2 I_2, CH_2Cl_2, 0 °C, −2 PhI.

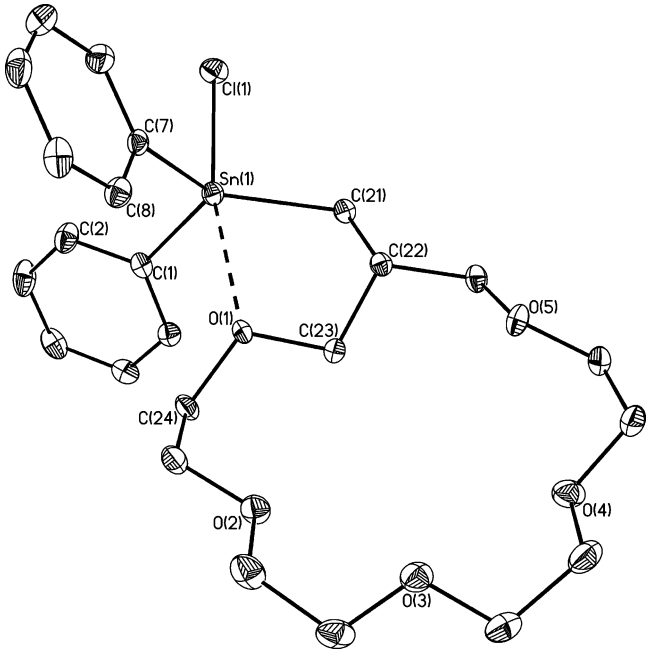


Figure 2. Molecular structure of **4** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

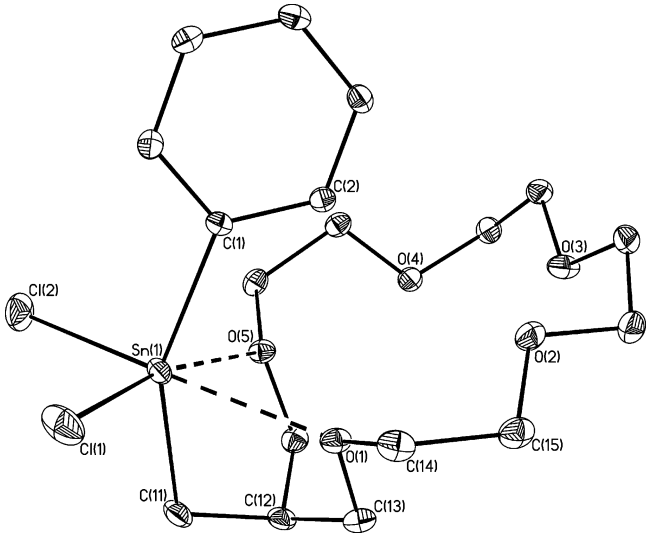


Figure 3. Molecular structure of **7** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

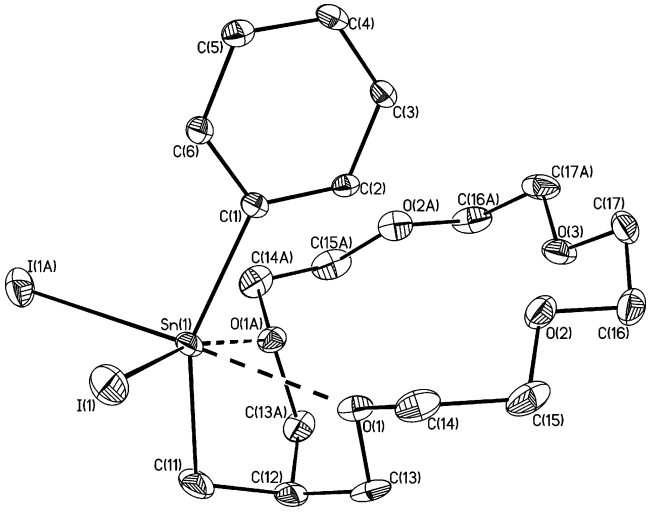


Figure 4. Molecular structure of **8** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

expected, the tin−halogen distances are longer than the corresponding distances in tetracoordinated triorganotin halides, with this effect being least pronounced for the triorganotin fluoride **5**.

Two-fold functionalization at the tin atom was achieved by reaction of the tetraorganostannane **1** with gaseous hydrogen chloride to give the diorganotin dichloride **7**, and with 2 molar equiv of iodine to give the diorganotin diiodide **8** (Scheme 1). Both compounds **7** and **8** are crystalline solids, but in contrast to the triorganotin halides **2**−**5**, they exhibit lower solubility in organic solvents.

The molecular structures of the diorganotin dihalides **7** and **8** are shown in Figures 3 and 4, respectively, and selected geometrical parameters are collected in Tables 3 and 4. The tin atoms in compounds **7** and **8** are each hexacoordinated by two carbon, two oxygen, and two halogen atoms (Cl for **7**, I for **8**), with an overall distorted octahedral *trans*−*cis*−*cis* configuration. The distortion is mainly the result of ligand constraint and especially manifested in (i) the decrease of the C(1)−Sn(1)−C(11) angles from 180° to 151.44(6)° for **7** and 150.5(2)° for **8**, (ii) the decrease of the O(1)−Sn(1)−O(5)/O(1A) angles from 90° to 74.11(0)° for **7** and 73.9(1)° for **8**, and (iii) the increase of the Cl(1)−Sn(1)−Cl(2) and I(1)−Sn(1)−I(1A) angles from

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Table 2. Selected Bond Angles (deg) for Compounds 1−5

	1	2	3	4	5
	X = C(13)	X = I(1)	X = Br(1)	X = Cl(1)	X = F(1)
C(7)−Sn(1)−C(1)	108.29(6)	114.2(1)	112.86(8)	112.33(7)	110.92(9)
C(21)−Sn(1)−C(1)	110.29(6)	121.1(1)	119.55(9)	119.76(7)	121.62(10)
C(21)−Sn(1)−C(7)	101.31(6)	119.8(1)	122.93(8)	123.21(7)	122.84(9)
C(1)−Sn(1)−O(1)		90.0(1)	87.79(7)	87.98(6)	86.50(8)
C(7)−Sn(1)−O(1)		86.03(9)	88.79(7)	88.63(6)	88.16(8)
C(21)−Sn(1)−O(1)		72.5(1)	72.79(7)	72.75(5)	74.86(8)
C(1)−Sn(1)−X		100.26(8)	97.03(6)	97.15(5)	96.26(8)
C(7)−Sn(1)−X	106.04(6)	97.57(8)	98.54(6)	98.05(5)	95.43(8)
C(21)−Sn(1)−X	120.88(6)	94.49(8)	96.09(6)	96.53(5)	99.50(8)
O(1)−Sn(1)−X		166.45(5)	168.82(3)	169.26(3)	174.34(6)
C(23)−O(1)−Sn(1)		110.4(2)	109.0(1)	108.96(9)	106.88(14)
C(24)−O(1)−Sn(1)		131.5(2)	124.5(1)	124.3(1)	124.29(15)
C(22)−C(21)−Sn(1)	119.8(1)	114.8(2)	114.1(2)	114.3(1)	112.02(17)

Table 3. Selected Bond Distances (Å) for Compounds 7 and 8

	7	8
	X(1) = Cl(1), X(2) = Cl(2), X(3) = O(5)	X(1) = I(1), X(2) = I(1a), X(3) = O(1a)
Sn(1)−X(1)	2.4234(4)	2.8050(3)
Sn(1)−X(2)	2.4240(4)	
Sn(1)−C(1)	2.128(2)	2.137(4)
Sn(1)−C(11)	2.123(2)	2.123(5)
Sn(1)−O(1)	2.522(1)	2.482(2)
Sn(1)−O(5)	2.4793(9)	

Table 4. Selected Bond Angles (deg) for Compounds 7 and 8

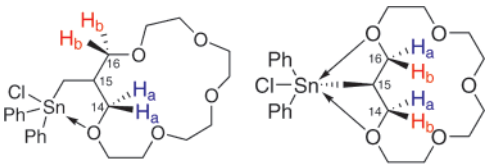
	7	8
	X(1) = Cl(1), X(2) = Cl(2), X(3) = O(5)	X(1) = I(1), X(2) = I(1a), X(3) = O(1a)
C(11)−Sn(1)−C(1)	151.44(6)	150.5(2)
C(1)−Sn(1)−X(1)	98.72(4)	99.51(8)
C(11)−Sn(1)−X(1)	99.47(4)	100.05(9)
C(1)−Sn(1)−X(2)	98.22(4)	
C(11)−Sn(1)−X(2)	100.67(4)	
X(1)−Sn(1)−X(2)	98.44(2)	96.33(1)
C(1)−Sn(1)−O(1)	84.80(4)	84.4(1)
C(11)−Sn(1)−O(1)	71.55(5)	72.2(1)
X(1)−Sn(1)−O(1)	96.05(3)	94.63(5)
X(2)−Sn(1)−O(1)	164.55(3)	
X(3)−Sn(1)−O(1)	74.11(3)	73.9(1)
C(1)−Sn(1)−O(5)	85.92(4)	
C(11)−Sn(1)−O(5)	72.60(5)	
X(1)−Sn(1)−O(5)	168.79(3)	
X(2)−Sn(1)−O(5)	90.94(2)	
C(13)−O(1)−Sn(1)	110.55(8)	111.3(2)
C(14)−O(1)−Sn(1)	129.09(8)	127.1(2)
C(21)−O(5)−Sn(1)	128.66(8)	
C(22)−O(5)−Sn(1)	111.13(8)	
C(12)−C(11)−Sn(1)	108.2(1)	108.3(3)

90° to 98.44(2) (**7**) and 96.33(1)° (**8**). The intramolecular Sn(1)−O(1) and Sn(1)−O(5) distances of 2.522(1) and 2.4793(9) Å in the diorganotin dichloride **7** and the Sn(1)−O(1) distance of 2.482(2) Å in the diorganotin diiodide **8** are slightly shorter than the corresponding distances in the triorganotin halides **2**−**5** (see above).

Structures in Solution. The tin atom in compound **1** is essentially tetracoordinated, as expected. It shows a ^{119}Sn NMR chemical shift of δ −110, which is close to δ −92 found for Ph_3SnMe.[41]

The intramolecular Sn−O coordination found in the solid state for the triorganotin halides **2**−**5** and the diorganotin dihalides **7** and **8**, respectively, is retained in solution, as evidenced by

Chart 3



4a **4b**

the ^{119}Sn NMR chemical shifts of δ −130 (**2**), −96 (**3**), −88 (**4**), −106 [$^1J(^{119}Sn-^{19}F)$ 2207 Hz] (**5**), −125 (**7**), and −266 (**8**) being low-frequency shifted with respect to related compounds having comparable substituent patterns at the tin atoms but lack any intramolecular or intermolecular coordination, such as the diphenylmethyltin iodide Ph_2MeSnI (δ −68),[42] the triorganotin fluoride $Ph_2(Me_3SiCH_2)SnF$ (δ 25, $^1J(^{119}Sn-^{19}F)$ 2380 Hz),[43] the diphenylethyltin chloride $Ph_2EtSnCl$ (δ 17),[44] the 1,2-bis(diphenylhalostannyl)ethanes $(Ph_2XSnCH_2)_2$, (X = I, δ −54; X = Br, δ −5; X = Cl, δ 2),[44] the bis(dichlorophenylstannyl)methane $(PhCl_2Sn)_2CH_2$ (δ 8),[45] and the 1,2-bis(diiodophenylstannyl)ethane $(PhI_2SnCH_2)_2$ (δ −169).[44] Moreover, the ^{119}Sn chemical shift for compound **4** (δ −88) is essentially temperature-independent (between 20 and −80 °C) and rather close to the ^{119}Sn MAS NMR chemical shift of δ −73.

Exemplarily, compound **4** was studied in more detail by ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C spectrum ($CDCl_3$) at room temperature of the triorganotin chloride **4** displayed only six resonances for the crown ether carbon atoms, indicating, on the ^{13}C NMR time scale, a symmetric structure **4b** with pairs of equivalent carbon atoms C6/C8, C5/C9, C3/C11, C2/C12, and C14/C16 rather than an unsymmetrical structure **4a** (Charts 3, 4).

This view is supported by a ^{1}H−^{13}C-HSQC experiment showing only one resonance for the C14 and C16 carbon atoms. No decoalescence of these signals was observed at −80 °C.

Worth mentioning is the ^{119}Sn NMR spectrum of the triorganotin thiocyanate **6** (see Supporting Information). It shows a triplet resonance (δ −155, $^1J(^{119}Sn-^{14}N)$ 141 Hz) as result of ^{119}Sn−^{14}N coupling and indicates a rather symmetric electron distribution in the SCN−Sn moiety. The ^{14}N NMR spectrum (see Supporting Information) exhibits a singlet resonance at δ −236 ($\nu_{1/2}$ = 65 Hz).

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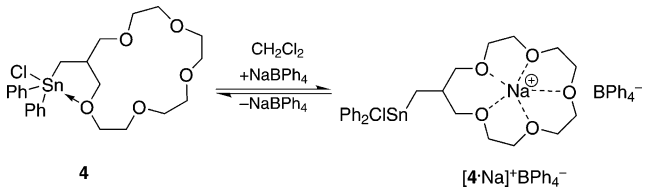
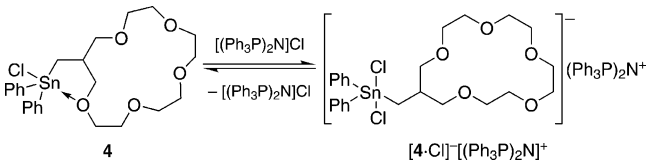
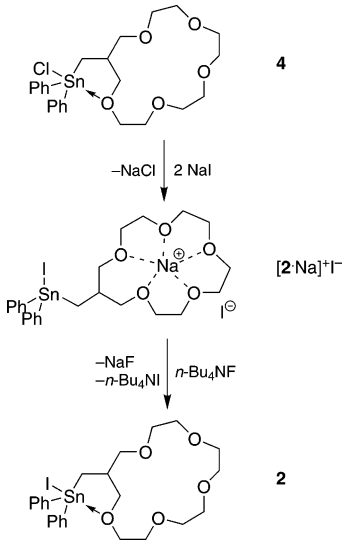
Scheme 2



Scheme 3



Scheme 4



Complexation Studies. The ^{119}Sn NMR spectrum at −40 °C of a solution of the triorganotin chloride **4** in CD_2Cl_2 to which had been added 1 molar equiv of sodium tetraphenyloborate, $NaBPh_4$, displayed one resonance at δ 13 ($\nu_{1/2}$ = 207 Hz), which is assigned to the sodium complex [**4**·Na]$^+$BPh$_4^-$ in which no O → Sn coordination takes place and in which the tin atom is four-coordinate. In addition to the ^{119}Sn NMR chemical shift, the latter statement is supported by a decrease of both the $^2J(^1H-^{119}Sn)$ and $^1J(^{13}C-^{119}Sn)$ couplings to 47 and 434 Hz, respectively, as compared with 72 and 548 Hz measured for the triorganotin chloride **4**. No ^{119}Sn NMR signal was observed at room temperature. Apparently, there is an equilibrium in which the Lewis acidic sodium cation and tin atom compete for the oxygen Lewis bases (Scheme 2). The equilibrium becomes slow at low temperature and shifts to the right. That the sodium cation is indeed coordinated by the crown ether oxygen atoms is supported by (i) the high-frequency shift of the ^{13}C resonance for the C14/C16 crown ether carbon atoms from δ 74.4 to δ 78.1 and the low-frequency shift of the ^{13}C signals for the C2−C12 carbon atoms by approximately 0.4 ppm (for numbering see Chart 4 in the Experimental Section) and (ii) by the ^{23}Na NMR spectrum ($CDCl_3/CD_3CN$, 4:1) showing a rather broad resonance at δ 1.94 ($\nu_{1/2}$ 573 Hz) in comparison to the sharp resonance at δ 1.84 ($\nu_{1/2}$ 71 Hz) observed in the absence of compound **4**. In CD_2Cl_2 solution of [**4**·Na]$^+$BPh$_4^-$, an even broader signal at δ 1.40 ($\nu_{1/2}$ 2232 Hz) was observed. Line broadening is a typical measure for the identification of crown ether complexes with sodium cations, whereas the ^{23}Na chemical shifts do not vary dramatically between free and complexed sodium cation.[46]

In order to check whether the ^{119}Sn NMR spectrum mentioned above can indeed be interpreted in terms of formation of [**4**·Na]$^+$BPh$_4^-$ (Scheme 2) and not with formation of the triorganotin cation [Ph_2Sn-CH_2-16-crown-5]$^+$, tetraphenylborate anion BPh$_4^-$, and NaCl, we reacted compound **2** with $AgClO_4$ in CH_3CN and, after the AgI had been filtered and the CH_3CN had been removed in vacuo, obtained a colorless oil. The ^{119}Sn NMR spectrum in $CDCl_3$ of this oil displayed a single resonance at δ −71. With caution, we assign this signal to [Ph_2-Sn-CH_2-16-crown-5]$^+$ClO$_4^-$. Under the assumption that exchange of a perchlorate anion by a tetraphenylborate anion will have only little influence on the ^{119}Sn chemical shift, this result confirms our interpretation concerning Scheme 2.

The ^{119}Sn NMR spectrum (CD_2Cl_2) at ambient temperature of a solution of the triorganotin chloride **4** to which had been added 1 molar equiv of [$(Ph_3P)_2$N]$^+$Cl$^-$ showed a broad resonance at δ −121 (integral 96, $\nu_{1/2}$ 970 Hz, signal c). At −70 °C two sharp resonances were observed at δ −89 (integral 65, signal d) and −199 (integral 35, signal e). Addition of a second molar equivalent of [$(Ph_3P)_2$N]$^+$Cl$^-$ causes (i) signal c to broaden further ($\nu_{1/2}$ 2300 Hz) and to shift to δ −140 and (ii) a change in the integral ratio of signals d and e to 47:53. The results are interpreted in terms of an equilibrium between the triorganotin chloride **4** (represented by signal d) and its triorganodichlorostannate complex [**4**·Cl]$^-$[$(Ph_3P)_2$N]$^+$ (represented by signal e) (Scheme 3) with, on the ^{119}Sn NMR time scale, the equilibrium being fast at ambient temperature and slow at −70 °C.

Interestingly, the thiocyanate anion, as its tetrabutylammonium salt, is not able to break the O→Sn coordination in the triorganotin chloride **4**; that is, the ^{119}Sn NMR spectrum of a solution of **4** in $CDCl_3$ to which had been added 1 molar equiv of *n*-Bu_4NSCN displayed a sharp resonance at δ −88, identical with the signal observed for a solution of pure **4**.

So far, we learned that the sodium cation as well as the chloride anion, as their soluble salts with appropriate counterions, are able to break the intramolecular O→Sn coordination in the triorganotin chloride **4**. However, the complexation ability of **4** is not strong enough to overcome the lattice energy of sodium chloride (790 kJ/mol)[47] and to solubilize the latter to give a ditopic zwitterionic complex [**4**·NaCl]; that is, no reaction was observed upon addition of NaCl to a solution of compound **4** in $CDCl_3$. The lattice energy of sodium iodide is lower and amounts to 705 kJ/mol.[47] The ^{119}Sn NMR spectrum at room temperature of a solution of compound **4** in CD_2Cl_2 to which had been added 1 molar equiv of NaI displayed two broad resonances at −87 ($\nu_{1/2}$ 454 Hz, integral 41, **4**) and −129 ($\nu_{1/2}$ 794 Hz, integral 59, **2**). At −70 °C both signals sharpened but did not significantly change their integral ratio. The ^{119}Sn NMR spectrum of compound **4** in CD_2Cl_2 that had been reacted with excess NaI and from which the precipitate had been filtered showed a single resonance at δ −61. This signal is assigned to the homotopic complex [**2**·Na]$^+$I$^-$ (Scheme 4), containing a four-coordinate tin atom (see δ −68 of tetracoordinated Ph_2-MeSnI for comparison). This assignment is supported by the

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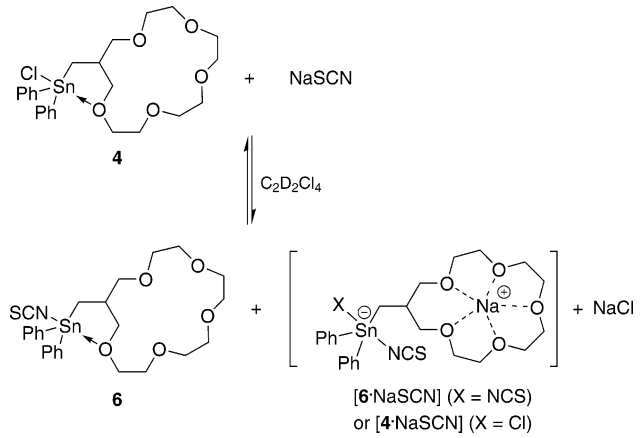
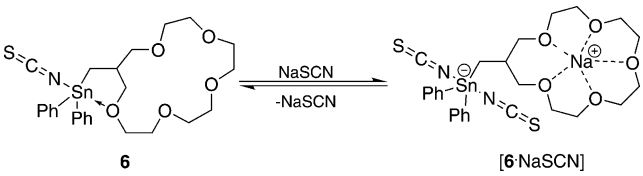
Scheme 5



Scheme 6



^{13}C NMR spectrum with the C14/C16 resonance being shifted to δ 77.6 and the ^1H NMR spectrum unambiguously indicating sodium ion coordination. Apparently, the Lewis acidity of the tin atom in [**2**·Na]$^+I^-$ (Scheme 4) is not high enough to induce charge separation under formation of a triorganodiiodostannate complex. Addition of tetrabutylammonium fluoride trihydrate, *n*-$Bu_4NF{\cdot}3H_2O$, to the solution caused precipitation of sodium fluoride and quantitative formation of the triorganotin iodide **2** (Scheme 4).

Sodium thiocyanate, NaSCN, has an even lower lattice energy of 682 kJ/mol.[47] The ^{119}Sn NMR spectrum at room temperature of a solution of compound **4** in $C_2D_2Cl_4$ to which had been added 1 molar equiv of NaSCN displayed three broad resonances at δ −89 ($\nu_{1/2}$ 219 Hz, integral 43, signal f, **4**), δ −157 ($\nu_{1/2}$ 325 Hz, integral 18, signal g), and δ −229 ($\nu_{1/2}$ 219 Hz, integral 39, signal h), respectively. Lowering the temperature to −20 °C caused the signals to sharpen and their integral ratio to change slightly (f:g:h = 48:14:38). Changing the molar ratio of **4**:NaSCN from 1:1 to 1:2 caused a change of the integral ratio of the signals as well (f:g:h = 41:10:49).

The signal at δ −157 is assigned to the triorganotin thiocyanate $Ph_2(NCS)Sn$-CH_2-16-crown-5 (**6**), with the assignment being confirmed by addition of the authentic compound. The signal at δ −229 can be assigned with caution to the ditopic complex [**4**·NaSCN] or [**6**·NaSCN] (Scheme 5). Given the smaller difference between the ^{119}Sn chemical shift observed (signal h) and that of compound **6** (72 ppm) and compound **4** (140 ppm), respectively, and the result shown in Scheme 6 (see below), the assignment of signal h to [**6**·NaSCN] is favored. The electrospray ionization mass spectrum (positive mode) of the authentic solution displayed mass clusters centered at *m*/*z* 602.2, 579.2, and 521.2 which are assigned to [$Ph_2(NCS)Sn$-CH_2-16-crown-5·Na]$^+$, [Ph_2ClSn-CH_2-16-crown-5·Na]$^+$, and [Ph_2Sn-CH_2-16-crown-5]$^+$, respectively, whereas the spectrum of pure compound **4** showed only the two latter mass clusters.

The existence of three different species being in equilibrium (Scheme 5) is further manifested by the ^1H NMR spectrum at −20 °C, which shows three Sn*CH*$_2$ resonances at δ 1.50, 1.56, and 1.79. At 87 °C only one resonance at δ 1.74 ($^2J(^1H-^{119}Sn)$ 78 Hz, $^3J(^1H-^1H)$ 6 Hz) was observed.

Notably, the equilibrium mixture as shown in Scheme 5 was also formed upon addition of an equimolar amount of sodium chloride to the solution of the triorganotin thiocyanate **6** in $CDCl_3$. However, it took the mixture 8 days to reach equilibrium, indicating kinetic control of the complexation.

The ^{119}Sn NMR spectrum ($CDCl_3$) of the triorganotin thiocyanate **6** to which had been added 1 molar equiv of sodium thiocyanate displayed two resonances at δ −155 ($\nu_{1/2}$ 418 Hz, integral 62) and −225 ($\nu_{1/2}$ 154 Hz, integral 38), respectively, indicating the equilibrium shown in Scheme 6. The latter signal is assigned with caution to the ditopic complex [**6**·NaSCN]. The equilibrium is further supported by observation of two ^{13}C resonances for the Sn*C*H_2 carbons at δ 18.9 and 23.0, respectively, being assigned to **6** and [**6**·NaSCN].

Notably, measuring the ^{119}Sn NMR spectrum of the same sample 10 days later revealed complete formation of [**6**·NaSCN] (only one sharp resonance at δ −225) and again indicates kinetic control of the complexation process.

Conclusion

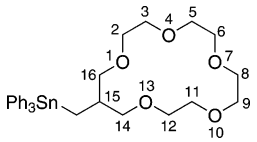
A variety of organotin-substituted crown ethers were prepared, the design of which allows intramolecular O→Sn coordination. Nevertheless, as it was shown exemplarily for the chlorodiphenylstannyl-substituted compound **4** in solution, this intramolecular O→Sn coordination is broken by addition of a chloride anion (as its $[(Ph_3P)_2N]^+$ salt) or sodium cation (as its Ph_4B^- salt), as well as by addition of sodium chloride or sodium thiocyanate, thus forming the corresponding ditopic complex [**4**·NaSCN] or [**6**·NaSCN]. Most interestingly, the latter process, that is, the dissolution of these salts, is kinetically controlled and might even take several days.

These results are promising, as they support the validity of the general concept for ditopic salt complexation and encourage future efforts for the design of related organometal-substituted crown compounds. One strategy to enable complexation of salts such as sodium or potassium fluoride having a high lattice energy should be to increase the Lewis acidity of the anion binding site and not allow the crown ether-oxygen atoms to interact with this Lewis acid.

Experimental Section

General Methods. All solvents were purified by distillation under nitrogen atmosphere from the appropriate drying agents. The hydrostannylation was carried out under nitrogen atmosphere. 15-Methylene-1,4,7,10,13-pentaoxacyclohexadecane[34] and triphenyltin hydride[48] were synthesized as described in the literature. The NMR experiments were carried out on a Bruker DRX 400, Bruker DPX 300, Varian Mercury 200, or Varian Inova 600 spectrometer. NMR experiments are carried out at ambient temperature unless a different temperature is given. Chemical shifts (δ) are given in ppm and are referenced to the solvent peaks with the usual values calibrated against tetramethylsilane (^1H, ^{13}C), $CFCl_3$ (^{19}F), NaCl solution in D_2O (^{23}Na), CH_3NO_2 (^{14}N), and tetramethylstannane (^{119}Sn). The numbering scheme for the crown ether moiety is pictured in Chart 4.

Chart 4



Electrospray mass spectra were recorded in the positive mode on a Thermoquest-Finnigan instrument using CH_3CN as the mobile phase. The samples were introduced as a solution in a mixture of CH_3CN and 1% formic acid (9:1 ratio) ($c = 10^{-4}$ mol L^{-1}) via a syringe pump operating at 0.5 μL/min. The capillary voltage was 4.5 kV, while the cone skimmer voltage was varied between 50 and 250 kV. Identification of the inspected ions was assisted by comparison of experimental and calculated isotope distribution patterns. The *m*/*z* values reported correspond to those of the most intense peak in the corresponding isotope pattern.

Crystallography. Intensity data for the colorless crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα (0.71073 Å) radiation at 173(1) K. The data collection covered almost the whole sphere of reciprocal space with three (**2**, **5**, **7**, **8**) and four (**1**, **3**, **4**) sets at different *k*-angles with 395 (**1**), 298 (**2**), 182 (**3**), 419 (**4**), 207 (**5**), 310 (**7**), and 263 (**8**) frames via ω-rotation [$\Delta/\omega = 1°$ (**1**, **2**, **4**, **7**, **8**) and $\Delta/\omega = 2°$ (**3**, **5**)] at two times 10 s (**3**, **4**), 12.5 s (**2**), and 60 s (**4**) per frame. The crystal-to-detector distances were 3.4 cm (**2**−**8**) and 4.4 cm (**1**). Crystal decays were monitored by repeating the initial frames at the end of data collection. The data were not corrected for absorption effects. Analyzing the duplicate reflections, there were no indications for any decay. The structures were solved by direct methods (SHELXS97[49]) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (SHELXL97[50]).

The H atoms were placed in geometrically calculated positions using a riding model with isotropic temperature factors constrained at 1.2 for non-methyl and at 1.5 for methyl groups times U_{eq} of the carrier C atom. In **7** one C atom is disordered over two positions with occupancies of 0.5 (C(27), C(27′)). Each solvent molecule CH_2Cl_2 in **3** and **4** is anisotropically refined with occupancies of 0.5. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 51. The figures were created by SHELXTL.[52]

Crystallographic data are given in Table 5, and selected bond distances and angles in Tables 1 and 2 (**1**−**5**) and Tables 3 and 4 (**3**, **4**).

Synthesis of (1,4,7,10,13-Pentaoxacyclohexadec-15-ylmethyl)-triphenylstannane (1). 15-Methylene-1,4,7,10,13-pentaoxacyclohexadecan (10 g, 40 mmol) and aibn (115 mg) were added to Ph_3SnH (14.26 g, 40 mmol). The mixture was stirred at 70 °C for 12 h followed by cooling to room temperature, addition of CH_2Cl_2 (50 mL), and filtration of the solution through Celite. After the solvent had been removed in vacuum a light yellow oil remained. The purification of this oil was achieved by column chromatography with silica gel and CH_2Cl_2. Elution with ethanol gave 18.6 g (78%) of **1**. ^{1}H NMR ($CDCl_3$) δ: 1.45 (d, $^3J(^1H-^1H) = 7.5$ Hz, $^2J(^1H-^{117/119}Sn) = 58.8$ Hz, 2H, Sn−CH_2), 2.43 (m, 1 H, CH), 3.28−3.69 (m, 20 H, CH_2-O-CH_2), 7.31−7.63 (m, 15 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 11.35 (Sn−CH_2−), 37.10 ($^2J(^{13}C-^{117/119}Sn) = 20.1$ Hz, C15), 69.47−70.72 (C2−C12), 74.20 (C14/C15), 128.13 ($^3J(^{13}C-^{117/119}Sn) = 48.0$ Hz, C_m), 128.36 ($^4J(^{13}C-^{117/119}Sn) = 11.5$ Hz, C_p), 136.86 ($^2J(^{13}C-^{117/119}Sn) = 35.5$ Hz, C_o), 140.39 ($^1J(^{13}C-^{117/119}Sn) = 497.1$ Hz, C_i). ^{119}Sn $\{^1H\}$ NMR (CH_2Cl_2, D_2O-Cap.) δ: −110.2. Anal. Calcd for $C_{30}H_{38}O_5Sn$ (597.33): C 60.3; H 6.4. Found: C 60.3; H 6.4. Mp: 60 °C.

Synthesis of Iodo(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)diphenylstannane (2). Iodine (2.98 g, 11.75 mmol) was added in small portions under ice cooling to a stirred solution of **1** (7.00 g, 11.75 mmol) in CH_2Cl_2 (50 mL). The reaction mixture was stirred overnight. The solvent and the iodobenzene were removed in vacuo (1×10^{-3} Torr). Addition of CH_2Cl_2 (20 mL), filtration, and evaporation of the solvent afforded 7.55 g (99% yield) of **3** as colorless crystals. ^{1}H NMR ($CDCl_3$) δ: 1.76 (d, $^3J(^1H-^1H) = 7.5$ Hz, $^2J(^1H-^{117/119}Sn) = 73.5$ Hz, 2 H, Sn−CH_2), 2.58 (m, 1 H, CH), 3.30−3.9 (m, 20 H, CH_2-O-CH_2), 7.30−7.90 (m, 10 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 20.46 (Sn−CH_2−), 37.78 (C15), 69.59−70.42 (C2−C12), 74.34 (C14/C16), 128.52 ($^3J(^{13}C-^{117/119}Sn) = 62.4$ Hz, C_m), 129.32 ($^4J(^{13}C-^{117/119}Sn) = 13.4$ Hz, C_p), 135.89 ($^2J(^{13}C-^{117/119}Sn) = 46.1$ Hz, C_o), 140.20 (C_i). ^{119}Sn-$\{^1H\}$ NMR (CH_2Cl_2, D_2O-Cap.) δ: −130.2. Anal. Calcd (%) for $C_{24}H_{33}IO_5Sn$ (647.13): C 44.5, H 5.1. Found: C 44.6, H 5.0. Mp: 102−103 °C.

Synthesis of Bromo(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)diphenylstannane (3). Bromine (1.3 g, 8.40 mmol) in dichloromethane (50 mL) was added dropwise to a cooled solution (−55 °C) of **1** (5.00 g, 8.40 mmol) in dichloromethane (100 mL). The reaction mixture was allowed to warm to room temperature over night to give a clear solution. From this solution all volatiles were removed in vacuo to afford a light yellow solid, which was recrystallized from ethanol to give colorless crystals (4.9 g, 98%).

^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K) δ: 1.64 (d, $^3J(^1H-^1H) = 8.0$ Hz, $^2J(^1H-^{117/119}Sn) = 76.8$ Hz, 2 H, Sn−CH_2), 2.47−2.70 (m, 1 H, CH), 3.28−3.84 (m, 20 H, CH_2-O-CH_2), 7.32−7.43 (m, 6 H, $Ph_{m,p}$), 7.69 (dd, $^3J(^1H-^1H) = 7.8$ Hz, $^4J(^1H-^1H) = 1.8$ Hz, $^3H(^1H-^{117/119}Sn) = 60$ Hz, 4 H, Ph_o). $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$, 298 K) δ: 18.55 ($^1J(^{13}C-^{117}Sn) = 507.3$ Hz, $^1J(^{13}C-^{119}Sn) = 531.0$ Hz, Sn−CH_2−), 37.28 (C(15)), 69.58−70.39 (C(2)−C(12)), 74.38 ($^3J(^{13}C-^{117/119}Sn) = 70.0$ Hz, C(14)/C(16)), 128.59 ($^3J(^{13}C-^{117/119}Sn) = 65.0$ Hz, C_m), 129.39 ($^4J(^{13}C-^{117/119}Sn) = 14.0$ Hz, C_p), 135.81 ($^2J(^{13}C-^{117/119}Sn) = 47.0$ Hz, C_o), 140.67 (C_i). ^{119}Sn$\{^1H\}$ NMR (149.21 MHz, $CDCl_3$, 298 K) δ: −96. Anal. Calcd for $C_{24}H_{33}BrO_5Sn \cdot {}^1/_2CH_2Cl_2$ (642.60): C 45.8 H 5.3. Found: C 46.0, H 5.2. Mp: 84−86 °C.

Synthesis of Chloro(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)diphenylstannane (4). AgCl (4.7 g, 32.5 mmol) was added to a solution of **3** (7.0 g, 10.8 mmol) in CH_3CN (150 mL) and stirred in the dark for 14 days. The resulting AgI and the nonreacted AgCl were filtered, and the filtrate was evaporated in vacuo to give a light yellow oil. The oil was dissolved in CH_2Cl_2/Et_2O (2:1) and cooled to −5 °C for several days. providing 5.9 g (98%) of pure **3**. ^{1}H NMR (CD_2Cl_2) δ: 1.58 (d, $^3J(^1H-^1H) = 8.0$ Hz, $^2J(^1H-^{117/119}Sn) = 40.2$ Hz, 2 H, Sn−CH_2), 2.59 (m, 1 H, CH), 3.30−3.85 (m, 20 H, CH_2-O-CH_2), 7.68−7.50 (m, 6 H, $Ph_{m,p}$), 7.64−7.83 (m, 4 H, Ph_o). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: 17.25 ($^1J(^{13}C-^{117}Sn) = 548.2$ Hz, $^1J(^{13}C-^{119}Sn) = 523.9$ Hz, Sn−CH_2−), 37.17 ($^2J(^{13}C-^{117/119}Sn) = 23.3$ Hz, C15), 69.78−70.45 (C2−C12), 74.43 ($^3J(^{13}C-^{117/119}Sn) = 71.9$ Hz, C14/C16), 128.65 ($^3J(^{13}C-^{117/119}Sn) = 64.2$ Hz, C_m), 129.46 ($^4J(^{13}C-^{117/119}Sn) = 13.6$ Hz, C_p), 135.84 ($^2J(^{13}C-^{117/119}Sn) = 46.7$ Hz, C_o), 141.09 ($^1J(^{13}C-^{117}Sn) = 636.7$ Hz, $^1J(^{13}C-^{119}Sn) = 726.3$ Hz, C_i). ^{119}Sn$\{^1H\}$ NMR (CD_2Cl_2) δ: −88. ^{119}Sn MAS δ: −73 ($\Delta\delta$ −278.7, η 0.8). Anal. Calcd for $C_{24}H_{33}ClO_5Sn \cdot {}^1/_2CH_2Cl_2$ (598.1): C 49.2, H 5.7. Found: C 49.1, H 5.9. Mp: 76−78 °C.

Synthesis of Fluoro(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)diphenylstannane (5). A solution of **2** (2 g, 3.10 mmol) in CH_2Cl_2 (50 mL) was treated with tetrabutylammonium fluoride (5.7 g, 31 mmol) and stirred for 12 h at room temperature. Washing with water (3×50 mL), drying over Na_2SO_4, and removing the solvent led to a colorless solid, which was recrystallized from CH_2Cl_2/*n*-hexane (1:1) at −5 °C, resulting in 1.0 g (63%) of colorless crystals. ^{1}H NMR ($CDCl_3$) δ: 1.41 (d, $^3J(^1H-^1H) = 8.0$ Hz, $^2J(^1H-^{117/119}Sn) = 80.3$ Hz, 2 H, Sn−CH_2), 2.57 (m, 1 H, CH), 3.32−3.86 (m, 20 H, CH_2-O-CH_2), 7.32−7.44 (m, 6 H, Sn−Ph $H_{m,p}$), 7.56−7.76 (m, $^3J(^1H-^{117/119}Sn) = 60.8$ Hz, Sn−Ph H_o). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 20.46 ($^2J(^{13}C-^{19}F) = 12.6$ Hz, Sn−CH_2−), 36.58 (C15), 69.62−70.36 (C2−C12), 74.42 ($^3J(^{13}C-^{117/119}Sn) = 69.0$

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Table 5. Crystallographic Data for Compound 1−5, 7, and 8

	1	2	3	4	5	7	8
formula	$C_{30}H_{38}O_5Sn$	$C_{24}H_{33}IO_5Sn$	$C_{24}H_{33}BrO_5Sn\cdot 0.5CH_2Cl_2$	$C_{24}H_{33}ClO_5Sn\cdot 0.5CH_2Cl_2$	$C_{24}H_{33}FO_5Sn$	$C_{18}H_{28}Cl_2O_5Sn$	$C_{18}H_{28}I_2O_5Sn$
fw	597.29	647.09	642.57	598.11	539.19	513.99	696.89
cryst syst	monoclinic	monoclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic
cryst size, mm	0.25 × 0.25 × 0.23	0.27 × 0.25 × 0.25	0.33 × 0.30 × 0.30	0.30 × 0.25 × 0.25	0.17 × 0.15 × 0.15	0.20 × 0.17 × 0.15	0.20 × 0.18 × 0.15
space group	$P2(1)/n$	Pc	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P2(1)/m$
a, Å	10.1916(1)	9.1684(1)	9.3718(8)	9.3160(6)	9.339(1)	8.9520(1)	8.6467(2)
b, Å	23.3846(3)	10.0578(2)	12.6614(7)	12.6372(6)	10.7975(9)	12.8877(2)	13.5974(3)
c, Å	11.7911(1)	13.9514(2)	12.7444(12)	12.7260(8)	12.386(2)	18.7612(3)	9.8469(2)
α, deg			114.571(5)	114.544(3)	97.413(7)		
β, deg	90.5754(6)	95.1086(8)	99.533(4)	9.695(2)	103.057(5)	102.8772(6)	98.525(1)
γ, deg			96.655(5)	96.533(4)	93.902(6)		
V, Å^3	2809.99(5)	1281.54(3)	1327.2(2)	1314.9(1)	1200.4(2)	2110.05(5)	1144.93(4)
Z	4	2	2	2	2	4	2
ρ_{calcd}, Mg/m^3	1.412	1.677	1.608	1.511	1.492	1.618	2.021
μ, mm^{-1}	0.945	2.232	2.600	1.206	1.103	1.489	3.835
F(000)	1232	640	646	610	552	1040	664
θ range, deg	3.13 to 27.48	2.93 to 27.48	2.99 to 27.48	2.92 to 27.46	3.12 to 25.35	3.16 to 27.48	2.93 to 27.49
index ranges	$-13 \le h \le 13$ $-30 \le k \le 30$ $-15 \le l \le 15$	$-11 \le h \le 11$ $-13 \le k \le 13$ $-18 \le l \le 17$	$-12 \le h \le 12$ $-15 \le k \le 15$ $-16 \le l \le 16$	$-12 \le h \le 12$ $-16 \le k \le 16$ $-16 \le l \le 15$	$-11 \le h \le 11$ $-13 \le k \le 12$ $-14 \le l \le 14$	$-11 \le h \le 11$ $-16 \le k \le 16$ $-24 \le l \le 23$	$-10 \le h \le 10$ $-17 \le k \le 17$ $-12 \le l \le 12$
no. of reflns collcd	25 528	12 175	15 271	17 271	13 966	20 778	9504
completeness to θ_{max}	99.8	99.5	97.5	99.7	99.2	99.4	98.5
no. of indep reflns/R_{int}	6431/0.028	2928/0.029	5939/0.034	6001/0.026	4353/0.047	4831/0.022	2702/0.027
no. of reflns obsd with ($I > 2\sigma(I)$)	5475	2704	4250	4592	3618	3699	1972
no. of refined params	325	280	307	307	289	235	133
GooF (F^2)	1.077	0.991	0.813	0.819	0.956	0.924	0.959
R1 (F) ($I > 2\sigma(I)$)	0.0206	0.0168	0.0264	0.0253	0.0282	0.0194	0.0282
wR2 (F^2) (all data)	0.0516	0.0319	0.0451	0.0424	0.0531	0.0433	0.0581
extinction coeff, $(\Delta/\sigma)_{max}$	0.001	0.001	0.001	0.001	0.001	0.001	0.001
largest diff peak/hole, e/Å^3	0.344/−0.452	0.267/−0.371	0.487/−0.538	0.448/−0.495	0.560/−0.560	0.265/−0.677	0.972/−1.156

Hz, C14/C16), 128.53 ($^3J(^{13}C-^{117/119}Sn)$ = 63.2 Hz, C_m), 129.47 ($^4J(^{13}C-^{117/119}Sn)$ = 13.6 Hz, C_p), 135.81 ($^2J(^{13}C-^{117/119}Sn)$ = 45.7 Hz, C_o), 140.63 ($^2J(^{13}C-^{19}F)$ = 13.6 Hz, C_i). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ: −189.3 (s, $^1J(^{19}F-^{117}Sn)$ = 2116.4 Hz, $^1J(^{19}F-^{119}Sn)$ = 2212.4 Hz, Sn−F). $^{119}Sn\{^1H\}$ NMR (CH_2Cl_2, D_2O-Cap.) δ: −106.3 (d, $^1J(^{119}Sn-^{19}F)$ = 2206.8 Hz. Anal. Calcd (%) for $C_{24}H_{33}FO_5Sn$ (539.22): C 53.5, H 6.2. Found: C 53.2, H 6.1. Mp: 108−109 °C.

Synthesis of Thiocyanato(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)diphenylstannane (6). AgSCN (1.0 g, 1.55 mmol) was added to a solution of **2** (0.77 g, 4.64 mmol) in CH_3CN (50 mL), and the reaction mixture was stirred in the dark for 3 days followed by filtration of the AgI formed and the nonreacted AgSCN. The filtrate was removed in vacuo to give a light yellow oil. The oil was dissolved in EtOH (30 mL) and cooled to −5 °C for several days, yielding 0.5 g (98%) of pure **6**. ^1H NMR (599.83 MHz, $CDCl_3$) δ: 1.52 (d, $^3J(^1H-^1H)$ = 6.0 Hz, $^2J(^1H-^{117/119}Sn)$ = 72.0 Hz, 2 H, Sn−CH_2), 2.57 (m, 1 H, CH), 3.25−3.85 (m, 20 H, CH_2−O−CH_2), 7.35−7.45 (m, 6 H, $Ph_{m,p}$), 7.55−7.73 (m, 4 H, Ph_o). $^{13}C\{^1H\}$ NMR (150.84 MHz, $CDCl_3$) δ: 14.58 (CH_2), 36.89-($^2J(^{13}C-^{117/119}Sn)$ = 21.1 Hz, C(15)), 70.09−70.54 (C(2)−C(12)), 74.66 ($^3J(^{13}C-^{117/119}Sn)$ = 69.4 Hz, C(14)/C(16)), 129.16 ($^3J(^{13}C-^{117/119}Sn)$ = 64.9 Hz, C_m), 130.15 (C_p], 136.07 [$^2J(^{13}C-^{117/119}Sn)$ = 46.8 Hz, C_o], 138.68 [C_i], 141,01 [N═C═S]. $^{14}N\{^1H\}$ NMR (28.91 MHz, $CDCl_3$) δ: −235.6 ($\nu_{1/2}$ = 65 Hz). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, CD_2Cl_2) δ: −154.9 (t, $^1J(^{119}Sn-^{14}N)$ = 142 Hz). Anal. Calcd (%) for $C_{25}H_{33}NO_5SSn$ (578.31): C 51.9, H 5.8, N 2.4. Found: C 50.9, H 5.7, N 2.5.

Synthesis of Dichloro(1,4,7,10,13-Pentaoxacyclohexadec-15-ylmethyl)phenylstannane (7). Hydrogen chloride gas (dried over molecular sieves) was bubbled through (1 h) a cooled solution (−78 °C) of **1** (2 g, 3.36 mmol) in CH_2Cl_2. All volatiles were removed under vacuum, and the remaining oil consisting of the triorganotin chloride **3** and the diorganotin dichloride **7** was warmed to room temperature. The oil was dissolved in Et_2O and kept at −5 °C for several days, providing, after filtration, 0.5 g (23%) of the diorganotin dichloride **7** as colorless crystals.

^1H NMR ($CDCl_3$) δ: 1.77 (d, $^3J(^1H-^1H)$ = 6.0 Hz, $^2J(^1H-^{117/119}Sn)$ = 93.4 Hz, 2 H, Sn−CH_2), 2.60 (m, 1 H, CH), 3.47−3.95 (m, 20 H, CH_2−O−CH_2), 7.34−7.45 (m, 3 H, $Ph_{m,p}$), 7.73−7.99 (m, 2 H, Ph_o). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 26.40 ($^1J(^{13}C-^{117}Sn)$ = 706.7 Hz, $^1J(^{13}C-^{119}Sn)$ = 738.8 Hz, Sn−CH_2−), 35.65 ($^2J(^{13}C-^{117/119}Sn)$ = 44.7 Hz C15), 69.69−70.26 (C2−C12), 73.74 ($^3J(^{13}C-^{117/119}Sn)$ = 61.2 Hz, C14/C16), 128.64 ($^3J(^{13}C-^{117/119}Sn)$ = 91.4 Hz, C_m), 130.22 ($^4J(^{13}C-^{117/119}Sn)$ = 18.4 Hz, C_p), 135.33 ($^2J(^{13}C-^{117/119}Sn)$ = 65.2 Hz, C_o), 142.97 ($^1J(^{13}C-^{117}Sn)$ = 929.3 Hz, $^1J(^{13}C-^{119}Sn)$ = 971.1 Hz, C_i). $^{119}Sn\{^1H\}$ NMR (CH_2Cl_2, D_2O-Cap.) δ: −125.1. Anal. Calcd (%) for $C_{18}H_{28}Cl_2O_5Sn$ (514.03): C 42.1, H 5.5. Found: C 42.1, H 5.6. Mp: 160−162 °C.

Synthesis of Diiodo(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)phenylstannane (8). Iodine (3.72 g, 15.50 mmol) was added in small portions under ice cooling to a stirred solution of **1** (4.37 g, 7.32 mmol) in CH_2Cl_2 (50 mL). The reaction mixture was stirred overnight. The solvent and the iodobenzene were removed in vacuo (1×10^{-3} Torr). Addition of CH_2Cl_2 (20 mL) to the residue and stirring for 5 min, followed by filtration and evaporation of the solvent afforded **8** (5.0 g, 98%) as yellow crystals. ^1H NMR ($CDCl_3$) δ: 2.16 (d, $^3J(^1H-^1H)$ = 7.0 Hz, $^2J(^1H-^{117/119}Sn)$ = 75.6 Hz, 2 H, Sn−CH_2), 2.57 (m, 1 H, CH), 3.30−3.9 (m, 20 H, CH_2−O−CH_2), 7.30−7.81 (m, 5 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 29.90 (Sn−CH_2−), 38.03 (C15), 69.67−70.38 (C2−C12), 73.32 (C14/C16), 128.51 ($^3J(^{13}C-^{117/119}Sn)$ = 85.5 Hz, C_m), 130.12 ($^4J(^{13}C-^{117/119}Sn)$ = 19.4 Hz, (C_p), 134.36 ($^2J(^{13}C-^{117/119}Sn)$ = 62.2 Hz, C_o), 140.84 (C_i). $^{119}Sn\{^1H\}$ NMR (CH_2Cl_2, D_2O-Cap.) δ: −266.1. Anal. Calcd (%) for $C_{18}H_{28}I_2O_5Sn$ (696.93): C 31.0, H 4.1. Found: C 31.4, H 4.0. Mp: 177−178 °C.

Complexation Studies. Reaction of 4 with $NaBPh_4$. $NaBPh_4$ (34.9 mg, 1.02×10^{-4} mol) was added to a solution of **3** (56.5 mg, 1.02×10^{-4} mol) in CD_2Cl_2. ^1H NMR (CD_2Cl_2) δ: 1.79 (d, $^3J(^1H-^1H)$ = 8 Hz, $^2J(^1H-^{117/119}Sn)$ = 56 Hz, 2 H, Sn−CH_2), 2.50 (m, 1 H, CH), 3.20−3.27 (m, 2 H, CH_2−O−CH_2), 3.40−3.65 (m, 18 H, CH_2−O−CH_2), 6.98 (t, 4 H BPh_4^-), 7.13 (t, 8 H, BPh_4^-), 7.43 (m, 8 H, BPh_4^-), 7.56−7.60 (m, 6 H, $Ph_{m,p}$), 7.65−7.75 (m, 4 H, Ph_o). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: 16.58 ($^1J(^{13}C-^{117}Sn)$ = 414.6 Hz, $^1J(^{13}C-^{119}Sn)$ = 434.7 Hz, Sn−CH_2−), 36.92 ($^2J(^{13}C-^{117/119}Sn)$ = 27.2 Hz, C15), 69.40−71.08 (C2−C12), 78.05 ($^3J(^{13}C-^{117/119}Sn)$ = 47.3 Hz, C14/C16), 122.20 (BPh_4^-) 126.05 (BPh_4^-), 126.66 ($^3J(^{13}C-^{117/119}Sn)$ = 60.4 Hz, C_m), 130.98 ($^4J(^{13}C-^{117/119}Sn)$ = 12.1 Hz, C_p), 135.94 ($^2J(^{13}C-^{117/119}Sn)$ = 47.3 Hz, C_o), 136.41 (BPh_4^-), 139.22 ($^1J(^{13}C-^{117}Sn)$ = 551.5 Hz, $^1J(^{13}C-^{119}Sn)$ = 576.6 Hz C_i), 164.17 (q, BPh_4^-). $^{23}Na\{^1H\}$ NMR (CD_2Cl_2) δ: 1.40 ($\nu_{1/2}$ = 2232 Hz). $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 298 K) δ: no signal observed. $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 238 K) δ: 13.2 ($\nu_{1/2}$ = 207 Hz).

Reaction of 4 with $[(Ph_3P)_2N]Cl$. $[(Ph_3P)_2N]Cl$ (116.3 mg, 2.03×10^{-4} mol) was added to a solution of **3** (112.5 mg, 2.03×10^{-4} mol) in CD_2Cl_2. $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 298 K) δ: −120.7 (96%). $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 203 K) δ: −89.2 (65%), −198.6 (35%).

Reaction of 4 with Excess $[(Ph_3P)_2N]Cl$. $[(Ph_3P)_2N]Cl$ (161.2 mg, 2.81×10^{-4} mol) was added to a solution of **3** (78.0 mg, 1.40×10^{-4} mol) in CD_2Cl_2. $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 298 K) δ: −144.0 (96%). $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 203 K) δ: −89.3 (47%), −198.3 (53%).

Reaction of 4 with Excess Me_4NF. $Me_4NF{\cdot}H_2O$ (55.9 mg, 3.38 $\times 10^{-4}$ mol) was added to a solution of **3** (94.0 mg, 1.69×10^{-4} mol) in CD_2Cl_2. $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 298 K) δ: −110.6 (d, $^1J(^{119}Sn-^{19}F)$ = 2223 Hz). $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 203 K) δ: −108.0 (d, $^1J(^{119}Sn-^{19}F)$ = 2187 Hz).

In Situ Reaction of 4 with NaI. NaI (22.3 mg, 1.49×10^{-4} mol) was added to a solution of **3** (82.7 mg, 1.49×10^{-4} mol) in CD_2Cl_2. $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 298 K) δ: −86.7 (41%, $\nu_{1/2}$ = 454 Hz), −129.4 (59%, $\nu_{1/2}$ = 794 Hz). $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 203 K) δ: −88.9 (48%), −129.5 (52%).

In Situ Reaction of 4 with Excess NaI. NaI (539 mg, 3.6×10^{-4} mol) was added to a solution of **3** (500 mg, 9.0×10^{-4} mol) in chloroform. The solution was refluxed for 1 h and stirred at room temperature for 12 h. Filtering of the solution and removing of all volatiles gave a yellow solid. ^1H NMR (CD_2Cl_2) δ: 2.22 (d, $^3J(^1H-^1H)$ = 8.0 Hz, $^2J(^1H-^{117/119}Sn)$ = 57.5 Hz, 2 H, Sn−CH_2), 2.46 (m, 1 H, CH), 3.02−3.06 (m, 2 H, CH_2−O−CH_2), 3.36−3.80 (m, 18 H, CH_2−O−CH_2), 7.30−7.44 (m, 6 H, $Ph_{m,p}$), 7.73−7.94 (m, 4 H, Ph_o). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: 20.75 ($^1J(^{13}C-^{117}Sn)$ = 415.1, $^1J(^{13}C-^{119}Sn)$ = 434.5, Sn−CH_2−), 37.00 ($^2J(^{13}C-^{117/119}Sn)$ = 25.3 Hz, C15), 68.97−70.34 (−CH_2−O−), 77.56 ($^3J(^{13}C-^{117/119}Sn)$ = 54.4 Hz, C14/C16), 128.51 ($^3J(^{13}C-^{117/119}Sn)$ = 60.4 Hz, C_m), 129.50 ($^4J(^{13}C-^{117/119}Sn)$ = 13.6 Hz, C_p), 136.38 ($^2J(^{13}C-^{117/119}Sn)$ = 47.6 Hz, C_o), 139.32 ($^1J(^{13}C-^{117}Sn)$ = 530.7 Hz, $^1J(^{13}C-^{119}Sn)$ = 554.1 Hz, C_i). $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2) δ: −61.

In Situ Reaction of 4 with NaSCN. NaSCN (5 mg, 6.21×10^{-5} mol) was added to a solution of **4** (34.5 mg, 6.21×10^{-5} mol) in $C_2D_2Cl_4$. ^1H NMR (300 K, $C_2D_2Cl_4$) δ: 1.75 (s, br, 2 H, Sn−CH_2), 2.59 (s, br, 1 H, CH), 3.00−4.0 (m, br, 20 H, CH_2−O−CH_2), 7.25−7.50 (m, 6 H, $Ph_{m,p}$), 7.75−7.25 (m, br, 4 H, Ph_o). $^{13}C\{^1H\}$ NMR (300 K, $C_2D_2Cl_4$) δ: 37.29 (C15), 69.00−72.00 (br, −CH_2−O−), 128.89 (C_m), 129.69 (C_p), 136.33 ($^2J(^{13}C-^{117/119}Sn)$ = 47.6 Hz, C_o). $^{119}Sn\{^1H\}$ NMR (300 K, $C_2D_2Cl_4$) δ: −89 ($\nu_{1/2}$ = 219 Hz, 43%), −157 ($\nu_{1/2}$ = 325 Hz, 18%), −229 ($\nu_{1/2}$ = 219 Hz, 39%).

^1H NMR (253 K, $C_2D_2Cl_4$) δ: 1.50, 1.56, and 1.79 (s, br, 2 H, Sn−CH_2), 2.42 and 2.59 (s, br, 1 H, CH), 2.80 (s, br, 2 H, CH_2−O−CH_2), 3.25−3.75 (m, br, 16 H, CH_2−O−CH_2),7.40−7.45 (m, 6 H, $Ph_{m,p}$), 7.64, 7.71, 7.97 (s, br, 4 H, Ph_o). $^{13}C\{^1H\}$ NMR (253

K, $C_2D_2Cl_4$) δ: 14.53, 17.45, 22.55 ($SnCH_2$), 36.98, 37.10, 37.28 (C15), 69.34−71.00 (br, -CH_2−O-), 74.72, 78.76 (C14/C16) 128.74, 129.25, 129.49 (C_m), 129.88, 130.17, 130.57 (C_p), 136.07, 136.63 (C_o), 140.89, 141.91 (C_i). $^{119}Sn\{^1H\}$ NMR (253 K, $C_2D_2Cl_4$) δ: −93 ($\nu_{1/2}$ = 50 Hz, 48%), −159 ($\nu_{1/2}$ = 92 Hz, 14%), −229 ($\nu_{1/2}$ = 107 Hz, 38%).

^1H NMR (360 K, $C_2D_2Cl_4$) δ: 1.74 (s, $^3J(^1H-^1H)$ = 6 Hz, $^2J(^1H-^{117/119}Sn)$ = 78, 2 H, Sn−CH_2), 2.63 (m, 1 H, CH), 3.32 (s, br, 2 H, CH_2−O−CH_2), 3.48−3.77 (m, br, 16 H, CH_2−O−CH_2),7.44−7.48 (m, 6 H, $Ph_{m,p}$), 7.84 (s, br, 4 H, Ph_o). $^{13}C\{^1H\}$ NMR (360 K, $C_2D_2Cl_4$) δ: 37.46 (C15), 70.13−70.70 (−CH_2−O−), 75.96 (C14/C16) 128.88 ($^3J(^{13}C-^{117/119}Sn)$ = 68 Hz, C_m), 129.71 (C_p), 136.29 ($^2J(^{13}C-^{117/119}Sn)$ = 47 Hz, C_o). $^{119}Sn\{^1H\}$ NMR (313 K, $C_2D_2Cl_4$) δ: no signal observed.

In Situ Reaction of 4 with 2 equiv of NaSCN. NaSCN (21 mg, 2.61 × 10^{-4} mol) was added to a solution of **4** (73 mg, 1.31 × 10^{-4} mol) in $C_2D_2Cl_4$. $^{119}Sn\{^1H\}$ NMR (300 K, $C_2D_2Cl_4$) δ: −90 ($\nu_{1/2}$ = 155 Hz, 41%), −157 ($\nu_{1/2}$ = 260 Hz, 10%), −232 ($\nu_{1/2}$ = 205 Hz, 48%).

In Situ Reaction of 6 with NaCl. NaCl (7 mg, 1.21 × 10^{-4} mol) was added to a solution of **6** (70 mg, 1.21 × 10^{-4} mol) in $CDCl_3$. $^{119}Sn\{^1H\}$ NMR (300 K, $CDCl_3$) δ: −85 ($\nu_{1/2}$ = 121 Hz, 25%), −156 ($\nu_{1/2}$ = 432 Hz, 58%), −229 ($\nu_{1/2}$ = 243 Hz, 17%).

In Situ Reaction of 6 with NaSCN. NaSCN (10 mg, 1.21 × 10^{-4} mol) was added to a solution of **6** (70 mg, 1.21 × 10^{-4} mol) in $CDCl_3$. ^1H NMR (300 K, $CDCl_3$) δ: 1.56, 1.84 (s, 2 H, Sn−CH_2), 2.55 (m, br, 1 H, CH), 3.86 (s, br, 2 H, CH_2−O−CH_2), 3.40−3.75 (m, br, 16 H, CH_2−O−CH_2),7.36 (m, 6 H, $Ph_{m,p}$), 7.71, 7.98 (s, br, 4 H, Ph_o). $^{13}C\{^1H\}$ NMR (300 K, $CDCl_3$) δ: 18.91, 23.30 ($SnCH_2$). 37.19 ($^2J(^{13}C-^{117/119}Sn)$ = 25 Hz, C15), 69.57−70.53 (−CH_2−O−), 78.89 (C14/C16), 128.66 (C_m), 129.40 (C_p), 136.78 (C_o), 137.70 (C_i), 142.32 (SCN). $^{119}Sn\{^1H\}$ NMR (300 K, $CDCl_3$) δ: −155 ($\nu_{1/2}$ = 418 Hz, 62%), −225 ($\nu_{1/2}$ = 154 Hz, 38%). $^{119}Sn\{^1H\}$ NMR (300 K, $CDCl_3$, after 10 days) δ: −225 ($\nu_{1/2}$ = 154 Hz, 100%).

In Situ Reaction of 4 with $AgClO_4$. $AgClO_4$ (0.236 g, 1.14 mmol) was added to a solution of **2** (0.737 g, 1.14 mmol) in CH_3CN (20 mL), and the reaction mixture was stirred in the dark for 2 days. After the resulting AgI had been filtered the solvent of the filtrate was evaporated in vacuo to give a colorless oil. $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ: −71.1

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Supporting Information Available: ORTEP drawings of the molecular structures of compounds **2**, **3**, and **5**, the ^{14}N and ^{119}Sn NMR spectra of compound **6**, and the ^{23}Na NMR spectra of $NaBPh_4$ and of **4** + $NaBPh_4$. CIF files for compounds **2**−**5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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