Organotin Compounds Ph_2XSnCH_2-[19]-crown-6 (X = Ph, F, Cl, Br, I, SCN) and $Ph_2ISnCH_2Sn(I)PhCH_2$-[19]-crown-6 as Ditopic Receptors for Potassium Salts‡

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The syntheses of the organotin-substituted crown ethers Ph_2XSnCH_2[19]-crown-6 (**1**, X = Ph; **2**, X = Br; **3**, X = I; **4**, X = Cl; **5**, X = F; **6**, X = SCN) and $Ph_2XSnCH_2Sn(Y)PhCH_2$-[19]-crown-6 (**7**, X = Y = Ph; **8**, X = Ph, Y = I; **9**, X = Y = I) and of the ditopic complexes **5**·KF, **6**·KSCN, and **9**·KF are reported. These compounds are characterized by elemental analyses, ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopies, electrospray mass spectrometry, and in the cases of **1**−**4**, **8**, **9**·H_2O, and **9**·KF also by single-crystal X-ray diffraction studies. The coordination geometry about the tin atoms in compounds **1** and **8** (Sn2) is distorted tetrahedral, whereas it is trigonal bipyramidal for the tin atoms in compounds **2**, **3**, **4**, **8** (Sn1), **9**·H_2O, and **9**·KF.

Introduction

In recent years so-called ditopic complexation of anions and cations has become a well-established subdiscipline in supramolecular host−guest chemistry, and both concepts and achievements in this field have been thoroughly reviewed.[1−12] Most of the ditopic receptors reported to date are purely organic and employ hydrogen bonding for anion recognition and Lewis-basic binding sites such as oxygen atoms in crown ethers for cation recognition. On the other hand, there are only few examples of ditopic receptors that make use of the Lewis acidity of organoelement/organometallic moieties or metal cations for anion binding. This is even more surprising as, to the best of our knowledge, Reetz's organoboron-substituted crown ether (A) was the first representative of this class of compounds that simultaneously binds cations and anions (here potassium fluoride, KF).[13] Later on, the concept was extended to organoaluminium- (B)[14] and organotin- (C−E) substituted crown ethers,[15−17] which were shown to complex lithium chloride, LiCl, and sodium thiocyanate, NaSCN, respectively, and to transport the latter through an organic membrane (Chart 1).

Attempts at ditopically complexing sodium salts of higher lattice energy such as sodium halides, NaX (X = F, Cl, I), with the organotin compounds D and E failed, presumably because of the monotin sites not being Lewis acidic enough to compensate for the electrostatic Na^+X^- attraction. Most recently, however, we have demonstrated the ability of compound F, which contains a second organotin moiety linked via a methylene bridge to the first tin atom and that makes possible chelation of fluoride anion to overcome even the high lattice energy of sodium fluoride and to solubilize the latter in acetonitrile.[18,19]

Independent from the compounds shown in Chart 1, there were also reports on ruthenium,[20] rhenium,[20] zinc,[21] and uranium[22] complexes that selectively recognize potassium

‡ Dedicated to Professor Rudolph Willem on the occasion of his 60th birthday.

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Chart 1

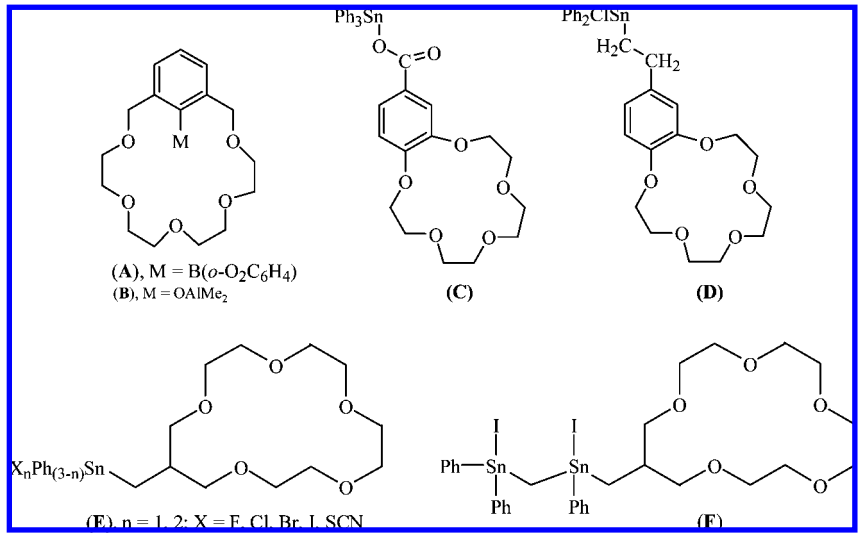
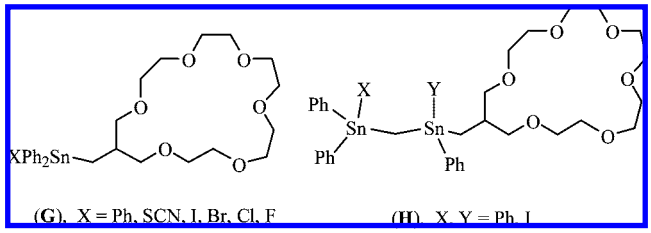


Chart 2



dihydrogen phosphate, sodium dihydrogen phosphate, sodium cyanide, or cesium chloride.

The organotin compounds depicted in Chart 1 contain crown-5 moieties that are specific for sodium cation. In continuation of our studies mentioned above we report here the synthesis, molecular structures, and complexation properties in polar as well as in nonpolar solvents of the corresponding organotin compounds of types G and H that contain crown-6 moieties being specific for potassium cation (Chart 2). We demonstrate that both the fluorine-substituted representative of G-type compounds and the bis(organoiodostannyl)methane-substituted crown ether of type H are capable of ditopically complexing potassium fluoride to the extent that the corresponding complexes could be isolated and characterized.

Results and Discussion

Synthesis Aspects and Molecular Structures in the Solid State. The reaction of 18-methylene-1,4,7,10,13,16-hexaoxacyclononadecane[23] with triphenyltin hydride provided the organotin-substituted crown ether **1** as a colorless oil that solidified after it had been kept for some days at room temperature (eq 1).

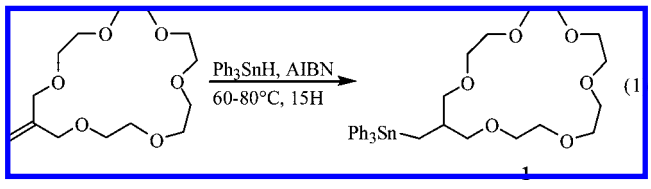


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Table 1. Selected Bond Distances (Å) for Compounds 1−4

	1 X = C(13)	2 X = Br(1)	3 X = I(1)	4 X = Cl(1)
Sn(1)−C(1)	2.145 (2)	2.124 (3)	2.138 (4)	2.137 (4)
Sn(41)−C(41)	2.147 (2)			
Sn(1)−C(7)	2.140 (2)	2.135 (3)	2.131 (4)	2.123 (4)
Sn(41)−C(47)	2.131 (2)			
Sn(1)−C(21)	2.143 (2)	2.115 (3)	2.128 (5)	2.111 (4)
Sn(41)−C(53)	2.157 (2)			
Sn(1)−X	2.149 (2)	2.5846 (4)	2.7896 (4)	2.4323 (11)
Sn(41)−C(61)	2.151 (2)			
Sn(1)−O1	2.9820 (13)	2.606 (2)	2.610 (2)	2.606 (2)
Sn(41)−O(41)	2.9963 (14)			

The molecular structure of compound **1** is shown in Figure 1, and selected bond distances and bonds angles are listed in Tables 1 and 2.

The unit cell contains two independent molecules of **1** with similar geometric parameters. The tin atoms Sn(1)/Sn(41) adopt monocapped tetrahedral configurations with the O(1)/O(41) atoms being the capping ones. They approach the Sn(1) and

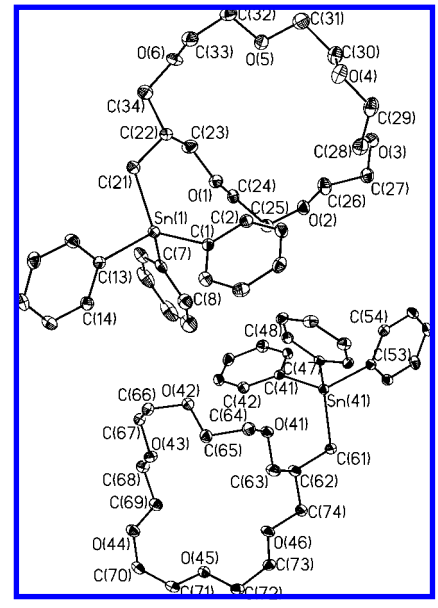


Figure 1. Molecular structure of **1** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

Table 2. Selected Bonds Angles (deg) for Compounds 1−4

	1	2 X = Br(1)	3 X = I(1)	4 X = Cl(1)
C(1)−Sn(1)−C(7)	109.47(8)	110.5(1)	110.4(1)	110.4(1)
C(1)−Sn(1)−C(21)	117.26(8)	119.5(1)	121.8(1)	124.0(2)
C(7)−Sn(1)−C(21)	117.14(9)	122.7(1)	120.1(2)	118.5(2)
C(1)−Sn(1)−C(13)	105.93(8)			
C(7)−Sn(1)−C(13)	102.44(8)			
C(13)−Sn(1)−C(21)	102.53(8)			
C(47)−Sn(41)−C(61)	118.33(8)			
C(47)−Sn(41)−C(41)	111.24(8)			
C(41)−Sn(41)−C(61)	109.70(8)			
C(41)−Sn(41)−C(53)	103.36(8)			
C(47)−Sn(41)−C(53)	104.21(8)			
C(53)−Sn(41)−C(61)	108.77(8)			
C(1)−Sn(1)−O(1)		84.14(8)	87.69(22)	86.9(1)
C(7)−Sn(1)−O(1)		87.10(8)	83.01(11)	83.9(1)
C(21)−Sn(1)−O(1)		72.77(9)	72.56(13)	73.3(11)
O(1)−Sn(1)-X		169.69(4)	169.37(6)	170.66(6)
O(1)−Sn(1)−C(13)	170.03(6)			
O(41)−Sn(1)−C(53)	168.80(6)			
C(1)−Sn(1)−X		99.80(7)	100.61(10)	99.48(11)
C(7)−Sn(1)−X		100.26(7)	100.03(10)	100.14(10)
C(21)−Sn(1)−X		97.08(8)	97.40(12)	97.43(11)
C(22)−C(21)−Sn(1)	118.5(2)	113.9(2)	111.9(3)	113.7(2)
C(62)−C(61)−Sn(41)	114.6(2)			

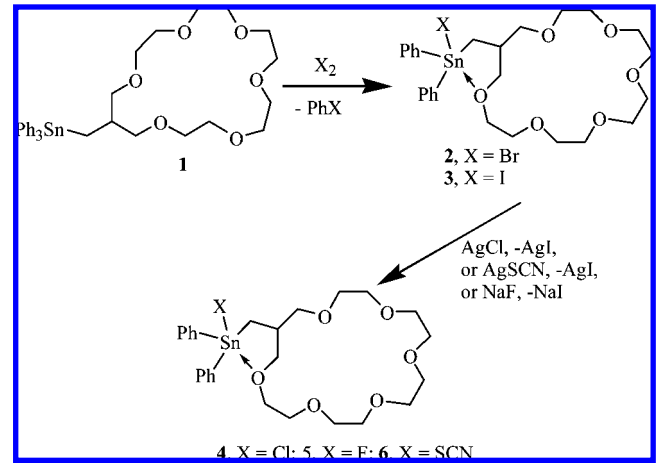
Sn(41) atoms via the tetrahedral faces defined by C(1), C(7), C(21) and C(41), C(47), C(61), respectively, at Sn(1)···O(1) and Sn(41)···O(41) distances of 2.9820(13) and 2.9963(14) Å, respectively. These distances are shorter than the sum of the van der Waals radii[24] of tin (2.20 Å) and oxygen (1.50 Å) and, notably, also shorter than the corresponding distance found in the closely related tetraorganotin compound Ph_3SnCH_2-[16]-crown-5 (3.206(1) Å).[17] This difference of approximately 0.2 Å sheds some light on the true nature of the intramolecular Sn···O interactions in tetraorganotin compounds such as **1** and Ph_3SnCH_2-[16]-crown-5. Both compounds have exactly the same substituent pattern at the tin atom, suggesting identical Lewis acidity as well as the same Lewis basicity of the crown ether oxygens O(1) and O(41). Consequently, the different Sn···O distances are the result of crystal-packing effects rather than of Lewis acid−Lewis base attraction. The Sn(1) and Sn(41) atoms lie 0.504(1) and 0.573(1) Å out of the corresponding plane in the direction of C(13) and C(53), respectively.

Treatment of **1** with 1 molar equiv of bromine and iodine gave the corresponding triorganotin bromide **2** and the triorganotin iodide **3**, respectively, in almost quantitative yield. Reaction of the triorganotin iodide **3** with an excess of AgCl in acetonitrile over a period of 14 days provided the triorganotin chloride **4**. In a similar manner, compound **3** was converted by reaction with NaF and AgSCN into the corresponding triorganotin fluoride **5** and triorganotin thiocyanate **6**, respectively (Scheme 1).

The triorganotin halides **2**−**4** are colorless crystalline solids, whereas the triorganotin fluoride **5** is an amorphous solid and the thiocyanate **6** is a viscous oil. They are all well soluble in common organic solvents such as $CHCl_3$, $CHCl_2$, toluene, and thf. The molecular structures of compounds **2**−**4** are rather similar, and only that of the triorganotin chloride **4** is illustrated in Figure 2; those of the triorganotin bromide and iodide are given in the Supporting Information (Figures S1, S2). Selected bond distances and bonds angles for **2**−**4** are listed in Tables 1 and 2.

The tin atoms in the triorganotin halides **2**−**4** are pentacoordinated and exhibit distorted trigonal-bipyramidal configurations (geometrical goodness $\Delta\sum(\theta)$[25] 55.6° (**2**), 54.3° (**3**), 55.8° (**4**)) with C(1), C(7), and C(21) occupying the equatorial and O(1) and the corresponding halogen atoms iodine, bromine, and chlorine, respectively, occupying the axial positions. The Sn(1) atom is displaced by 0.332(2) (**2**), 0.345(2) (**3**), and 0.330(2) (**4**) Å from the trigonal plane in the direction of X(1). The Sn(1)−O(1) distances are rather similar and fall between 2.606(2) (**2**, **4**) and 2.610(2) Å (**3**). They are slightly longer than those measured for the corresponding triorganotin halides Ph_2XSnCH_2-[16]-crown-5[17] (X = I, 2.554(2) Å; X = Cl, 2.571(1) Å) and comparable with other related[26−28] five-coordinate tin compounds having Sn−O chelation. As result of the intramolecular O(1)→Sn(1) coordination, the Sn(1)−I(1), Sn(1)−Br(1), and Sn(1)−Cl(1) distances of 2.7896(4), 2.5846(4), and 2.4323 (11) Å are longer than the corresponding distances in tetracoordinated triorganotin halides[29] and exceed the sums of the covalent radii[24] of the respective atoms by 0.06 (**3**) and 0.04 (**2**, **4**) Å, respectively.

Scheme 1



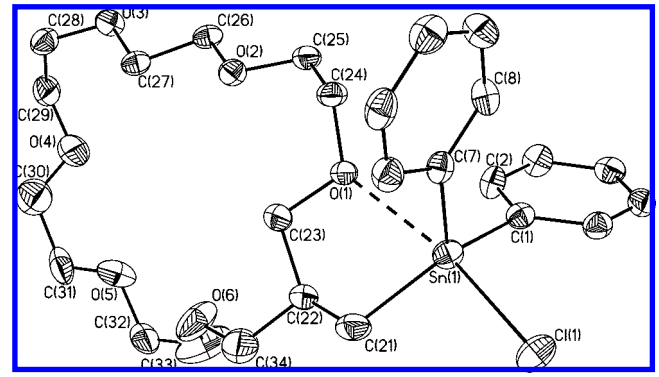


Figure 2. Molecular structure of **4** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

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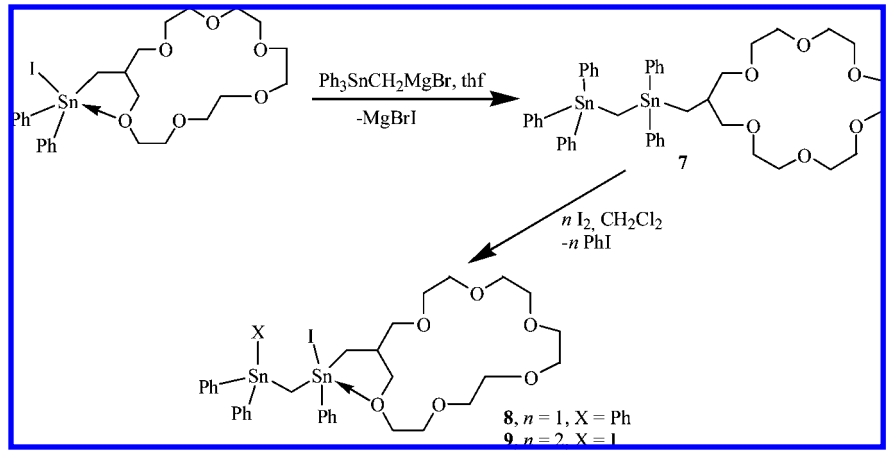
Scheme 2



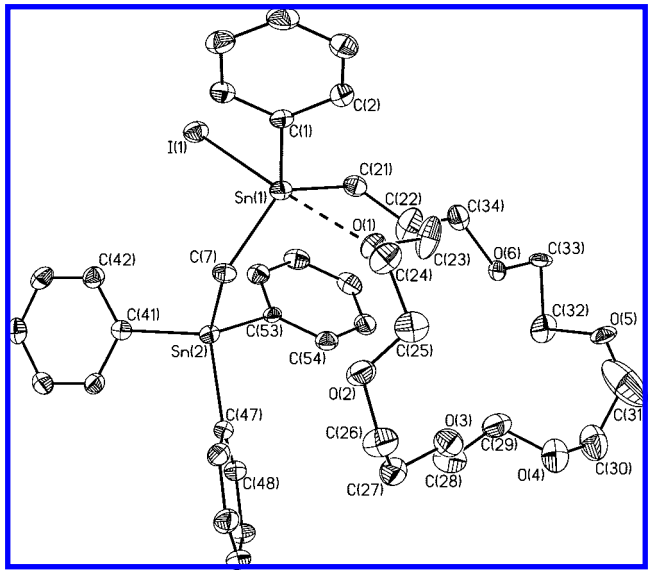


Figure 3. Molecular structure of **8** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

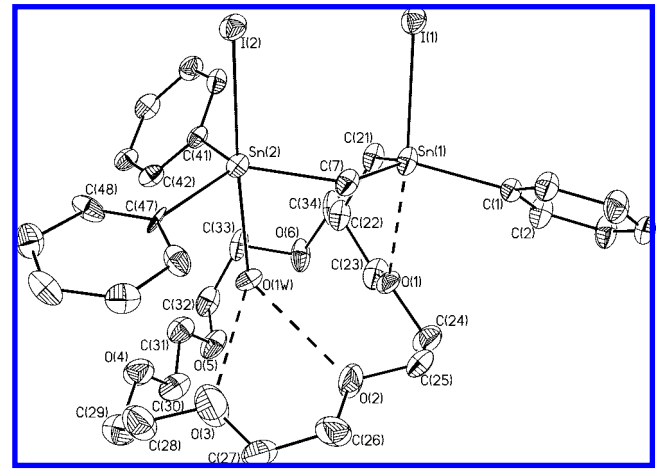


Figure 4. Molecular structure of **9**·H_2O showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

Reaction in thf of the triorganotin iodide **3** with triphenylstannylmethylmagnesium bromide[30] provided the bis(organostannyl) methane-substituted crown ether **7** as a colorless oil. Its treatment with 1 and 2 molar equiv of iodine gave the mono- and diiodine-substituted compounds **8** and **9**, respectively, as slightly yellow, sharp-melting crystalline materials (Scheme 2).

Single crystals were grown from ethanol at −15 °C (**8**) or by slow evaporation (**9**). For compound **9** single crystals of its aqua complex, hereafter referred to as **9**·H_2O, were obtained.

The molecular structures of **8** and **9**·H_2O are shown in Figures 3 and 4, respectively, and selected geometric parameters are collected in Tables 3 and 4.

Like for the triorganotin iodide **3**, the Sn(1) atom in compound **8** is pentacoordinated and exhibits a distorted trigonal-bipyramidal configuration (geometrical goodness $\Delta\Sigma(\theta)$[25] 66.0°) with C(1), C(7), and C(21) occupying the equatorial and O(1) and I(1) the axial positions, the Sn(1)−O(1) distance of 2.465(2) Å being shorter and the Sn(1)−I(1) distance of 2.8210(4) Å being longer than the corresponding distances in compound **3**. The Sn(1) atom is displaced by 0.255(2) Å in the direction of I(1) from the trigonal plane defined by C(1), C(7), and C(21). The configuration at Sn(2) is distorted tetrahedral with angles varying between 106.08(12)° (C41−Sn2−C47) and 115.86(12)° (C7−Sn2−C41).

Both of the tin atoms in **9**·H_2O are pentacoordinated and show a distorted trigonal-bipyramidal configuration (geometrical goodness $\Delta\Sigma(\theta)$[25] 60.2° (Sn1), 64.2°(Sn2)) with the carbon atoms C(1), C(7), C(21) (at Sn1), and C(7), C(41), C(47) (at Sn2) occupying the equatorial and O(1), I((1) (at Sn1) and O(1W), I(2) (at Sn2) occupying the axial positions. The Sn(1) atom is displaced by 0.292(3) Å in the direction of I(1) and the Sn(2) atom is displaced by 0.265(3) Å in the direction of I(2) from the planes defined by the corresponding carbon atoms.

Table 3. Selected Bond Distances (Å) for Compounds 8, 9·H_2O, and 9·KF

	8	**9**·H_2O	**9**·KF
Sn(1)−C(1)	2.140(3)	2.156(5)	2.151(6)
Sn(1)−C(7)	2.134(3)	2.119(4)	2.115(5)
Sn(1)−C(21)	2.132(3)	2.129(4)	2.154(5)
Sn(1)−I(1)	2.8210(4)	2.8019(6)	2.9581(7)
Sn(1)−O(1)	2.465(2)	2.644(3)	
Sn(1)−F(1)			2.198(3)
Sn(2)−C(7)	2.134(3)	2.128(4)	2.116(5)
Sn(2)−C(41)	2.148(3)	2.135(5)	2.144(5)
Sn(2)−C(47)	2.148(3)	2.205(5)	2.137(6)
Sn(2)−C(53)	2.156(3)		
Sn(2)−I(2)		2.8442(5)	2.8706(6)
Sn(2)−F(1)			2.266(3)
Sn(2)−O(1W)		2.516(3)	

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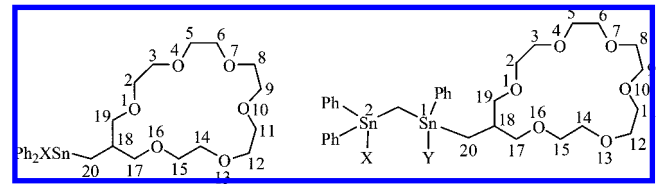
Table 4. Selected Bond Angles (deg) for Compounds 8, 9·H_2O, and 9·KF

	8 X = I(2)	**9**·H_2O X = I(2)	**9**·KF X = I(2)
C(1)−Sn(1)−C(7)	113.4(1)	112.0(2)	117.8(2)
C(1)−Sn(1)−C(21)	116.3(1)	115.5(2)	117.7(2)
C(7)−Sn(1)−C(21)	126.1(1)	126.8(2)	122.5(2)
C(1)−Sn(1)−I(1)	98.37(9)	102.4(1)	95.3(2)
C(7)−Sn(1)−I(1)	97.08(8)	98.9(1)	92.6(2)
C(21)−Sn(1)−I(1)	95.33(9)	93.0(1)	96.2(2)
O(1)−Sn(1)−I(1)	168.71(5)	165.60(8)	
Sn(1)−C(7)−Sn(2)	118.6(1)	117.6(2)	105.8(2)
C(7)−Sn(2)−C(41)	115.9(1)	122.5(2)	115.2(2)
C(7)−Sn(2)−C(47)	110.5(1)	120.4(2)	123.3(2)
C(7)−Sn(2)−X	110.4(1)	95.6(1)	95.0(1)
C(41)−Sn(2)−C(47)	106.1(1)	112.6(2)	117.6(2)
C(41)−Sn(2)−X		98.6(1)	97.5(2)
C(47)−Sn(2)−X		97.1(1)	97.4(2)
O(1W)−Sn(2)−I(2)		176.31(7)	
F(1)−Sn(1)−I(1)			171.12(7)
F(1)−Sn(2)−I(2)			172.10(8)
Sn(1)−F(1)−Sn(2)			98.2(1)

The intramolecular Sn(1)−O(1) distance of 2.644(3) Å is longer than those in compounds **2**−**4** and $Ph_2ISnCH_2Sn(I)PhCH_2$-[16]-crown-5·H_2O (2.555(2) Å).[18] The Sn(2)−O(1W) distance involving the water molecule being sandwich-like trapped between Sn(2) and the crown ether-oxygen atoms O(2) and O(3) amounts to 2.516(3) Å. This distance is slightly longer than those of 2.440(3) and 2.469(4) Å found in the aqua complexes $Ph_2ISnCH_2Sn(I)PhCH_2$-[16]-crown-5·H_2O[18] and $[Ph_2ClSn(CH_2)_2]$-15-benzocrown-5·H_2O,[16] respectively. As in these compounds, in the aqua complex **9**·H_2O the complexation of the water molecule is supported by two hydrogen bridges with O(1W)···O(2) and O(1W)···O(3) distances of 2.877(5) and 2.823(4) Å, respectively. Like for the triorganotin iodide **3**, the Sn(1)−I(1) and Sn(2)−I(2) distances of 2.8019(6) and 2.8442(5) Å, respectively, exceed the sum of the covalent radii of tin (1.40 Å) and iodine (1.33 Å).

Structures in Solution. The structures in solution of compounds **1**−**9** are similar to those of the analogous organostannyl-substituted [16]-crown-5 derivatives.[17] Thus, as expected, the tin atoms in the tetraorganostannanes **1** and **7** and the Sn(2) atom in compound **8** are essentially tetracoordinated, as evidenced by ^{119}Sn NMR chemical shifts ranging between δ −105 (**1**) and −55 (**7**), being close to δ −92 and −60 reported for Ph_3SnMe[31] and Ph_2SnMe_2,[32] respectively. On the other hand, the low-frequency ^{119}Sn NMR chemical shifts in $CDCl_3$ of δ −93 (**2**), −126 (**3**), −83 (**4**), −104 [$^1J(^{119}Sn-^{19}F)$ 2200 Hz] (**5**), −154 [$^1J(^{119}Sn-^{14}N)$ = 256 Hz] (**6**), −85 (Sn1 in **8**), and −79 (Sn1 in **9**·H_2O) indicate for compounds **2**−**6**, **8**, and **9**·H_2O that the intramolecular O→Sn interactions are retained, with a more detailed reasoning for this statement being given in ref 17 by comparison with the ^{119}Sn chemical shifts of tetracoordinated organotin compounds, having comparable substituent patterns at the tin atoms but lacking any intra- or intermolecular coordination. As a representative example of the monotin compounds **2**−**6**, the ^{119}Sn MAS NMR spectrum of the triorganotin iodide **3** was recorded. It shows a chemical shift of δ −128, which is close to the ^{119}Sn NMR chemical shift (δ −126) found in solution. The ^{119}Sn MAS NMR spectrum of compound **9**·H_2O shows resonances at δ −67 (Sn1) and −171 (Sn2). The former is close to the chemical shift of δ −79 in solution and confirms unambiguously the persistence of the O→Sn1 coordination, while the latter is rather high-field shifted in comparison with the chemical shift δ −55 of Sn2 and indicates that the intermolecular O(W)→Sn2 interaction is not preserved in solution. Similarly to the related aqua complex $[Ph_2ClSn(CH_2)_2]$-15-benzocrown-5·H_2O,[16] in solution compound **9**·H_2O might be in fast equilibrium with **9** + H_2O, with the population of the latter dominating at ambient temperature. However, this was not investigated in more detail. Moreover, the ^{1}H NMR spectra (400.13 MHz) of compounds **8** and **9**·H_2O show, as a result of their diastereotopism, AB- and ABX-type resonances for the SnCH_2Sn [**8**: δ 1.30/1.42, $^2J(^1H-^1H)$ 12 Hz; **9**: δ 1.73/1.93, $^2J(^1H-^1H)$ 12 Hz, $^2J(^1H-^{119/117}Sn)$ 67 Hz] and SnCH_2CH [**8**: δ 0.90/1.40, $^2J(^1H-^1H)$ 12 Hz, $^3J(^1H-^1H)$ 7 Hz; **9**·H_2O: δ 1.12/1.49, $^2J(^1H-^1H)$ 12 Hz, $^3J(^1H-^1H)$ 7 Hz] protons, respectively, which indicate the Sn(1) atoms (for numbering see Chart 3) to be configurationally stable on the ^{1}H NMR time scale. This enhanced configurational stability is the result of intramolecular O→Sn coordination and resembles the N→Sn-induced enhanced configurational stability of the tin atom in $(2\text{-}Me_2NCH_2C_6H_4)MePhSnBr$.[33]

Chart 3



In analogy with Ph_2XSnCH_2-[16]-crown-5[17] (X = F, Cl, Br, I) and in contrast to their nonsymmetric structure in the solid state, compounds **2**−**6** exhibit, at ambient temperature and on the ^{13}C NMR time scale, symmetric structures in solution, as was evidenced by the ^{13}C spectra showing for each compound seven resonances for the crown ether carbon atoms (C18, C19/C17, C2/C15, C3/C14, C5/C12, C6/C11, and C8/C9).

The electrospray ionization mass spectra, hereafter referred to as ESI-MS, in the positive mode of compounds **2**−**6** are characterized by the observation of a mass cluster centered at *m*/*z* 565.2 that is assigned to $(Ph_2SnCH_2\text{-}[19]\text{-crown-}6)^+$. The ESI-MS (positive mode) of compound **9** showed mass clusters centered at *m*/*z* 901.0 and 805.1 that are assigned to $\{Ph_2ISnCH_2Sn\text{-}PhCH_2\text{-}[19]\text{-crown-}6\}^+$ and $\{Ph_2(CH_3O)SnCH_2SnPhCH_2\text{-}[19]\text{-crown-}6\}^+$.

Complexation Studies. The complexation behavior of the monotin-substituted crown ether derivatives **2**−**6** toward potassium salts is similar to that of the triorganotin derivatives Ph_2XSnCH_2-[16]-crown-5[17] (X = F, Cl, Br, I, NCS) toward sodium salts. Thus, the ^{119}Sn spectra at room temperature of solutions of the triorganotin thiocyanate **6** in CD_3CN/D_2O (4:1) and $CDCl_3$ to each of which had been added 1 molar equiv of KSCN showed single resonances at δ −232 ($\nu_{1/2}$ = 426 Hz) and −240 ($\nu_{1/2}$ = 162 Hz), respectively. These signals are assigned to the ditopic complex [**6**·KSCN] (Scheme 3), with the chemical shifts being close to that reported for the related complex $\{Ph_2(NCS)SnCH_2\text{-}[16]\text{-crown-}5\cdot NaSCN\}$ (δ −225, in $CDCl_3$).[17]

The formation of the complex [**6**·KSCN] in CD_3CN/D_2O (4:1) gets further support from (i) the ^{13}C NMR, showing high-frequency chemical shifts of 2.5, 5.3, and 0.3 ppm of the C(*ipso*), C20, and C17/C19 resonances, respectively, and (ii) the ^{1}H NMR of the crown ether protons, showing high-frequency shifts of 0.1 ppm.

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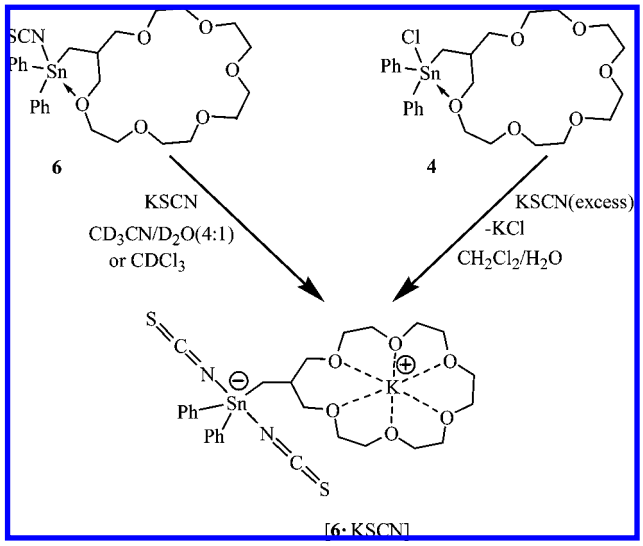
Scheme 3



The electrospray ionization mass spectrum of the authentic solution (**6** + KSCN in CD_3CN/D_2O (4:1)) displayed in the positive mode mass clusters centered at *m/z* 662.2 and 565.3, which are assigned to $[Ph_2(SCN)SnCH_2$-19-crown-6·K$]^+$ and $[Ph_2SnCH_2$-19-crown-6$\}]^+$. In the negative mode a mass cluster centered at *m/z* 682.3 was observed, which is assigned with caution to $[Ph_2(SCN)Sn$-CH_2-19-crown-6·SCN$]^-$. The calculated value for the latter is, however, *m/z* 681.1.

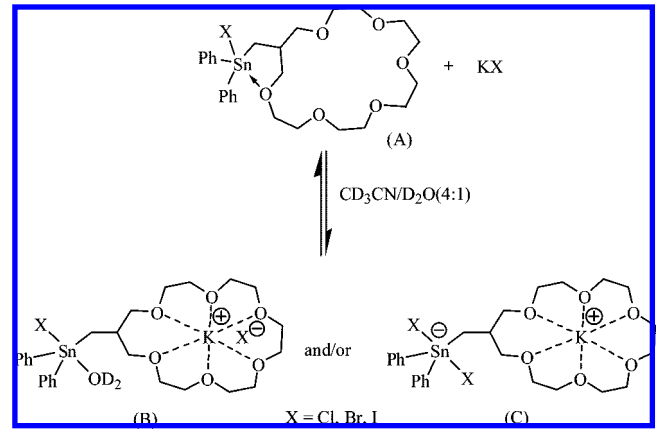
Finally, analytically pure [**6**·KSCN] was obtained as a colorless oil by reaction in dichloromethane/water of the triorganotin chloride **4** with excess potassium thiocyanate, KSCN (Scheme 3).

From the investigations on the complexation behavior of Ph_2XSnCH_2-[16]-crown-5 (X = Cl, SCN)[17] toward NaSCN and NaCl, respectively, we know that redistribution reactions take place involving the ditopic complex Na$\{Ph_2(NCS)_2SnCH_2$-[16]-crown-5$\}$. A similar behavior holds for $[Ph_2(SCN)SnCH_2$-19-crown-6] toward KCl, with K$\{Ph_2(SCN)_2SnCH_2$-[19]-crown-6$\}$ being involved in the equilibrium. Details are given in the Supporting Information.

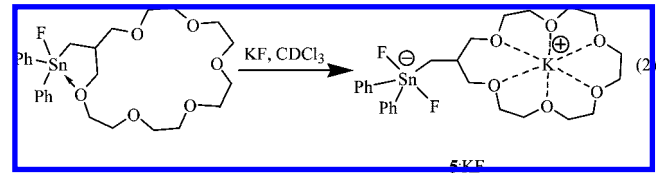
The ^{119}Sn NMR spectra in CD_3CN/D_2O solutions of the triorganotin halides **2**, **3**, and **4** to which had been added molar equivalents of potassium bromide, KBr, potassium iodide, KI, and potassium chloride, KCl, respectively, showed single resonances at δ −105, −124, and −122 that are close to the chemical shifts of the parent compounds (**2**, δ −101; **3**, δ −132; **4**, δ −91). Together with the ^{1}H and ^{13}C NMR spectra showing little but unambiguous differences especially of the crown ether resonances between salt-free and salt-containing solutions, these results indicate an equilibrium between A and B, and/or C, as shown in Scheme 4.

The position of this equilibrium depends on the identity of the halogen X and the concentration of the salt KX (X = Br, I, Cl) and reflects the interplay between the strengths of O→Sn, O→K^+, Sn−X, and K−X bonds, the hydration energies of K^+ and X^-, and the donor strength of X^- toward the tin atom. Thus, for X = I^- formation of C seems to be rather unlikely. Indeed, it appears that the strongest shift of the equilibrium shown in Scheme 4 toward B and/or C is observed in the case for X = Br and Cl, respectively. Thus, the ^{119}Sn NMR spectra of solutions in CD_3CN/D_2O (7:1) of the organotin bromide **2** and organotin chloride **4** to which had been added 3 molar equiv of KBr and 2 molar equiv of KCl, respectively, showed chemical shifts at δ −125 and −130.

Scheme 4

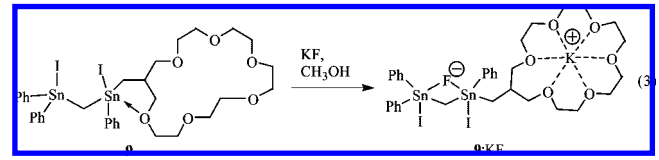


The ^{119}Sn NMR spectrum of a solution in $CDCl_3$ of the triorganotin fluoride **5** to which had been added 1 molar equiv of tetrabutylammonium fluoride trihydrate, *n*-$Bu_4NF·3H_2O$, showed a doublet resonance at δ −106 [$^1J(^{119}Sn-^{19}F)$ 2084 Hz, integral 27] and a triplet resonance at δ −267 [$^1J(^{119}Sn-^{19}F)$ 1860 Hz, integral 73], indicating an equilibrium between compound **5** and its triorganodifluorostannate complex [**5**·F]$^-$*n*-Bu_4N^+. In the latter, fluoride anion successfully competes with the crown ether oxygen atom for coordination at the tin atom. Most importantly, the reaction of the triorganotin fluoride **5** with potassium fluoride, KF, provided the corresponding ditopic complex **5**·KF as a colorless, crystalline, sharp-melting material (eq 2).



Its ^{119}Sn and ^{19}F NMR spectra show a triplet resonance at δ −277 [$^1J(^{119}Sn-^{19}F)$ 1910 Hz] and a singlet resonance at δ −157.7 [$^1J(^{19}F-^{119}Sn)$ 1912 Hz], respectively, and indicate the complex to be kinetically inert on the corresponding NMR time scales. That the potassium cation is indeed coordinated by the crown ether moiety follows from the ^{1}H and ^{13}C NMR spectra, which are different as compared to those of the triorganotin fluoride **5**.

Reaction of the bis(organostannyl)methane-substituted crown ether **9** in methanol with potassium fluoride, KF, provided the corresponding complex **9**·KF as a single crystalline material (eq 3).



The molecular structure of **9**·KF is shown in Figure 5, and selected bond distances and bond angles are given in Tables 3 and 4, respectively.

Complex **9**·KF is composed of a dinuclear organotin and a crown ether moiety that are linked by a methylene group (C21). Both tin atoms are pentacoordinated and each shows a distorted trigonal-bipyramidal configuration (geometrical goodness $\Delta\sum(\vartheta)^{25}$ 73.9° (Sn1), 66.2° (Sn2)) with the carbon atoms C(1),

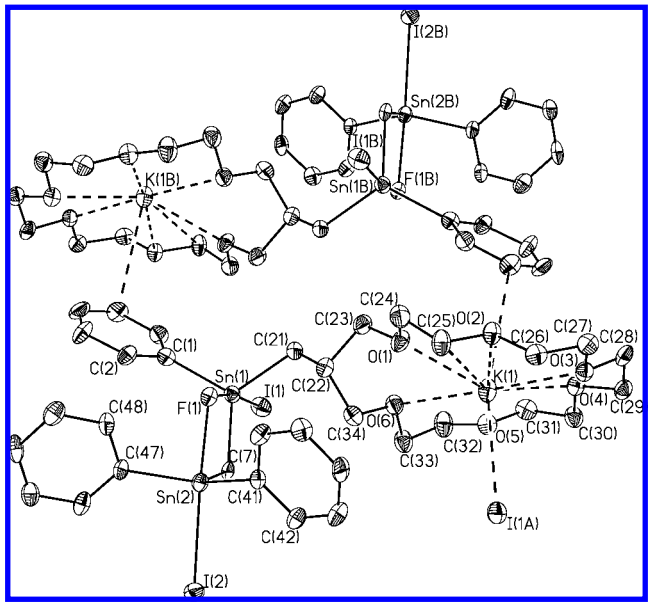


Figure 5. Molecular structure of **9**·KF showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

C(7), C(21) (at Sn1) and C(7), C(41), C(47) (at Sn2) occupying the equatorial and F(1), I(1) (at Sn1) and F(1), I(2) (at Sn2) occupying the axial positions. The Sn(1) atom is displaced by 0.175(4) Å in the direction of I(1) and the Sn(2) atom is displaced by 0.246(3) Å in the direction of I(2) from the planes defined by the corresponding carbon atoms. These data indicate the configurations of the Sn(1) and Sn(2) atoms in **9**·KF to be similar to the tin atoms in $[(Ph_2ISn)_2CH_2 \cdot F]^-[Et_4N]^+$ ($\Delta\sum(\vartheta)^{25}$ 72.3°, 69.1°) but somewhat less distorted than those of the tin atoms in the related ditopic complex $\{Ph_2ISnCH_2Sn(I)PhCH_2$-[16]-crown-5$\} \cdot NaF \cdot CH_3OH$ ($\Delta\sum(\vartheta)^{25}$ 70.2°, 58.4°).[19] As in the latter compound (Δ(Sn−F) 0.128 Å), the Sn(1)−F(1)−Sn(2) bridge in **9**·KF is unsymmetric (Δ(Sn−F) 0.068 Å), whereas it is almost symmetric in $[(Ph_2ISn)_2CH_2 \cdot F]^-[Et_4N]^+$ (Δ(Sn−F) 0.017 Å).[34] The origins for these differences are likely the high ionic character of the Sn−F bond[35] and the $CH_3O-H \cdots F$ bridge in $\{Ph_2ISnCH_2Sn(I)PhCH_2$-[16]-crown-5$\} \cdot NaF \cdot CH_3OH$. In complex **9**·KF, like for the sodium fluoride complex mentioned above,[19] the short Sn(1)−F(1) distance (2.198(2) Å) is associated with the long Sn(1)−I(1) distance (2.9581(7) Å), whereas the long Sn(2)−F(1) distance (2.266(3) Å) is associated with the short Sn(2)−I(2) distance (2.8706(6) Å). This is in line with the usual trend being observed for triorganostannates that contain a C_3SnXY substituent pattern and that exhibit a combination of short Sn−X/long Sn−Y bonds, or vice versa.[36]Further similarities between the structures of **9**·KF and $\{Ph_2ISnCH_2Sn(I)PhCH_2$-[16]-crown-5$\} \cdot NaF \cdot CH_3OH$[19] are the intramolecular F(1)···H(6A), F(1)···H(8A), F(1)···H(14A), and F(1)···H(22A) distances of 2.504, 2.524, 2.363, and 2.558 Å, respectively, being shorter than the sum of the van der Waals radii[24] of fluorine (1.50−1.60 Å) and hydrogen (1.20−1.45 Å) (see Figure S3 in the Supporting Information). The Sn(1)−I(1) distance in **9**·KF of 2.9581(7) Å is the longest among the intramolecularly coordinated triorganotin iodides $[(Ph_2ISn)_2CH_2 \cdot F]^-[Et_4N]^+$,[34] $\{Ph_2ISnCH_2Sn(I)PhCH_2$-[16]-crown-5$\} \cdot H_2O$,[18] $\{Ph_2ISnCH_2Sn(I)PhCH_2$-[16]-crown-5$\} \cdot NaF \cdot CH_3OH$,[19] **3**, **8**, and **9**·H_2O. The origin for this additional lengthening is very likely the intermolecular electrostatic I(1A)···K(1) attraction, giving rise to a distance of 3.8294(15) Å, which is only 0.2964 Å longer than the corresponding distance in crystalline potassium iodide, KI,[37] and which compensates part of the charge separation. As a result of this I(1A)···K(1) attraction, compound **9**·KF forms a polymeric chain in the crystal lattice.

The structure of the crown ether moiety is characterized by the potassium cation being coordinated by the six crown ether oxygen atoms at K−O distances ranging between 2.718(4) (K1−O5) and 2.894(4) Å (K1−O6), which is comparable to the K−O distances of 2.722(14) and 2.913(15) Å as reported for the complex formed by a rhenium(I) bipyridine-substituted crown ether and KCl.[38] In addition to the K−O and K···I interactions, there are K(1)···C(17b) and K(1)···C(25) distances of 3.498(6) and 3.506(7) Å, respectively, which are shorter than the sum of the van der Waals radii[24] of potassium and carbon. The potassium cation is placed 0.349(2) Å above the least plane defined by the six oxygen atoms O(1)−O(6), in the direction of I(A).

The ditopic complex **9**·KF is preserved in solution and exhibits a similar behavior to the corresponding complex $\{Ph_2ISnCH_2Sn(I)PhCH_2$-[16]-crown-5$\} \cdot NaF$.[18,19] On the ^{19}F and ^{119}Sn NMR time scales **9**·KF is kinetically labile at ambient temperature and kinetically inert at low temperature. These statements are substantiated by the following experimental facts: (i) In contrast to compound **9**·H_2O, the ^1H NMR spectrum (400.13 MHz, $CDCl_3$) of complex **9**·KF displays a broad singlet resonance for the $SnCH_2Sn$ protons at δ 1.41 ($^2J(^1H-^{117/119}Sn)$ 76.5 Hz) and a broad doublet resonance for the $SnCH_2CH$ protons at δ 1.05 ($^2J(^1H-^1H)$ 6 Hz, $^2J(^1H-^{117/119}Sn)$ 69 Hz). The data indicate loss of diastereotopism of the methylene protons associated with decreased configurational stability of the tin atom. (ii) The ^{19}F NMR spectrum (282.40 MHz, $CDCl_3$) shows a broad singlet at δ −105.0 ($\nu_{1/2}$ 226 Hz). At 238 K the singlet narrows, shifts to δ −102.7 ($\nu_{1/2}$ 112 Hz), and shows an unresolved $^1J(^{19}F-^{117/119}Sn)$ coupling of 668 Hz. The satellite-to-signal-to-satellite integral ratio of 15.45:69.43:15.12 is close to the calculated one of 17.16:65.68:17.16. This ratio as well as the magnitude of the $^1J(^{19}F-^{117/119}Sn)$ coupling confirms the existence of a Sn−F−Sn bridge. (iii) The ^{119}Sn NMR spectrum of a solution of compound **9** in $CDCl_3$ to which had been added 1 molar equiv of potassium fluoride, KF, showed two broad resonances at δ −105 ($\nu_{1/2}$ 1550 Hz) and −153 ($\nu_{1/2}$ 1230 Hz), which are low-frequency-shifted as compared to the two singlets at δ −55 and −79 detected for compound **9**. At 238 K decoalescence into two equally intense doublet resonances at δ −99 [$^1J(^{119}Sn-^{19}F)$ 683 Hz] and −151 [$^1J(^{119}Sn-^{19}F)$ 692 Hz] was observed.

The ESI-MS also supports the identity of complex **9**·KF in solution. In the positive mode there are mass clusters centered at *m/z* 1067, 959, and 791 that are assigned to $\{Ph_2ISnCH_2SnIPhCH_2$-[19]-crown-6·K$\}^+$, $\{Ph_2ISnCH_2SnPhCH_2$-[19]-crown-6·KF$\}^+$, and $\{Ph_2SnCH_2SnPhCH_2$-[19]-crown-6·F$\}^+$, respectively.

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(35) Beckmann, J.; Horn, D.; Jurkschat, K.; Rosche, F.; Schürmann, M.; Zachwieja, U.; Dakternieks, D.; Duthie, A.; Lim, A. E. K. *Eur. J. Inorg. Chem.* **2003**, 164.
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Conclusions

The combination of the potassium cation-specific crown ether [19]-crown-6 with mono- and ditin moieties, respectively, provided novel host molecules that are capable of complexing potassium thiocyanate, KSCN, and potassium fluoride, KF, in ditopic fashion. The fact that in contrast to {Ph_2FSnCH_2-[16]-crown-5}, which was shown to be unable to complex sodium fluoride, the corresponding triorganotin fluoride {Ph_2FSnCH_2-[19]-crown-6} complexes potassium fluoride, KF, is traced to the lower lattice energy of the latter. With a variety of robust organotin-substituted crown ethers now at hand, future work will be devoted to explore the ability of these host molecules to selectively transport salts through organic membranes.

Experimental Section

General Methods. Solvents were dried and distilled from the appropriate desiccants prior to use. All manipulations were performed under an inert atmosphere of nitrogen or argon. Literature procedures were used to prepare 1,4,7,10,13,16-hexaoxacyclononadecane[23] and triphenyltin hydride.[39] The atom numbering of the crown ether fragment is shown in Chart 3.

NMR Spectroscopy. NMR spectra were recorded on Bruker DRX 500, DRX 400, and DPX 300, Varian Nova 600, and Varian Mercury 200 spectrometers with broadband decoupling of ^{119}Sn at 111.92 MHz, ^{19}F at 282.4 MHz, and ^{13}C at 100.61 MHz. Chemical shifts δ are given in ppm and referenced to tetramethylstannane (^{119}Sn), $CFCl_3$ (^{19}F), and tetramethylsilane (^{1}H, ^{13}C). Solid state ^{119}Sn NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer equipped with a double-bearing CP/MAS probe at room temperature. CP/MAS (cross-polarization/magic angle spinning) experiments were used with a repetition delay of 10s, and the contact time was set at 2 ms. Two spinning rates (4000−7000 Hz) were used to identify the isotropic chemical sfift. The number of scans varied between 500 and 1000. The ^{119}Sn chemical shifts were calibrated using tetracyclohexyltin (δ = −97.35).

Complexation Studies. The samples for NMR analyses were prepared by dissolving ca. 50 mg of the triorganotin halide and the corresponding amounts of the potassium salt in deuterated solvents. The potassium salts used for the complexation studies were dried in vacuo (10^{-6} mbar) at 100 °C for one day and stored under nitrogen.

Electrospray Mass Spectra. Spectra were recorded on a Thermoquest-Finnigan instrument using CH_3CN as the mobile phase. The samples were introduced as solution in CH_3CN via a syringe pump operating at 0.5 μL/min. The capillary voltage was 4.5 kV, while the cone skimmer voltage varied between 50 and 250 kV. Identification of the expected 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 3 (**2**, **9**·H_2O, **9**·KF), 4 (**3**), and 5 (**1**, **4**, **8**) sets at different κ-angles with 513 (**1**), 263 (**2**), 454 (**3**), 421 (**4**), 512 (**8**), 272 (**9**·H_2O), and 249 (**9**·KF) frames via ω-rotation (Δ/ω = 1°) at two times 15 s (**3**, **9**·H_2O), 40 s (**1**), 50 s (**2**), 70 s (**4**), 80 s (**8**), and 150 s (**9**·KF) per frame. The crystal-to-detector distance was 3.4 cm (**1**, **2**, **4**, **8**, **9**·H_2O, **9**·KF) and 4.4 cm (**3**). Crystal decay was monitored by repeating the initial frames at the end of data collection. The data were not corrected for absorption effects. Analyzing the duplicate reflections showed no indication for any decay. The structure was solved by direct methods with SHELXS97[40] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods with SHELXL97.[41]

The H atoms were placed in geometrically calculated positions using a riding model with isotropic temperature factors constrained at 1.2 for nonmethyl and at 1.5 for methyl groups times U_{eq} of the carrier C atom.

Disordered crown ether rings were found in **2** with occupancies of 0.5 (O(6), O(6′), C(33), C(33′)), in **3** with occupancies of 0.5 (O(4), O(4′)), and in **8** with occupancies of 0.4 (O(5), O(6), (C(32), (C(33)) and 0.6 (O(5′), O(6′), (C(32′), (C(33′)).

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from International Tables for X-ray Crystallography.[42] The figures were created by SHELXTL.[43] Crystallographic data are given in Table 5, selected bond distances and angles for **1**−**4** in Tables 1 and 2, and those for **8**, **9**·H_2O, and **9**·KF in Tables 3 and 4.

Synthesis of (1,4,7,10,13,16-Hexaoxacyclononadec-18-methyl)-triphenylstannane (1). 18-Methylene-1,4,7,10,13,16-hexaoxacyclononadecane (5.12 g, 17.643 mmol) was mixed with triphenyltin hydride, Ph_3SnH (6.18 g, 17.643 mmol). After a small quantity of AIBN (100 mg) had been added, the mixture was stirred at 60−80 °C for 15 h followed by cooling to room temperature. Addition of CH_2Cl_2 (80 mL) followed by filtration through Celite and removal of the solvent in vacuo afforded a viscous oil. Purification of the oil by column chromatography with silica gel/CH_2Cl_2 and elution with ethanol gave 8.06 g (71%) of **1** as a viscous oil, which solidified after it had been kept a few days at room temperature, mp 48 °C. Single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in CH_2Cl_2/*n*-hexane.

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ: 1.45 (d, $^3J(^1H-^1H)$ = 7.3 Hz, $^2J(^1H-^{117}Sn)$ = 51.5 Hz, $^2J(^1H-^{119}Sn)$ = 65.7 Hz, 2H, Sn-CH_2), 2.38 (m, 1H, CH), 3.28−3.71 (complex pattern, 24H, CH_2-O-CH_2), 7.31−7.53 (15H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.63 MHz) δ: 11.4 ($^1J(^{13}C-^{117}Sn)$ = 398 Hz, $^1J(^{13}C-^{119}Sn)$ = 417 Hz, C20), 37.3 ($^2J(^{13}C-^{117/119}Sn)$ = 20 Hz, C18), 70.2, 70.6, 70.7, 70.8, (C2−C15), 74.5 ($^3J(^{13}C-^{117/119}Sn)$ = 48 Hz, C17/C19), 128.2 ($^3J(^{13}C-^{117/119}Sn)$ = 49 Hz, C_m), 128.4 ($^4J(^{13}C-^{117/119}Sn)$ = 12 Hz, C_p), 136.9 ($^2J(^{13}C-^{117/119}Sn)$ = 36 Hz, C_o), 140.2 ($^1J(^{13}C-^{117}Sn)$ = 474 Hz, $^1J(^{13}C-^{119}Sn)$ = 496 Hz), C_i). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 111.93 MHz) δ: −106. Anal. Calcd for $C_{32}H_{42}O_6Sn$ (641.39): C 59.9; H 6.6. Found: C 59.8; H 6.8.

Synthesis of Bromo(1,4,7,10,13,16-hexaoxacyclononadec-18-methyl)diphenylstannane (2). To a cooled solution (−55 °C) of **1** (1.05 g, 1.637 mmol) in dichloromethane (30 mL) was added dropwise a solution of bromine (0.26 g, 1.637 mmol) in dichloromethane (15 mL). After the addition had been completed, the mixture was stirred and warmed to room temperature overnight. From the clear solution obtained, the solvent and the bromobezene formed were removed in vacuo (10^{-3} mm Hg) to afford a light yellow solid, which was recrystallized from ethanol to give 0.71 g (68%) of **2** as colorless crystals, mp 85 °C.

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ: 1.69 (d, $^3J(^1H-^1H)$ = 8.04 Hz, $^2J(^1H-^{117}Sn)$ = 68.5 Hz, $^2J(^1H-^{119}Sn)$ = 83.6 Hz, 2H, Sn-CH_2), 2.56 (m, 1H, CH), 3.32−3.75 (complex pattern, 24H, CH_2-O-CH_2), 7.34−7.77 (10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.63 MHz) δ: 18.9 ($^1J(^{13}C-^{117}Sn)$ = 503 Hz, $^1J(^{13}C-^{119}Sn)$ = 527 Hz, C20), 37.4 ($^2J(^{13}C-^{117/119}Sn)$ = 23 Hz, C18), 70.3, 70.5, 70.6, 70.8, 70.9 (C2−C15), 74.4 ($^3J(^{13}C-^{117/119}Sn$ = 66 Hz, C17/C19),

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Table 5. Crystallographic Data and Structure Refinements for Compounds 1−4, 8, 9·H_2O, and 9·KF

	1	2	3	4	8	9·H_2O	9·KF
formula	$C_{32}H_{42}O_6Sn$	$C_{26}H_{37}BrO_6Sn$	$C_{26}H_{37}IO_6Sn$	$C_{26}H_{37}ClO_6Sn$	$C_{39}H_{49}IO_6Sn_2$	$C_{33}H_{44}I_2O_6Sn_2·H_2O$	$C_{33}H_{44}FI_2KO_6Sn_2$
fw	641.35	644.16	691.15	599.70	978.06	1045.88	1085.96
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
cryst size, mm	0.12 × 0.10 × 0.10	0.18 × 0.16 × 0.16	0.22 × 0.22 × 0.20	0.10 × 0.10 × 0.08	0.16 × 0.14 × 0.14	0.24 × 0.22 × 0.20	0.10 × 0.10 × 0.06
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a, Å	13.7101(5)	9.8780(5)	10.0164(2)	9.8090(5)	11.0743(6)	12.3109(8)	12.4106(15)
b, Å	14.2590(7)	22.5904(14)	22.4277(6)	22.6677(18)	13.8150(10)	23.0720(14)	19.896(2)
c, Å	15.8087(7)	13.0178(5)	13.1163(3)	12.9588(9)	14.8912(14)	13.6159(5)	15.6208(11)
α, deg	80.987(18)	90	90	90	63.678(4)	90	90
β, deg	86.130(2)	108.916(3)	109.6686(10)	108.653(4)	87.735(6)	103.304(3)	94.869(7)
γ, deg	87.754(2)	90	90	90	72.193(4)	90	90
V, Å^3	3044.1(2)	2748.0(2)	2774.59(11)	2730.0(3)	1931.8(3)	3763.6(4)	3843.2(7)
Z	4	4	4	4	2	4	4
ρ_{calcd}, Mg/m^3	1.399	1.557	1.655	1.459	1.681	1.846	1.877
μ, mm^{-1}	0.880	2.420	2.070	1.070	2.135	3.009	3.058
F(000)	1328	1304	1376	1232	968	2024	2096
θ range, deg	2.93 to 25.35	3.26 to 27.45	3.19 to 27.51	2.91 to 27.47	2.95 to 27.45	3.06 to 25.35	2.62 to 25.34
index ranges	$-16 \le h \le 16$ $-17 \le k \le 17$ $-18 \le l \le 18$	$-12 \le h \le 12$ $-29 \le k \le 29$ $-16 \le l \le 15$	$-12 \le h \le 12$ $-29 \le k \le 29$ $-17 \le l \le 16$	$-12 \le h \le 12$ $-29 \le k \le 29$ $-16 \le l \le 15$	$-14 \le h \le 14$ $-16 \le k \le 17$ $-19 \le l \le 19$	$-14 \le h \le 14$ $-27 \le k \le 24$ $-16 \le l \le 16$	$-14 \le h \le 14$ $-23 \le k \le 23$ $-18 \le l \le 18$
no. of reflns collcd	44 260	22 494	28 956	36 315	31 302	28 815	28 344
completeness to θ_{max}	99.8	99.3	99.8	99.8	99.4	99.8	99.8
no. of indep reflns/R_{int}	11 135/0.022	6239/0.034	6345/0.031	6242/0.039	8794/0.036	6881/0.04	7010/0.054
no. of reflns obsd with $I > 2\sigma(I)$	8387	3669	4585	2831	4695	3329	2763
no. of refined params	703	325	316	302	469	397	406
GooF (F^2)	0.936	0.862	1.091	0.801	0.739	0.657	0.517
R1(F) ($I > 2\sigma(I)$)	0.0252	0.0307	0.0340	0.0385	0.0281	0.0291	0.0285
wR2(F^2) (all data)	0.0539	0.0614	0.0872	0.0886	0.0469	0.0468	0.0509
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001	0.001	0.001	0.000	0.000
largest diff peak/hole, e/Å^3	0.646/−0.542	1.027/−0.676	1.534/−0.907	1.163 /−0.806	0.660/−0.881	0.641/−1.012	0.861 /−0.617

128.6 ($^3J(^{13}C-^{117/119}Sn)$ = 63 Hz, C_m), 129.4 ($^4J(^{13}C-^{117/119}Sn)$ = 14 Hz, C_p), 135.8 ($^2J(^{13}C-^{117/119}Sn)$ = 48 Hz, C_o), 140.6 ($^1J(^{13}C-^{117}Sn)$ = 617 Hz, $^1J(^{13}C-^{119}Sn)$ = 645 Hz), C_i). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 111.93 MHz) δ: −93. Anal. Calcd for $C_{26}H_{37}BrO_6Sn$ (644.18): C 48.5; H 5.8. Found: C 48.5; H 5.5.

Synthesis of Iodo(1,4,7,10,13,16-hexaoxacyclononadec-18-methyl)diphenylstannane (3). Over a period of 3 h, iodine (2.39 g, 9.355 mmol) was added in small portions at 0 °C to a stirred solution of **1** (6.0 g, 9.355 mmol) in CH_2Cl_2 (100 mL). Stirring was continued, and the reaction mixture was warmed to room temperature overnight. Dichloromethane and iodobenzene were removed in vacuo (10^{-3} mm Hg) to give a yellow solid. The latter was recrystallized from ethanol at −5 °C to afford 5.26 g (81%) of pure **3**, mp 100 °C. Single crystals of **3** suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in ethanol.

^1H NMR ($CDCl_3$, 400.13 MHz) δ: 1.80 (d, $^3J(^1H-^1H)$ = 7.8 Hz, $^2J(^1H-^{117}Sn)$ = 65.0 Hz, $^2J(^1H-^{119}Sn)$ = 80.6 Hz, 2H, Sn-CH_2), 2.56 (m, 1H, CH), 3.31−3.76 (complex pattern, 24H, CH_2-O-CH_2), 7.33−7.77 (10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.63 MHz) δ: 20.7 ($^1J(^{13}C-^{117}Sn)$ = 481 Hz, $^1J(^{13}C-^{119}Sn)$ = 504 Hz, C20), 38.0 ($^2J(^{13}C-^{117/119}Sn)$ = 25 Hz, C18), 70.3, 70.5, 70.6, 70.8, 70.9 ((C2−C15), 74.3 ($^3J(^{13}C-^{117/119}Sn)$ = 65 Hz, C17/C19), 128.5 ($^3J(^{13}C-^{117/119}Sn)$ = 63 Hz, C_m), 129.3 ($^4J(^{13}C-^{117/119}Sn)$ = 14 Hz, C_p), 135.9 ($^2J(^{13}C-^{117/119}Sn)$ = 47 Hz, C_o), 140.1 ($^1J(^{13}C-^{117}Sn)$ = 592 Hz, $^1J(^{13}C-^{119}Sn)$ = 620 Hz), C_i). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 111.93 MHz) δ: −126. ^{119}Sn MAS NMR (149.20 MHz) δ: −128. Anal. Calcd for $C_{26}H_{37}IO_6Sn$ (691.18): C 45.2; H 5.4. Found: C 45.2; H 5.4.

Synthesis of Chloro(1,4,7,10,13,16-hexaoxacyclononadec-18-methyl)diphenylstannane (4). To a solution of **3** (0.50 g, 0.723 mmol) in CH_3CN (20 mL) was added excess silver chloride, AgCl (0.46 g, 3.210 mmol). The resulting mixture was stirred at room temperature and in the dark for 14 days. After the AgI formed and the nonreacted AgCl had been removed by filtration the solvent was evaporated under vacuum. The slightly yellow oil thus obtained was dissolved in ethanol and cooled at −5 °C to give 0.38 g (88%) of pure **4**, mp 65 °C. Crystals of **4** suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in CH_2Cl_2/*n*-hexane.

^1H NMR ($CDCl_3$, 400.13 MHz) δ: 1.60 (d, $^3J(^1H-^1H)$ = 8.0 Hz, $^2J(^1H-^{117}Sn)$ = 70.5 Hz, $^2J(^1H-^{119}Sn)$ = 85.6 Hz, 2H, Sn-CH_2), 2.56 (m, 1H, CH), 3.34−3.75 (complex pattern, 24H, CH_2-O-CH_2), 7.35−7.78 (10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.63 MHz) δ: 17.6 ($^1J(^{13}C-^{117}Sn)$ = 515 Hz, $^1J(^{13}C-^{119}Sn)$ = 543 Hz, C20), 37.2 ($^2J(^{13}C-^{117/119}Sn)$ = 23 Hz, C18), 70.3, 70.5, 70.6, 70.7, 70.8 (C2−C15), 74.4 ($^3J(^{13}C-^{117/119}Sn)$ = 67 Hz, C17/C19), 128.6 ($^3J(^{13}C-^{117/119}Sn)$ = 65 Hz, C_m), 129.4 ($^4J(^{13}C-^{117/119}Sn)$ = 14 Hz, C_p), 135.8 ($^2J(^{13}C-^{117/119}Sn)$ = 47 Hz, C_o), 140.8 ($^1J(^{13}C-^{117}Sn)$ = 634 Hz, $^1J(^{13}C-^{119}Sn)$ = 663 Hz), C_i). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 111.93 MHz) δ: −83. Anal. Calcd for $C_{26}H_{37}ClO_6Sn$ (596.73): C 52.0; H 6.2. Found: C 51.5; H 6.2.

Synthesis of Fluoro(1,4,7,10,13,16-hexaoxacyclononadec-18-methyl)diphenylstannane (5). A solution of **3** (2.0 g, 2.894 mmol) in CH_2Cl_2 (20 mL) was mixed with a solution of NaF (1.22 g, 28.940 mmol) in water (30 mL). The biphasic mixture was stirred at room temperature for 3 days. The organic phase was then separated and dried over $MgSO_4$. Removing the solvent in vacuo afford 1.02 g (60%) of **5** as a colorless oil, which solidified after it had been kept at room temperature for some days, mp 77 °C.

^1H NMR ($CDCl_3$, 400.13 MHz) δ: 1.46 (d, $^3J(^1H-^1H)$ = 9 Hz, $^2J(^1H-^{117}Sn)$ = 72.0 Hz, $^2J(^1H-^{119}Sn)$ = 87.0 Hz, 2H, Sn-CH_2), 2.55 (m, 1H, CH), 3.42−3.77 (complex pattern, 24H, CH_2-O-CH_2), 7.38−7.78 (10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.63 MHz) δ: 13.9 ($^1J(^{13}C-^{117/119}Sn)$ = 553 Hz, C20), 36.8 ($^2J(^{13}C-^{117/119}Sn)$ = 21 Hz, C18), 70.3, 70.4, 70.6, 70.7, 70.8 (C2−C15), 74.4 ($^3J(^{13}C-^{117/119}Sn)$ = 65 Hz, C17/C19), 128.5 ($^3J(^{13}C-^{117/119}Sn)$ = 63 Hz, C_m), 129.5 ($^4J(^{13}C-^{117/119}Sn)$ = 14 Hz, C_p), 135.8 ($^2J(^{13}C-^{117/119}Sn)$ = 47 Hz, C_o), 140.6 ($^1J(^{13}C-^{117}Sn)$ = 683 Hz, $^1J(^{13}C-^{119}Sn)$ = 713 Hz, C_i). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282.4 MHz, 293 K) δ: −188.0 ($^1J(^{19}F-^{117}Sn)$ = 2105 Hz, $^1J(^{19}F-^{119}Sn)$ = 2203 Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 111.93 MHz) δ: −104 (d, $^1J(^{119}Sn-^{19}F)$ = 2200 Hz). Anal. Calcd for $C_{26}H_{37}FO_6Sn$ (583.28): C 53.8; H 6.4. Found: C 52.4; H.6.7.

Synthesis of Thiocyanato(1,4,7,10,13,16-hexaoxacyclononadec-18-methyl)diphenylstannane (6). To a solution of **3**(1.02 g, 1.476 mmol) in CH_3CN (50 mL) was added excess AgSCN (0.73 g, 4.427 mmol). The reaction mixture was stirred at room temperature and in the dark for 10 days, followed by filtration of the AgI formed and the nonreacted AgSCN. Removing the solvent in vacuo gave 0.55 g (60%) of **6** as slightly yellow oil.

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ: 1.59 (d, $^3J(^1H-^1H) = 4.0$ Hz, $^2J(^1H-^{117}Sn) = 68.0$ Hz, $^2J(^1H-^{119}Sn) = 84.0$ Hz, 2H, Sn-CH_2), 2.57 (m, 1H, CH), 3.44−3.76 (complex pattern, 24H, CH_2-O-CH_2), 7.43−7.76 (10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.63 MHz) δ: 15.4 (C20), 37.4 (C18), 70.8, 70.9, 71.0, 71.2 (C2−C15), 75.1 (C17/C19), 128.3 ($^3J(^{13}C-^{117/119}Sn) = 65$ Hz, C_m), 130.3 (C_p), 136.3 ($^2J(^{13}C-^{117/119}Sn) = 45$ Hz, C_o), 139.1 (C_i). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 111.93 MHz) δ: −154 (t, $^1J(^{119}Sn-^{14}N) = 256$ Hz). Anal. Calcd for $C_{27}H_{37}NO_6SSn$ (596.73): C 52.1; H 6.0; N 2.3. Found: C 51.4; H 5.7; N 2.6.

Synthesis of 18-({Diphenyl[(triphenylstannyl)methyl]stannyl}methyl)-1,4,7,10,13,16-hexaoxanonadecane (7). A solution of (bromomagnesiummethyl)triphenylstannane, prepared from (bromomethyl)triphenylstannane (2.27 g, 5.113 mmol) and magnesium (0.13 g, 5.349 mmol) in THF (60 mL), wad added dropwise to a stirred solution of iodo({1,4,7,10,13,16-hexaoxanonadec-18-yl}methyl)diphenylstannane (3.0 g, 4.340 mmol) in THF (50 mL) for a period of 2 h. After the addition had been completed, the reaction mixture was heated at reflux overnight and then cooled to room temperature. Cold water (60 mL) was added, and the mixture was extracted three times with 50 mL of ether. The combined organic phases were dried with $MgSO_4$ and the solvents evaporated in vacuo to give the crude product. It was purified by column chromatography (Al_2O_3, CH_2Cl_2, ethyl acetate) to yield 1.11 g (27.5%) of **7** as a colorless oil.

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ: 0.81 (s, $^2J(^1H-^{117/119}Sn) = 61.7$ Hz, 2H, Sn-CH_2-Sn), 1.01 (d, $^3J(^1H-^{117/119}Sn) = 7.5$ Hz, $^2J(^1H-^{117}Sn) = 48$ Hz, $^2J(^1H-^{119}Sn) = 64.0$ Hz, 2H, Sn-CH_2), 2.13 (m, 1H, C*H*), 3.21−3.68 (complex pattern, 24H, CH_2-O-CH_2), 7.22−7.47 (25H, Ph). ^{13}C NMR ($CDCl_3$, 100.63 MHz) δ: −15.2 ($^1J(^{13}C-^{117}Sn) = 262/273$ Hz, $^1J(^{13}C-^{119}Sn) = 287/300$ Hz, Sn-*C*H_2-Sn), 12.5 ($^1J(^{13}C-117Sn) = 388$ Hz, $^1J(^{13}C-^{119}Sn) = 406$ Hz, Sn*C*H_2), 37.6 ($^2J(^{13}C-^{117/119}Sn) = 19$ Hz, C18), 70.8, 71.1, 71.2, 71.3 (C2−C15), 75.1 (C17/C19), 74.6 ($^3J(^{13}C-^{117/119}Sn) = 50$ Hz, C17/C19), 128.5 ($^3J(^{13}C-^{117/119}Sn) = 48$ Hz, $SnPh_2$, C_m), 128.7 ($SnPh_2$, C_p), 128.8 ($^3J(^{13}C-^{117/119}Sn) = 48.3$ Hz, $SnPh_3$, C_m), 129.1 ($^4J(^{13}C-^{117/119}Sn) = 11$ Hz, $SnPh_3$, C_p), 136.9 ($^2J(^{13}C-^{117/119}Sn) = 37$ Hz, $SnPh_2$, C_o), 137.3 ($^2J(^{13}C-^{117/119}Sn) = 38$ Hz, $SnPh_3$, C_o), 140.2 ($^3J(^{13}C-^{117/119}Sn) = 9$ Hz, $^1J(^{13}C-^{117}Sn) = 483$ Hz, $^1J(^{13}C-^{119}Sn) = 505$ Hz, $SnPh_3$, C_i), 142.2 ($^3J(^{13}C-^{117/119}Sn) = 12$ Hz, $^1J(^{13}C-^{117}Sn) = 457$ Hz, $^1J(^{13}C-^{119}Sn) = 479$ Hz, $SnPh_2$, C_i). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 111.92 MHz) δ: −55 ($^2J(^{119}Sn-^{117/119}Sn) = 231$ Hz, $SnPh_2$), −76 ($^2J(^{119}Sn-^{117/119}Sn) = 227$ Hz, $SnPh_3$). Anal. Calcd (%) for $C_{45}H_{54}O_6Sn_2$ (928.34): C 58.2, H 5.9. Found: C 58.2, H 6.0.

Synthesis of 18-({Iodophenyl[(triphenylphenylstannyl)methyl]stannyl}methyl)-1,4,7,10,13,16-hexaoxanonadecane (8). Iodine (107.1 mg, 0.422 mmol) was added in small portions and under ice cooling to a stirred solution of **7** (392.0 mg, 0.422 mmol) in CH_2Cl_2 (20 mL). Stirring was continued while warming to room temperature overnight. The solvent and the iodobenzene were removed in vacuo (10^{-3} mmHg) to afford a slightly yellow oil. The oil was dissolved in ethanol (8 mL), and the solution was cooled at −15 °C for some days to give 260.0 mg (60.2%) of **8** as a colorless crystalline solid, mp 88−90 °C.

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ: 0.91 (dd, $^2J(^1H-^1H) = 13.1$ Hz, $^3J(^1H-^1H) = 6.5$ Hz, 1H, Sn-CH*H′*), 1.25−1.46 (m, 3H, Sn-C*H*H′-Sn and Sn-CH_2-Sn), 2.10 (m, 1H, C*H*), 3.14−3.76 (complex pattern, 24H, CH_2−-O-CH_2), 7.34−7.76 (20H, Ph). ^{13}C NMR ($CDCl_3$, 100.63 MHz) δ: −5.7 ($^1J(^{13}C-^{117}Sn) = 282$ Hz, $^1J(^{13}C-^{119}Sn) = 294$ Hz, Sn-*C*H_2-Sn), 20.6 ($^1J(^{13}C-^{117}Sn) = 471$ Hz, $^1J(^{13}C-^{119}Sn) = 494$ Hz, Sn*C*H_2), 38.1 ($^2J(^{13}C-^{117/119}Sn) = 20$ Hz, C18), 70.0, 70.7, 70.9, 71.0, 71.2, 71.3, 71.4 (C2−C15), 74.5/74.8 (C17/C19), 128.8 ($^3J(^{13}C-^{117/119}Sn) = 60$ Hz, SnIPh, C_m), 128.9 ($^3J(^{13}C-^{117/119}Sn) = 52$ Hz, $SnPh_3$, C_m), 129.4 ($^4J(^{13}C-^{117/119}Sn) = 12$ Hz, $SnPh_3$, C_p), 129.6 ($^4J(^{13}C-^{117/119}Sn) = 12$ Hz, $SnIPh_2$, C_p), 135.4 ($^2J(^{13}C-^{117/119}Sn) = 48$ Hz, SnIPh, C_o), 137.7 ($^2J(^{13}C-^{117/119}Sn) = 39$ Hz, $SnPh_3$, C_o), 139.7 ($^3J(^{13}C-^{117/119}Sn) = 14$ Hz, $^1J(^{13}C-^{117}Sn) = 497$ Hz, $^1J(^{13}C-^{119}Sn) = 521$ Hz, $SnPh_3$, C_i), 143.4 ($^3J(^{13}C-^{117/119}Sn) = 22$ Hz, $^1J(^{13}C-^{117}Sn) = 547$ Hz, $^1J(^{13}C-^{119}Sn) = 572$ Hz, $SnIPh_2$, C_i). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 111.92 MHz) δ: −62 ($^2J(^{119}Sn-^{117/119}Sn) = 293/310$ Hz, $SnPh_3$), −85 ($^2J(^{119}Sn-^{117/119}Sn) = 294/312$ Hz, SnIPh). Anal. Calcd (%) for $C_{39}H_{49}IO_6Sn_2$ (977.98): C 47.9, H 5.0. Found: C 48.1, H 4.9.

Synthesis of the Aqua Complex of 18-({Iodophenyl[(iododiphenylphenylstannyl)methyl]stannyl}methyl)-1,4,7,10,13,16-hexaoxanonadecane (9·H$_2$O). Iodine (0.55 g, 2.154 mmol) was added in small portions and under ice cooling to a stirred solution of **7** (1.0 g, 1.077 mmol) in CH_2Cl_2 (50 mL). The reaction mixture was stirred while warming at room temperature overnight. The solvent and the iodobenzene were removed in vacuo (10^{-3} mm Hg) to afford a yellow oil. The oil was dissolved in ether (10 mL), and the solution was cooled at −20 °C for several days to give 0.7 g (63%) of **9** as a yellow solid. Single crystals of **9**·H_2O (mp 68−70 °C) suitable for X-ray diffraction analysis were obtained by slow evaporation of an ethanol solution of **9** at room temperature.

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ: 1.12/1.49 (ABX-type resonance, $^2J(^1H-^1H) = 11.5$ Hz, $^3J(^1H-^1H) = 7.1$ Hz, 2H, Sn-CH_2), 1.73/1.93 (AB-type resonance, $^2J(^1H-^1H) = 11.3$ Hz, $^2J(^1H-^{117}Sn) = 56.7$ Hz, $^2J(^1H-^{119}Sn) = 78.0$ Hz, 2H, Sn-CH_2-Sn), 2.24 (1H, C*H*), 3.21−3.64 (complex pattern, 24H, CH_2-O-CH_2), 7.29−7.81 (15H, Ph). ^{13}C NMR ($CDCl_3$, 100.63 MHz) δ: 4.0 ($^1J(^{13}C-^{117}Sn) = 288/301$ Hz, $^1J(^{13}C-^{119}Sn) = 324/339$ Hz, Sn-*C*H_2-Sn), 20.9 ($^1J(^{13}C-^{117}Sn) = 483$ Hz, $^1J(^{13}C-^{119}Sn) = 505$ Hz, Sn*C*H_2), 38.2 ($^2J(^{13}C-^{117/119}Sn) = 25$ Hz, C_{18}), 70.8, 71.0, 71.2, 71.3 (C_2-C_{15}), 74.5 (C_{17}/C_{19}), 129.0 ($^3J(^{13}C-^{117/119}Sn) = 62$ Hz, SnIPh, C_m), 129.2 ($^3J(^{13}C-^{117/119}Sn) = 63$ Hz, $SnIPh_2$, C_m), 129.8 ($^4J(^{13}C-^{117/119}Sn) = 13$ Hz, SnIPh, C_p), 130.4 ($^4J(^{13}C-^{117/119}Sn) = 14$ Hz, $SnIPh_2$, C_p), 135.5 ($^2J(^{13}C-^{117/119}Sn) = 48$ Hz, SnIPh, C_o), 137.0 ($SnIPh_2$, C_o), 138.4 (SnIPh, C_i), 142.1 ($^3J(^{13}C-^{117/119}Sn) = 28$ Hz, SnIPh, C_i). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 111.92 MHz) δ: −55 ($^2J(^{119}Sn-^{117/119}Sn) = 256$ Hz, $SnIPh_2$), −79 ($^2J(^{119}Sn-^{117/119}Sn) = 261$ Hz, SnIPh). ^{119}Sn MAS NMR (149.20 MHz) δ: −67, −171. Anal. Calcd (%) for $C_{33}H_{44}I_2O_6Sn_2 \cdot H_2O$ (1045.94): C 37.9, H 4.4. Found: C 37.8, H 4.3.

Synthesis of 5·KF. Potassium fluoride (7.6 mg, 0.130 mmol) was added to a solution of **5** (75.86 mg, 0.130 mmol) in CH_2Cl_2 (7 mL), and the mixture was stirred at room temperature for 2 days. The reaction mixture was filtered, and the filtrate was dried over molecular sieves. *n*-Hexane (5 mL) was added, and slow evaporation of the solvent gave 42.5 mg (51%) of **5**·KF as a colorless crystalline solid, mp 230 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz, 293 K) δ: 1.26 (d, $^3J(^1H-^1H) = 8.0$ Hz, $^2J(^1H-^{117/119}Sn) = 82.8$ Hz, 2H, Sn-CH_2), 2.55 (m, 1H, CH), 3.36−3.64 (complex pattern, 24H, CH_2-O-CH_2), 7.28−8.16 (10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$,100.63 MHz, 293 K) δ: 19.4 (C20), 36.0 (C18), 69.7, 69.8, 69.9, 70.2 (C2−C15), 76.4 (C17/C19), 127.6 ($^3J(^{13}C-^{117/119}Sn) = 67$ Hz, C_m), 128.1 (C_p), 136.6 ($^2J(^{13}C-^{117/119}Sn) = 49$ Hz, C_o), 145.9 (broad, C_i). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282.4 MHz, 293 K) δ: −157.7 ($^1J(^{19}F-^{117}Sn) = 1838$ Hz, $^1J(^{19}F-^{119}Sn) = 1912$ Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 111.92 MHz, 293 K) δ: − 277 (t, $^1J(^{119}Sn-^{19}F) = 1919$ Hz). Anal. Calcd (%) for $C_{26}H_{37}F_2KO_6Sn$ (641.38): C 48.7, H 5.8. Found: C 48.3, H 6.2.

Synthesis of 6·KSCN. A solution of potassium thiocyanate (175.0 mg, 1.801 mmol) in water (6 mL) was mixed with a solution of **4** (83.3 mg, 0.139 mmol) in CH_2Cl_2 (6 mL). The biphasic mixture was stirred at room temperature for 2 days. The organic phase was separated and dried over molecular sieves for 24 h. After the molecular sieves had been filtered the solvent was removed in vacuo to give 0.086 g (86%) of **6**·KSCN as a colorless oil. ^{1}H NMR ($CDCl_3$, 400.13 MHz, 293 K) δ: 1.52 (broad, $^2J(^1H-^{117/119}Sn) = 75.0$ Hz, 2H, Sn-CH_2), 2.55 (m, 1H, CH), 3.39−3.60 (m, 24H, CH_2-O-CH_2), 7.33−8.06 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.63 MHz, 293 K) δ: 23.6 (C20), 38.0 (C18), 70.1, 70.2, 70.4, 70.8 (C2−C15), 78.6 (broad, C17/C19,), 128.6 ($^3J(^{13}C-^{117/119}Sn)$ = 69 Hz, C_m), 129.2 (C_p), 136.9 ($^2J(^{13}C-^{117/119}Sn)$ = 48 Hz, C_o), 142.5 (C_i). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 111.92 MHz, 293 K) δ: −246. Anal. Calcd for $C_{28}H_{37}N_2KO_6S_2Sn$ (725.55): C 46.7; H 5.2; N 3.9. Found: C 47.0; H 5.5; N 3.4.

Synthesis of 9·KF. Potassium fluoride (1.3 mg, 1.95×10^{-5} mol) was added to a methanol solution of **9**·H_2O (20.0 mg, 1.95×10^{-5} mol) at room temperature, and the mixture was stirred for 30 min. The solvent was allowed to completely evaporate at ambient temperature to give a yellow solid residue. This residue was dissolved in dichloromethane, and the solution was filtered. Slow diffusion of the CH_2Cl_2 solution with ether gave 11 mg (51.4%) of **9**·KF as a yellow crystalline solid, mp 185 °C. Anal. Calcd (%) for $C_{33}H_{44}FI_2KO_6Sn_2$ (1086.02): C 36.5, H 4.1. Found: C 36.8, H 3.9. ^{1}H NMR ($CDCl_3$, 400.13 MHz, 293 K) δ: 1.05 ($^2J(^1H-^1H)$ = 6.3 Hz, $^2J(^1H-^{117/119}Sn)$ = 68.5 Hz, 2H, Sn-CH_2), 1.41 ($^2J(^1H-^{117/119}Sn)$ = 76.5 Hz, 2H, Sn-CH_2-Sn), 2.24 (1H, C*H*), 3.29−3.49 (complex pattern, 24H, CH_2-O-CH_2), 7.24−7.97 (15H, Ph). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282.4 MHz) 293 K: δ −105 (broad, $\nu_{1/2}$ = 226 Hz), 238 K: δ −102.7 ($^1J(^{19}F-^{117}Sn)$ = 668 Hz. $^{119}Sn\{^1H\}$ NMR (111.92 MHz) 293 K: δ −105 (broad, $\nu_{1/2}$ = 1550 Hz), −153 (broad, $\nu_{1/2}$ = 1230 Hz); 238 K: δ −99 (d, $^1J(^{119}Sn-^{19}F)$ = 683 Hz), −151(d, $^1J(^{119}Sn-^{19}F)$ = 692 Hz).

Complexation Studies. In Situ Reaction of 2 with 1 equiv of KBr in CD_3CN/D_2O (4:1). KBr (9.3 mg, 0.078 mmol) was added to a solution of **2** (50.0 mg, 0.078 mmol) in CD_3CN/D_2O (4:1). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, 293 K) δ: −105.

In Situ Reaction of 2 with 3 equiv of KBr in CD_3CN/D_2O (7:1). KBr (18.6 mg, 0.156 mmol) was added to a solution of **2** (50 mg, 0.078 mmol) in CD_3CN/D_2O (7:1). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, 293 K) δ: −125.

In Situ Reaction of 3 with 1 equiv of KI in CD_3CN/D_2O (4:1). KI (12.0 mg, 0.072 mmol) was added to a solution of **3** (50.0 mg, 0.072 mmol) in CD_3CN/D_2O (4:1). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, 293 K) δ: −124.

In Situ Reaction of 4 with 1 equiv of KCl in CD_3CN/D_2O (7:1). KCl (6.3 mg, 0.084 mmol) was added to a solution of **4** (50.0 mg, 0.084 mmol) in CD_3CN/D_2O (7:1). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, 293 K) δ: −122.

In Situ Reaction of 4 with 2 equiv of KCl in CD_3CN/D_2O (8:1). KCl (12.6 mg, 0.168 mmol) was added to a solution of **4** (50 mg, 0.084 mmol) in CD_3CN/D_2O (8:1). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, 293 K) δ: −130.

In Situ Reaction of 5 with 1 equiv of *n*-Bu_4NF in $CDCl_3$. *n*-Bu_4NF (32.4 mg, 0.103 mmol) was added to a solution of **5** (59.9 mg, 0.103 mmol) in $CDCl_3$. $^{19}F\{^1H\}$ NMR (282.4 MHz, 293 K) δ: −150.0 ($^1J(^{19}F-^{117/119}Sn)$ = 1809.0 Hz), −187. $^{119}Sn\{^1H\}$ NMR (111.92 MHz, 293 K) δ: −267.0 (t, 73%, $^1J(^{117/119}Sn-^{19}F)$ = 1860.0 Hz), −106 (d, 27%, $^1J(^{117/119}Sn-^{19}F)$ = 2084.0 Hz).

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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