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Intramolecularly Coordinated Bis(crown ether)-Substituted Organotin Halides as Ditopic Salt Receptors

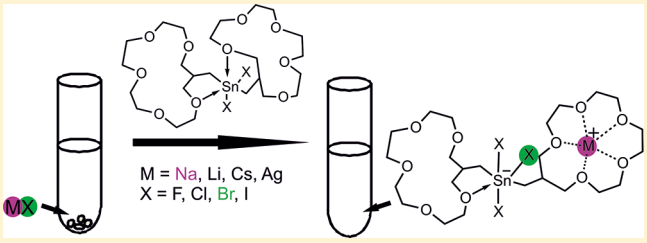
Verena Arens,[†] Christina Dietz,[†] Dieter Schollmeyer,[‡] and Klaus Jurkschat*[,†]

[†]Lehrstuhl für Anorganische Chemie II, Technische Universität Dortmund, D-44221 Dortmund, Germany

[‡]Institut für Organische Chemie, Johannes Gutenberg Universität Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany

Supporting Information

ABSTRACT: The synthesis of the bis(crown ether)-substituted organostannanes $X_2Sn(CH_2\text{-}[16]\text{-crown-}5)_2$ (**3**, X = I; **4**, X = Br; **5**, X = Cl; **6**, X = F) and $X_2Sn(CH_2\text{-}[13]\text{-crown-}4)_2$ (**10**, X = I; **11**, X = Br; **12**, X = F) is reported. The compounds have been characterized by ^{1}H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectroscopy, elemental analyses, and electrospray ionization mass spectrometry (ESI-MS). Single-crystal X-ray diffraction analyses reveal a distorted-octahedral *cis,cis,trans* configuration of the tin atoms in compounds **4**−**6** and **10**−**12** as a result of intramolecular O→Sn coordination. The ability of the host molecules to form mono- and ditopic complexes with various halide salts in different solvents, including water, has been investigated by NMR spectroscopy and ESI-MS.



INTRODUCTION

Ditopic receptors are molecules that complex the cation as well as the anion of an ion pair. Such molecules have attracted increasing interest in the last two decades, because it has been noticed that the complexation of ions by host molecules depends on the identity and the concentration of counterions: that is to say, the interaction of host molecules with their guests can be restricted by ion pair effects. Consequently, the use of ion pair receptors should lead to higher affinities and improved selectivity in comparison to that of monotopic receptors. However, while the development of receptors for cations or anions started in the late 1960s,[1−4] the first artificial receptor for ion pairs was reported in 1991.[5] This is due to challenges in synthesizing these host molecules and to the complexity of the several component mixtures arising from their application as ditopic receptors. However, in recent years the simultaneous complexation of anions and cations by ditopic receptors has become a well-established area in host−guest chemistry. This is evidenced by numerous publications and reviews reporting different strategies of ion pair recognition.[6−10] However, there are only a few examples of ditopic receptors containing Lewis-acidic organoelement or organometallic centers, as most of the published host molecules are merely organic compounds, despite the fact that the first representative of this class of compounds was the organoboron-substituted crown ether **A** (Chart 1) Receptor **A**,[5] the analogous organoaluminum compound **B**,[11] and the organotin-substituted crown ether **C**[12] are able to bind potassium fluoride (KF), lithium fluoride (LiF), and sodium thiocyanate (NaSCN) as separate ions but suffer from their instability under noninert conditions, limiting their potential applications (Chart 1). More robust ditopic receptors of types **D**−**F** (Chart 1), applying kinetically inert Sn−C bonds to link the organotin moiety with the cation binding site, were reported by our group in the last few years.[13−15,16a] To the best of our knowledge, the only examples containing two crown ether moieties attached to one tin atom are diorganotin dicarboxylates of the type $n\text{-}Bu_2Sn(OCOR)_2$ (R = benzo-18-crown-6, benzo-15-crown-5) (**G** in Chart 1), the complexation properties of which toward salts were, however, not investigated.[16b] In a continuation of our systematic studies on organotin-substituted crown ethers we report here bis(crown ether)-substituted organotin halides of type **H** (Chart 1) and investigations of the complexation behavior of these compounds toward different halide salts in different solvents.

RESULTS AND DISCUSSION

Synthetic Aspects and Molecular Structures in the Solid State. The synthesis of compounds **1**−**6** is summarized in Scheme 1. The reaction of iodido(1,4,7,10,13-pentaoxahexadec-15-ylmethyl)diphenylstannane[14] with $LiAlH_4$ provided the mono(crown ether)-substituted triorganohydridostannane **1**. Hydrostannation at 70 °C of 15-methylene-1,4,7,10,13-pentaoxacyclohexadecane with triorganohydridostannane **1** gave the bis(crown ether)-substituted tetraorganostannane **2**. The diorganotindihalide derivatives **3**−**5** were obtained by the reaction of the tetraorganostannane **2** with 2 molar equiv of iodine (I_2), bromine (Br_2), or iodine chloride (ICl), respectively. The diorganodifluoridostannane **6** was obtained in dichloromethane at room temperature by treatment of the diorganodiiodidostannane **3** with 2 molar equiv of silver fluoride (AgF). The preparation of compounds **8**−**12** is analogous to that of compounds **1**−**4** and **6** (Scheme 1). The reaction of the triorganobromidostannane **7**, which had been

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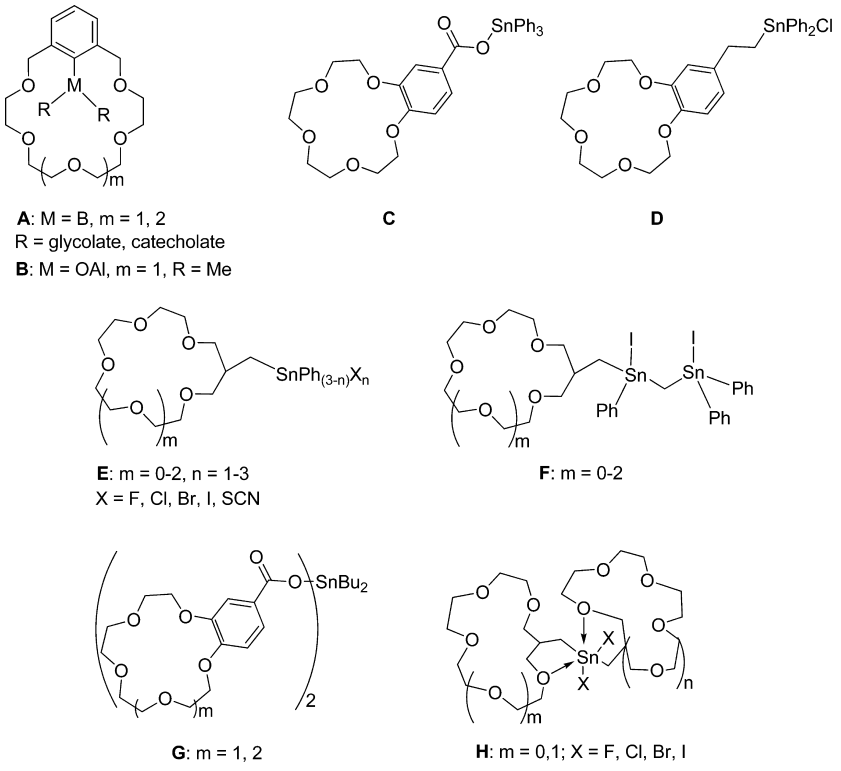
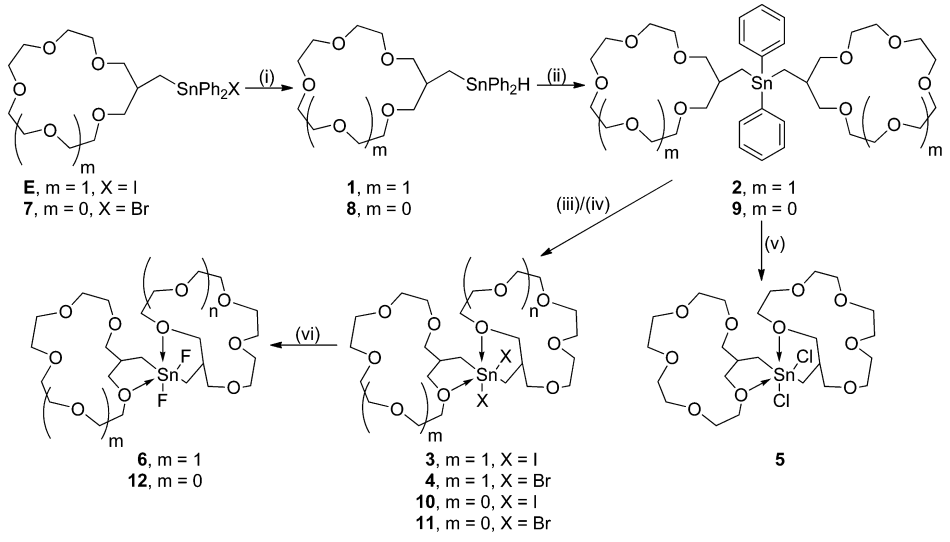
Chart 1



Scheme 1. [a]



[a]Conditions: (i) $LiAlH_4$, Et_2O, 0 °C; (ii) 15-methylene-1,4,7,10,13-pentaoxacyclohexadecane, aibn, 70 °C; (iii) for X = I, 2 I_2, CH_2Cl_2, 0 °C, −2 PhI; (iv) for X = Br, 2 Br_2, CH_2Cl_2, −2PhBr; (v) 2 ICl, CH_2Cl_2, 0 °C, −2 PhI; (vi) 2 AgF, CH_2Cl_2/H_2O, room temperature, −2 AgI.

prepared by the addition of 1 equiv of bromine at low temperatures to (1,4,7,10-tetraoxacyclotridec-12-ylmethyl)-triphenylstannane,[16] with $LiAlH_4$ afforded triorganohydridostannane **8**. Hydrostannation of 12-methylene-1,4,7,10-tetraoxacyclotridecan with the triorganohydridostannane **8** gave the tetraorganostannane **9**. The diorganodiiodidostannane **10** and the diorganodibromidostannane **11** were obtained by the reaction of the tetraorganostannane **9** with 2 equiv of iodine (I_2) and bromine (Br_2), respectively, while the diorganodifluoridostannane **12** was produced by reacting the diorganodiiodido derivative **10** with 2 molar equiv of silver fluoride (AgF).

While the tri- and tetraorganotin compounds **1**, **2**, **8**, and **9** are viscous oils, the diorganodiiodidostannane **3** solidified after standing for several weeks at room temperature. The diorganotin dihalide derivatives **4**−**7** and **10**−**12** are colorless to slightly yellow solids. The triorganohydridostannane **1** is well soluble in benzene and chloroform. Compounds **2**−**7** and **10**−**12** are readily soluble in dichloromethane, chloroform, toluene and benzene, display moderate solubility in acetonitrile, hexane,

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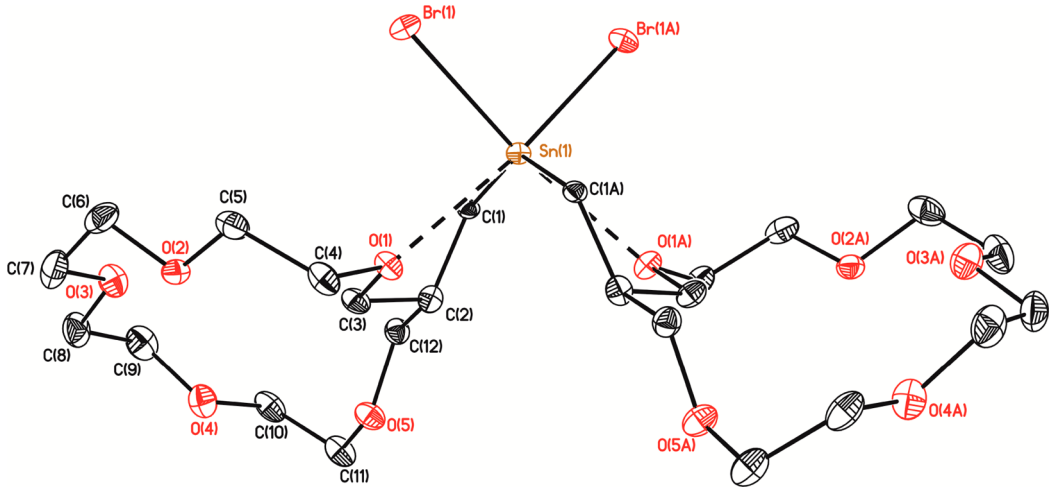

Figure 1. Molecular structure of the diorganodibromidostannane **4** showing 30% probability displacement ellipsoids and crystallographic numbering scheme. The hydrogen atoms are omitted for clarity. Symmetry operation for generation of symmetry-equivalent atoms: (A) $-x, y, -z + {}^{1}/_{2}$.

and alcohols, and have sufficient solubility in water to record ^{1}H NMR spectra.

As a representative of compounds **4**–**6** the molecular structure of the diorganodibromidostannane **4** as determined by single-crystal X-ray diffraction analysis is shown in Figure 1. The compounds **5** and **6** are isostructural with compound **4**, and their structures are given in the Supporting Information (Figures S1 and S2). Selected bond lengths and bond angles of compounds **4**–**6** are summarized in Tables 1 and 2. One of the

Table 1. Selected Bond Lengths (Å) in Compounds 4–6

	4 (X = Br)	**5** (X = Cl)	**6** (X = F)
Sn(1)–C(1)	2.136(2)	2.117(2)	2.102(2)
Sn(1)–X(1)	2.5552(4)	2.4067(6)	1.9610(13)
Sn(1)–O(1)	2.5752(19)	2.5598(14)	2.5672(16)

Table 2. Selected Bond Angles (deg) for Compounds 4–6

	4 (X = Br)	**5** (X = Cl)	**6** (X = F)
C(1A)–Sn(1)–C(1)	141.74(16)	142.69(11)	144.53(12)
C(1A)–Sn(1)–X(1A)	107.97(8)	107.41(6)	105.90(8)
C(1)–Sn(1)–X(1A)	98.26(8)	98.12(6)	98.41(7)
X(1A)–Sn(1)–X(1)	92.77(2)	92.99(3)	92.77(9)
C(1)–Sn(1)–O(1A)	82.90(9)	83.15(7)	84.31(8)
C(1A)–Sn(1)–O(1A)	72.79(9)	72.97(7)	72.39(7)
X(1)–-Sn(1)–O(1)	84.33(5)	84.49(3)	85.72(6)
X(1)–Sn(1)–O(1A)	169.08(4)	169.41(3)	169.79(6)
O(1A)–Sn(1)–O(1)	100.39(9)	99.80(7)	97.52(7)

crown ether moieties, one halogen atom, and half of the tin atom are created by symmetry through a C_2 axis. The tin atoms in compounds **4**–**6** show distorted-octahedral *cis,cis,trans* environments and are surrounded by two halogen atoms, two crown ether oxygen atoms, and two crown ether carbon atoms. The distortion is most perceivable by (i) the decrease of the C(1)–Sn(1)–C(1A) angles from 180° to 141.74(16)° (**4**), 142.69(11)° (**5**), and 144.53(12)° (**6**), (ii) the increase of the O(1)–Sn(1)–O(1A) angles from 90° to 100.39(9)° (**4**), 99.80(7)° (**5**), and 97.52(7)° (**6**), and (iii) the decrease of the X(1)–Sn(1)–O(1A) angles from 180° to 169.08(4)° (**4**), 169.41(3)° (**5**), and 169.79(6)° (**6**). The intramolecular Sn(1)–O(1) distances fall in the range between 2.5752(19) Å (**4**) and 2.5598(14) Å (**5**) and are much shorter than the sum of the van der Waals radii[17] of tin (2.17 Å) and oxygen (1.50 Å). The distances are slightly longer than in the crown ether substituted diorganotin dihalides X_2PhSn-CH_2-[16]-crown-5 (X = Cl, 2.522(1)/2.4793(9) Å; X = I, 2.482(2) Å)[14] or the intramolecularly coordinated diorganotin dihalide $(H_3COOCC_2H_4)_2SnBr_2$ (2.529(3)/2.533(3) Å).[18] The Sn–X bonds (**4**, X = Br, 2.5552(4) Å; **5**, X = Cl, 2.4067(6) Å; **6**, X = F, 1.9610(13) Å) are longer than in the tetracoordinated dicyclohexyltin dihalides $(C_6H_{11})_2SnX_2$ (X = Br, 2.516(2)/2.492(3) Å; X = Cl, 2.393(4)/2.400(5) Å)[19a] and diphenyltin dibromide, Ph_2SnBr_2 (2.4710(3)/2.4947(9) Å)[19b] but shorter than in the intermolecularly coordinated diorganotin dihalide Me_2SnX_2·2(*N*-methylpyrrolidine) (X = Br, 2.6738(10)/2.6761(12) Å; X = Cl, 2.4737(7)/2.4768(8) Å).[20]

As result of the *cis* orientation of the oxygen and the halogen atoms the crown ether moieties are on the same side of the molecule, thus forming a butterfly-like structure. This arrangement suggests that the two crown ether moieties should be able to complex *one* larger cation, which prefers a higher coordination number, instead of two sodium cations.

The molecular structure of diorganodibromidostannane **11** is shown in Figure 2; those of the iodido- and fluorido-substituted compounds **10** and **12** are given in the Supporting Information (Figures S3 and S4). Selected bond lengths and bond angles of compounds **10**–**12** are summarized in Tables 3 and 4. One crown ether moiety, one halogen atom, and half of the tin atom in compounds **10** and **11** are created by a C_2 axis. The structure of compound **10** is isostructural with that of **11**, while that of **12** is very similar to that of **10** and **11** but lacks the C_2 symmetry. In all three structures the tin atoms, being surrounded by two halogen atoms, two crown ether oxygen atoms, and two crown ether carbon atoms, feature a distorted-octahedral *cis,cis,trans* environment. The distortion is manifested by (i) the decrease of the C(1)–Sn(1)–C(1A)/C(101) angles from 180° to 153.4(2)° (**10**), 155.6(1)° (**11**), and 145.70(12)° (**12**), (ii) the decrease of the O(1)–Sn(1)–O(1A) angles from 90° to 88.59(11)° (**10**) and 87.59(9)° (**11**) and the increase of the O(1)–Sn(1)–O(101) angle from 90° to 115.14(7)° (**12**), and (iii) the decrease of the X(1)–Sn(1)–O(1A)/O(101) angles from 180° to 173.41(6)° (**10**), 171.27(4)° (**11**), and 164.58(7)° (**12**).

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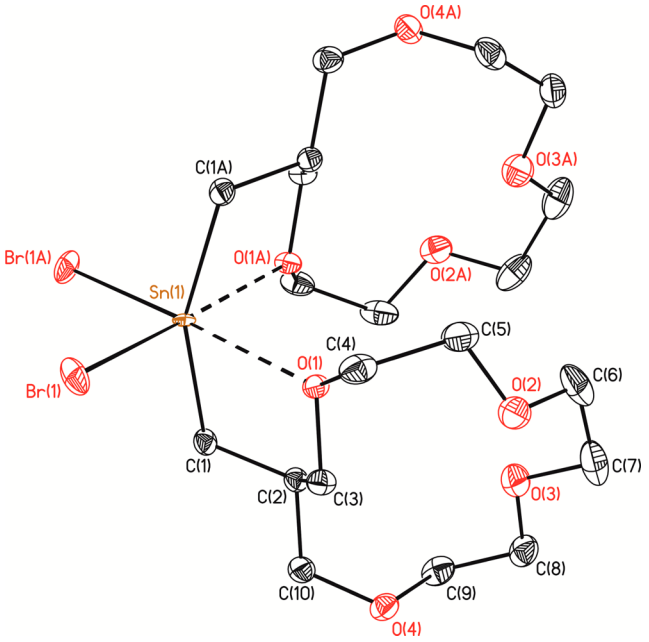


Figure 2. Molecular structure of diorganodibromidostannane **11** showing 30% probability displacement ellipsoids and crystallographic numbering scheme. The hydrogen atoms and the disordered bromine and tin atoms are omitted for clarity. Symmetry operation for generation of symmetry-equivalent atoms: (A) $-x + 1, y, -z + {}^{1}/_{2}$.

Table 3. Selected Bond Lengths (Å) in Compounds 10–12

	10 (X = I)	**11** (X = Br)	**12** (X = F)
Sn(1)–C(1)	2.126(4)	2.130(5)	2.121(3)
Sn(1)–C(101)			2.109(3)
Sn(1)–O(1)	2.474(2)	2.480(4)	2.507(2)
Sn(1)–O(101)			2.527(2)
Sn(1)–X(1)	2.8068(6)	2.6152(14)	2.0041(17)
Sn(1)–X(2)			1.9918(17)

Table 4. Selected Bond Angles (deg) in Compounds 10–12

	10 (X = I)	**11** (X = Br)	**12** (X = F)
C(1A)/C(101)–Sn(1)–C(1)	153.4(2)	155.6(1)	145.70(12)
C(1)–Sn(1)–O(1A)/O(101)	85.56(11)	86.74(8)	87.38(11)
C(1)–Sn(1)–O(1)	75.41(11)	75.65(8)	73.96(10)
O(1A)/O(101)–Sn(1)–O(1)	88.59(11)	87.59(9)	115.14(7)
C(1A)/C(101)–Sn(1)–X(1)	98.05(10)	97.07(7)	101.04(11)
C(1)–Sn(1)–X(1)	99.34(9)	98.72(7)	103.73(11)
O(1A)/O(101)–Sn(1)–X(1)	173.41(6)	171.27(4)	164.58(7)
O(1)–Sn(1)–X(1)	87.01(6)	87.18(5)	78.68(7)
X(1)–Sn(1)–X(1A)/X(2)	97.78(2)	98.83(2)	88.99(7)

The Sn–O distances in compounds **10–12** are considerably shorter than the Sn–O distances in compounds **4–6**. The shortening of the Sn–O distances in [13]-crown-4- in comparison to [16]-crown-5-substituted derivatives has been noticed before[16] and is probably due to steric effects combined with the higher rigidity of the smaller ring. The longest Sn–O distances are found in the difluorido-substituted compound **12** (2.507(2)/2.527(2) Å), and the shortest ones are found in the diiodido-substituted derivative **10** (2.474(2) Å). The shortening of the Sn–O distances results in an elongation of the corresponding Sn–X bond lengths.

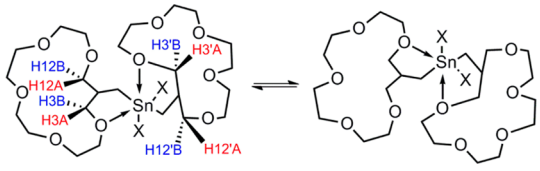
The crown ether moieties in these three compounds display a parallel arrangement. The distance between the crown ether rings is approximately that of the crown ether diameter (5–8 Å). Thus, a cavity is formed that holds potential for the complexation of larger cations.

Structures in Solution. The ^{119}Sn NMR spectra of the triorganohydridostannanes **1** (δ −147, $^{1}J(^{119}\mathrm{Sn}-^{1}\mathrm{H})$ = 1903 Hz) and **8** (δ −147, $^{1}J(^{119}\mathrm{Sn}-^{1}\mathrm{H})$ = 1921 Hz) and of the tetraorganostannanes **2** (δ −82) and **9** (δ −78) display single resonances. Their chemical shifts are comparable to those of triphenylhydridostannane (Ph_3SnH; δ −148, $^{1}J(^{119}\mathrm{Sn}-^{1}\mathrm{H})$ = 1936 Hz),[21] dineohexyldiphenylstannane (δ −64), and dicyclohexyldiphenylstannane (δ −107),[22] thus indicating tetracoordinated tin atoms.

The ^{119}Sn NMR spectra of the organotinhalide derivatives **3–7** and **10–12** display resonances at δ −221 (**3**), −137 (**4**), −112 (**5**), −236 (**6**), −96 (**7**), −227 (**10**), −135 (**11**) and −235 (**12**). These resonances are shifted to low frequency in comparison to those of tetracoordinated diorganotin dihalides (Me_2SnI_2, δ −159;[23] t-Bu_2SnBr_2, δ 77;[24] t-Bu_2SnCl_2, δ 56[25]), indicating retention of the intramolecular O→Sn coordination in solution. The ^{119}Sn NMR signals of the difluorido-substituted compounds **6** and **12** are triplets, indicating kinetically inert Sn–F bonds on the ^{119}Sn NMR time scale. As the ^{119}Sn NMR signals of the other diorganotindihalide compounds **4**, **5**, **7**, **10**, and **11** are sharp, it is assumed that their Sn–X bonds are also kinetically inert.

The ^{1}H and ^{13}C NMR spectra suggest hypercoordination of the tin atoms as well. As a representative, the spectra of the diorganotin difluoride **6** are discussed here. In the ^{1}H NMR spectrum (Supporting Information, Figure S5), two doublets of doublets, representing four protons each, are displaced from the complex pattern of the other crown ether protons. The existence of these doublets of doublets indicates diastereotopic protons at C3/C3′ and C12/C12′. The fact that there is only one doublet for H1 *and* H1′ and one multiplet for H2 *and* H2′ shows the equivalence of the two crown ether rings. The same conclusion can be drawn from the ^{13}C NMR spectrum, containing only seven signals. Two of them are assigned to C1/C1′ (δ 20.0) and C2/C2′ (δ 35.2), and the other five signals represent four equivalent crown ether carbon atoms each. The resonance for C3/C3′/C12/C12′ (δ 74.0) can be identified by its ^{119}Sn satellites ($^{3}J(^{13}\mathrm{C}-^{119}\mathrm{Sn})$ = 98 Hz). Thus, there are two types of protons at C3 and C12, but C3 and C12 are equal, which proves that there are diastereotopic protons at these carbon atoms. These findings suggest an intramolecular O→Sn coordination, in which the four oxygen atoms O1, O1′, O5, and O5′ have to be incorporated to the same degree. As an increase of the coordination number in solution in comparison to the coordination number in the solid state is unlikely, there probably is a fast exchange of the coordinating oxygen atoms on the NMR time scale (Scheme 2).

Scheme 2. Behavior of the Diorganotin Dihalides 3–6 in Solution



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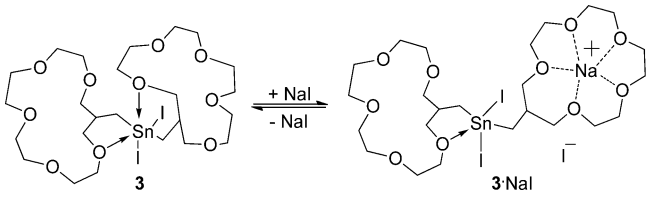
Complexation Studies. *(i). Diorganodiiodidostannanes **3** and **10**.* No effect on the ^{1}H, ^{13}C, and ^{119}Sn NMR signals was observed upon addition of 1 or 2 molar equiv of tetraphenylphosphonium iodide (Ph_4PI) to a solution of the diorganodiidostannane **3** in $CDCl_3$, while the addition of 2 equiv of tetraethylammonium fluoride ($Et_4NF{\cdot}2H_2O$) gave the diorganodifluorido stannane **6** within a few minutes. Apparently, iodide anion by itself cannot change the coordination sphere of the tin atom, which is probably due to the strong interaction of the crown ether oxygen atoms with the tin atom, while the presence of fluoride anion causes a halide ion exchange instead of the formation of a stannate complex.

The ^{119}Sn NMR spectrum of a solution of compound **3** in CD_3CN to which had been added 2 molar equiv of sodium iodide (NaI) displayed a broad signal at δ −207 that is slightly shifted to high frequency in comparison to that of the pure compound (δ −220). The ^{1}H and ^{13}C NMR spectra showed a variation of the chemical shift of all signals that was dependent on the sodium iodide concentration, as well. The H1 doublet was shifted from δ 1.91 ($^{3}J(^{1}H-^{1}H)$ = 8.4 Hz, $^{2}J(^{1}H-^{119}Sn)$ = 84/87 Hz) to δ 2.10 after addition of 1 molar equiv of the salt and to δ 2.39 ($^{3}J(^{1}H-^{1}H)$ = 7.3 Hz, $^{2}J(^{1}H-^{119}Sn)$ = 64 Hz) after addition of a second equivalent. The center of the H2 multiplet was shifted from δ 2.52 to 2.54 by the addition of the first equivalent and to δ 2.66 by the addition of the second equivalent of sodium iodide. The complex pattern for the crown ether protons was narrowed to a smaller region. One of the H3/H12 doublet of doublets was no longer observed but was probably hidden under the resonances of the other crown ether protons. The other doublet of doublets displayed a strong variation in one of the coupling constants (from J = 6.8 Hz to J = 1.8 Hz), whereas the other coupling constant was hardly changed (from J = 9.3 Hz to J = 9.5 Hz). The fact that one of the coupling constants was almost unchanged while the other was noticeably decreased is further evidence for a geminal coupling, as the angle between two protons at the same carbon atom is fixed in comparison to the angle of two protons at different carbon atoms. The ^{13}C NMR spectra of a solution of pure **3** in CD_3CN as well as of a solution of **3** in CD_3CN to which had been added 2 molar equiv of sodium iodide displayed seven signals. All signals were shifted by the addition of the salt. The C1 signal suffered the biggest change, as it moved from δ 34.8 to 40.0 and was considerably sharpened after the addition of sodium iodide. The chemical shift for the C2 carbon atoms remained almost unchanged (δ 38.4 with $^{2}J(^{13}C-^{119}Sn)$ = 36 Hz to δ 39.1 with $^{2}J(^{13}C-^{119}Sn)$ = 34/36 Hz). The C3/C12 signal, which was identified by its ^{119}Sn coupling, shifted from δ 73.9 ($^{3}J(^{13}C-^{117/119}Sn)$ = 102/106 Hz) to δ 77.6 ($^{3}J(^{13}C-^{117/119}Sn)$ = 78/80 Hz). The other four crown ether carbon atom signals were found between δ 71.4 and 70.0 in the pure compound and were distributed over a wider area by the addition of the salt (between δ 71.0 and 69.6). These observations suggest an interaction of the crown ether rings with the sodium cation. No evidence for the nonequivalence of the crown ether rings, even after adding only 1 equiv of salt, was observed. Either there is a fast equilibrium in which the Lewis-acidic sodium cation and the tin atom compete for the oxygen Lewis bases or *one* sodium cation is bound cooperatively by both crown ether rings. The iodide anion probably does not bind to the tin atom. Most likely, the diiodidodiorganostannane **3** forms the homotopic complex **3**·NaI with sodium cation, while the iodide anion is kept nearby through electrostatic interactions with the cation (Scheme 3).

Scheme 3. Reaction of Compound 3 with NaI



The addition of an excess of sodium iodide to a solution of the diorganotin diiode derivative **3** in water led to a significant change of the ^{1}H NMR spectrum as well. Because of the low solubility in water, no ^{13}C and ^{119}Sn NMR spectra were recorded. In the ^{1}H NMR spectrum of the pure compound, there is one doublet of doublets for the H3A/H12A protons shifted to high frequency and the doublet of doublets assigned to the H3B/H12B protons shifted to low frequency from the complex pattern of the H4−H11 protons between δ 3.81 and 3.60. The center of the H2 multiplet was found at δ 2.46 and the doublet for the H1 protons at δ 1.44 ($^{2}J(^{1}H-^{119}Sn)$ = 94 Hz). The addition of NaI caused a high-frequency shift of all resonances. The doublets of doublets were no longer observed, but there was only one complex pattern for all 40 CH_2O protons between δ 4.09 and 3.87. The center of the H2 multiplet shifted to δ 2.79 and the H1 doublet to δ 2.06 ($^{2}J(^{1}H-^{119}Sn)$ = 80 Hz). This shows the ability of compound **3** to complex sodium iodide in an aqueous environment.

The behavior of compound **10** toward lithium, sodium, and cesium iodides was studied by NMR spectroscopy. No effect on the spectra was observed after the addition of sodium and cesium iodide, while the addition of lithium iodide resulted in a significant change in the spectra. The ^{119}Sn NMR resonance shifted with broadening from δ −226 ($\nu_{1/2}$ = 31 Hz) to δ −216 ($\nu_{1/2}$ = 243 Hz). All signals in the ^{1}H NMR spectra were shifted to high frequency by the addition of the salt. The H3/H10 doublet of doublets was still observed, while the H3B/H10B doublet of doublets probably coincided with the H4−H9 multiplet. The geminal coupling constant in the H3A/H10A doublets of doublets hardly changed, while the vicinal coupling constant decreased from 7 to 3 Hz. The H1 doublet shifted from δ 1.93 to 2.25, and the $^{2}J(^{1}H-^{119}Sn)$ coupling constant decreased from 86 to 70 Hz. The most obvious changes in the ^{13}C NMR were the high-frequency shift of the C1 signal by 5 ppm and of the C3/C10 signal by 4 ppm and the low-frequency shift of the C4−C9 resonances. These observations indicate the complexation of lithium cations by the crown ether moieties. The preservation of the H3/H10 doublet of doublets and the broadening of the ^{119}Sn resonance suggest an equilibrium between **10** and its complex with LiI. In the latter, the iodide anion is probably not bound to the Lewis-acidic tin atom, as the direction and the magnitude of the change of the chemical shift of the ^{119}Sn NMR resonance indicate.

*(ii). Diorganodibromidostannanes **4** and **11**.* No effect on the ^{1}H and ^{13}C NMR signals was observed after 1 or 2 molar equiv of tetraphenylphosphonium bromide (Ph_4PBr) had been added to a solution of the diorganodibromidostannane **4** in $CDCl_3$, indicating the coordination sphere of the tin atom was not affected by the bromide anion itself. Adding successively 1, 2, and 3 equiv of sodium perchlorate, ($NaClO_4$) to a solution of

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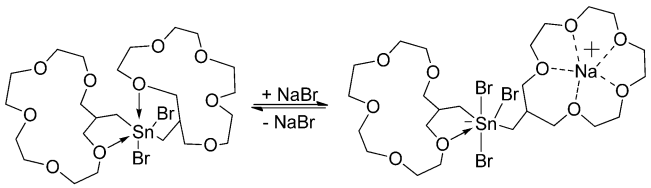
4 in $CDCl_3$ shows, however, that up to 2 molar equiv of $NaClO_4$ easily dissolved, while a third equivalent did not dissolve at all. This indicates the simultaneous complexation of two sodium cations by compound **4**. The complexation was verified by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of the pure compound **4** displayed a doublet of doublets resonance at δ 3.84 for H3A/H12A, a complex pattern between δ 3.78 and 3.63 for H4−H11, a doublet of doublets resonance at δ 3.46 for H3B/H12B, a multiplet centered at δ 2.57 for H2, and a doublet for H1 at δ 1.65 ($^2J(^1H-^{119}Sn)$ = 93 Hz). The variation of the ^1H NMR spectrum after the addition of the salt was manifested by (i) the merging of the doublets of doublets for the H3/H12 protons and the multiplet for the H4−H11 protons into one multiplet between δ 3.82 and 3.53 and (ii) the transformation of the H1 doublet into a broad singlet at δ 1.79 ($^2J(^1H-^{117/119}Sn)$ = 80 Hz). In the ^{13}C NMR spectrum the most obvious change was the disappearance of the C1 signal after the addition of the salt.

The addition of 1 equiv of NaBr to a solution of **4** in $CDCl_3$ resulted in neither the dissolution of the salt nor in a change in the NMR spectra, while the same experiment in both CD_3CN and CD_3OD led to the dissolution of the salt and a change of the ^1H and ^{119}Sn spectra. The ^1H NMR spectrum of a solution of **4** in CD_3CN to which had been added NaBr was quite similar to that of a solution of **4** to which had been added $NaClO_4$. This showed the complexation of sodium cations by the crown ether moieties of **4**. The ^{119}Sn NMR resonance was shifted from δ −142 to −178. This low-frequency shift is probably due to the coordination of an additional bromide anion to the Lewis-acidic tin atom and suggests that compound **4** is able to ditopically complex NaBr in acetonitrile (Scheme 4).

Scheme 4. Reaction of Compound 4 with NaBr



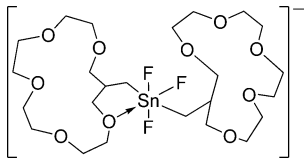
Remarkably, the solubility of compound **4** in CD_3CN and even more so in CD_3OD was significantly increased by the addition of the salt. Due to the low solubility no ^{119}Sn NMR signal was observed for **4** in CD_3OD. However, after NaBr had been added to the solution, the ^{119}Sn NMR spectrum showed a resonance at δ −115. As the changes of the ^1H NMR spectra after the addition of the salt are comparable to those of the spectra in CD_3CN, it is concluded that compound **4** can complex NaBr in methanol as well.

Attempts at complexing, with both crown ether moieties, one cation that prefers a higher coordination number were not successful. The addition of neither $LaBr_3·H_2O$ nor $MgBr_2$ to a solution of **4** in CD_3CN caused dissolution of the salt or a significant change of the NMR spectra in comparison to those of the pure compound.

Comparison of the NMR spectra of a solution of pure **11** in CD_3CN and a solution of **11** to which had been added LiBr showed that **11** can complex LiBr. The variations in the spectra were quite similar to those observed in the spectra of **4** and of **4** to which had been added NaBr. The ESI mass spectrum (negative mode) of this solution displayed among other peaks a mass cluster centered at m/z 765.0, which is assigned to $[\mathbf{11}·Br]^-$, proving that **11** is able to complex a bromide anion.

*(iii). Diorganodifluoridostannanes **6** and **12**.* In addition to compounds **3** and **4**, the addition of an adequate anion source to a solution of **6** resulted in a change in the NMR spectra. The ^{119}Sn NMR spectrum at room temperature of a solution of **6** in CD_3CN to which had been added 1 molar equiv of $Et_4NF·2H_2O$ showed no signal. After a second molar equivalent of $Et_4NF·2H_2O$ had been added, a broad resonance at δ −330 ($\nu_{1/2}$ = 518 Hz) was observed. The ^{19}F NMR spectra of these solutions displayed several signals, but no coupling to tin was observed. The ^{119}Sn NMR spectrum at T = 223 K (Supporting Information, Figure S7) of a solution of **6** in CD_2Cl_2 to which had been added 1 molar equiv of $Et_4NF·2H_2O$ showed a doublet of triplets resonance at δ −333 ($^1J(^{119}Sn-^{19}F)$ = 2656 Hz, signal a) and a triplet resonance at δ −242 ($^1J(^{119}Sn-^{19}F)$ = 2892 Hz, signal b, **6**). The ^{19}F NMR (Supporting Information, Figure S6) spectrum of this solution displayed three signals at δ −117.8 ($^1J(^{19}F-^{117/119}Sn)$ = 2522/2645 Hz, signal c), δ −160.5 ($^1J(^{19}F-^{117/119}Sn)$ = 2570/2672 Hz, signal d), and δ −164.7 ($^1J(^{19}F-^{117/119}Sn)$ = 2816 Hz, not resolved, signal e; **6**). Addition of a second molar equivalent of fluoride anion caused the triplet ^{119}Sn resonance (b) to disappear and signal (a) to remain. The ^{19}F NMR spectrum at T = 213 K of this solution showed the signal (e) to disappear and the signals (c) and (d) to remain. At this temperature, the signals (c) and (d) appeared as a slightly broadened doublet ($^2J(^{19}F-^{19}F)$ = 20 Hz) and triplet ($^2J(^{19}F-^{19}F)$ = 20 Hz), respectively. The signals (a), (c), and (d) are assigned to the tetraethylammonium diorganotrifluoridostannate salt $NEt_4[\mathbf{6}·F]$. The NMR experiments unambiguously indicate that compound **6** can complex only one fluoride anion. Of the three fluorine atoms at the tin atom, two are chemically and magnetically equivalent while the third atom is different (Chart 2). The ^1H and ^{13}C NMR spectra of

Chart 2



these solutions at room temperature showed one set of signals for the crown ether moieties, revealing that the latter are equivalent. Apparently, the diorganotrifluorido stannate anion $[\mathbf{6}·F]^-$ is kinetically inert on the ^{19}F and ^{119}Sn NMR time scales at low temperature but kinetically labile at room temperature on these and the ^1H and ^{13}C NMR time scales.

No effect on the NMR spectra was observed after the addition of LiF and NaF to a solution of **6** in $CDCl_3$ or CD_3CN. This showed that the complexation ability of compound **6** is not high enough to overcome the lattice energy of lithium and sodium fluoride in organic solvents. Adding sodium fluoride to a solution of **6** in water resulted in the salting out of most of the receptor. The ^1H NMR spectra of a solution of pure **6** in D_2O and a solution of **6** in D_2O to which had been added NaF differed slightly. It could not be clarified if these changes in the spectra and the decrease of solubility were due to the complexation of the salt or to an increase of the capacity of the solvent, which was caused by the addition of the salt.

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The ^{19}F and ^{119}Sn NMR spectra of a solution of **6** in CD_3CN or CD_3OD to which had been added CsF displayed no signals at room temperature which could be assigned to **6** or a complex of **6**. The ^{1}H and ^{13}C NMR spectra were slightly changed by the addition of the salt. This suggests equilibrium, which is fast on the NMR time scale at room temperature. The ^{119}Sn NMR spectrum at 213 K displayed one triplet at δ −255 and one very broad resonance at δ −337. The ^{19}F NMR spectrum at the same temperature showed several signals. None of them matches with pure **6**. These observations point at an interaction of **6** with CsF, but 213 K is not cold enough to freeze the equilibrium and no statement can be made about this interaction.

Adding 2 equiv of silver fluoride to a solution of **6** in CD_3CN resulted in the disappearance of the ^{119}Sn NMR signal. The ^{19}F NMR spectrum of this solution displayed one rather broad resonance at δ −138 ($\nu_{1/2}$ = 1200 Hz) and one sharp resonance at δ −130. The latter was assigned to "free" fluoride anion and the former with caution to a complex of **6** with AgF. The ^{1}H and ^{13}C NMR spectra of the solutions of **6** to which had been added AgF also differed from those of the pure compound. The most obvious changes were the shifting of the C1 signal by almost 3 ppm from δ 20.8 to 23.7 and the overlapping of two of the crown ether signals after the addition of the salt. These observations suggest a complexation of silver fluoride by compound **6**. This finding is supported by the fact that the silver ion containing solution did not darken, even after several weeks of exposure to light.

The behavior of compound **12** toward lithium, cesium, and silver fluorides was studied by NMR spectroscopy. No effect on the NMR spectra was observed after the addition of lithium fluoride to a solution of **12** in CD_3CN. The addition of cesium fluoride to a solution of **12** in $CDCl_3$ resulted in the broadening of the H1 and H2 signals in the ^{1}H NMR spectrum and the disappearance of the ^{19}F NMR signal. The effect of the addition of silver fluoride was comparable to the addition of silver fluoride to a solution of **6**, which suggests that **12** is able to build a complex with silver fluoride.

Remarkably, compounds **6** and **12** do not interact with lithium or sodium fluoride, although they contain crown ether moieties designed for the complexation of lithium and sodium cations, respectively, but they do interact with silver fluoride. The lattice energies of these three fluoride salts are in the same region (LiF, 1037 kJ/mol; NaF, 926 kJ/mol; AgF, 969 kJ/mol); therefore, this effect is probably due to the better solubility of silver fluoride in comparison to the alkali-metal fluorides.

CONCLUSION

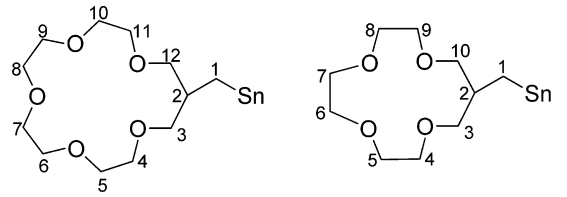
A series of bis(crown ether)-substituted organotin dihalides was synthesized and completely characterized, and their ability in the ditopic complexation of alkali-metal salts was investigated. In the solid state as well as in solution in all compounds both crown ether moieties coordinate the tin atoms via intramolecular O→Sn interactions. By the addition of sodium halide salts, only one of these two O→Sn interactions is broken in favor of forming mono- and ditopic complexes **3**·NaI and **4**·NaBr, respectively. There was no evidence for the existence in solution or in the solid state of the complexes **3**·2NaI and **4**·2NaBr. On the other hand, the diorganotin difluorides **6** and **12** are not able to compensate for the high lattice energy of both lithium and sodium fluoride by formation of the corresponding ditopic complexes. Nevertheless, rupture of the O→Sn coordination in compound **6** by $Et_4NF{\cdot}2H_2O$ to give the corresponding diorganotrifluoridostannate salt takes place. For future investigations the presence of hydrogen bonds between the crown ether oxygen atoms and water must also be taken into account. These might compete with the metal cations for interaction with the crown ether.

EXPERIMENTAL SECTION

General Methods. All solvents were purified by distillation under an argon atmosphere from the appropriate drying agents. The hydrostannation was carried out under an argon atmosphere as well. 15-Methylene-1,4,7,10,13-pentaoxacyclohexadecane, iodido(1,4,7,10,13-pentaoxahexadec-15-ylmethyl)diphenylstannane, (1,4,7,10-tetraoxacyclotridec-12-ylmethyl)triphenylstannane, and 12-methylene-1,4,7,10-tetraoxacyclotridecan were synthesized as described in the literature. The NMR experiments were carried out on a Bruker DRX 400, a Bruker DPX 300, or a Varian Mercury 200 spectrometer. NMR experiments were carried out at ambient temperature unless otherwise stated. Chemical shifts (δ) are given in ppm and are referenced to the solvent peaks with the values calibrated against tetramethylsilane (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), and tetramethylstannane (^{119}Sn).

The partial assignments of the ^{13}C NMR data for the crown ether moieties refer to the numbering schemes in Chart 3.

Chart 3



Synthesis of Hydrido(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)diphenylstannane, Ph_2HSnCH_2-[16]-crown-5 (1). Iodido(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)-diphenylstannane[1] (2.00 g, 3.09 mmol) was added to an ice-cooled slurry of $LiAlH_4$ (0.50 g, 13.16 mmol) in diethyl ether (100 mL). After the reaction mixture had been stirred for 15 min at 0 °C and a further 3 h at room temperature, the reaction was quenched by adding 30 mL of degassed potassium sodium tartrate solution. After the phases were separated, the organic phase was washed with degassed potassium sodium tartrate solution (4 × 100 mL), dried over magnesium sulfate, and filtered. Evaporating the solvent in vacuo yielded 1.00 g (1.92 mmol, 62%) of **1** as a colorless oil. Crude **1** was used in the next step without further purification. ^{1}H NMR (300.13 MHz, C_6D_6, 293 K): δ 7.78−7.58 (m, $4H_o$, $^{3}J(^{1}H-^{117/119}Sn)$ = 48 Hz), 7.35−7.17 (m, $6H_{m/p}$), 6.56 (s, 1H, Sn-*H*), 3.76−3.71 (m, 2H, H3A/H12A), 3.54−3.25 (m, 18H, H4−H11+ H3B/H12B), 2.45 (m, 1H, H2), 1.24 (dd, 2H, H1, $^{3}J(^{1}H-^{1}H)$ = 7 Hz, $^{2}J(^{1}H-^{1}H)$ = 2 Hz, $^{2}J(^{1}H-^{117/119}Sn)$ = 60 Hz). $^{13}C\{^{1}H\}$ NMR (100.63 MHz, C_6D_6) δ: 141.25 (C_i, $^{1}J(^{13}C-^{117/119}Sn)$ = 463/485 Hz), 137.85 (C_o, $^{2}J(^{13}C-^{117/119}Sn)$ = 35 Hz), 128.96 (C_p, $^{4}J(^{13}C-^{117/119}Sn)$ = 11 Hz, 128.93 (C_m, $^{3}J(^{13}C-^{117/119}Sn)$ = 47 Hz), 75.07 (C3/C12, $^{3}J(^{13}C-^{117/119}Sn)$ = 50 Hz, 71.82, 71.33, 71.31, 70.48, 38.33 (C2, $^{2}J(^{13}C-^{117/119}Sn)$ = 24 Hz, 11.70 (C1, $^{1}J(^{13}C-^{117/119}Sn)$ = 414/433 Hz). $^{119}Sn\{^{1}H\}$ NMR (111.92 MHz, C_6D_6, 293 K): δ −147. ^{119}Sn NMR (111.92 MHz, C_6D_6): δ −147 (d, $^{1}J(^{119}Sn-^{1}H)$ = 1903 Hz). Anal. Calcd for $C_{24}H_{34}O_5Sn$ (521.23): C, 55.30; H, 6.57. Found: C, 54.3; H, 6.65.

Synthesis of Bis(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)diphenylstannane, Ph_2SnCH_2-[16]-crown-5 (2). Compound **1** (1.00 g, 1.92 mmol), 15-methylene-1,4,7,10,13-pentaoxacyclohexadecane (0.50 g, 2.01 mmol), and a small quantity of AIBN (0.05 g) were mixed and stirred for 15 h at 70 °C. After cooling of the mixture to room temperature, addition of 70 mL of CH_2Cl_2, filtration through Celite, and evaporation of the solvent in vacuo, 1.49 g (1.91 mmol, 99%) of **2** was obtained as a colorless oil. Crude **2** was used in

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the next step without further purification. ^{1}H NMR (300.13 MHz, $CDCl_3$, 293 K): δ 7.56−7.38 (m, 4H$_o$), 7.29−7.19 (m, 6H$_{m/p}$), 3.69−3.20 (m, 40H, H3−H12), 2.29−2.16 (m, 2H, H2), 1.19 (d, 4H, H1, $^{3}J(^{1}H-^{1}H)$ = 7 Hz, $^{2}J(^{1}H-^{117/119}Sn)$ = 57 Hz). $^{13}C\{^{1}H\}$ NMR (100.63 MHz, $CDCl_3$): δ 142.51, 136.57, 127.92, 113.43, 74.26 ($^{3}J(^{13}C-^{117/119}Sn)$ 47 Hz, C3/C12), 70.81, 70.66, 70.42, 69.70, 37.12 (C2), 11.54 (C1). $^{119}Sn\{^{1}H\}$ NMR (111.92 MHz, $CDCl_3$, 293 K): δ −82. Anal. Calcd for $C_{36}H_{56}O_{10}Sn\cdot 0.5\ CH_2Cl_2$ (767.53): C, 54.12; H, 7.09. Found: C, 54.20; H, 7.35.

Synthesis of Diiodidobis(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)stannane, I_2SnCH_2-[16]-crown-5 (3). Over a period of 12 h, iodine (0.97 g, 3.84 mmol) was added in small portions to an ice-cooled, stirred solution of **2** (1.49 g, 1.91 mmol) in dichloromethane (10 mL). After complete addition of the iodine, the reaction mixture was warmed to room temperature and stirred for a further 30 h. Evaporation of the solvent and most of the formed iodobenzene in vacuo (10^{-3} mbar) gave a dark red, viscous oil. Recrystallization of this oil from ethanol allowed separation of diiodido(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)-phenylstannane. Removal of the remaining iodobenzene in vacuo afforded 1.23 g (1.42 mmol, 74%) of **3** as a dark red, viscous oil, which solidified upon standing for several days. ^{1}H NMR (300.13 MHz, $CDCl_3$, 293 K): δ 3.79 (dd, 4H, H3A/H12A, $^{2}J(^{1}H-^{1}H)$ = 9.2 Hz, $^{3}J(^{1}H-^{1}H)$ = 7.0 Hz), 3.72−3.55 (m, 32H, H4−H11), 3.41 (dd, 4H, H3B/H12B, $^{2}J(^{1}H-^{1}H)$ = 9.2 Hz, $^{3}J(^{1}H-^{1}H)$ = 7.7 Hz), 2.69−2.37 (m, 2H, H2), 1.86 (d, 4H, H1, $^{3}J(^{1}H-^{1}H)$ = 8.6 Hz, $^{2}J(^{1}H-^{117/119}Sn)$ = 85 Hz). $^{13}C\{^{1}H\}$ NMR (75.48 MHz, $CDCl_3$, 293 K): δ 73.3 (C3/C12, $^{3}J(^{13}C-^{117/119}Sn)$ = 98 Hz), 70.7, 70.4, 70.3, 70.2, 37.4 (C2, $^{2}J(^{13}C-^{117/119}Sn)$ = 37 Hz), 33.0 (C1). $^{119}Sn\{^{1}H\}$ NMR (111.92 MHz, $CDCl_3$, 293 K): δ −227. ^{1}H NMR (300.13 MHz, CD_3CN, 293 K): δ 3.80 (dd, 4H, H3A/H12A, $^{2}J(^{1}H-^{1}H)$ = 9.3 Hz, $^{3}J(^{1}H-^{1}H)$ = 6.8 Hz), 3.73−3.47 (m, 32H, H4−H11), 3.39 (dd, 4H, H3B/H12B, $^{2}J(^{1}H-^{1}H)$ = 9.1 Hz, $^{3}J(^{1}H-^{1}H)$ = 7.7 Hz), 2.55−2.45 (m, 2H, H2), 1.91 (d, 4H, H1, $^{3}J(^{1}H-^{1}H)$ = 8.4 Hz, $^{2}J(^{1}H-^{117/119}Sn)$ = 85 Hz). $^{13}C\{^{1}H\}$ NMR (75.48 MHz, CD_3CN, 293 K): δ 72.9 (C3/C12, $^{3}J(^{13}C-^{117/119}Sn)$ = 102 Hz/106 Hz), 70.4, 70.2, 70.1, 70.0, 37.4 (C2, $^{2}J(^{13}C-^{117/119}Sn)$ = 38 Hz), 33.8 (br s, C1). $^{119}Sn\{^{1}H\}$ NMR (111.92 MHz, CD_3CN, 293 K): δ −220. ^{1}H NMR (300.13 MHz, D_2O): δ 3.76 (dd, 4H, H3A/H12A, $^{2}J(^{1}H-^{1}H)$ = 10 Hz, $^{3}J(^{1}H-^{1}H)$ = 7 Hz), 3.81−3.60 (m, 32H, H4−H11), 3.51 (dd, 4H, H3B/H12B, $^{2}J(^{1}H-^{1}H)$ = 10 Hz, $^{3}J(^{1}H-^{1}H)$ = 7 Hz), 2.53−2.39 (m, 2H, H2, $^{3}J(^{1}H-^{117/119}Sn)$ = 75 Hz), 1.44 (d, 4H, H1, $^{3}J(^{1}H-^{1}H)$ = 8 Hz, $^{2}J(^{1}H-^{117/119}Sn)$ = 93 Hz). Anal. Calcd for $C_{24}H_{46}I_2O_{10}Sn$ (867.14): C, 33.24; H, 5.35. Found: C, 33.45; H, 5.40. Mp: 115 °C.

Synthesis of Dibromidobis(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)stannane, $Br_2Sn(CH_2$-[16]-crown-5)$_2$ (4). A solution of elemental bromine (0.91 g, 5.71 mmol) in dichloromethane (30 mL) was added drop by drop to an ice-cooled solution of **2** (2.19 g, 2.86 mmol) in dichloromethane (100 mL). The reaction mixture was warmed to room temperature and stirred for a further 15 h. All volatile material was removed in vacuo. The residue was extracted with toluene, and the extract was dried. Recrystallization of the residue in ethanol afforded 2.16 g (2.80 mmol, 98%) of compound **4** as a white, microcrystalline solid. Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation of a toluene solution of the compound. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 3.84 (dd, 4H, H3A/H12A, $^{3}J(^{1}H-^{1}H)$ = 7 Hz, $^{2}J(^{1}H-^{1}H)$ = 9 Hz), 3.78−3.63 (m, 32H, H4−H11), 3.46 (dd, 4H, H3B/H12B, $^{3}J(^{1}H-^{1}H)$ = 7.32 Hz, $^{2}J(^{1}H-^{1}H)$ = 8.78 Hz), 2.57 (m, 2H, H2, $^{3}J(^{1}H-^{117/119}Sn)$ = 75 Hz), 1.65 (d, 4H, H1, $^{3}J(^{1}H-^{1}H)$ = 8.42 Hz, $^{2}J(^{1}H-^{117/119}Sn)$ = 93 Hz). ^{1}H NMR (300.13 MHz, CD_3CN): δ 3.82−3.77 (m, 4H, H3A/H12A), 3.74−3.49 (m, 32 H, H4−H11), 3.42−3.36 (m, 4H, H3B/H12B), 2.48 (m, 2H, H2), 1.61 (d, 4H, H1, $^{3}J(^{1}H-^{1}H)$ = 8 Hz, $^{2}J(^{1}H-^{117/119}Sn)$ = 83/86 Hz). ^{1}H NMR (300.13 MHz, CD_3OD): δ 2.60−2.54 (m, 4H, H3A/H12A), 2.52−2.30 (m, 32 H, H4−H11), 2.21−2.16 (m, 4H, H3B/H12B), 1.35−1.25 (m, 2H, H2), 0.35 (d, 4H, H1, $^{3}J(^{1}H-^{1}H)$ = 8 Hz, $^{2}J(^{1}H-^{117/119}Sn)$ = 94 Hz).$^{13}C\{^{1}H\}$ NMR (100.63 MHz, $CDCl_3$): δ 73.45 (C3/C12), 70.36 (C4/C11, $J(^{13}C-^{117/119}Sn)$ = 48 Hz), 69.95, 69.91, 69.69, 36.18 (C2), 31.26 (br s, C1). $^{119}Sn\{^{1}H\}$ NMR (111.92 MHz, $CDCl_3$): δ −137. $^{119}Sn\{^{1}H\}$ NMR (111.92 MHz, CD_3CN): δ −142. $^{119}Sn\{^{1}H\}$ NMR (111.92 MHz, CD_3OD): no signal observed. Anal. Calcd for $C_{24}H_{46}Br_2O_{10}Sn$ (773.13): C, 37.28; H, 6.00. Found: C, 37.25; H, 5.95. Mp: 123 °C.

Synthesis of Dichloridobis(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)stannane, $Cl_2Sn(CH_2$-[16]-crown-5)$_2$ (5). A solution of iodine chloride (0.42 g, 2.60 mmol) in dichloromethane (20 mL) was added dropwise to an ice-cooled solution of **2** (1.00 g, 1.30 mmol) in dichloromethane (30 mL). The reaction mixture was warmed to room temperature and was stirred for a further 15 h. All volatile material was evaporated in vacuo. The residue was extracted with hot hexane, and the extract was dried. Recrystallization of the residue afforded 0.05 g (0.072 mmol, 0.6%) of compound **5** as colorless crystals. These crystals were suitable for single-crystal X-ray diffraction analysis. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 3.81 (dd, 4H, H3A/H12A, $^{2}J(^{1}H-^{1}H)$ = 9 Hz, $^{3}J(^{1}H-^{1}H)$ = 7 Hz), 3.76−3.55 (m, 34H, H4−H11), 3.43 (dd, 4H, H3B/H12B, $^{2}J(^{1}H-^{1}H)$ = 9 Hz, $^{3}J(^{1}H-^{1}H)$ = 7 Hz), 2.66−2.35 (m, 2H, H2, $^{3}J(^{1}H-^{117/119}Sn)$ = 54 Hz), 1.43 (d, 4H, H1, $^{3}J(^{1}H-^{1}H)$ = 8 Hz, $^{2}J(^{1}H-^{117/119}Sn)$ = 96/100 Hz). ^{13}C NMR (100.63 MHz, $CDCl_3$): δ 73.97 (C3/C12, $^{3}J(^{13}C-^{117/119}Sn)$ = 104 Hz), 70.73, 70.32, 70.27, 69.89, 36.02 (C2, $^{2}J(^{13}C-^{117/119}Sn)$ = 32 Hz), 28.77 (C1). $^{119}Sn\{^{1}H\}$ NMR (111.92 MHz, $CDCl_3$): δ −112. Anal. Calcd for $C_{24}H_{46}Cl_2O_{10}Sn$ (684.23): C, 42.13; H, 6.78. Found: C, 40.85; H, 6.25. Mp: 136 °C.

Synthesis of Difluoridobis(1,4,7,10,13-pentaoxacyclohexadec-15-ylmethyl)stannane, $F_2Sn(CH_2$-[16]-crown-5)$_2$ (6). Silver fluoride (AgF; 0.22 g, 1.71 mmol), was added to a solution of 0.74 g (0.86 mmol) of **3** in 10 mL of dichloromethane. The resulting mixture was stirred at room temperature in the dark for 8 h. Removal of the formed silver iodide by filtration and evaporation of the solvent in vacuo afforded 0.55 g (0.84 mmol, 98%) of **6** as a slightly yellow oil, which became solid upon standing at room temperature. Single crystals of **6** suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation of a solution of **6** in CH_2Cl_2/hexane. ^{1}H NMR (300.13 MHz, $CDCl_3$, 293 K): δ 3.77−3.53 (m, 36H, H4−H11+H3A/H12A), 3.44−3.39 (dd, 4H, H3B/H12B), 2.39 (m, 2H, H2), 1.11 (d, 4H, H1, $^{3}J(^{1}H-^{1}H)$ = 7.7 Hz, $^{2}J(^{1}H-^{119}Sn)$ = 101 Hz). $^{13}C\{^{1}H\}$ NMR (100.63 MHz, $CDCl_3$, 293 K): δ 74.0 (C3/C12, $^{3}J(^{13}C-^{117/119}Sn)$ = 95 Hz), 70.6 ($J(^{13}C-^{117/119}Sn)$ = 29.2 Hz), 70.3, 70.2, 69.7 ($J(^{13}C-^{117/119}Sn)$ = 130.2 Hz), 35.3 (C2), 20.0 (C1). ^{19}F NMR (282.38 MHz, $CDCl_3$, 293 K): δ −167.8 (s, $^{1}J(^{19}F-^{117/119}Sn)$ = 2760/2889 Hz). $^{119}Sn\{^{1}H\}$ NMR (111.92 MHz, $CDCl_3$, 293 K): δ −236 (t, $^{1}J(^{119}Sn-^{19}F)$ = 2889 Hz). ^{1}H NMR (300.13 MHz, CD_3CN, 293 K): δ 3.75−3.51 (m, 36H, H4−H11+H3A/H12A), 3.41−3.36 (dd, 4H, H3B/H12B), 2.32 (m, 2H, H2), 1.05 (d, 4H, H1, $^{3}J(^{1}H-^{1}H)$ = 8.1 Hz, $^{2}J(^{1}H-^{117/119}Sn)$ = 101.4 Hz). $^{13}C\{^{1}H\}$ NMR (100.63 MHz, CD_3CN, 293 K): δ 74.7 (C3/C12, $J(^{13}C-^{117/119}Sn)$ = 99.1 Hz), 71.5, 71.1, 71.0, 70.7, 36.4 (C2, $^{2}J(^{13}C-^{117/119}Sn)$ = 27.2 Hz), 20.8 (C1). ^{19}F NMR (282.38 MHz, CD_3CN, 293 K): δ −167.4 (s, $^{1}J(^{19}F-^{117/119}Sn)$ = 2760/2887 Hz). $^{119}Sn\{^{1}H\}$ NMR (111.92 MHz, CD_3CN, 293 K): δ −236 (t, $^{1}J(^{119}Sn-^{19}F)$ = 2887 Hz). ^{1}H NMR (300.13 MHz, D_2O, 293 K): δ 3.85−3.58 (m, 36H, H4−H11+H3A/H12A), 3.50−3.42 (dd, 4H, H3B/H12B), 2.42 (m, 2H, H2), 1.19 (d, 4H, H1, $^{3}J(^{1}H-^{1}H)$ = 7.3 Hz, $^{2}J(^{1}H-^{117/119}Sn)$ = 97 Hz). ^{19}F NMR (282.37 MHz, CD_2Cl_2, 293 K): δ −167.7 (s,$^{1}J(^{19}F-^{117/119}Sn)$ = 2763/2879 Hz). $^{119}Sn\{^{1}H\}$ NMR (111.92 MHz, CD_2Cl_2, 293 K): δ −234 (t, $^{1}J(^{119}Sn-^{19}F)$ = 2878 Hz). ^{19}F NMR (282.37 MHz, CD_2Cl_2, −49 °C): δ −164.8 (s, $^{1}J(^{19}F-^{117/119}Sn)$ = 2811 Hz), $^{119}Sn\{^{1}H\}$ NMR (111.92 MHz, CD_2Cl_2, −49 °C): δ −242 (t, $^{1}J(^{119}Sn-^{19}F)$ = 2884 Hz). Anal. Calcd for $C_{24}H_{46}F_2O_{10}Sn$ (651.32): C, 44.26; H 7.12. Found: C, 44.3; H 6.9, Mp: 110 °C.

Synthesis of Bromido(1,4,7,10-tetraoxacyclotridec-12-ylmethyl)diphenylstannane, $BrPh_2SnCH_2$-[13]-crown-4 (7). A solution of elemental bromine (2.20 g, 13.79 mmol) in dichloromethane (85 mL) was added dropwise to a solution of (1,4,7,10-tetraoxacyclotridec-12-ylmethyl)triphenylstannane (7.63 g, 13.79 mmol) in dichloromethane (160 mL) at −55 °C. The reaction mixture was warmed to room temperature and stirred for a further 15

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h. All volatile material was removed in vacuo (10^{-3} mbar). Recrystallization of the residue in ethanol afforded 6.90 g (12.41 mmol, 90%) of bromido(1,4,7,10-tetraoxacyclotridec-12-ylmethyl)-diphenylstannane (**7**) as a colorless solid. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.79−7.76 (m, 4H$_o$, $^3J(^1H-^{117/119}Sn)$ = 63 Hz), 7.46−7.36 (m, 6H$_{m/p}$), 3.78−3.73 (m, 2H), 3.62−3.34 (m, 14H), 2.74−2.62 (m, 1H, H2, $^3J(^1H-^{117/119}Sn)$ = 156/162 Hz), 1.76 (d, 2H, H1, $^3J(^1H-^1H)$ = 6 Hz, $^2J(^1H-^{117/119}Sn)$ = 75/77 Hz). $^{13}C\{^1H\}$-NMR (75.47 MHz, $CDCl_3$): δ 140.74 (C_i, $^1J(^{13}C-^{117/119}Sn)$ = 631 Hz), 135.76 (C_o, $^2J(^{13}C-^{117/119}Sn)$ = 47/50 Hz), 129.39 (C_p, $^4J(^{13}C-^{117/119}Sn)$ = 14 Hz), 129.59 (C_m, $^3J(^{13}C-^{117/119}Sn)$ = 62/65 Hz), 71.14 (C3/C10, $^3J(^{13}C-^{117/119}Sn)$ = 38 Hz), 70.02, 69.54 (C4/C9, $J(^{13}C-^{117/119}Sn)$ = 39 Hz), 69.17, 36.57 (C2, $^2J(^{13}C-^{117/119}Sn)$ = 29 Hz), 18.38 (C1, $^1J(^{13}C-^{117/119}Sn)$ = 499/521 Hz). $^{119}Sn\{^1H\}$ NMR (111.92, $CDCl_3$): δ −96. Anal. Calcd for $C_{22}H_{29}BrO_4Sn$ (556.08): C, 47.52; H, 5.26. Found: C, 47.15; H, 5.10. Mp: 137.1 °C.

Synthesis of Hydrido(1,4,7,10-tetraoxacyclotridec-12-ylmethyl)diphenylstannane, HPh_2SnCH_2-[13]-crown-4 (8). Bromidotriorganostannane **7** (4.00 g, 7.19 mmol) was added to an ice-cooled suspension of $LiAlH_4$ (1.00 g, 26.32 mmol) in diethyl ether (125 mL). The reaction mixture was warmed to room temperature within 6 h. To destroy the excess $LiAlH_4$ and to remove the aluminum salts, a degassed, aqueous solution of potassium sodium tartrate was added until hydrogen formation ceased. Afterward, the organic phase was washed with potassium sodium tartrate solution several times. The organic phase was separated, dried with magnesium sulfate, and filtered. Evaporation of the solvent provided 3.09 g (90%) of hydrido(1,4,7,10-tetraoxacyclotridec-12-ylmethyl)diphenylstannane (**8**) as a colorless oil, which was contaminated with the crown ether substituted distannane ([13]-crown-4-$CH_2(Ph)_2Sn)_2$. The crude product was used in the next step without further purification. ^{1}H NMR (300.13 MHz, C_6D_6): δ 7.61−7.58 (m, 4H$_o$, $^2J(^1H-^{117/119}Sn)$ = 50 Hz), 7.22−7.09 (m, 6H$_{m/p}$), 6.48 (t, 1H, Sn−H, $^3J(^1H-^1H)$ = 2 Hz, $^1J(^1H-^{117/119}Sn)$ = 1831/1921 Hz), 3.65 (dd, 2H, H3A/H10A, $^3J(^1H-^1H)$ = 6 Hz, $^2J(^1H-^1H)$ = 9 Hz), 3.44−3.21 (m, 18H, H3B/H10B + H4−H9), 2.41−2.32 (m, 1H, H2), 1.14 (dd, 2H, H1, $^3J(^1H-^1H)$ = 2 Hz, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 60 Hz). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, C_6D_6): δ −147. Anal. Calcd for $C_{22}H_{30}O_4Sn$ (477.18): C, 55.37; H, 6.54. Found: C, 55.10; H, 6.70.

Synthesis of Bis(1,4,7,10-tetraoxacyclotridec-12-ylmethyl)-diphenylstannane, $Ph_2Sn(CH_2$-[13]-crown-4$)_2$ (9). Triorganohydridostannane **8** (3.09 g, 6.47 mmol), 12-methylene-1,4,7,10-tetraoxacyclotridecane (1.31 g, 6.47 mmol), and AIBN (50 mg) were mixed and stirred for 15 h at 70 °C. The reaction mixture was cooled to room temperature and dissolved in dichloromethane, and the solution was filtered through Celite. Evaporation of the solvent afforded 2.98 g of a mixture of $Ph_2Sn(CH_2$-[13]-crown-4$)_2$ (**9**) and the crown ether substituted distannane ([13]-crown-4-$CH_2(Ph)_2Sn)_2$. The crude product was used in the next steps without further purification. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.49−7.48 (m, 4H$_o$), 7.26−7.17 (m, 6H$_{m/p}$), 3.67−3.19 (m, 40H, H3−H10), 2.19−2.08 (m, 2H, H2), 1.24 (d, 4H, H1, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 57 Hz). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −78 ($^1J(^{119}Sn-^{13}C)$ = 382/450 Hz). Anal. Calcd for $C_{32}H_{48}O_8Sn$ (679.43): C, 56.47; H, 7.02. Found: C, 56.10; H, 6.75.

Synthesis of Diiodidobis(1,4,7,10-tetraoxacyclotridec-12-ylmethyl)stannane, $I_2Sn(CH_2$-[13]-crown-4$)_2$ (10). Elemental iodine (2.20 g, 8.7 mmol) was added in small portions to a cooled solution of **9** (2.95 g, 4.3 mmol) in dichloromethane (50 mL). Afterward, the reaction mixture was warmed to room temperature and stirred for a further 15 h. All volatile material was removed in vacuo. Recrystallization in ethanol afforded 1.76 g (2.3 mmol, 52%) of compound **10** as a light yellow, microcrystalline solid. Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in dichloromethane/hexane. ^{1}H NMR (499.79 MHz, $CDCl_3$): δ 3.87 (dd, 4H, H3A/H10A, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^1H)$ = 9 Hz), 3.74−3.60 (m, 24 H, H4−H9), 3.57 (dd, 4H, H3B/H10B, $^3J(^1H-^1H)$ = 6 Hz, $^2J(^1H-^1H)$ = 9 Hz), 2.63−2.55 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 159 Hz), 1.96 (d, 4H, H1, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 78/84 Hz). ^{1}H NMR (400 MHz, CD_3CN): δ 3.87 (dd, 4H, H3A/H10A, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^1H)$ = 9 Hz), 3.54−3.72 (m, 24H, H4−H9), 3.51 (dd, 4H, H3B/H10B, $^3J(^1H-^1H)$ = 6 Hz, $^2J(^1H-^1H)$ = 9 Hz), 2.51−2.63 (m, 2H, H2), 1.93 (d, 4H, H1, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 83/87 Hz). $^{13}C\{^1H\}$ NMR (125.68 MHz, $CDCl_3$): δ 71.00 (C3/C10, $^3J(^{13}C-^{117/119}Sn)$ = 70/75 Hz), 70.36, 70.10, 69.52, 37.33 (C2), 31.33 (br s, C1). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_3CN): δ 72.03 (C3/C10, $^3J(^{13}C-^{117/119}Sn)$ = 80/84 Hz), 71.25 (C4/C9, $^{2/5}J(^{13}C-^{117/119}Sn)$ = 130/134 Hz), 70.91, 70.42, 38.16 (C2, $^2J(^{13}C-^{117/119}Sn)$ = 40 Hz), 33.78 (br s, C1). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −227. $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_3CN): δ −226. Anal. Calcd for $C_{20}H_{38}I_2O_8Sn$ (779.03): C, 30.84; H, 4.92. Found: C, 30.90; H, 4.50. Mp: 146 °C.

Synthesis of Dibromidobis(1,4,7,10-tetraoxacyclotridec-12-ylmethyl)stannane, $Br_2Sn(CH_2$-[13]-crown-4$)_2$ (11). A solution of elemental bromine (1.62 g, 10.1 mmol) in dichloromethane (30 mL) was added dropwise to an ice-cooled solution of **9** (3.45 g, 5.1 mmol) in dichloromethane (70 mL). The reaction mixture was warmed to room temperature and stirred for a further 15 h. All volatile material was removed from the reaction mixture. Recrystallization in ethanol afforded 1.53 g (2.24 mmol, 44%) of **11** as a colorless, amorphous solid. Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation of a dichloromethane solution of compound **11**. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 3.81 (dd, 4H, H3A/H10A, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^1H)$ = 9 Hz), 3.75−3.56 (m, 28H, H3B/H10B+H4−H9), 2.70−2.57 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 169/180 Hz), 1.72 (d, 4H, H1, $^3J(^1H-^1H)$ = 6 Hz, $^2J(^1H-^{117/119}Sn)$ = 88/90 Hz). ^{1}H NMR (300.13 MHz, CD_3CN): δ 3.80 (dd, 4H, H3A/H10A, $^3J(^1H-^1H)$ = 8 Hz, $^2J(^1H-^1H)$ = 9 Hz), 3.73−3.50 (m, 24H, H4−H9), 3.54 (dd, 4H, H3B/H10B, $^3J(^1H-^1H)$ = 6 Hz, $^2J(^1H-^1H)$ = 9 Hz), 2.66−2.53 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 163 Hz), 1.65 (d, 4H, H1, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 90/94 Hz). ^{1}H NMR (400.13 MHz, CD_3OD): δ 3.84 (dd, 4H, H3A/H10A, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^1H)$ = 9 Hz), 3.79−3.61 (m, 28H, H3B/H10B+H4−H9), 2.68−2.62 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 170/178 Hz), 1.71 (d, 4H, H1, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 89/93 Hz). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_3OD): δ 72.56, 71.60, 71.37, 70.83, 37.89 (C2), no C1 signal was observed. $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −135. $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_3CN): δ −147. Anal. Calcd for $C_{20}H_{38}Br_2O_8Sn$ (685.03): C, 35.07; H, 5.59. Found: C, 35.14; H, 5.35. Mp: 129 C.

Synthesis of Difluorido(1,4,7,10-tetraoxacyclotridec-12-ylmethyl)diphenylstannane, $F_2Sn(CH_2$-[13]-crown-4$)_2$ (12). Silver fluoride (59 mg, 0.47 mmol) was added to a solution of **10** (181 mg, 0.23 mmol) in dichloromethane. The reaction mixture was stirred for 5 h in the dark. Afterward, the formed silver iodide was removed by filtration. The evaporation of the solvent gave 130 mg (0.23 mmol) of **12** as a colorless amorphous solid. Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation of a dichloromethane solution of compound **12**. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 3.75−3.53 (m, 32H, H3−H10), 2.62−2.47 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 198 Hz), 1.26 (d, 4H, H1, $^3J(^1H-^1H)$ = 6 Hz, $^2J(^1H-^{117/119}Sn)$ = 97 Hz). ^{1}H NMR (300.13 MHz, CD_3CN): δ 3.72−3.41 (m, 32H, H3−H10), 2.53−2.45 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 184/193 Hz), 1.19 (br s, 4H, H1, $^2J(^1H-^{117/119}Sn)$ = 96 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ 72.04 (C3/C10, $^3J(^{13}C-^{117/119}Sn)$ = 59/61 Hz), 70.88, 70.61, 70.09, 36.23 (C2, $^2J(^{13}C-^{117/119}Sn)$ = 32 Hz), 20.47 (br s, C1). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ −168 ($^1J(^{19}F-^{117/119}Sn)$ = 2710/2831 Hz). ^{19}F NMR (282.40 MHz, CD_3CN): δ −164 ($^1J(^{19}F-^{117/119}Sn)$ = 2800 Hz). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −235 ($^1J(^{119}Sn-^{19}F)$ = 2834 Hz). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_3CN): δ −235 ($^1J(^{119}Sn-^{19}F)$ = 2816 Hz). Anal. Calcd for $C_{20}H_{38}F_2O_8Sn$ (563.22): C, 42.65; H, 6.80. Found: C, 42.50; H, 6.75. Mp: 131 °C.

Complexation Studies. *Reaction of **3** with 1 equiv of Ph_4PI.* A 131.0 mg portion (0.15 mmol, 1 equiv) of **3** and 49.0 mg (0.15 mmol, 1 equiv) of Ph_4PI were dissolved in acetonitrile-d_3/chloroform-d 1/1. ^{1}H NMR (300.13 MHz, $CD_3CN/CDCl_3$, 293 K): δ 7.93−7.56 (m,

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20H, Ph_4P^+), 3.79 (dd, 4H, H3A/H12A, $J(^1H-^1H)$ = 9.2 Hz, $J(^1H-^1H)$ = 7.0 Hz), 3.72−3.50 (m, 32H, H4−H11), 3.39 (dd, 4H, H3B/H12B, $J(^1H-^1H)$ = 9.0 Hz, $J(^1H-^1H)$ = 7.5 Hz), 2.55−2.45 (m, 2H, H2), 1.89 (d, 4H, H1, $^3J(^1H-^1H)$ = 8.1 Hz, $^2J(^1H-^{117/119}Sn)$=85 Hz). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CD_3CN/CDCl_3$, 293 K): δ 135.6 (d, $J(^{13}C-^{31}P)$ = 3 Hz), 132.6 (d, $J(^{13}C-^{31}P)$ = 325 Hz), 132.6 (d, $J(^{13}C-^{31}P)$ = 302 Hz), 118.3, 73.0 ($^3J(^{13}C-^{117/119}Sn)$ = 106 Hz), 70.5, 70.2, 70.1, 70.1, 37.4, 33.7. $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CD_3CN/CDCl_3$, 293 K): δ −222.

*Reaction of **3** with 2 equiv of Ph_4PI:* A 115.0 mg (0.13 mmol, 1 equiv) portion of **3** and 85.0 mg (0.27 mmol, 2 equiv) of Ph_4PI were dissolved in acetonitrile-d_3/chloroform-d 1/1. ^1H NMR (300.13 MHz, $CD_3CN/CDCl_3$, 293 K): δ 7.93−7.58 (m, 40H, Ph_4P^+), 3.79 (dd, 4H, H3A/H12A, $J(^1H-^1H)$ = 9.0 Hz, $J(^1H-^1H)$ = 76.8 Hz), 3.73−3.53 (m, 32H, H4−H11), 3.39 (dd, 4H, H3B/H12B, $J(^1H-^1H)$ = 9.2 Hz, $J(^1H-^1H)$ = 7.7 Hz), 2.57−2.43 (m, 2H, H2), 1.88 (d, 4H, H1, $^3J(^1H-^1H)$ = 8.4 Hz, $^2J(^1H-^{117/119}Sn)$ = 85 Hz). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CD_3CN/CDCl_3$, 293 K): δ 135.6 (d, $J(^{13}C-^{31}P)$ = 3 Hz), 132.6 (d, $J(^{13}C-^{31}P)$ = 325 Hz), 132.6 (d, $J(^{13}C-^{31}P)$ = 302 Hz), 118.3, 73.0 (C3/C10, $^3J(^{13}C-^{117/119}Sn)$ = 106 Hz), 70.5, 70.2, 70.1, 70.1, 37.4, 33.7. $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CD_3CN/CDCl_3$, 293 K): δ −222.

*Reaction of **3** with 2 equiv of $Et_4NF{\cdot}2H_2O$.* To a solution of 87 mg (100 μmol) **3** in 600 μL of chloroform-d was added 37 mg (200 μmol) of $Et_4NF{\cdot}2H_2O$. ^1H NMR (300.13 MHz, $CDCl_3$): δ 3.79 (dd, 4H, H3A/H12A, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 3.76−3.59 (m, 32H, H4−H11), 3.46 (dd, 4H, H3B/H12B, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 3.44 (q, 16H, CH_2N, $^3J(^1H-^1H)$ = 7 Hz), 2.48−2.38 (m, 2H, H2), 1.39 (tt, 24H, CH_3CH_2N, $^3J(^1H-^1H)$ = 7 Hz, ^7J = 2 Hz), 1.14 (d, 4H, H1, $^3J(^1H-^1H)$ =8 Hz, $^2J(^1H-^{117/119}Sn)$ = 100/104 Hz). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ −166.8 ($^1J(^{19}F-^{117/119}Sn)$ = 2746/2889 Hz). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −236 ($^1J(^{119}Sn-^{19}F)$ = 2886 Hz).

*Reaction of **3** with 1 equiv of NaI in CD_3CN.* A 50.2 mg (58 μmol) portion of **3** and 8.7 mg (58 μmol) of sodium iodide were dissolved in 600 μL of CD_3CN. ^1H NMR (400.13 MHz, CD_3CN): δ 3.72−3.57 (m, 40H, H3−H12), 2.58−2.49 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 112 Hz), 2.10 (d, 4H, H1, $^3J(^1H-^1H)$ = 8 Hz, $^2J(^1H-^{117/119}Sn)$ = 76/80 Hz). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_3CN): δ 75.47 (C3/C12, $^3J(^1H-^{117/119}Sn)$ = 87 Hz), 71.25, 70.67, 70.56, 70.48, 38.59 (C2, $^2J(^1H-^{117/119}Sn)$ = 39 Hz), 36.25 (C1, br s, $w_{1/2}$ = 4 Hz).

*Reaction of **3** with 2 equiv of NaI in CD_3CN.* A 79 mg (0.09 mmol, 1 equiv) portion of **3** and 27 mg (0.18 mmol, 2 equiv) of sodium iodide were dissolved in acetonitrile-d_3. ^1H NMR (300.13 MHz, CD_3CN, 293 K): δ 3.73 (dd, $^2J(^1H-^1H)$ = 9.5 Hz, $^3J(^1H-^1H)$ = 1.8 Hz, 4H, CH_2OCH_2), 3.69−3.51 (m, 36H, CH_2OCH_2), 2.70−2.62 (m, 2H, $SnCH_2CHR$), 2.38 (d, $^3J(^1H-^1H)$ = 7.3 Hz, $^2J(^1H-^{117/119}Sn)$ = 76 Hz), 4H, $SnCH_2CHR$). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_3CN, 293 K): δ 77.0 ($^3J(^{13}C-^{117/119}Sn)$ = 80 Hz), 70.3, 69.1, 69.0, 68.9, 39.9, 38.4 ($^1J(^{13}C-^{117/119}Sn)$ = 36 Hz). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_3CN, 293 K): δ −207.

*Reaction of **3** with an Excess of NaI in D_2O.* A 30 mg (35 μmol) portion of **3** and 50 mg (350 μmol, 10 equiv) of sodium iodide were dissolved in 550 μL of D_2O. ^1H NMR (300.13 MHz, D_2O): δ 4.09−3.87 (m, 40H, H3−H12), 2.79 (m, 2H, H2), 2.06 (d, 4H, H1, $^3J(^1H-^1H)$ = 8 Hz, $^2J(^1H-^{117/119}Sn)$ = 60 Hz).

*Reaction of **4** with 1 equiv of Ph_4PBr in $CDCl_3$.* A 77.88 mg (98.9 μmol) portion of **4** and 41.48 mg (98.9 μmol) of Ph_4PBr were dissolved in 600 μL of $CDCl_3$. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.80−7.89 (m, 4H, Ph_4P^+), 7.72 (td, 8H, Ph_4P^+, J = 7.78, 3.51 Hz), 7.54 (dd, 8H, Ph_4P^+, J = 12.92, 7.40 Hz), 3.73 (dd, 4H, H3A/H12A, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 3.45−3.68 (m, 32H), 3.36 (dd, 4H, H3B/H12B, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 8 Hz), 2.46 (m, 2H, H2), 1.53 (d, 4H, H1, $^3J(^1H-^1H)$ = 8 Hz, $^2J(^1H-^{117/119}Sn)$ = 93 Hz). $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$): δ 135.56 (d, $J(^{13}C-^{31}P)$ = 3 Hz), 134.04 (d, $J(^{13}C-^{31}P)$ = 11 Hz), 130.56 (d, $J(^{13}C-^{31}P)$ = 13 Hz), 117.02 (d, $J(^{13}C-^{31}P)$ = 89 Hz), 73.44 (C3/C12, $^3J(^{13}C-^{117/119}Sn)$ = 195 Hz), 70.35, 69.94, 69.90, 69.68, 36.17 (C2, $^3J(^{13}C-^{117/119}Sn)$ = 35 Hz), 31.25 (C1, br s).

*Reaction of **4** with 2 equiv of Ph_4PBr in $CDCl_3$.* A 72.6 mg (92.3 μmol) portion of **4** and 44.4 mg (184.5 μmol) of Ph_4PBr were dissolved in 600 μL of $CDCl_3$. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.89−7.77 (m, 8H, Ph_4P^+), 7.71 (td, 16H, Ph_4P^+, J = 7.78, 3.51 Hz), 7.53 (dd, 16H, Ph_4P^+, J = 13.05, 7.53 Hz), 3.73 (dd, 4H H3A/H12A, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 3.68−3.43 (m, 32H, H4−H11), 3.35 (dd, 4H, H3B/H12B, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 8 Hz), 2.50−2.39 (m, 2H, H2), 1.52 (d, 4H, H1, $^3J(^1H-^1H)$ =8.03 Hz, $^2J(^1H-^{117/119}Sn)$ = 94 Hz). ^{13}C NMR (100.63 MHz, $CDCl_3$): δ 135.53 (d, Ph_4P^+, J = 2.92 Hz), 134.00 (d, Ph_4P^+, J = 11 Hz), 130.54 (d, Ph_4P^+, J = 14 Hz), 117.00 (d, Ph_4P^+, J = 89 Hz), 73.41 (C3/C12, $^3J(^{13}C-^{117/119}Sn)$ = 195 Hz), 70.34, 70.04, 69.79, 69.66, 36.14 (C2), 31.23 (C1).

*Reaction of **4** with 2 equiv of $NaClO_4$ in $CDCl_3$.* A 37.5 mg (48.5 μmol) portion of **4** and 11.9 mg (96.9 μmol) of $NaClO_4$ were dissolved in 600 μL of $CDCl_3$. ^1H NMR (400.13 MHz, $CDCl_3$): δ 3.82−3.53 (m, 40H, H3−H12), 2.59−2.50 (m, 2H, H1, $^3J(^1H-^{117/119}Sn)$ = 116 Hz), 1.79 (br s, 4H, H1, $\nu_{1/2}$= 23 Hz, $^2J(^1H-^{117/119}Sn)$ = 80 Hz). ^{13}C NMR (100.63 MHz, $CDCl_3$): δ 74.77 (br s, $\nu_{1/2}$ = 30 Hz), 70.26, 69.99−69.76, 36.49 (C2), no C1 signal was observed.

*Reaction of **4** with 1 equiv of NaBr in $CDCl_3$.* A 10.2 mg (99.3 μmol) portion of NaBr was added to a solution of 78.2 mg (99.3 μmol) of **4** in 600 μL of $CDCl_3$. ^1H NMR (400 MHz, $CDCl_3$): δ 3.78 (dd, 4H H3A/H12A, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 3.73−3.53 (m, 32H, H4−H11), 3.50 (m, dd, 4H, H3B/H12B, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 2.63−2.49 (m, 2H, H2), 1.70 (d, $^3J(^1H-^1H)$=8 Hz, 8 H, $^2J(^1H-^{117/119}Sn)$ = 87 Hz).

*Reaction of **4** with 1 equiv of NaBr in CD_3CN.* A 73.5 mg (95.1 μmol) portion of **4** and 9.8 mg (95.1 μmol) of NaBr were dissolved in 600 μL of CD_3CN. ^1H NMR (300 MHz, CD_3CN): δ 3.82−3.20 (m, 40H, C3−C12), 2.83−2.59 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 105 Hz), 1.85 (d, 4H, H1, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 87/93 Hz). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_3CN): δ −178.

*Reaction of **4** with 1 equiv of NaBr in CD_3OD.* A 61.0 mg (78.9 μmol) portion of **4** and 8.1 mg (78.9 μmol) of NaBr were dissolved in 600 μL of CD_3OD. ^1H NMR (300.13 MHz, CD_3OD): δ 3.85−3.54 (m, 40H, H3−H12), 2.75−2.52 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 123 Hz), 1.84 (d, 4H, H1, $^3J(^1H-^1H)$ = 4 Hz, $^2J(^1H-^{117/119}Sn)$ = 123 Hz). $^{119}Sn\{^1H\}$-NMR (111.92 MHz, CD_3OD): δ −115.

*Reaction of **4** with 2 equiv of of $LaBr_3{\cdot}H_2O$ in CD_3CN.* A 55 mg (140 μmol) portion of $LaBr_3{\cdot}H_2O$ was added to a solution of 54.2 mg (70.1 μmol) of **4** in 600 μL of CD_3CN. ^1H NMR (300 MHz, CD_3CN): δ 3.80 (dd, 4H H3A/H12A, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 3.76−3.48 (m, 32H, H4−H11), 3.40 (dd, 4H H3B/H12B, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 2.55−2.43 (m, 2H, H2), 1.62 (d, 4H, H1, $^3J(^1H-^1H)$ = 8 Hz, $^2J(^1H-^{117/119}Sn)$ = 91/95 Hz). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_3CN): δ −143.

*Reaction of **4** with 1 equiv of $MgBr_2$ in CD_3CN.* A 14.1 mg (76.7 μmol) portion of $MgBr_2$ was added to a solution of 60.4 mg (76.7 μmol) of **4** in 600 μL of CD_3CN. ^1H NMR (400 MHz, CD_3CN): δ 3.79 (dd, 4H H3A/H12A, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 3.74−3.50 (m, 32H, H4−H11), 3.39 (dd, 4H H3B/H12B, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 2.55−2.43 (m, 2H, H2), 1.59 (d, 4H, H1, $^3J(^1H-^1H)$ = 8 Hz, $^2J(^1H-^{117/119}Sn)$ = 92/95 Hz). ^{13}C NMR (101 MHz, CD_3CN): δ 74.13 (C3/C12, $^3J(^{13}C-^{117/119}Sn)$ = 105/109 Hz), 71.15, 70.75, 70.72, 70.62, 37.17 (C2, $^2J(^{13}C-^{117/119}Sn)$ = 34 Hz), 32.34 (C1).

*Reaction of **6** with 1 equiv of $Et_4NF{\cdot}2H_2O$ in CD_3CN.* A 76.7 mg (0.12 mmol, 1 equiv) portion of **6** and 21.8 mg (0.12 mmol, 1 equiv) of $Et_4NF{\cdot}2H_2O$ were dissolved in 600 μL of CD_3CN. ^1H NMR (300.13 MHz, CD_3CN, 293 K): δ 3.66−3.44 (m, 36H, H3A/H12A + H4−H11), 3.37−3.32 (m, 4H, H3B/H12B), 3.18 (q, 8H, Et_4N^+, $^3J(^1H-^1H)$ = 7.2 Hz), 2.26 (m, 2H, H2), 1.20 (tt, 12H, Et_4NF^+ $J(^1H-^1H)$ = 7.2 Hz, $J(^1H-^1H)$ = 1.9 Hz), 0.84 (d, 4H, H1, $^3J(^1H-^1H)$ = 7.3 Hz, $^2J(^1H-^{117/119}Sn)$ = 105.0/109.8 Hz). ^{19}F−NMR (282.38 MHz, CD_3CN, 293 K): δ −126.0, −129.4, −150.8, −150.8, −153.9. $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_3CN, 293 K): no resonance observed.

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*Reaction of **6** with 2 equiv of $Et_4NF{\cdot}2H_2O$ in CD_3CN.* A 84.1 mg (0.13 mmol) portion of **6** and 47.8 mg (0.26 mmol, 2 equiv) of $Et_4NF{\cdot}2H_2O$ were dissolved in 600 μL of CD_3CN. ^1H NMR (300.13 MHz, CD_3CN, 293 K): δ 3.63−3.42 (m, 36H, H3A/H12A + H4−H11), 3.36−3.30 (m, 4H, H3B/H12B), 3.20 (q, 16H, Et_4N^+, $^3J(^1H-^1H)$ = 7.3 Hz), 2.23 (m, 2H, H2), 1.20 (tt, 24 H, Et_4N^+, $J(^1H-^1H)$ = 7.3 Hz, $J(^1H-^1H)$ = 1.8 Hz), 0.79 (d, 4H, H1, $^3J(^1H-^1H)$ = 7.3 Hz, $^2J(^1H-^{117/119}Sn)$ = 106.1 Hz). ^{19}F NMR (282.38 MHz, CD_3CN): δ −126.70, −129.06 (d, $^2J(^{19}F-^{19}F)$ = 16.06 Hz, $^1J(^{19}F-^{117/119}Sn)$ = 2599/2720 Hz), −136.05 (quintet, $^2J(^{19}F-^{19}F)$ = 16.06 Hz, $^1J(^{19}F-^{117/119}Sn)$ = 1170 Hz), −150.73, −150.79, −153.7. $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_3CN): δ −330 ($w_{1/2}$ = 518 Hz).

*Reaction of **6** with 1 equiv of $Et_4NF{\cdot}2H_2O$ in CD_2Cl_2 at 213 K.* A 61.2 mg (0.094 mmol) portion of **6** and 17.4 mg (0.094 mmol) of $Et_4NF{\cdot}2H_2O$ were dissolved in 600 μL of CD_2Cl_2, and the resulting solution was investigated by NMR spectroscopy at 213 K. ^{19}F NMR (282.38 MHz, CD_2Cl_2, 213 K): δ −117.8 (s, $^1J(^{19}F-^{117/119}Sn)$ = 2522/2645 Hz), −160.5 (s, $^1J(^{19}F-^{117/119}Sn)$ = Hz),−164.7 (br s, $^1J(^{19}F-^{117/119}Sn)$ = Hz). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_2Cl_2, 213 K): δ −333 (q, $^1J(^{119}Sn-^{19}F)$ = 2656 Hz), −242 (t, $^1J(^{119}Sn-^{19}F)$ = 2892 Hz).

*Reaction of **6** with 2 equiv of $Et_4NF{\cdot}2H_2O$ in CD_2Cl_2 at 213 K.* A 65.4 mg (0.100 mmol) portion of **6** and 37.2 mg (0.201 mmol) of $Et_4NF{\cdot}2H_2O$ were dissolved in 600 μL of CD_2Cl_2, and the resulting solution was investigated by NMR spectroscopy at 213 K. ^{19}F NMR (282.38 MHz, CD_2Cl_2, 213 K): δ −118.1 (d, $^2J(^{19}F-^{19}F)$ = 18.4 Hz, $^3J(^{19}F-^{117/119}Sn)$ = 2547/2647 Hz), −159.7 (t, $^2J(^{19}F-^{19}F)$ = 22.9 Hz, $^3J(^{19}F-^{117/119}Sn)$ = 2552/2666 Hz) (+ signals without coupling to $^{117/119}Sn$ at δ −128.04, −129.84, −129,89, −151.00, −151.12, −151.54). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_2Cl_2, 213 K): δ −333 (q, $^1J(^{119}Sn-^{19}F)$ = 2662 Hz).

*Reaction of **6** with an Excess of LiF in $CDCl_3$.* An excess of LiF was added to a solution of **6** in 600 μL of $CDCl_3$. ^1H NMR (200.13 MHz, $CDCl_3$, 293 K): δ 3.82−3.55 (m, 36H, H3A/H12A + H4−H11), 3.49−3.41 (m, 4H, H3B/H12B), 2.42 (m, 2H, H2), 1.14 (d, 4H, H1, $^3J(^1H-^1H)$ = 8.06 Hz, $^2J(^1H-^{117/119}Sn)$ = 99.7/103.6 Hz). ^{19}F NMR (188.28 MHz, $CDCl_3$, 293 K): δ −168.86 (s, $^1J(^{19}F-^{117/119}Sn)$ = 2751.1/2893.2 Hz).

*Reaction of **6** with 1 equiv of NaF in CD_3CN.* A 2.5 mg (0.06 mmol) portion of NaF was added to a solution of 39.1 mg (0.06 mmol) of **6** in 600 μL of CD_3CN. ^1H NMR (200.13 MHz, CD_3CN, 293 K): δ 3.77−3.51 (m, 36H, H3A/H12A + H4−H11), 3.43−3.34 (m, 4H, H3B/H12B), 2.33 (m, 2H, H2), 1.05 (d, 4H, H1, $^3J(^1H-^1H)$ = 8.06 Hz, $^2J(^1H-^{117/119}Sn)$ = 99.0/103.3 Hz).

*Reaction of **6** with 2 equiv of NaF in CD_3CN.* A 4.9 mg (0.12 mmol) portion of NaF was added to a solution of 38.3 mg (0.06 mmol) of **6** in 600 μL of CD_3CN. ^1H NMR (200.13 MHz, CD_3CN, 293 K): δ 3.77−3.51 (m, 36H, H3A/H12A + H4−H11), 3.43−3.34 (m, 4H, H3B/H12B), 2.33 (m, 2H, H2), 1.05 (d, 4H, H1, $^3J(^1H-^1H)$ = 7.82 Hz, $^2J(^1H-^{117/119}Sn)$ = 98.7/103.1 Hz).

*Reaction of **6** with 2 equiv of CsF in CD_3CN.* An 18.1 mg (0.12 mmol) portion of CsF was added to a solution of 77.8 mg (0.12 mmol) of **6** in 600 μL of CD_3CN. ^1H NMR (300.13 MHz, CD_3CN, 293 K): δ 3.70−3.54 (m, 36H, H3A/H12A + H4−H11), 3.43−3.37 (m, 4H, H3B/H12B), 2.33 (m, 2H, H2), 1.02 (d, 4H, H1, $^3J(^1H-^1H)$ = 7.7 Hz, $^2J(^1H-^{117/119}Sn)$ = 101.0/104.3 Hz). ^{19}F NMR (282.38 MHz, CD_3CN): δ −150.8 (no coupling to $^{119/117}Sn$ observed). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_3CN): no resonance observed.

*Reaction of **6** with 1 equiv of CsF in CD_3OD.* A 19.1 mg (0.126 mmol) portion of CsF was added to a solution of 81.8 g (0.126 mmol) of **6** in 600 μL of CD_3OD, and the solution was investigated by NMR spectroscopy at 213 K. ^{19}F NMR (282.38 MHz, CD_3OD, 213 K): δ −126 (?), −152 (CsF), −160 (br s). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_3OD, 213 K): δ −256 (t, $^1J(^{19}F-^{119}Sn)$ = 2918 Hz), −337 (q, $^1J(^{19}F-^{119}Sn)$ = 2684 Hz).

*Reaction of **10** with 2 equiv of CsI in CD_3CN.* A 40.0 mg (154 μmol) portion of CsI was added to a solution of 60.0 mg (77 μmol) of **10** in 600 μL of CD_3CN. ^1H NMR (400.13 MHz, CD_3CN): δ 3.87 (dd, 4H, H3A/H10A, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 3.73−3.54 (m, 32 H, H4−H9), 3.51 (dd, 4H, H3A/H10A, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 6 Hz), 2.56 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 148 Hz), 1.93 (d, 4H, H1, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 83/86 Hz). ^{13}C NMR (100.63 MHz, CD_3CN): δ 72.02 (C3/C10), 71.23, 70.89, 70.40, 38.15 (C2), 33.78 (C1).

*Reaction of **10** with 2 equiv of LiI in CD_3CN.* A 21.1 mg (158 μmol) portion of LiI was added to a solution of 61.5 mg (79 μmol) of **10** in 600 μL of CD_3CN. ^1H NMR (400.13 MHz, CD_3CN): δ 3.89 (dd, 4H, H3A/H10A, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 3 Hz), 3.81−3.58 (m, 28H, H4−H9 + H3B/H10B), 2.80−2.68 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 142 Hz), 2.25 (d, 4H, H1, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 70 Hz). ^{13}C NMR (100.63 MHz, CD_3CN): δ 76.07 (C3/C10, $^3J(^{13}C-^{117/119}Sn)$ = 80/84 Hz), 69.21, 68.32, 68.07, 39.07 (br s, C1, $\nu_{1/2}$ = 8 Hz), 38.17 (C2, $^2J(^{13}C-^{117/119}Sn)$ = 38 Hz). ^{119}Sn NMR (111.92 MHz, CD_3CN): δ −216 ($\nu_{1/2}$ = 243 Hz).

*Reaction of **10** with an Excess of NaI in CD_3CN.* A 50.0 mg (334 μmol) portion of NaI was added to a solution of 60.0 mg (77 μmol) of **10** in 600 μL of CD_3CN. ^1H NMR (400.13 MHz, CD_3CN): δ 3.87 (dd, 4H, H3A/H10A, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 3.73−3.54 (m, 32 H, H4−H9), 3.51 (dd, 4H, H3A/H10A, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 6 Hz), 2.56 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 148 Hz), 1.93 (d, 4H, H1, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 83/86 Hz). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_3CN): δ 72.02 (C3/C10), 71.23, 70.89, 70.40, 38.15 (C2), 33.78 (C1).

*Reaction of **11** with 1 equiv of LiBr in CD_3CN.* A 6.9 mg (80 μmol) portion of LiBr was added to a solution of 54.7 mg (80 μmol) of **11** in 600 μL of CD_3CN. ^1H NMR (300.13 MHz, CD_3CN, 293 K): δ 3.80−3.54 (m, 32H, H3−H10), 2.85−2.67 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 149 Hz), 1.81 (d, 4H, H1, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 89/93 Hz). ^1H NMR (300.13 MHz, CD_3CN, 253 K): δ 3.81−3.48 (m, 32H, H3−H10), 2.82−2.62 (m, 2H, H2, $^2J(^1H-^{117/119}Sn)$ = 145 Hz), 1.76 (d, 4H, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 94 Hz). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_3CN, 293 K): δ −172 ($\nu_{1/2}$ = 227 Hz).

*Reaction of **11** with an Excess of LiBr in CD_3OD.* A 19.8 mg portion of LiBr werewas added to a solution of 30.2 mg of **11** in 600 μL of CD_3OD. ^1H NMR (400.13 MHz, CD_3OD): δ 3.91 (dd, 2H, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 3.82 (dd, 4H, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 3.77−3.56 (m, 26H), 2.57−2.69 (m, 2H, H2, $^3J(^1H-^1H)$ = 172 Hz), 1.68 (d, 4H, H1, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 89/94 Hz). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_3OD): δ 72.39 (C3/C10), 71.44, 71.21, 70.65, 37.72 (C2), 31.71 (C1).

*Reaction of **11** with 1 equiv of $CsClO_4$ in CD_3CN.* A 17.4 mg (75 μmol) portion of $CsClO_4$ was added to a solution of 51.4 mg (75 μmol)of **11** in 600 μL of CD_3CN. ^1H NMR (300.13 MHz, CD_3CN): δ 3.80 (dd, 4H, H3A/H10A, $^2J(^1H-^1H)$ = 9 Hz, $^3J(^1H-^1H)$ = 7 Hz), 3.73−3.47 (m, 28H, H4−H9+H3B/H10B), 2.59 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 165 Hz), 1.65 (d, 4H, H1, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 90/94 Hz). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, CD_3CN): δ −147 ($\nu_{1/2}$ = 25 Hz).

*Reaction of **12** with an Excess of LiF in CD_3CN.* A 10 mg (385 μmol) portion of LiF was added to a solution of 30 mg (53 μmol) of **12** in 600 μL of CD_3CN. ^1H NMR (200.13 MHz, CD_3CN): δ 3.84−3.34 (m, 32H, H3−H10), 2.62−2.35 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 182/194 Hz), 1.19 (d, 4H, H1, $^3J(^1H-^1H)$ = 5 Hz, $^2J(^1H-^{117/119}Sn)$ = 98 Hz). ^{13}C NMR (75.47 MHz, CD_3CN): δ 72.03 (C3/C10, $^3J(^{13}C-^{117/119}Sn)$ = 59 Hz), 70.87, 70.60, 70.08, 36.22 (C2, $^2J(^{13}C-^{117/119}Sn)$ = 33 Hz), 20.49 (br s, C1, $\nu_{1/2}$ = 33 Hz). ^{19}F NMR (188.29 MHz, CD_3CN): δ −152.2 (3%), −165 (97%, $^1J(^{19}F-^{117/119}Sn)$ = 2760 Hz). ^{119}Sn NMR (111.92 MHz, CD_3CN): δ −235 (t, $^1J(^{119}Sn-^{19}F)$ = 2822 Hz).

*Reaction of **12** with an Excess of CsF in $CDCl_3$.* A 40 mg (263 μmol) portion of CsF was added to a solution of 30 mg (53 μmol) of **12** in 600 μL of $CDCl_3$. ^1H NMR (200.13 MHz, $CDCl_3$): δ 3.72−3.49 (m, 32H, H3−H10), 2.58−2.33 (m, 2H, H2), 1.11 (d, $^3J(^1H-^1H)$ = 6 Hz, $^2J(^1H-^{117/119}Sn)$ = 102 Hz, 4H, H1). ^{19}F NMR (188.29 MHz, $CDCl_3$): no signal observed.

*Reaction of **12** with 1 equiv of AgF in CD_3CN.* A 6.5 mg (52 μmol) portion of AgF was added to a solution of 29.1 mg (52 μmol) of **12** in

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600 μL of CD_3CN. ^1H NMR (200.13 MHz, CD_3CN): δ 3.74−3.36 (m, 32H), 2.41−2.17 (m, 2H, H2, $^3J(^1H-^{117/119}Sn)$ = 145 Hz), 1.02 (d, 4H, H1, $^3J(^1H-^1H)$ = 7 Hz, $^2J(^1H-^{117/119}Sn)$ = 105/108 Hz). ^{13}C NMR (75.47 MHz, CD_3CN): δ 72.97 (s, 1 C), 72.19 (s, 2 C), 70.56 (s, 2 C), 70.19−70.41 (m, 7 C), 69.85 (d, *J* = 2 Hz, 5 C), 36.20 (s, 1 C), 35.98 (s, 1 C), 24.05 (s, 1 C). ^{19}F NMR (188.29 MHz, CD_3CN): δ −129 (br. s, $\nu_{1/2}$ = 152 Hz, 80%), −130 (s, 20%).

Crystallography. Intensity data for crystals of **4**−**6**, **10**, and **12** were collected on a XcaliburS CCD diffractometer (Oxford Diffraction) and for crystal **11** on a SMART APEX2 CCD diffractometer (Bruker) using Mo Kα radiation at 110 K. All structures were solved with direct methods using SHELXS-97.[26] Refinements were carried out against F^2 by using SHELXL-97.[26] The C−H hydrogen atoms were positioned with idealized geometries and refined using a riding model. All non-hydrogen atoms were refined using anisotropic displacement parameters. In compound **11** Sn1 and Br1 are disordered and split into two positions. Their occupancies were allowed to refine freely until a constant number was obtained (second FVAR 0.87544). For decimal rounding of numerical parameters and su values the rules of IUCr have been employed.[27]

CCDC-902174 (**4**), CCDC-902175 (**5**), CCDC-902176 (**6**), CCDC-902177 (**10**), CCDC-902178 (**11**) and CCDC-902179 (**12**) contain supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files for compounds **4**−**6** and **10**−**12**, molecular structures for **5**, **6**, **10**, and **12** (Figures S1−S4), ^1H, ^{19}F, and ^{119}Sn NMR spectra of **6** (Figures S5−S7), and crystallographic data (Tables S1 and S2). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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