Organotin-Substituted Crown Ethers for Ditopic Complexation of Anions and Cations[‡]

Gregor Reeske,[a] Markus Schürmann,[a] Burkhard Costisella,[a] and Klaus Jurkschat*[a]

Dedicated to Prof. W.-W. Du Mont on the occasion of his 60th birthday

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The syntheses of the organotin-substituted crown ethers *m*-($Ph_2XSnCH_2CH_2$)-15-benzocrown-5 (**2**, X = Ph; **3**, X = I; **4**, X = Cl; **5**, X = NCS) and the salt [*m*-($Ph_3SnCH_2CH_2$)-15-benzocrown-5·Na]$^+SCN^-$ (**2a**) are reported. Compounds **2a** and **4** (as its aqua complex **4**·H_2O) are characterized by single-crystal X-ray diffraction sudies. Multinuclear NMR spectroscopy and electrospray mass spectrometry reveal the triorganotin chloride **4** to be a ditopic host towards sodium rhodanide. This statement is further supported by the ability of compound **4** to transport sodium rhodanide through an organic membrane.

Introduction

The simultaneous recognition and sensing of anions and cations is a new area of increasing research activities.[1,2] Practical applications of ion-pair recognition range from complexation of zwitterionic amino acids and peptides,[3,4] the transport of ion pairs across biological membranes[5–12] to solubility enhancement of ion pairs in nonpolar solvents for ion extraction.[13] Ion-pair receptors known so far are based on the combination of crown compounds or calixarenes with (i) ammonium groups exploiting hydrogen bonding[14,15] or (ii) Lewis acidic groups.[16–20] Straightforward examples of the latter case involve the work of Reetz et al.[18a] on an organoboron-substituted crown ether, and Willem et al.[18b] who reported the sodium rhodanide complex of triorganotin carboxylates containing the [18]crown-6 and [15]crown-5 substituents. However, an essential shortcoming of the latter compounds is the kinetic lability of the tin–carboxylate bond, which makes the corresponding zwitterionic complexes unstable in solution.[18b]

In continuation of our own studies on organotin halides as Lewis acids for selective complexation of anions[21–23] we report here the synthesis and structures of kinetically more stable carbon-bonded organotin-functionalized crown ethers and demonstrate that such compounds are able to complex and transport sodium rhodanide in nonpolar organic solvents.

Results and Discussion

Synthetic Aspects and Molecular Structures in the Solid State

The reaction of 4-vinylbenzo-15-crown-5[24,25] (**1**) with triphenyltin hydride provided [2-(6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxabenzocyclopentadec-2-yl)ethyl]-triphenylstannane (**2**) as a colorless oil (Scheme 1).

Treatment of the tetraorganostannane **2** with 1 molequiv. of iodine gave the triorganotin iodide **3**. The latter was quantitatively converted into its chloride derivative **4** by reaction with AgCl in acetonitrile over a period of 14 d. The reaction of triorganotin iodide **3** with AgSCN in CH_3CN gave the triorganotin rhodanide **5** in quantitative yield.

The treatment of **2** with NaSCN in ethanol provided the corresponding sodium rhodanide complex **2a** as a colorless solid. Single crystals of **2a** suitable for X-ray diffraction analyses were obtained by recrystallization from dichloromethane/*n*-hexane.

The molecular structure of **2a** is shown in Figure 1 and selected geometric parameters are collected in Table 1.

The sodium cation is coordinated by five oxygen atoms with Na–O distances ranging between 2.317(7) and 2.469(6) Å. These values are in line with those reported for similar compounds.[18] The rhodanide anion is located close

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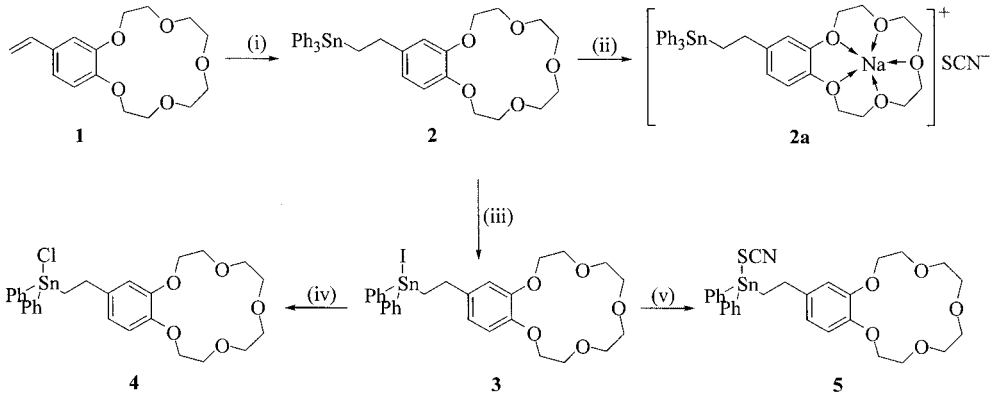
[a] Lehrstuhl für Anorganische Chemie II der Universität Dortmund,
44221 Dortmund, Germany
Fax: +49-231-7555048
E-mail: klaus.jurkschat@uni-dortmund.de



Scheme 1. Synthesis of the organotin-substituted crown ethers. i) Ph_3SnH, AIBN; ii) NaSCN, EtOH; iii) I_2, CH_2Cl_2, – PhI; iv) AgCl, CH_3CN, – AgI; v) AgSCN, CH_3CN, – AgI.

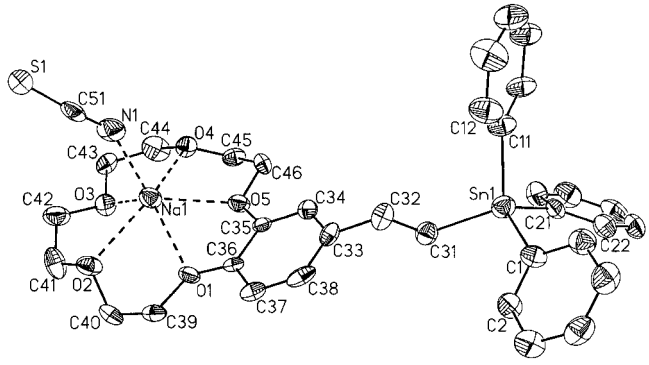


Figure 1. Molecular structure of the sodium rhodanide complex **2a**. Atomic displacement parameters are drawn at 30% probability level.

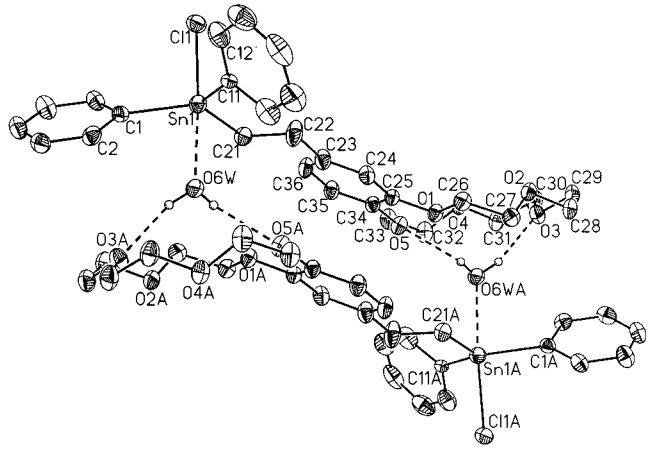


Figure 2. Molecular structure of $4 \cdot H_2O$. Atomic displacement parameters are drawn at 30% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for **2a**.

Sn–C(11)	2.141(9)	Na–N	2.344(9)
Sn–C(21)	2.125(9)	Na–O(1)	2.453(5)
Sn–C(31)	2.141(7)	Na–O(2)	2.438(6)
S–C(51)	1.625(11)	Na–O(3)	2.313(7)
N–C(51)	1.164(10)	Na–O(4)	2.469(6)
		Na–O(5)	2.375(6)
C(1)–Sn–C(11)	108.0(4)	O(1)–Na-(O3)	117.0(2)
C(1)–Sn–C(21)	110.5(4)	O(2)–Na–O(4)	141.0(3)
C(1)–Sn–C(31)	108.0(4)	O(3)–Na-(O2)	71.5(2)
C(21)–Sn–C(11)	105.5(4)	O(3)–Na-(O4)	70.5(3)
C(21)–Sn–C(31)	112.0(4)	O(3)–Na-(O5)	120.0(3)
C(31)–Sn–C(11)	111.0(3)	O(5)–Na-(O1)	62.75(20)
O(1)–Na–O(4)	125.5(2)	O(5)–Na-(O2)	127.5(2)
O(1)–Na–O(2)	66.5(2)	O(5)–Na-(O4)	67.5(2)

to the sodium cation with an Na–N distance of 2.344(9) Å. The tin atom shows the expected tetrahedral configuration.

Crystallization of the triorganotin chloride **4** at –5 °C from CH_2Cl_2/Et_2O (1:2) in the presence of air moisture afforded single crystals of the aqua complex $4 \cdot H_2O$ as its CH_2Cl_2 solvate.

The molecular structure of $4 \cdot H_2O$ is shown in Figure 2, selected geometric parameters are collected in Table 2.

Table 2. Selected bond lengths [Å] and angles [°] for $4 \cdot H_2O$.

Sn–C(1)	2.125(4)	O(1)–C(26)	1.430(5)
Sn–C(11)	2.109(4)	O(2)–C(27)	1.406(5)
Sn–C(21)	2.125(4)	O(5)–C(33)	1.430(5)
Sn–Cl(1)	2.453(1)		
Sn–O(6W)	2.469(4)		
O(1)–C(25)	1.359(5)		
C(1)–Sn–Cl(1)	95.0(12)	C(11)–Sn–Cl(1)	96.5(11)
C(1)–Sn–O(6W)	81.0(16)	C(11)–Sn–O(6W)	86.5(14)
Cl(1)–Sn–O(6W)	176.0(11)	C(21)–Sn–C(1)	121.5(17)
C(11)–Sn–C(1)	116.0(16)	C(21)–Sn–Cl(1)	96.0(13)
C(11)–Sn–C(21)	118.5(17)	C(21)–Sn–O(6W)	83.5(16)

The compound crystallizes monoclinically with one molecule in the unit cell. The tin atom in $4 \cdot H_2O$ is pentacoordinate and adopts a distorted trigonal-bipyramidal configuration [geometrical goodness $\Delta(\Sigma\vartheta) = 68.5°$].[26,27] The equatorial positions are occupied by C(1), C(11), C(21) and the axial positions by Cl(1) and the water oxygen atom. The tin atom is displaced by 0.22 Å from the plane defined by C(1), C(11), C(21) in the direction of Cl(1). The Sn(1)–Cl(1) and Sn–O(6W) distances of 2.453(1) and 2.469(4) Å, respectively, are comparable with those of other aqua complexes of organotin chlorides.[28,29] In CH_2Cl_2 solution, compound

4·H_2O shows a dissociation equilibrium between **4**·H_2O and **4** + H_2O. The equilibrium is fast on the NMR time-scale with the population of **4** + H_2O dominating at room temperature (δ^{119}Sn = 2 ppm). However, at –70 °C the aqua complex **4**·H_2O dominates (δ^{119}Sn = –155 ppm). These results are supported by NOE decoupling experiments at different temperatures. At room temperature the water proton resonance shows a large NOE to the resonances of the crown ether ring suggesting hydrogen bonding to the oxygen atoms of the latter. Upon lowering of the temperature, this NOE becomes smaller, which implies a larger distance between the crown ether protons and the water protons.

Complexation Studies

In comparison to the organotin-substituted crown ether **2**, the ^{13}C NMR spectrum of its sodium complex **2a** shows low-field shifts of approximately 2 ppm for the crown ether carbon resonances. The same effect was observed for the ^{13}C NMR spectrum ($CDCl_3/CD_3CN$, 4:1) of the chlorodiphenylstannyl-substituted crown ether **4** to which 1 mol-equiv. of sodium tetraphenylborate ($NaBPh_4$) had been added. This clearly indicates complexation of the sodium cation by the crown ether. The ^{119}Sn NMR spectrum of the same solution showed a single resonance at δ = –9.2 ppm indicating, as expected, no coordination of the tetraphenylborate anion.

The ^{119}Sn NMR spectrum at –70 °C of a CD_2Cl_2 solution of the triorganotin chloride **4,** to which 1 mol-equiv. of $[(Ph_3P)_2N]Cl$ had been added, showed a single resonance at δ = –198 ppm indicating the in situ formation of the dichlorotriorganostannate [**4**·Cl][$(Ph_3P)_2N$] (**4a**). In a similar manner, addition of $n$$Bu_4NSCN$ to a solution of the triorganotin rhodanide **5** afforded, in situ, the complex [**5**·SCN][$n$$Bu_4N$] (**5a**). Its ^{119}Sn NMR spectrum at –70 °C showed a single resonance at δ = –253 ppm. The ^{119}Sn NMR spectrum at –70 °C of a solution of the chlorodiphenylstannyl-substituted crown ether **4**, to which 1 mol-equiv. of Bu_4NSCN had been added, showed three resonances at δ = –198 ppm (signal a, integral 18), –216 ppm (signal b, integral 69) and –253 ppm (signal c, integral 13). Addition of a further 3 mol-equiv. of Bu_4NSCN changed the integral ratios of signals (a), (b) and (c) to 9, 69, and 21, respectively. Signals (a) and (c) are assigned to **4a** and **5a**, respectively, whereas signal (b) is tentatively assigned to [**4**·SCN][$n$$Bu_4N$] (**4b**). The latter assignment is supported by the observation of the same ^{119}Sn chemical shift of a CD_2Cl_2 solution of the triorganotin rhodanide **5** to which 1 mol-equiv. of $[(Ph_3P)_2N]Cl$ had been added, and by the fact that organostannate complexes of type $[R_3SnXY]^-$ are more stable than their corresponding symmetrically substituted derivatives $[R_3SnX_2]^-$ and $[R_3SnY_2]^-$.[30] The ^{119}Sn NMR spectra at room temperature of all the solutions mentioned above showed no resonances, indicating fast exchange between the species present in the corresponding samples.

The ^{119}Sn NMR spectrum at room temperature of a solution of the triorganotin chloride **4** in CD_2Cl_2 to which 1 mol-equiv. of NaSCN had been added showed in comparison to compound **4** a low-frequency-shifted single broad resonance at δ = –225 ppm ($\nu_{1/2}$ = 2013 Hz) which at –60 °C shifted to δ = –248 ppm ($\nu_{1/2}$ = 937 Hz). The ^{13}C NMR spectrum of the same solution showed $^1J(^{13}C\text{-}^{117/119}Sn)$ coupling constants of 595/621 and 716/751 Hz to the Sn–CH_2 and Sn–C_i carbon atoms, respectively, that are larger than the corresponding couplings of 426/446 and 540/566 Hz measured for compound **4**. Both the ^{119}Sn chemical shifts and the $^1J(^{13}C\text{-}^{117/119}Sn)$ coupling constants clearly indicate the tin atom in the complex [**4**·NaSCN] to be pentacoordinate. The ultimate evidence for the coordination of the rhodanide anion to the tin atom stems (i) from the observation of a $^2J(^{13}C\text{-}^{117/119}Sn)$ coupling of 59 Hz to the rhodanide carbon atom and (ii) from an HMBC correlation experiment showing a ^5J coupling of the *o*-phenyl protons to the rhodanide carbon atom. The binding of the sodium cation to the crown ether oxygen atoms is clearly evidenced by similar high-frequency shifts of the ^{13}C resonances for the crown ether carbon atoms as observed for the sodium complex **2a** (see above).

These results unambiguously prove that the chlorodiphenylstannyl-substituted crown ether **4** is a ditopic receptor simultaneously binding the sodium cation and rhodanide anion.

This statement obtains further support from electrospray mass spectrometry (ESMS) and transport experiments. Thus, the ESMS spectrum (negative mode) of a solution of the triorganotin chloride **4** to which NaSCN had been added showed mass clusters at m/z = 685.14 and 766.22 which are assigned to $[\mathbf{5} + SCN]^-$ and $[\mathbf{5} + 2\ SCN + Na]^-$, respectively. In the positive mode the spectrum showed a major mass cluster at m/z = 650.05 which is assigned to $[\mathbf{5}\cdot Na]^+$. Minor mass clusters at m/z = 569.07 and 609.06 were also present which were assigned to $[\mathbf{4} - Cl]^+$ and $[\mathbf{4} - Cl + OH + Na]^+$, respectively.

The transport properties of the chlorodiphenylstannyl-substituted crown ether **4** were investigated by a U-tube experiment (Figure 3).

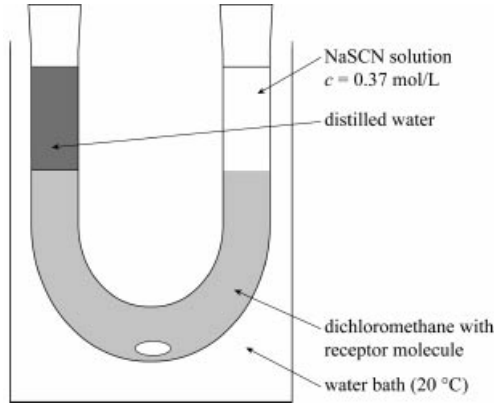


Figure 3. Schematic presentation of the U-tube experiment.

Figure 4 demonstrates the superior capability of compound **4** over triphenyltin chloride and the unsubstituted 15-benzocrown-5 to transport NaSCN from an aqueous

phase through a dichloromethane layer into another aqueous phase. This apparently becomes possible by the simultaneous complexation of the sodium cation and the rhodanide anion by the ditopic host **4**.

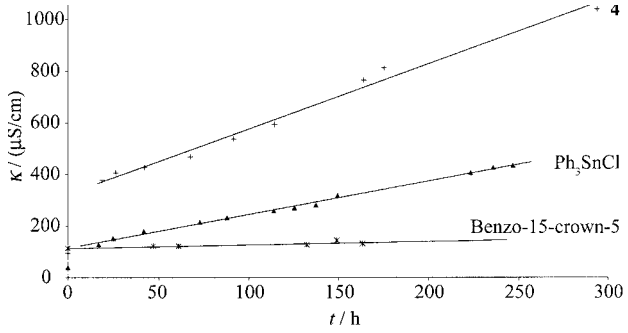


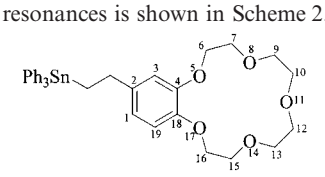
Figure 4. Plot of the electric conductivity vs. time illustrating the different ability of the triorganotin chloride **4**, triphenyltin chloride, and the unsubstituted crown ether benzo-15-crown-5 to transport sodium rhodanide through a dichloromethane layer. The concentration of **4**, Ph_3SnCl as well as that of the crown ether was 0.0268 mol/L.

Conclusions

Linking a chlorodiorganostannyl moiety via a dimethylene spacer with a crown ether was shown to provide the robust ditopic host **4** for the complexation of sodium rhodanide. It even serves for the efficient extraction of the latter from an aqueous solution. Given the large variety of crown ethers and related compounds such as azacrowns and cryptands on the one hand and the experience with mono- bi- and multicentered organometal-based Lewis acids on the other, the concept of combining representatives of these classes of compounds in one molecule appears to be promising for designing tailor-made hosts for the complexation of any salt.

Experimental Section

General Methods: All solvents were purified by distillation under nitrogen from appropriate drying agents. The hydrostannylation was carried out under nitrogen. 4-Vinylbenzo-15-crown-5[24,25] and triphenyltin hydride[31] were synthesized as described in the literature. The NMR experiments were carried out with Bruker DRX 500, Bruker DRX 400, DPX 300, Varian Nova 600 and Varian Mercury 200 spectrometers. Chemical shifts δ are given in ppm and are referenced to the solvent peaks with the usual values calibrated against tetramethylsilane (^1H, ^{13}C) and tetramethylstannane (^{119}Sn). The numbering of the carbon atoms applied for the assignment of the ^{13}C resonances is shown in Scheme 2.



Scheme 2.Numbering scheme for the assignment of the ^{13}C NMR resonances.

The ability of compound **4** to transport the rhodanide anion through an organic phase was investigated by U-tube experiments as shown in Figure 3. The conductivity was determined with an apparatus of the type LF530 from the company Wissenschaftlich-Technische Werkstätten. The cell was calibrated at 20 °C with an NaCl standard solution. The rhodanide transported to the aqueous layer was identified by reaction with iron(III).

Complexation Studies: The samples for ^1H, ^{13}C and ^{119}Sn NMR spectroscopy were prepared by dissolving the triorganotin chloride **4** (ca. 80 mg) and the corresponding amounts of $NaBPh_4$, nBu_4NSCN and NaSCN in deuterated solvents. The ^1H (400.1 MHz) and ^{13}C (100.6 MHz) spectra were recorded at 303 K whereas the ^{119}Sn (149.4 MHz) NMR spectra were recorded at both 303 and 208 K. NaSCN was dried in vacuo (10^{-3} Torr) at 100 °C for several days and stored under nitrogen. $NaBPh_4$ and nBu_4NSCN were stored in a desiccator.

Crystallography: Crystals of **2a** were grown from ethanol and of **4**·H_2O from a CH_2Cl_2/Et_2O solution at –5 °C. Crystallographic data are collected in Table 3. Intensity data for the colorless crystals were collected with a Nonius KappaCCD diffractometer with graphite-monochromated Mo-K_α radiation. The data collections covered almost the whole sphere of the reciprocal space with 2 (**2a**), 4 (**4**·H_2O) sets at different κ angles and 203 (**2a**), 424 (**4**·H_2O) frames by ω-rotation (Δ/ω = 1°) at 2×90 s (**2a**), 70 s (**4**·H_2O) per frame. Crystal decay was monitored by repeating the initial frames at the end of the data collection. After analysis of the duplicate reflections, there was no indication of any decay. The structures were solved by direct methods (SHELXS97[32]) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (SHELXL97[33]). The H atoms were placed in geometrically calculated positions using a riding model with U_{iso} constrained at 1.2 times U_{eq} of the carrier C atom, whereas the H atoms [H(6W1), H(6W1)] (**4**·H_2O) bonded to the water molecule O(6W) were located in the difference Fourier map and refined isotropically. In **2a** there are two C atoms disordered over two sites with occupancies of 0.5 [C(42), C(43), C(43′), C(44′)], whereas C(43′) is refined isotropically. In **4**·H_2O one Cl atom of the solvent molecule CH_2Cl_2 is disordered over two sites with occupancies of 0.9 [Cl(3) and 0.1 Cl(3′)]. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref.[34] The figures were created by SHELXTL.[35] CCDC-248340 (**2a**) and -248341 (**4**·H_2O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[2-(6,7,9,10,12,13,15,16-Octahydro-5,8,11,14,17-pentaoxabenzocyclopentadec-2-yl)ethyl]triphenylstannane (2): 4-Vinylbenzo-15-crown-5 (12.8 g, 44 mmol) and AIBN (115 mg) were added to Ph_3SnH (26.7 g, 41 mmol). The mixture was stirred at 70 °C for 12 h. After cooling to room temperature, CH_2Cl_2 (40 mL) was added and the solution was filtered through Celite. The filtrate was concentrated to give a yellow oil. The latter was purified by column chromatography (silica gel, CH_2Cl_2). Elution with ethanol gave 16.9 g (60%) of **2** as a slightly yellow oil. ^1H NMR (400.1 MHz, $CDCl_3$, 300 K): δ = 1.80 [t, $^3J(^1H\text{-}^1H)$ = 7.7, $^3J(^1H\text{-}^{117/119}Sn)$ = 54.5 Hz, 3 H, Sn–CH_2], 2.93 [t, $^3J(^1H\text{-}^1H)$ = 7.7, $^2J(^1H\text{-}^{117/119}Sn)$ = 56.9 Hz, 2 H, CH_2–Ar], 3.72–3.79 [m, 8 H, H(9)–H(13)], 3.82–3.85 [m, 2 H, H(7)], 3.87–3.93 [m, 2 H, H(15)], 3.94–3.98 [m, 2 H, H(6)], 4.07–4.10 [m, 2 H, H(16)], 6.62 {d, ^3J[H(1)-H(19)] = 2.0 Hz, 1 H, H(19)}, 6.66 {dd, ^3J[H(1)-H(19)] = 2.0, ^4J[H(1)-H(3)] = 8.2 Hz, 1 H, H(1)}, 6.73 {d, ^4J[H(1)-H(3)] = 8.2 Hz, 1 H, H(3)}, 7.32–7.45 (m, 15 H, $SnPh_3$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 300 K): δ = 13.1 [$^1J(^{13}C\text{-}^{117/119}Sn)$ = 383 Hz, Sn–CH_2], 32.0 [$^2J(^{13}C\text{-}^{117/119}Sn)$ = 18 Hz, CH_2–Ar], 69.1 [C(6)], 69.7 [C(16)], 69.8 [C(7)],

Table 3. Crystallographic data of **2a** and **4**·H_2O.

	2·NaSCN	**4**·H_2O
Empirical formula	$C_{34}H_{38}O_5Sn$·NaSCN	$C_{29}H_{35}Cl_3O_5Sn$·H_2O
Formula mass [g/mol]	726.40	706.63
Crystal system	monoclinic	triclinic
Crystal size	0.08 × 0.04 × 0.04	0.15 × 0.13 × 0.13
Space group	$P2_1/b$	$P\bar{1}$
a [Å]	22.0800(17)	10.6889(3)
b [Å]	9.9015(7)	12.1158(3)
c [Å]	16.0185(9)	13.1338(4)
α [°]	90.00	84.0147(10)
β [°]	103.277(3)	76.4871(11)
γ [°]	90.00	69.7220(12)
V [Å^3]	3408.4(4)	1550.80(7)
Z	4	2
$\rho_{calcd.}$ [mg/m^3]	1.416	1.513
μ [mm^{-1}]	0.864	1.121
F(000)	1488	720
θ range [°]	2.98–25.04	3.17–25.36
Index ranges	$-26 \le h \le 25$	$-12 \le h \le 12$
	$-11 \le k \le 11$	$-13 \le k \le 14$
	$-17 \le l \le 17$	$-15 \le l \le 15$
No. of reflections collected	18544	19140
Completeness of θ_{max} (%)	89.0	99.8
No. of independent reflections/$R_{int.}$	5367/0.085	5680/0.037
No. of reflections observed with [$I > 2\sigma(I)$]	1522	3606
No. of refined parameters	410	369
GoF(F^2)	0.597	0.920
$R_1(F)$ [$I > 2\sigma(I)$]	0.0399	0.0427
$wR_2(F^2)$ (all data)	0.0944	0.1006
$(\Delta/\sigma)_{max.}$	0.001	0.001
Largest difference peak/hole [e/Å^3]	0.259/–0.219	0.826/–0.779

69.9 [C(15)], 70.8–71.3 [C(9)–C(13)], 114.1 [C(19)], 114.5 [C(3)], 120.4 [C(1)], 128.4 [^3J(^{13}C-$^{117/119}$Sn) = 47 Hz, Sn–Ph C(*m*)], 128.8 [^4J(^{13}C-$^{117/119}$Sn) = 10 Hz Sn–Ph, C(*p*)], 137.0 [^2J(^{13}C-$^{117/119}$Sn) = 36 Hz, Sn–Ph C(*o*)], 138.1 [^3J(^{13}C-$^{117/119}$Sn) = 55 Hz, C(2)], 138.7 [Sn–Ph C(*i*)], 147.3 [C(18)], 149.1 [C(4)] ppm. ^{119}Sn{^{1}H} NMR (149.2 MHz, CH_2Cl_2, D_2O capillary, 300 K): δ = –103 ppm. $C_{34}H_{38}O_5Sn$ (645.37): calcd. C 63.3, H 5.9; found C 63.0, H 5.9.

Iodo[2-(6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxabenzocyclopentadec-2-yl)ethyl]diphenylstannane (3): Iodine (2.78 g, 10.97 mmol) was added in small portions to a magnetically stirred solution of **2** (7.07 g, 10.97 mmol) in CH_2Cl_2 (50 mL) in an ice bath. The reaction mixture was stirred overnight. The solvent and the iodobenzene were removed in vacuo. Addition of CH_2Cl_2 (20 mL), filtration and evaporation of the solvent afforded 7.46 g (97%) of **2** as a slightly yellow oil. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 2.09 [t, ^3J(^{1}H-^{1}H) = 8.0, ^2J(^{1}H-$^{117/119}$Sn) = 52.6 Hz, 2 H, Sn–CH_2], 2.30 [t, ^3J(^{1}H-^{1}H) = 8.0, ^3J(^{1}H-$^{117/119}$Sn) = 88.5 Hz, 2 H, Ar-CH_2], 3.68–3.75 (m, 8 H, OCH_2), 3.77–3.82 (m, 4 H, OCH_2), 3.83–3.88 (m, 4 H, OCH_2), 3.91–3.96 (m, 4 H, OCH_2), 4.01–4.07 (m, 4 H, OCH_2), 6.65 (s, 1 H, Ar-H), 6.68 (s, 2 H, Ar-H), 7.30–7.50 (m, 10 H, Sn–Ph) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$, 300 K): δ = 19.9 (Sn–CH_2), 31.8 (CH_2–Ar), 68.6–70.7 [C(6)–C(16)], 114.1 [C(3)], 114.5 [C(19)], 120.5 [C(1)], 128.6 [^3J(^{13}C-$^{117/119}$Sn) = 58 Hz, Sn–Ph C(*m*)], 129.7 [Sn–Ph C(*p*)], 135.8 [^2J(^{13}C-$^{117/119}$Sn) = 47 Hz, Sn–Ph C(*o*)], 136.3 [C(2)], 137.2 [Sn–Ph C(*i*)], 147.4 [C(18)], 148.9 [C(4)] ppm. ^{119}Sn{^{1}H} NMR (111.91 MHz, CH_2Cl_2, D_2O capillary): δ = –130 ppm. $C_{24}H_{33}IO_5Sn$ (695.17): calcd. C 48.4, H 4.8; found C 48.3, H 4.9.

Aqua Complex of Chloro[2-(6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxabenzocyclopentadec-2-yl)ethyl]diphenylstannane (4·H_2O): AgCl (3.08 g, 21.48 mmol) was added to a solution of **3** (7.46 g, 10.47 mmol) in CH_3CN (100 mL). After stirring in darkness for 14 d, the solution was filtered. The solvent was evaporated to give a light yellow oil. The latter was dissolved in CH_2Cl_2/Et_2O (2:1) and cooled to –5 °C for several days to give 3 g (73%) of **4** as colorless crystals. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 300 K): δ = 2.08 [t, ^3J(^{1}H-^{1}H) = 7.8, ^2J(^{1}H-$^{117/119}$Sn) = 59.2 Hz, 2 H, Sn–CH_2], 3.08 [t, ^3J(^{1}H-^{1}H) = 7.8, ^3J(^{1}H-$^{117/119}$Sn) = 87.8 Hz, 2 H, CH_2–Ar], 3.62–3.67 [m, 8 H, H(9)–H(13)], 3.74–3.77 [m, 2 H, H(7)], 3.78–3.83 [m, 2 H, H(15)], 3.87–3.91 [m, 2 H, H(6)], 3.99–4.04 [m, 2 H, H(16)], 6.67–6.75 (m, 3 H, Ar), 7.39–7.78 (m, 10 H, Sn–Ph) ppm. ^{13}C{^{1}H} NMR (100.63 MHz, CD_2Cl_2 300 K): δ = 20.9 [^1J(^{13}C-^{117}Sn) = 426, ^1J(^{13}C-^{119}Sn) = 446 Hz, Sn–CH_2], 31.0 [^2J(^{13}C-$^{117/119}$Sn) = 23 Hz, CH_2–Ar], 68.4 [C(6)], 68.8 [C(16)], 69.3 [C(7)], 69.4 [C(15)], 70.1–70.6 [C(9)–C(13)], 113.6 [C(19)], 114.0 [C(3)], 120.3 [C(1)], 128.8 [^3J(^{13}C-$^{117/119}$Sn) = 59 Hz, Sn–Ph C(*m*)], 129.9 [^4J(^{13}C-$^{117/119}$Sn) = 13 Hz Sn–Ph C(*p*)], 135.8 [^2J(^{13}C-$^{117/119}$Sn) = 47 Hz, Sn–Ph C(*o*)], 137.3 [^3J(^{13}C-$^{117/119}$Sn) = 61 Hz, C(2)], 139.6 [^1J(^{13}C-^{117}Sn = 540, ^1J(^{13}C-^{119}Sn) = 566 Hz, Sn–Ph C(*i*)], 146.6 [C(18)], 148.3 [C(4)] ppm. ^{119}Sn{^{1}H} NMR (111.9 MHz, CD_2Cl_2, 298 K): δ = 2 ppm. ^{119}Sn{^{1}H} NMR (111.9 MHz, CD_2Cl_2, 193 K): δ = –155 ppm. $C_{28}H_{33}ClO_5Sn$·H_2O (621.74): calcd. C 54.1, H 5.7; found C 53.7, H 5.7.

[2-(6,7,9,10,12,13,15,16-Octahydro-5,8,11,14,17-pentaoxabenzocyclopentadec-2-yl)ethyl]diphenyl(thiocyanato)stannane (5): AgSCN (8.30 g, 50.04 mmol) was added to a solution of **3** (3.50 g, 5.04 mmol) in CH_3CN (150 mL). The reaction mixture was stirred in darkness for 12 h followed by filtration from AgI and unreacted AgSCN. The filtrate was concentrated to give a light yellow solid. The latter was recrystallized from methanol to give 3.0 g (98%) of **5** as a colorless solid. ^{1}H NMR (400.13 MHz, CD_3OD, 300 K): δ = 1.93 [t, ^3J(^{1}H-^{1}H) = 7.5, ^2J(^{1}H-$^{117/119}$Sn) = 67.3 Hz, 2 H, Sn–

CH_2], 3.12 [t, $^3J(^1H\text{-}^1H)$ = 7.8, $^3J(^1H\text{-}^{117/119}Sn)$ = 102.4 Hz, 2 H, CH_2–Ar], 3.55–4.00 (m, 16 H, CH_2O), 6.65–6.90 (m, 3 H, Ar), 7.29–7.64 (m, 10 H, Sn–Ph) ppm. $^{13}C\{^1H\}$ NMR (150.84 MHz, CD_2Cl_2, 300 K): δ = 23.3 (Sn–CH_2), 31.6 [$^2J(^{13}C\text{-}^{117/119}Sn)$ = 28 Hz, CH_2–Ar], 66.6–68.7 (CH_2O), 113.1 [C(19)/C(3)], 120.8 [C(1)], 128.6 [$^3J(^{13}C\text{-}^{117/119}Sn)$ = 64 Hz, $SnPh_2$ C(*m*)], 129.3 [$SnPh_2$ C(*p*)], 135.4 [SCN, determined by HMBC experiment], 136.4 [$^2J(^{13}C\text{-}^{117/119}Sn)$ = 46 Hz, $SnPh_2$ C(*o*)], 138.2 [$SnPh_2$ C(*i*)], 138.4 [C(2)], 141.9 [C(18)], 145.6 [C(4)] ppm. $^{119}Sn\{^1H\}$ NMR (111.9 MHz, $CDCl_3$): δ = –180 ($\nu_{1/2}$ = 1930 Hz) ppm.

Sodium Rhodanide Complex 2a: The triorganotin chloride **2** (1 g, 1.55 mmol) and NaSCN (0.170 g, 1.55 mmol) were dissolved in ethanol (5 mL) and the mixture was heated at reflux for 1 h. The reaction mixture was cooled to room temperature providing 700 mg (62%) of **2a** as colorless crystals. ^1H NMR (400.1 MHz, $CDCl_3$, 300 K): δ = 1.77 [t, $^3J(^1H\text{-}^1H)$ = 8.28, $^2J(^1H\text{-}^{117/119}Sn)$ = 52.2 Hz, 2 H, $SnCH_2$], 2.93 [t, $^3J(^1H\text{-}^1H)$ = 8.28, $^3J(^1H\text{-}^{117/119}Sn)$ = 56.5 Hz, 2 H, CH_2–Ar], 3.71 (m, 4 H, OCH_2), 3.79 (m, 4 H, OCH_2), 3.86 (m, 2 H, OCH_2), 3.93 (m, 4 H, OCH_2), 4.11 (m, 2 H, OCH_2), 6.58 [s, 1 H, H(3)], 6.70 [s, 2 H, H(1), H(19)], 7.43–7.33 (m, 15 H, Sn–Ph) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$ 300 K): δ = 13.0 (Sn–CH_2), 31.8 (CH_2–Ar), 69.0–66.5 [C(6)–C(16)], 112.3 [C(19)], 112.4 [C(3)], 121.0 [C(1)], 128.4 [$^3J(^{13}C\text{-}^{117/119}Sn)$ = 49 Hz, Sn–Ph C(*m*)], 128.8 [$^4J(^{13}C\text{-}^{117/119}Sn)$ = 11 Hz, Sn–Ph C(*p*)], 136.8 [$^2J(^{13}C\text{-}^{117/119}Sn)$ = 35 Hz, Sn–Ph C(*o*)], 138.5 [C(2)], 138.7 [Sn–Ph C(*i*)], 144.6 [C(4)], 146.3 [C(18)] ppm. $^{119}Sn\{^1H\}$ NMR (149.2 MHz, $CDCl_3$): δ = –104 ppm. $C_{35}H_{38}NNaO_5SSn$ (726.45): calcd. C 57.7, H 5.3, N 1.9; found C 58.0, H 5.3, N 1.9.

Complex [4·Na][BPh_4]: ^1H NMR (400.1 MHz, $CDCl_3/CD_3CN$, 4:1, 300 K): δ = 2.08 [t, $^3J(^1H\text{-}^1H)$ = 7.9, $^2J(^1H\text{-}^{117/119}Sn)$ = 56.8 Hz, 2 H, Sn–CH_2], 3.12 [t, $^3J(^1H\text{-}^1H)$ = 7.8, $^3J(^1H\text{-}^{117/119}Sn)$ = 52.0 Hz, 2 H, CH_2–Ar], 3.58–3.67 [m, 8 H, H(9)–H(13)], 3.68–3.77 [m, 2 H, H(7)], 3.78–3.82 [m, 2 H, H(15)], 3.88–3.92 [m, 2 H, H(6)], 3.98–4.04 [m, 2 H, H(16)], 6.76–6.80 (m, 3 H, Ar), 6.87 (m, BPh_4^-), 7.02 [t, $^3J(^1H\text{-}^1H)$ = 7.2 Hz, BPh_4^-], 7.37–7.60 (m, 10 H, Sn–Ph) ppm. $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3/CD_3CN$, 4:1, 300 K): δ = 20.5 (Sn–CH_2), 30.3 (CH_2–Ar), 66.3 [C(6)], 66.7 [C(16)], 67.2 [C(7)], 67.3 [C(15)], 67.8–68.1 [C(9)–C(13)], 112.9 [C(19)], 113.1 [C(3)], 116.3 (BPh_4^-), 121.1 [C(1)], 121.3 (BPh_4^-), 124.1 (BPh_4^-), 128.2 [$^3J(^{13}C\text{-}^{117/119}Sn)$ = 59 Hz, Sn–Ph, C(*m*)], 129.3 [$^4J(^{13}C\text{-}^{117/119}Sn)$ = 14 Hz, Sn–Ph C(*p*)], 135.2 [$^2J(^{13}C\text{-}^{117/119}Sn)$ = 43 Hz, Sn–Ph C(*o*)], 135.4 (BPh_4^-), 137.5 [C(2)], 139.2 [Sn–Ph C(*i*)], 144.6 [C(18)], 146.1 [C(4)], 162.7–164.2 (q, BPh_4^-) ppm. $^{119}Sn\{^1H\}$ NMR (149.2 MHz, $CDCl_3/CD_3CN$, 4:1, 300 K): δ = –9 ppm.

Complex [$n$$Bu_4N$][4·SCN]: ^1H NMR (400.1 MHz, CD_2Cl_2, 300 K): δ = 0.93 [t, $^3J(^1H\text{-}^1H)$ = 8 Hz, 12 H, $n$$Bu_4N^+$ CH_3], 1.29 [q, $^3J(^1H\text{-}^1H)$ = 7.3 Hz, 8 H, $n$$Bu_4N^+$ CH_2], 1.45 (m, 8 H, $n$$Bu_4N^+$ CH_2), 1.91 [t, $^3J(^1H\text{-}^1H)$ = 8.8, $^2J(^1H\text{-}^{117/119}Sn)$ = 74.8 Hz, 2 H, Sn–CH_2], 2.93 (m, 8 H, $n$$Bu_4N^+$ N–CH_2), 3.0 [t, $^3J(^1H\text{-}^1H)$ = 8.8, $^3J(^1H\text{-}^{117/119}Sn)$ = 52.3 Hz, 2 H, CH_2–Ar], 3.65 [s, 8 H, H(9)–H(13)], 3.75–3.84 [m, 4 H, H(7) H(15)], 3.98–4.05 [m, 4 H, H(6) H(15)], 6.72–6.84 (m, 3 H, Ar), 7.25–7.40 [m, 6 H, Sn–Ph H(*m*), H(*p*)], 7.84–8.20 [m, $^3J(^1H\text{-}^{117/119}Sn)$ = 30.6 Hz, 4 H, Sn–Ph H(*o*)]. $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 300 K): δ = 13.3 ($n$$Bu_4N^+$), 19.5 ($n$$Bu_4N^+$), 23.6 ($n$$Bu_4N^+$), 31.5 ($CH_2$–Ar), 58.5 ($n$$Bu_4N^+$), 68.4 [C(6)], 69.0 [C(16)], 69.3 [C(7)], 69.4 [C(15)], 70.1–70.5 [C(9)–C(13)], 113.9 [C(19)], 114.1 [C(3)], 120.2 [C(1)], 127.6 [$^3J(^{13}C\text{-}^{117/119}Sn)$ = 64 Hz, Sn–Ph, C(*m*)], 128.1 [Sn–Ph C(*p*)], 136.7 [$^2J(^{13}C\text{-}^{117/119}Sn)$ = 47 Hz, Sn–Ph C(*o*)], 138.9 [C(2)], 146.8 [C(18)], 148.8 [C(4)] ppm. $^{119}Sn\{^1H\}$ NMR (149.2 MHz, CD_2Cl_2, 300 K): no resonance found. $^{119}Sn\{^1H\}$ NMR (149.2 MHz, CD_2Cl_2, 208 K): δ = –253 (13%), –217 (69%), –198 (18%) ppm.

Complex [$n$$Bu_4N$][5·SNC]: $^{119}Sn\{^1H\}$ NMR (149.2 MHz, CD_2Cl_2, 203 K): δ = 308 (3%), –252 (97%) ppm.

Complex [$(Ph_3P)_2N$][5·Cl]: $^{119}Sn\{^1H\}$ NMR (149.2 MHz, CD_2Cl_2, 203 K): δ = –250 (19%), –214 (64%), –197 (17%) ppm.

Complex 4·NaSCN: ^1H NMR (400.1 MHz, CD_2Cl_2, 300 K): δ = 1.96 [t, $^3J(^1H\text{-}^1H)$ = 8.3, $^2J(^1H\text{-}^{119/117}Sn)$ = 66.0 Hz, 2 H, Sn–CH_2], 3.10 [t, $^3J(^1H\text{-}^1H)$ = 8.0, $^3J(^1H\text{-}^{117/119}Sn)$ = 84.8 Hz, 2 H, CH_2–Ar], 3.47–3.60 [m, 8 H, H(9)–H(13)], 3.61–3.70 [m, 4 H, H(7), H(15)], 3.80–3.92 [m, 4 H, H(6), H(16)], 6.61–6.80 (m, 3 H, Ar), 7.30–7.79 (m, 10 H, Sn–Ph) ppm. $^{13}C\{^1H\}$ NMR (150.84 MHz, CD_2Cl_2, 300 K): δ = 24.8 [$^1J(^{13}C\text{-}^{117}Sn)$ = 595, $^1J(^{13}C\text{-}^{119}Sn)$ = 621 Hz, Sn–CH_2], 31.5 [$^2J(^{13}C\text{-}^{117/119}Sn)$ = 32 Hz, CH_2–Ar], 67.2–69.2 [C(6)–C(16)], 113.5 [C(19)], 113.6 [C(3)], 121.8 [C(1)], 128.3 [$^3J(^{13}C\text{-}^{117/119}Sn)$ = 66 Hz, Sn–Ph, C(*m*)], 129.1 [$^4J(^{13}C\text{-}^{117/119}Sn)$ = 13 Hz, Sn–Ph C(*p*)], 135.6 [N=C=S, $^2J(^{13}C\text{-}^{117/119}Sn)$ = 59 Hz], 136.5 [$^2J(^{13}C\text{-}^{117/119}Sn)$ = 45 Hz, Sn–Ph C(*o*)], 139.2 [$^3J(^{13}C\text{-}^{117/119}Sn)$ = 68 Hz, C(2)], 142.7 [$^1J(^{13}C\text{-}^{117}Sn)$ = 716, $^1J(^{13}C\text{-}^{119}Sn)$ = 751 Hz, Sn–Ph C(*i*)], 144.9 [C(18)], 146.7 [C(4)] ppm. $^{119}Sn\{^1H\}$ NMR (149.2 MHz, CD_2Cl_2, 298 K): δ = –225 ($\nu_{1/2}$ = 2013 Hz) ppm. $^{119}Sn\{^1H\}$ NMR (149.2 MHz, CD_2Cl_2, 203 K): δ = –248 ($\nu_{1/2}$ = 937 Hz) ppm. ESMS (+p): *m*/z = 650.1 [$Ph_2Sn(SCN) - C_{16}H_{23}O_5$]·$Na^+$. ESMS (–p): *m*/*z* = 685.1 [$Ph_2Sn(SCN)_2 - C_{16}H_{23}O_5$]$^-$, 766.2 [$Ph_2Sn(SCN)_2 - C_{16}H_{23}O_5$·NaSCN]$^-$.

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