Functionalization of 1,3-Phenylene-16-crown-5 *via* Direct Lithiation

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1,3-Phenylene-16-crown-5 (**1**) was selectively and quantitatively lithiated at the intraannular 2-position with *n*-butyllithium, making functionalization of this system easier than that of the 1,3-xylylene crown ethers. The lithiation yielded the corresponding (2-lithio-1,3-phenylene)-16-crown-5 (**2**) without cleavage of the polyether ring. Subsequent reaction with deuterium oxide, dimethyl disulfide, iodine, carbon dioxide, dimethyltin dichloride (0.5 molar equiv), mercury dibromide (0.5 molar equiv), benzyl bromide, and magnesium dibromide yielded (2-deuterio-1,3-phenylene)-16-crown-5 (**3**), [2-(methylthio)-1,3-phenylene]-16-crown-5 (**4**), (2-iodo-1,3-phenylene)-16-crown-5 (**5**), (2-carboxy-1,3-phenylene)-16-crown-5 (**6**), dimethylbis[(1,3-phenylene-16-crown-5)-2-yl]stannane (**7**), bis[(1,3-phenylene-16-crown-5)-2-yl]mercury (**8**), 2-benzyl-1,3-phenylene-16-crown-5 (**9**), and [2-(bromomagnesio)-1,3-phenylene]-16-crown-5 (**10**), respectively. Functionalized analogues of this crown ether have not been reported previously. X-ray crystal structures of **6**, **7**, and **10** were determined. According to the crystal structure of **6**, the carboxylic substituent takes part in intramolecular hydrogen bonding with a transannular crown ether oxygen (O(8)). The crystal structure of **7** is the first one for a bis(crown ether)tin(IV) compound and reveals close proximity between tin and four of the ten crown ether oxygens. In the Grignard reagent **10** the magnesium is hexacoordinated in a distorted-octahedral fashion with the bromine and a THF oxygen in the apical positions and three of the five crown ether oxygens plus carbon C(1) in planar positions. It is the first example of a crown ether Grignard reagent in which the metal center is not completely intramolecularly coordinated.

Introduction

Crown ethers play an increasingly important role in chemistry. Various syntheses of crown ethers with intraannular functional groups have been described. Initially, 2-functionalized 1,3-bis(bromomethyl)benzenes were reacted with the appropriate oligo(ethylene glycol) to yield a crown ether with the desired intraannular functionality. In the case of carboxy-[1] and hydroxy-substituted[2] crown ethers, the functionalities require protection during crown ether formation, as they are not stable under the strongly basic conditions required for the ring closure. This generally led to multistep processes with low overall yields. An exception was the quantitative formation of (2-hydroxy-1,3-xylylene)-15-crown-4 and -18-crown-5 from the intraannular ether cleavage reactions of the analogous methoxy compounds with organomagnesium reagents.[3]

Other examples of intraannular functionalization *after* the formation of the crown ether have been reported. 2-Substituted-1,3-xylylene crown ethers, obtained from the corresponding lithium precursors, have been synthesized by Reinhoudt *et al.*[4] and by our group.[5] In these papers the organolithium precursors were prepared by bromine−lithium exchange. More convenient would be direct lithiation of 1,3-xylylene crown ethers; unfortunately, this cannot be achieved due to the reactivity of the benzylic hydrogens toward lithium reagents.[4,6] Therefore, crown ethers in which the oxygens are directly bonded to the aromatic ring, such as 1,3-phenylene-16-crown-5 (**1**), are of interest, in par-

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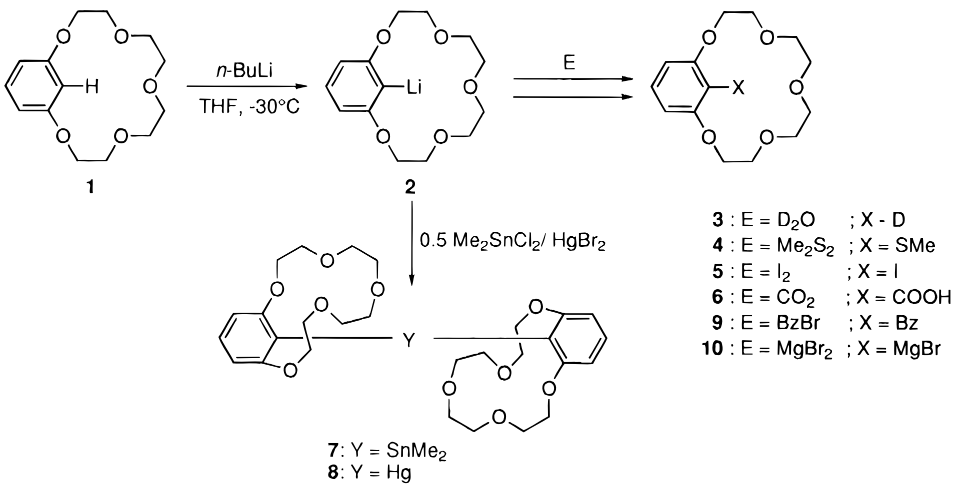
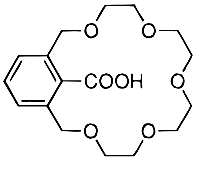
Scheme 1



ticular as 1,3-dimethoxybenzene is known to easily undergo lithiation at the 2-position.[7] With the exception of methoxy-substituted derivatives,[8] intraannular functionalized 1,3-phenylene crown ethers have not been reported previously.

In this paper, we report the successful lithiation of **1** to furnish its organolithium derivative **2** and the synthesis of a variety of intraannular substituted derivatives of **1** by the reaction of **2** with deuterium oxide, dimethyl disulfide, iodine, carbon dioxide, dimethyltin dichloride (0.5 molar equiv), mercury dibromide (0.5 molar equiv), benzyl bromide, and magnesium dibromide, yielding the compounds **3**–**10**, respectively (Scheme 1).

For three compounds the X-ray crystal structures were determined. The crystal structure of the carboxylic acid **6** was of interest in order to compare it with that of the previously reported (2-carboxy-1,3-xylylene)-18-crown-5 (**11**).[1,9]

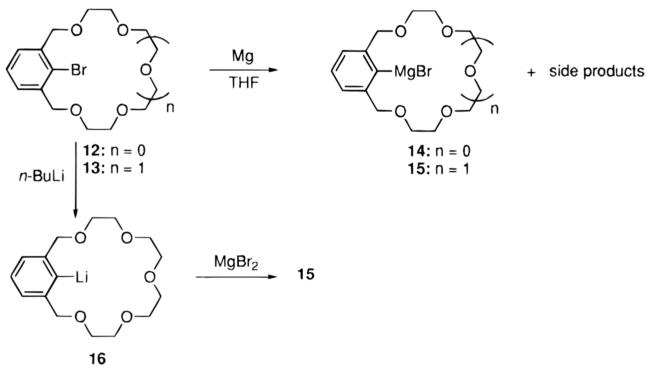


11

The crystal structure of the organotin compound **7** was of interest because it is the first bis(crown ether)tin(IV) compound. Unfortunately, a crystal structure could not be determined from single crystals obtained from the mercury compound **8**.

Previously, we reported that the reaction of the 2-bromo-1,3-xylylene crown ethers **12** and **13** with magnesium metal to prepare the 2-(bromomagnesio)-1,3-xylylene crown ethers **14** and **15** (Scheme 2) was accompanied by extensive crown ether ring cleavage, especially in the case of **15**.[10] Therefore, **15** was prepared preferentially *via* the organolithium precursor **16** (Scheme 2).[5] This method was also applied for the synthesis of the Grignard reagent **10**. The X-ray crystal structure of **10** was determined in order to relate it with those of **14** and **15**. Indeed, an interesting difference was observed: while in **14** and **15**, the magnesium is only coordinated *intramolecularly* to crown ether oxygens, **10** turned out to contain hexacoordinated magnesium by inclusion of an *intermolecular* coordinative bond to one molecule of THF.

Scheme 2



Results and Discussion

Lithiation of 1,3-Phenylene-16-crown-5 (1). Direct lithiation of the crown ether **1** with *n*-butyllithium proceeded in high yield. The reaction conditions were optimized by varying the reaction temperature, the reaction time, and the solvent. Best results were obtained when *n*-butyllithium (1.0–1.1 molar equiv) was added to **1** dissolved in THF (about 0.1 M) at −30 °C (Scheme 1). A few minutes after the addition of *n*-butyllithium to **1** in THF, a white suspension was formed, indicating that **2** has a low solubility. The crown ether ring is stable under these reaction conditions; ether cleavage induced by deprotonation of OCH_2CH_2O units[11,12] does not occur.

The yield of **2** was determined by a quenching reaction with either deuterium oxide or dimethyl disulfide (Scheme 1); the products **3** and **4** were isolated in 72%

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Table 1. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) of 6

(a) Bond Distances (Å)

C(15)−C(16)	1.376(4)	C(1)−C(19)	1.395(4)	C(20)−O(22)	1.331(3)
C(16)−C(17)	1.388(5)	C(19)−C(15)	1.392(4)	O(22)−H(22)	0.84(4)
C(17)−C(18)	1.376(5)	C(19)−C(20)	1.498(4)	H(22)···O(8)	1.93(4)
C(18)−C(1)	1.384(4)	C(20)−O(21)	1.199(3)		

(b) Bond Angles (deg)

O(21)−C(20)−C(19)	123.0(3)	O(22)−H(22)···O(8)	153(4)
O(22)−C(20)−C(19)	117.2(2)	C(20)−O(22)−H(22)	114(3)
C(1)−C(19)−C(20)	120.3(2)	O(21)−C(20)−O(22)	119.8(3)
C(15)−C(19)−C(20)	120.2(2)		

(c) Torsion Angles (deg)

C(16)−C(15)−C(19)−C(20)	−178.8(3)	O(2)−C(1)−C(19)−C(20)	0.6(4)
C(18)−C(1)−C(19)−C(20)	178.3(3)	O(14)−C(15)−C(19)−C(20)	−2.2(4)
C(1)−C(19)−C(20)−O(21)	−94.7(3)	O(2)−C(3)−C(4)−O(5)	−62.2(6)
C(15)−C(19)−C(20)−O(21)	83.7(4)	O(5)−C(6)−C(7)−O(8)	41.8(5)
C(1)−C(19)−C(20)−O(22)	86.0(3)	O(8)−C(9)−C(10)−O(11)	−61.8(4)
C(15)−C(19)−C(20)−O(22)	−95.6(3)	O(11)−C(12)−C(13)−O(14)	67.1(3)
O(21)−C(20)−O(22)−H(22)	179(4)		

and 79% yield, respectively, while almost no starting material was detected by GC−MS and ^{1}H NMR spectroscopy. Compound **2** was used for further intraannular functionalizations. In some reactions with electrophiles, **1** (hydrolyzed material) was formed as a byproduct; on the extremely small scale of the reactions (usually 0.20 mmol), even minimal traces of water will give a significant amount of hydrolysis.

Synthesis of (2-Iodo-1,3-phenylene)-16-crown-5 (5). When **2** was quenched with an excess of solid iodine, (2-iodo-1,3-phenylene)-16-crown-5 (**5**) was obtained (Scheme 1). The excess iodine was removed by addition of an aqueous solution of sodium thiosulfate. The corresponding iodo derivative of 1,3-xylylene-18-crown-5 was synthesized from **13** *via* **15** or **16** by reaction of either one of the latter compounds with iodine (Scheme 2).[5] For practical reasons, the synthesis of a 2-halogen-functionalized crown ether such as **5** *via* the organolithium intermediate is superior to halogen functionalization *before* formation of the crown ether ring.

Synthesis and Crystal Structure of (2-Carboxy-1,3-phenylene)-16-crown-5 (6). The carboxylic acid **6** was obtained in good yield by the reaction of **2** with carbon dioxide and subsequent acidification (Scheme 1). Suitable crystals for an X-ray crystal structure determination were obtained by recrystallization of **6** from dichloromethane/diethyl ether.

The crystal structure of **6** is shown in Figure 1. A selection of bond distances and angles and torsion angles is presented in Table 1. The atoms C(4)/C(41) and O(5)/O(51) are disordered with populations of 0.565(6) and 0.435(6) for the atoms C(4), O(5) and C(41), O(51), respectively. The syn-clinal values of the torsion angles of the OCH$_2$CH$_2$O units vary from 41.8(5) to 67.1(3)°.

The carboxylic C(20) is almost in the plane of the aromatic ring. The angle between the plane formed by the carboxy group (C(20), O(21), O(22)) and the aromatic C(19) and the aromatic ring is 85.04(16)°, while the angle between the carboxy group and the aromatic ring in the structure of **11** is 59°.[9] This difference is largely due to the different conformations of the crown ether moieties in **6** and **11**. In **11**, the crown ether unit is more or less twisted around the C(4)−C(1)−C(OOH) axis of the aromatic ring with roughly half of its atoms above and the other half below the aromatic plane;[9] in contrast, in **6** the average plane of the crown ether unit is approximately perpendicular to the aromatic plane, so that the carboxyl group has to adopt a perpendicular orientation in order to achieve hydrogen bonding to the opposite oxygen O(8) (hydrogen bond distance H(22)···O(8) = 1.93(4) Å; the angle O(22)−H(22)···O(8) is 153(4)°). The corresponding hydrogen bond to the central oxygen in **11** is slightly shorter (1.84 Å).[9]

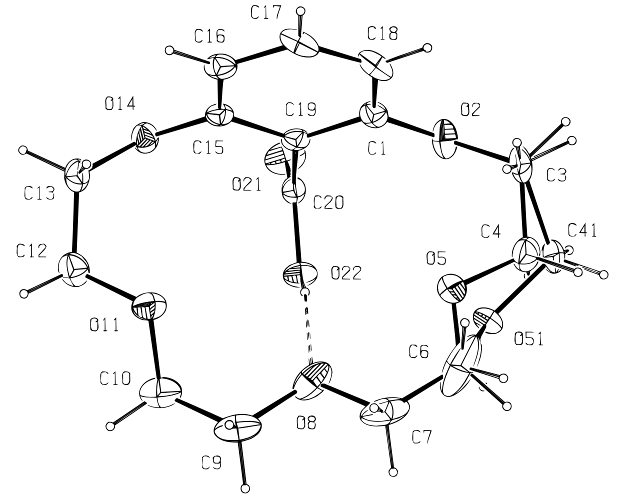

Figure 1. ORTEP[27] drawing of complex **6** at the 30% probability level.

Similar to the situation in **11**, the C···O nonbonded distances of **6** involving the electrophilic carboxy C(20) and the two nucleophilic crown ether oxygens O(2) and O(14) (C(20)···O(2), 2.736(4) Å; C(20)···O(14), 2.742(4) Å) are shorter than the van der Waals contact (3.22 Å); this may in part be due to attractive dipole−dipole interactions (O···C═O),[13] but probably, it is largely imposed by geometric restraints, as both the aryl oxygens and the carboxyl carbon are *ortho* substituents at an aryl moiety.

Synthesis and Crystal Structure of Dimethylbis[(1,3-phenylene-16-crown-5)-2-yl]stannane (7). The organotin compound **7** was synthesized from **2** and dimethyltin dichloride in the molar ratio 2:1 (Scheme 1). Suitable crystals for an X-ray crystal structure determination were obtained after recrystallization of **7** from diethyl ether. The crystal structure of **7** is shown

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Table 2. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) of 7

(a) Bond Distances (Å)			
Sn(1)−C(19)	2.148(3)	Sn(1)−C(39)	2.133(3)
Sn(1)−C(38)	2.152(2)	Sn(1)−C(40)	2.134(3)
(b) Bond Angles (deg)			
C(19)−Sn(1)−C(39)	113.19(11)	C(19)−Sn(1)−C(38)	110.98(11)
C(38)−Sn(1)−C(39)	106.16(11)	Sn(1)−C(19)−C(1)	118.7(2)
C(38)−Sn(1)−C(40)	113.66(11)	Sn(1)−C(19)−C(15)	123.2(2)
C(19)−Sn(1)−C(40)	107.63(12)	Sn(1)−C(38)−C(20)	119.4(2)
C(39)−Sn(1)−C(40)	105.20(12)	Sn(1)−C(38)−C(34)	123.1(2)
(c) Torsion Angles (deg)			
C(38)−Sn(1)−C(19)−C(1)	−67.9(2)	C(35)−C(34)−C(38)−Sn(1)	−179.7(2)
C(38)−Sn(1)−C(19)−C(15)	114.0(2)	C(37)−C(20)−C(38)−Sn(1)	−179.5(3)
C(39)−Sn(1)−C(19)−C(1)	172.8(2)	O(2)−C(1)−C(19)−Sn(1)	4.6(3)
C(39)−Sn(1)−C(19)−C(15)	−5.3(3)	O(14)−C(15)−C(19)−Sn(1)	−4.5(3)
C(40)−Sn(1)−C(19)−C(1)	57.0(2)	O(21)−C(20)−C(38)−Sn(1)	−3.6(4)
C(40)−Sn(1)−C(19)−C(15)	−121.1(2)	O(33)−C(34)−C(38)−Sn(1)	2.5(4)
C(19)−Sn(1)−C(38)−C(20)	−43.8(3)	O(2)−C(3)−C(4)−O(5)	−66.7(3)
C(19)−Sn(1)−C(38)−C(34)	−137.8(3)	O(5)−C(6)−C(7)−O(8)	78.9(3)
C(39)−Sn(1)−C(38)−C(20)	79.6(3)	O(8)−C(9)−C(10)−O(11)	166.9(3)
C(39)−Sn(1)−C(38)−C(34)	−98.8(3)	O(11)−C(12)−C(13)−O(14)	72.3(3)
C(40)−Sn(1)−C(38)−C(20)	−165.2(2)	O(21)−C(22)−C(23)−O(24)	71.5(3)
C(40)−Sn(1)−C(38)−C(34)	16.3(3)	O(24)−C(25)−C(26)−O(27)	−84.8(3)
C(16)−C(15)−C(19)−Sn(1)	178.1(2)	O(27)−C(28)−C(29)−O(30)	171.5(2)
C(18)−C(1)−C(19)−Sn(1)	−178.4(2)	O(30)−C(31)−C(32)−O(33)	−97.7(3)

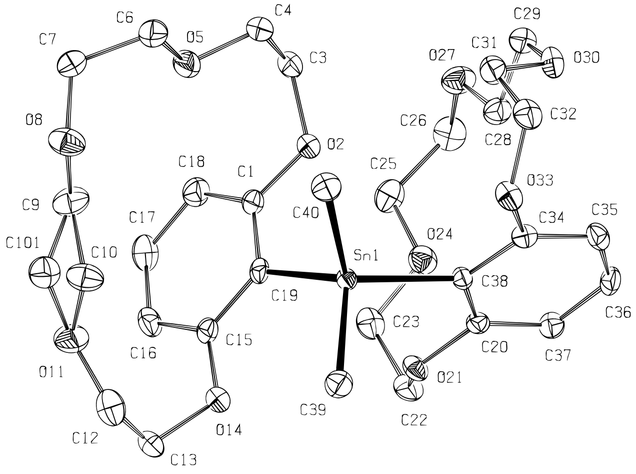

Figure 2. ORTEP[27] drawing of complex **7** at the 30% probability level. The hydrogen atoms are omitted for clarity.

in Figure 2. A selection of bond distances and angles and torsion angles is presented in Table 2.

The structure shows that the conformations of the two crown ether rings are different. The atom C(10)/C(101) in one of the two crown ether rings (A) is disordered with populations of 0.74(2) and 0.26(2) for the atoms C(10) and C(101), respectively. The angles between the aromatic rings and the mean planes of their crown ether moieties are 84.06(10) and 73.77(11)° for A and B, respectively; the two aromatic rings are almost orthogonal (87.73(14)°). The absolute values of the torsion angles of the OCH_2CH_2O units vary from 66.7(3) to 171.5(2)°.

The bond lengths of the tin atom to the aromatic carbons C(19) and C(38) are in the same range (Sn(1)−C(19), 2.148(3) Å; Sn(1)−C(38), 2.152(2) Å), as are the bond lengths of the tin atom to the methyl carbons (Sn(1)−C(39), 2.133(3); Sn(1)−C(40), 2.134(3) Å). The coordination sphere around the tin atom is distorted tetrahedral.

The nonbonded distances of Sn−O(2) (3.075(2) Å), Sn−O(14) (3.2231(19) Å), Sn−O(21) (3.0748(18) Å), and Sn−O(33) (3.2421(19) Å) are shorter than the sum of the van der Waals radii (3.78 Å); in view of the unfavorable orientation of the C−O−C bisectors which point away from the tin atom, this is probably a matter of steric congestion rather than intramolecular coordinative interaction.

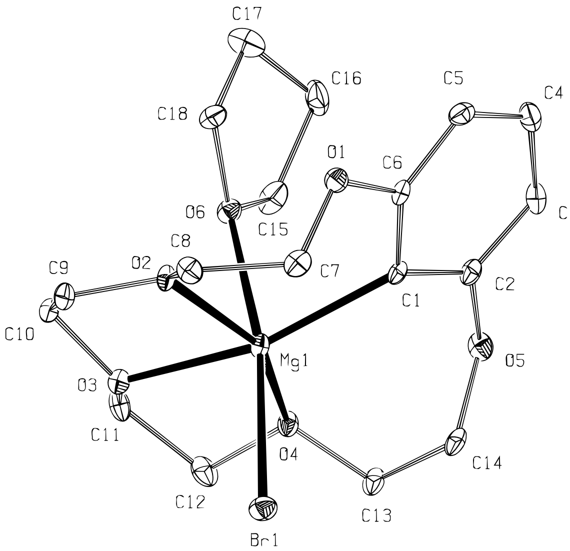

Figure 3. ORTEP[27] drawing of complex **10** at the 30% probability level. The hydrogen atoms are omitted for clarity.

Synthesis and Crystal Structure of [2-(Bromomagnesio)-1,3-phenylene]-16-crown-5 (10). The Grignard reagent **10** was obtained by addition of magnesium dibromide to the suspension of the organolithium reagent **2** (Scheme 1). The ^1H NMR spectrum of **10** could not be obtained, due to its low solubility in THF and toluene. Crystals suitable for an X-ray crystal structure determination were obtained by storing a dilute solution of **10** in THF at −20 °C.

The crystal structure of **10** is shown in Figure 3 (note that the numbering of the structure is that given in the figure; it differs from the IUPAC numbering which is used in the structures of **6** and **7**). A selection of structural parameters (bond distances and angles and torsion angles) is given in Table 3.

Table 3. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) of 10

(a) Bond Distances (Å)

Mg(1)−C(1)	2.193(3)	Mg(1)−O(2)	2.081(3)	Mg(1)−O(4)	2.096(3)
Mg(1)−Br(1)	2.6599(12)	Mg(1)−O(3)	2.136(3)	Mg(1)−O(6)	2.315(3)

(b) Bond Angles (deg)

Br(1)−Mg(1)−C(1)	106.81(8)	O(4)−Mg(1)−O(6)	89.02(10)
Br(1)−Mg(1)−O(2)	92.74(8)	O(2)−Mg(1)−C(1)	103.16(11)
Br(1)−Mg(1)−O(3)	89.99(7)	O(3)−Mg(1)−C(1)	163.19(11)
Br(1)−Mg(1)−O(4)	90.46(7)	O(4)−Mg(1)−C(1)	102.37(12)
Br(1)−Mg(1)−O(6)	170.17(9)	O(6)−Mg(1)−C(1)	82.88(11)
O(2)−Mg(1)−O(3)	76.10(11)	Mg(1)−C(1)−C(2)	121.5(2)
O(3)−Mg(1)−O(4)	76.21(11)	Mg(1)−C(1)−C(6)	120.0(2)
O(2)−Mg(1)−O(4)	152.12(12)	Mg(1)−O(6)−C(15)	122.0(2)
O(2)−Mg(1)−O(6)	83.21(11)	Mg(1)−O(6)−C(18)	121.8(2)
O(3)−Mg(1)−O(6)	80.35(10)		

(c) Torsion Angles (deg)

Br(1)−Mg(1)−C(1)−C(2)	105.2(2)	Mg(1)−C(1)−C(2)−O(5)	−27.9(4)
Br(1)−Mg(1)−C(1)−C(6)	−104.8(2)	O(1)−C(7)−C(8)−O(2)	62.7(3)
Mg(1)−C(1)−C(2)−C(3)	147.4(2)	O(2)−C(9)−C(10)−O(3)	51.4(4)
Mg(1)−C(1)−C(6)−C(5)	−145.7(3)	O(3)−C(11)−C(12)−O(4)	−52.8(4)
Mg(1)−C(1)−C(6)−O(1)	29.7(4)	O(4)−C(13)−C(14)−O(5)	−62.5(4)

A comparison of the crystal structure of **10** with those of **14**[10] and **15**[5] is of interest. In **14**, the magnesium is intramolecularly coordinated to the four crown ether oxygens and is electronically (and sterically) sufficiently saturated, so that the coordination of additional THF molecules is not required. In **15**, the magnesium is similarly coordinated to four of the five crown ether oxygens without extra solvent molecules. On the other hand, the structure of **10** shows coordination of the magnesium atom to only three of the five crown ether oxygens, while one extra THF molecule serves to complete the hexacoordination. The reason for this difference is obvious: in **14**, the benzylic oxygens O(1) and O(4) are able to weakly coordinate to magnesium, forming a five-membered chelate ring, as does one of the benzylic oxygens in **15**; in contrast, in **10** a coordinative interaction of magnesium with O(1) and O(5) would involve four-membered rings, which obviously is unfavorable. Indeed, the C−O−C bisectors of O(1) and O(5) point away from magnesium, thus indicating that there is no coordinating interaction.

The intramolecular bonds (Mg(1)−C(1), 2.193(3) Å; Mg(1)−Br(1), 2.6599(12) Å; Mg(1)−O(2), 2.081(3) Å; Mg(1)−O(3), 2.136(3) Å; Mg(1)−O(4), 2.096(3) Å) are slightly longer than those normally found in Grignard reagents,[14] as a result of the higher coordination number. The Mg(1)−Br(1) bond elongation may be accompanied by a slight additional polarization of this bond. The intermolecular Mg(1)−O(6) bond (2.315(3) Å) is longer than in “normal” Grignard reagents;[14] thus, the THF molecule is bound relatively weakly.

The coordination sphere around the magnesium atom can be regarded as distorted octahedral, while those of **14** and **15** are pentagonal pyramidal and distorted octahedral, respectively.[5,10] Due to the geometric restraints of the molecular skeleton, the angles in **10** deviate from the ideal octahedral value of 90°. In particular, the angles involving the Mg−Br bond show notable deviations. Notable is the small Br(1)−Mg(1)−C(1) angle (106.81(8)°); in Grignard reagents, it is usually between 120 and 130°, while in octahedral structures similar to **10**, it is reduced to 99−111°.[15] As expected, the angles inside the five-membered chelate rings are relatively small (O(2)−Mg(1)−O(3), 76.10(11)°; O(3)−Mg(1)−O(4), 76.21(11)°).

Quite unusual is the fact that the magnesium atom is strongly elevated from the plane of the aromatic ring; the C(4)−C(1)−Mg(1) angle is 152.4° (deviation from planarity 27.6!), the torsion angle Mg(1)−C(1)−C(6)−C(5) being 145.7(3)°. While a detailed discussion of this phenomenon will be deferred to a future comprehensive analysis of the available data, it is of interest to point out that inspection of known X-ray structures of organomagnesium compounds[5,10] reveals that, in the vast majority, the carbon−magnesium bond is oriented in the plane of the aromatic ring. Only for crown ethers and related polyethers, deviations from planarity of 1−5° are observed, with **14** thus far showing the largest deviation of 10.3°.[5] Again, as pointed out above, we feel that constraints of the crown ether skeleton are responsible. The torsion angles of the OCH_2CH_2O units vary from 51.4(4) to 62.7(3)°.

Conclusions

The results of this investigation illustrate the ease of intraannular functionalization of the crown ether **1** *via* the organolithium precursor **2**. Metal exchange reactions of **2** allow the synthesis of other organometallic crown ethers.

The crystal structure of the organotin compound **7** was determined because it is the first bis(crown ether)-tin(IV) compound. According to the crystal structure of the organomagnesium compound **10**, the magnesium atom is intramolecularly coordinated to three of the five crown ether oxygens, and the coordination sphere is completed by intermolecular coordination to the oxygen of one THF molecule; the carbon−magnesium bond shows a remarkable deviation of 27.6° from the plane of the aromatic ring.

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Experimental Section

General Comments. The crown ether **1**[16] was synthesized according to Kellogg *et al.*[17] by reaction of the dicesium salt of resorcinol with tetraethylene glycol dibromide in DMF (dried by distillation from CaO). Tetraethylene glycol dibromide was prepared by the reaction of tetraethylene glycol and phosphorus tribromide;[18] the ^{1}H NMR spectrum was similar to the one previously reported.[19] Lithiation reactions were performed in standard glassware with ground joints under argon or nitrogen. THF and diethyl ether were predried on NaOH and distilled from $LiAlH_4$. The synthesis of the Grignard reagent **10** was also carried out in standard glassware under nitrogen; its crystallization was performed in fully sealed glassware by using high-vacuum techniques. For this crystallization, extremely dry THF was prepared by distillation from liquid Na/K alloy after predrying on NaOH. A solution of dry magnesium dibromide was prepared by the reaction of dibromoethane and doubly sublimed magnesium in THF. Concentrations of "total base" and Mg^{2+} of the organomagnesium solution were determined by titration of a hydrolyzed sample with acid−base and EDTA complexation, respectively.[20] The starting materials tetraethylene glycol (Merck), phosphorus tribromide (Merck), resorcinol (Baker), cesium carbonate (Janssen), *n*-butyllithium (Janssen, Acros), deuterium oxide (Janssen), dimethyl disulfide (Aldrich), iodine (Janssen), dimethyltin dichloride (Aldrich), mercury dibromide (Merck), benzyl bromide (Aldrich), and dibromoethane (Janssen) were commercially available. Column chromatography was performed over aluminum oxide 90, activity II−III (Merck). TLC chromatography was carried out on aluminum sheets coated with silica gel 60 F_{254} (Merck). NMR spectra were measured on a Bruker AC 200 (^{1}H NMR, 200.13 MHz; ^{13}C, ^{13}C{^{1}H}, 2D{^{13}C,^{1}H} NMR, 50.32 MHz) or a Bruker MSL 400 (^{1}H NMR, NOESY/COSY, 400.13 MHz; ^{119}Sn NMR, 149.21 MHz). The ^{13}C chemical shifts were obtained from the ^{13}C{^{1}H} NMR and the coupling constants $J(^{13}\mathrm{C}-^{1}\mathrm{H})$ from the ^{13}C NMR spectra. The correlation between carbons and hydrogens was found by 2D{^{13}C,^{1}H} NMR. GC−MS analyses were performed on a HP 5890 II GC/5971 A MSD combination, operating at 70 eV and equipped with a Chrompack CP sil 5CB 50 m/0.21 mm column. Mass spectra and HRMS measurements were performed on a Finnigan MAT 90 mass spectrometer (direct inlet system). The characteristic fragments of the mass spectra of crown ethers were in agreement with those reported elsewhere.[21] Melting points were measured on a Büchi melting point apparatus and were not corrected. Elemental analyses were carried out at the Micro Analytical Department, Rijksuniversiteit Groningen, Groningen, The Netherlands.

Crystal Structure Determination of 6, 7, and 10. Crystals suitable for X-ray structure determination were glued to the top of a glass fiber and transferred into the cold nitrogen stream of an Enraf-Nonius CAD4-T diffractometer on a rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of the setting angles of a set of 25 well-centered reflections (SET4[22]) in the ranges of $9.92^\circ < \theta < 13.68^\circ$, $11.43^\circ < \theta < 13.76^\circ$, and $9.92^\circ < \theta < 13.87^\circ$ for **6**, **7**, and **10**, respectively. Reduced-cell calculations did not indicate higher lattice symmetry.[23] Crystal data and details on data collection are given in Table 4.

Data were corrected for Lp effects and for the linear decay of three periodically measured reference reflections during X-ray exposure time. An empirical absorption/extinction correction (DIFABS,[24] as implemented in PLATON[29]) was applied for **10**.

The structure of **6** was solved by automated direct methods (SHELXS86[25]). The structures of **7** and **10** were solved by automated Patterson methods and subsequent different Fourier techniques (DIRDIF-92[26]). All structures were refined on F^2 using full-matrix least-squares techniques (SHELXL-93[27]); no observance criteria were applied during refinement. Both **6** and **7** displayed conformational disorder in the crown ether moiety.

Hydrogen atoms were included in the refinement on calculated positions as riding on their carrier atoms, except for the hydroxy hydrogen of **6**, which was located on a difference Fourier map and subsequently included in the refinement. The methyl hydrogen atoms of **7** were refined as a rigid group, allowing for rotation around the Sn−C bonds. All non-hydrogen atoms, except for the disordered atoms of **7**, were refined with anisotropic thermal parameters. The hydrogen atoms of the other compounds were included in the refinement with a fixed isotropic thermal parameter related to the value of the equivalent isotropic thermal parameter of their carrier atoms. The hydroxy hydrogen atom of **6** was refined with an individual isotropic parameter.

Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 28 for all compounds. Geometrical calculations and illustrations were performed with PLATON.[29] All calculations were performed on a DEC station 5000.

Preparation of 2,5,8,11,14-Pentaoxabicyclo[13.3.1]-nonadeca-1(19),15,17-triene (1,3-Phenylene-16-crown-5; 1).[16] The crown ether **1** was synthesized by the reaction of the dicesium salt of resorcinol with tetraethylene glycol dibromide in DMF, in a yield (24%) slightly higher than that previously reported.[17] To avoid extensive dimer and polymer formation and to optimize the yield of the monomeric crown ether, high-dilution conditions (2×10^{-2} M) were applied. The crown ether **1** was separated from the 2:2 ring closure byproduct and the byproducts of higher molecular weight by column chromatography over aluminum oxide. During the elution, the eluent was gradually changed in 10% increments from pure petroleum ether (40−60 °C) to pure THF. The crystallization of pure **1** was accomplished from diethyl ether/pentane at −20 °C, which yielded a white solid, mp 45−46 °C (lit.[17] oil). ^{1}H NMR (for numbering of the atoms, see Figure 4) (400.13 MHz, $CDCl_3$, ref C*H*Cl_3 at 7.27 ppm): δ 3.599−3.631 (m, 4H, O(2)CH_2C*H*$_2$O(3)), 3.663−3.696 (m, 4H, O(2)C*H*$_2$$CH_2$O-(3)), 3.796−3.821 (m, 4H, O(1)CH_2C*H*$_2$O(2)), 4.290−4.315 (m, 4H, O(1)C*H*$_2$$CH_2$O(2)), 6.545 (dd, $^{3}J = 8.15$ Hz, $^{4}J = 2.36$ Hz, 2H, aryl H(4,6)), 7.117 (t, $^{3}J = 8.15$ Hz, 1H, aryl H(5)), 7.124 (t, $^{4}J = 2.36$ Hz, 1H, aryl H(2)). The ^{1}H NMR spectrum was analyzed with the help of a NOESY spectrum (^{1}H NMR, 400.13 MHz). ^{13}C NMR (50.32 MHz, $CDCl_3$, ref *C*DCl_3 at 77 ppm): δ

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Table 4. Crystallographic Data for 6, 7, and 10

	6	7	10
Crystal Data			
formula	$C_{15}H_{20}O_7$	$C_{30}H_{44}O_{10}Sn$	$C_{18}H_{27}BrMgO_6$
mol wt	312.32	683.38	443.62
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	13.0757(7)	9.4563(14)	15.5270(12)
b, Å	11.8147(12)	20.744(3)	9.7157(7)
c, Å	9.934(2)	17.617(2)	14.549(2)
β, deg	103.535(10)	117.953(9)	117.789(8)
V, Å^3	1492.0(4)	3052.6(8)	1941.7(4)
D_{calcd}, g cm^{-3}	1.390	1.487	1.517
Z	4	4	4
F(000)	664	1416	920
μ(Mo Kα), cm^{-1}	1.1	8.9	21.5
cryst size, mm	0.20 × 0.20 × 0.80	0.25 × 0.28 × 0.40	0.3 × 0.3 × 0.3
Data Collection			
T, K	150	150	150
θ_{min}, θ_{max}, deg	1.18, 25.00	0.98, 27.50	1.48, 27.50
wavelength, Å	0.710 73 (Mo Kα, graphite monochr)	0.710 73 (Mo Kα, graphite monochr)	0.710 73 (Mo Kα, graphite monochr)
scan type	ω	ω	$\omega/2\theta$
$\Delta\omega$, deg	$0.69 + 0.35 \tan\theta$	$0.50 + 0.35 \tan\theta$	$0.81 + 0.35 \tan\theta$
horiz, vert aperture, mm	$3.00 + 1.50 \tan\theta$, 4.00	$3.00 + 1.50 \tan\theta$, 4.00	2.55, 4.00
X-ray exposure time, h	22	13	19
linear decay, %	0.7	2.0	0.5
ref reflns	$112, 1\bar{1}2, 0\bar{3}2$	$\bar{2}16, \bar{3}24, \bar{1}73$	$32\bar{2}, \bar{4}2\bar{1}, 22\bar{3}$
data set	−16 to +16, −15 to 0, −12 to +12	−12 to +12, 0−26, −18 to +22	−17 to +20, 0−12, −18 to +14
total no. of data	5490	11 224	7669
total no. of unique data	2626 (R_{int} = 0.0820)	6997 (R_{int} = 0.0322)	4444 (R_{int} = 0.0401)
DIFABS cor range			0.893−1.131
Refinement			
no. of refined params	222	397	235
final R1[a]	0.0559 (1637, $I > 2\sigma(I)$)	0.0325 (5657, $I > 2\sigma(I)$)	0.0478 (2824, $I > 2\sigma(I)$)
final wR2[b]	0.1321	0.0687	0.0823
goodness of fit	1.027	1.045	0.969
w^{-1} [c]	$\sigma^2(F^2) + (0.0438P)^2 + 0.13P$	$\sigma^2(F^2) + (0.0251P)^2 + 0.81P$	$\sigma^2(F^2) + (0.0286P)^2$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, 0.000	0.000, 0.001	0.000, 0.001
min and max residual density, e Å^{-3}	−0.28, 0.26	−0.59, 0.40	−0.47, 0.56

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$.

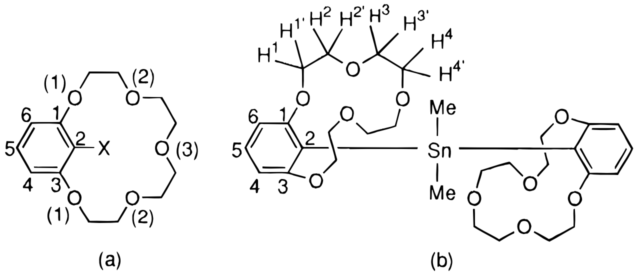

Figure 4. Atom numbering used for the NMR spectra of (a) **1**−**6** and (b) **7**.

68.72 (t, ^1J = 143 Hz, 2C, O(1)CH_2CH_2O(2)), 70.30 (t, ^1J = 141 Hz, 2C, O(1)CH_2CH_2O(2)), 70.57 (t, ^1J = 140 Hz, 2C, O(2)CH_2CH_2O(3)), 70.73 (t, ^1J = 141 Hz, 2C, O(2)CH_2CH_2O(3)), 103.74 (dtd, ^1J = 160 Hz, ^3J = 4.9 Hz, ^4J = 1.4 Hz, 1C, aryl C(2)), 110.05 (dddd, ^1J = 160 Hz, ^3J = 7.8 Hz, ^3J = 4.7 Hz, ^2J = 1.1 Hz, 2C, aryl C(4,6)), 129.34 (d, ^1J = 159 Hz, 1C, aryl C(5)), 160.23 (s, 2C, aryl C(1,3)). GC−MS: *m/z* (relative intensity) 268 ($M^{\bullet+}$, $C_{14}H_{20}O_5$, 80), 181 (7), 154 (9), 137 (39), 136 (32), 117 (7), 110 (48), 92 (100), 89 (9), 76 (42), 73 (51), 64 (68), 45 (80).

Synthesis of 19-Lithio-2,5,8,11,14-pentaoxabicyclo[13.3.1]nonadeca-1(19),15,17-triene ((2-Lithio-1,3-phenylene)-16-crown-5; 2). To a solution of **1** in THF (0.20 mmol in 2 mL of THF) under argon or nitrogen was added 1.1 molar equiv of *n*-butyllithium (1.6 M in hexane) at −30 °C. A white suspension appeared after about 5 min. The reaction exchange was complete after 1 h, after which time **2** was quenched with an electrophile.

19-Deuterio-2,5,8,11,14-pentaoxabicyclo[13.3.1]nonadeca-1(19),15,17-triene ((2-Deuterio-1,3-phenylene)-16-crown-5; 3). An excess (0.5 mL, 27.63 mmol) of deuterium oxide was added at −30 °C to the suspension of **2** (0.28 mmol in 5 mL of THF) under nitrogen. The reaction mixture was warmed slowly to room temperature, after which 5 mL of 1 M HCl was added. The volatile materials were removed by evaporation, the residue was extracted with dichloromethane (3 × 10 mL), and the combined organic layers were washed with 5 mL of water, dried over $MgSO_4$, filtered, and evaporated to dryness, to yield a pale yellow oil (0.054 g, yield 72%, 98% deuterium incorporation according to GC−MS spectrum), which was identified by GC−MS and ^{1}H NMR spectroscopy as nearly pure **3**. It was crystallized from diethyl ether/pentane at −20 °C, yielding a white solid, mp 44−46.5 °C. The ^{1}H NMR spectrum (200.13 MHz, $CDCl_3$, ref C*H*Cl_3 at 7.27 ppm) was identical with that of **1**, except for the signal of the aryl H(4,6) being a doublet (δ 6.54, d, ^3J = 8.1 Hz, 2H) and for the absence of the aryl H(2) signal. The ^{13}C NMR spectrum (50.32 MHz, $CDCl_3$, *C*DCl_3 at 77 ppm) was identical with that of **1** except for the signal of the aryl C(2) being a triplet (δ 103.45, t, $^1J(C-{}^2H)$ = 25 Hz, 1C) of low intensity, and the signal of the aryl C(4,6) (δ 110.05, ddd, ^1J = 161 Hz, ^3J = 7.7 Hz, ^2J = 1.3 Hz, 2C). GC−MS: *m/z* (relative intensity) 269 ($M^{\bullet+}$, $C_{14}H_{19}{}^2HO_5$, 97), 182 (8), 155 (10), 138 (35), 137 (35), 117 (7), 111 (47), 93 (100), 89 (7), 77 (43), 73 (49), 65 (63), 45 (53). HRMS: calcd for $C_{14}H_{19}{}^2HO_5$ 269.1374, found 269.1373 ± 0.0005.

19-(Methylthio)-2,5,8,11,14-pentaoxabicyclo[13.3.1]nonadeca-1(19),15,17-triene ([2-(Methylthio)-1,3-phenylene]-16-crown-5; 4). An excess (0.06 mL, 0.67 mmol) of dimethyl disulfide was added at −30 °C to the suspension of

2 (0.19 mmol in 3 mL of THF) under argon. The reaction mixture was warmed slowly to room temperature and worked up as for **3**. After evaporation of the solvent, **4** (0.047 g, yield 79%) was obtained as an oil, which crystallized upon standing; it was identified by GC−MS and ^{1}H NMR spectroscopy as nearly pure **4**. Repeated crystallizations from diethyl ether at −20 °C yielded a white solid, mp 69.5−70 °C. ^{1}H NMR (200.13 MHz, $CDCl_3$, ref $C\mathit{H}Cl_3$ at 7.27 ppm): δ 2.42 (s, 3H, SMe), 3.19−3.88 (m, 12H, $C\mathit{H}_2O(2)C\mathit{H}_2C\mathit{H}_2O(3)$), 4.32−4.56 (m, 4H, $O(1)C\mathit{H}_2CH_2O(2)$), 6.66 (d, ^{3}J = 8.2 Hz, 2H, aryl H(4,6)), 7.14 (t, ^{3}J = 8.2 Hz, 1H, aryl H(5)). ^{13}C NMR (50.32 MHz, $CDCl_3$, ref $\mathit{C}DCl_3$ at 77 ppm): δ 17.94 (q, ^{1}J = 140 Hz, 1C, SMe), 69.77 (t, ^{1}J = 144 Hz, 2C, $O(1)\mathit{C}H_2CH_2O(2)$), 70.15, 70.74, and 70.87 (3 × t, ^{1}J = 141 Hz, 6C, $\mathit{C}H_2O(2)\mathit{C}H_2\mathit{C}H_2O(3)$), 109.86 (ddd, ^{1}J = 159 Hz, ^{3}J = 8.3 Hz, ^{2}J = 1.8 Hz, 2C, aryl C(4,6)), 118.86 (s, 1C, aryl C(2)), 128.08 (d, ^{1}J = 159 Hz, 1C, aryl C(5)), 160.73 (s, 2C, aryl C(1,3)). GC−MS: *m/z* (relative intensity) 314 ($M^{\bullet+}$, $C_{15}H_{22}O_5S$, 74), 267 ($[M - SMe]^+$, 3), 226 (10), 200 (10), 182 (17), 167 (23), 156 (100), 139 (19), 123 (30), 111 (17), 95 (17), 73 (9), 45 (32). HRMS: calcd for $C_{15}H_{22}O_5{}^{32}S$ 314.1188, found 314.1189 ± 0.0006. Anal. Calcd for $C_{15}H_{22}O_5S$: C, 57.30; H, 7.05. Found: C, 57.03; H, 7.17.

19-Iodo-2,5,8,11,14-pentaoxabicyclo[13.3.1]nonadeca-1(19),15,17-triene ((2-Iodo-1,3-phenylene)-16-crown-5; 5). An excess (0.133 g, 0.52 mmol) of solid iodine was added at −30 °C to the suspension of **2** (0.20 mmol in 2 mL of THF) under argon. The reaction mixture was warmed slowly to room temperature, after which 5 mL of an aqueous solution of sodium thiosulfate (2 g, 12.65 mmol) was added. The workup procedure was as described for **3**, yielding 0.067 g of the crude product as a slightly yellow solid; it was identified by GC−MS as a mixture of **1** (14%) and **5** (86%). The crude product was recrystallized from diethyl ether/dichloromethane, which yielded a white solid (0.054 g, yield 69%), mp 102−103.5 °C. ^{1}H NMR (200.13 MHz, $CDCl_3$, ref $C\mathit{H}Cl_3$ at 7.27 ppm): δ 3.18−3.94 (m, 12H, $C\mathit{H}_2O(2)C\mathit{H}_2C\mathit{H}_2O(3)$), 4.27−4.58 (m, 4H, $O(1)C\mathit{H}_2CH_2O(2)$), 6.59 (d, ^{3}J = 8.2 Hz, 2H, aryl H(4,6)), 7.17 (t, ^{3}J = 8.2 Hz, 1H, aryl H(5)). ^{13}C NMR (50.32 MHz, $CDCl_3$, ref $\mathit{C}DCl_3$ at 77 ppm): δ 69.94 (t, ^{1}J = 142 Hz, 2C, 2 × OCH_2), 70.45 (t, ^{1}J = 144 Hz, 2C, $O(1)\mathit{C}H_2CH_2O(2)$), 70.88 and 70.97 (2 × t, ^{1}J = 140 Hz, 4C, 4 × OCH_2), 85.91 (td, ^{3}J = 7.6 Hz, ^{4}J = 1.5 Hz, 1C, aryl C(2)), 109.59 (ddd, ^{1}J = 160 Hz, ^{3}J = 8.2 Hz, ^{2}J = 1.6 Hz, 2C, aryl C(4,6)), 128.81 (d, ^{1}J = 160 Hz, 1C, aryl C(5)), 159.92 (s, 2C, aryl C(1,3)). GC−MS: *m/z* (relative intensity) 394 ($M^{\bullet+}$, $C_{14}H_{19}IO_5$, 100), 267 ($[M - I]^+$, 2), 262 (7), 236 (13), 218 (83), 205 (9), 190 (13), 161 (26), 151 (15), 133 (17), 107 (25), 89 (23), 73 (22), 45 (91). HRMS: calcd for $C_{14}H_{19}IO_5$ 394.0276, found 394.0271 ± 0.0005. Anal. Calcd for $C_{14}H_{19}IO_5$: C, 42.66; H, 4.86. Found: C, 42.07; H, 4.92.

Synthesis of 2,5,8,11,14-Pentaoxabicyclo[13.3.1]nonadeca-1(19),15,17-triene-19-carboxylic Acid ((2-Carboxy-1,3-phenylene)-16-crown-5; 6). The suspension of **2** (0.20 mmol in 2 mL of THF) was cooled to −65 °C, and over 30 min carbon dioxide was bubbled through it. Subsequently, the reaction mixture was poured rapidly into a beaker containing a slurry of crushed dry ice and anhydrous diethyl ether. When the carboxylation mixture had reached room temperature, water was added, and the volatile materials were removed by evaporation. The aqueous phase was washed once with 10 mL of toluene and once with 10 mL of hexane, after which 5 mL of 20% H_2SO_4 was added to liberate the acid, which was extracted with dichloromethane (4 × 10 mL). The combined organic layers were washed with 5 mL of water and dried over $MgSO_4$. After filtration, the solvent was evaporated, yielding **6** (0.044 g, yield 71%) as an oil, which crystallized upon standing; according to the ^{1}H NMR spectrum, the compound was nearly pure. Repeated crystallizations from dichloromethane/pentane yielded a white solid, mp 224−226 °C. ^{1}H NMR (200.13 MHz, $CDCl_3$, ref $C\mathit{H}Cl_3$ at 7.27 ppm): δ 3.46−3.83 (m, 12H, $C\mathit{H}_2O(2)C\mathit{H}_2C\mathit{H}_2O(3)$), 4.27−4.48 (m, 4H, $O(1)C\mathit{H}_2CH_2O(2)$), 6.64 (d, ^{3}J = 8.3 Hz, 2H, aryl H(4,6)), 7.26 (t, ^{3}J = 8.3 Hz, 1H, aryl H(5)), 10.08 (brs, 1H, COOH). ^{13}C NMR (50.32 MHz, $CDCl_3$, ref $\mathit{C}DCl_3$ at 77 ppm): 69.93, 70.18, and 70.34 (3 × t, ^{1}J = 142 Hz, 8C, 4 × C_2H_4), 109.54 (dd, ^{1}J = 161 Hz, ^{3}J = 7.0 Hz, 2C, aryl C(4,6)), 119.10 (t, ^{3}J = 6.3 Hz, 1C, aryl C(2)), 130.71 (d, ^{1}J = 160 Hz, 1C, aryl C(5)), 157.11 (s, 2C, aryl C(1,3)), 166.17 (s, 1C, COOH). MS (direct inlet): *m/z* (relative intensity) 312 ($M^{\bullet+}$, $C_{15}H_{20}O_7$, 85), 295 ($[M - OH]^+$, 6), 267 ($[M - COOH]^+$, 5), 225 (17), 207 (13), 180 (100), 177 (8), 162 (40), 136 (79), 133 (16), 108 (46), 89 (17), 73 (23), 45 (65). HRMS: calcd for $C_{15}H_{20}O_7$ 312.1209, found 312.1203 ± 0.0005. Anal. Calcd for $C_{15}H_{20}O_7$: C, 57.69; H. 6.45. Found: C, 56.95; H, 6.55.

Colorless crystals, suitable for X-ray crystal structure determination, were obtained by slow recrystallization from dichloromethane/diethyl ether by cooling from room temperature to −20 °C.

Synthesis of Dimethylbis(2,5,8,11,14-pentaoxabicyclo[13.3.1]nonadeca-1(19),15,17-trien-19-yl)stannane (Dimethylbis[(1,3-phenylene-16-crown-5)-2-yl]stannane; 7). A solution of dimethyltin dichloride (0.022 g, 0.10 mmol in 5 mL of THF) was added dropwise (over a period of 20 min) to the suspension of **2** (0.20 mmol in 2 mL of THF) at −30 °C. After a few minutes, the white suspension changed to a clear solution; it was slowly warmed to room temperature, after which 5 mL of water was added. The volatile materials were removed by evaporation, and the residue was extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with 5 mL of water, dried over $MgSO_4$, filtered, and evaporated to dryness, yielding 0.061 g of a crude oil. According to the ^{1}H NMR spectrum, two compounds were present: **1** and **7** (molar ratio **1**:**7** = 61:31, corresponding to a 48% yield of **7**). Purification and isolation of a small amount (about 5 mg) of the pure **7** were carried out by column chromatography (analogous to the purification of **1**), followed by repeated crystallization from diethyl ether at −20 °C. Pure **7** was obtained as a white solid, mp 146 °C. The ^{1}H NMR spectrum was analyzed with the help of the program PANIC[30] (a version of the LAO-COON type programs[31]) on a Bruker Aspect 3000 computer. ^{1}H NMR (for numbering of the atoms, see Figure 4) (400.13 MHz, $CDCl_3$, ref $C\mathit{H}Cl_3$ at 7.27 ppm): δ 0.632 (s, Sn satellites $^{2}J(^{119}Sn-H)$ = 61.44 Hz, $^{2}J(^{117}Sn-H)$ = 58.66, 6H, $SnMe_2$), 3.070 (ddd, $^{2}J(H^4-H^{4'})$ = −10.92 Hz, $^{3}J(H^{3'}-H^{4'})$ = 4.68 Hz, $^{3}J(H^3-H^{4'})$ = 7.37 Hz, 4H, $H^{4'}$), 3.237 (dt, $^{2}J(H^4-H^{4'})$ = −10.92 Hz, $^{3}J(H^{3'}-H^4)$ = 4.78 Hz, $^{3}J(H^3-H^4)$ = 4.79 Hz, 4H, H^4), 3.302−3.394 (m, $^{2}J(H^3-H^{3'})$ = −10.14 Hz, $^{3}J(H^3-H^4)$ = 4.79 Hz, $^{3}J(H^3-H^{4'})$ = 7.37 Hz, $^{3}J(H^{3'}-H^4)$ = 4.78 Hz, $^{3}J(H^{3'}-H^{4'})$ = 4.68 Hz, 8H, H^3, $H^{3'}$), 3.581 (dd, $^{2}J(H^2-H^{2'})$ = −13.16 Hz, $^{3}J(H^1-H^2)$ = $^{3}J(H^1-H^{2'})$ = 5.44 Hz, $^{3}J(H^{1'}-H^2)$ = $^{3}J(H^{1'}-H^{2'})$ = 3.11 Hz, 8H, H^2, $H^{2'}$), 3.901 (dt, $^{2}J(H^1-H^{1'})$ = −13.38 Hz, $^{3}J(H^{1'}-H^2)$ = $^{3}J(H^{1'}-H^{2'})$ = 3.11 Hz, 4H, $H^{1'}$), 4.528 (dt, $^{2}J(H^1-H^{1'})$ = −13.38 Hz, $^{3}J(H^1-H^2)$ = $^{3}J(H^1-H^{2'})$ = 5.44 Hz, 4H, H^1), 6.575 (d, ^{3}J = 8.41 Hz, Sn satellites $^{4}J(Sn-H)$ = 17.43 Hz, 4H, aryl H(4,6)), 7.118 (t, ^{3}J = 8.10 Hz, 2H, aryl H(5)). The ^{1}H NMR spectrum was analyzed with the help of NOESY and COSY spectra (^{1}H NMR, 400.13 MHz). ^{13}C NMR (50.32 MHz, $CDCl_3$, ref $\mathit{C}DCl_3$ at 77 ppm): δ 67.09, 69.86, 70.95, and 71.04 (4 × t, ^{1}J = 142 Hz, 8C, 4 × C_2H_4), 107.11 (dd, ^{1}J = 159 Hz, ^{3}J = 7.3 Hz, 4C, aryl C(4,6)), 123.00 (s, 2C, aryl C(2)), 129.08 (d, ^{1}J = 157 Hz, 2C, aryl C(5)), 164.39 (s, 4C, aryl C(1,3)). The Sn satellites were not observed due to the low concentration. ^{119}Sn NMR (149.21 MHz, $CDCl_3$, ref $Me_4\mathit{Sn}$ at 0 ppm): δ −99.73 (s, 1Sn). MS (direct inlet): *m/z* (relative intensity) 669 ($[M - Me]^+$, $C_{29}H_{41}O_{10}{}^{120}Sn$, 100), 417 ($Ar^{120}Sn^{+}Me_2$, 38), 387 ($Ar^{120}Sn$, 6), 45 (29). Parent ion mass: calcd for $C_{29}H_{41}O_{10}{}^{116}Sn$ ($[M - Me]^+$, ^{116}Sn) 665.1721, found 665.1714 ± 0.0010. Anal. Calcd for $C_{30}H_{44}O_{10}Sn$: C, 52.73; H, 6.49. Found: C, 52.00; H. 6.37.

Colorless crystals, suitable for X-ray crystal structure determination, were obtained by slow recrystallization from diethyl ether by cooling from room temperature to −20 °C.

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[30] Program, PANIC, Bruker Program Library.

[31] Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863.

Synthesis of Bis(2,5,8,11,14-pentaoxabicyclo[13.3.1]-nonadeca-1(19),15,17-trien-19-yl)mercury (Bis[(1,3-phenylene-16-crown-5)-2-yl]mercury; 8). At −30 °C, *n*-BuLi (0.50 mmol in 0.31 mL of hexane) was added to a solution of **1** (0.129 g, 0.48 mmol) in 5 mL of THF under a nitrogen atmosphere. After the mixture was stirred for 50 min at −30 °C, $HgBr_2$ (0.080 g, 0.22 mmol as a suspension in 0.5 mL of THF) was added, after which the cooling bath was removed. Subsequently, the reaction mixture was stirred for 16 h at room temperature, after which diluted hydrochloric acid was added. The THF was removed by evaporation, the organic material was extracted with diethyl ether, and the ether layer was dried ($MgSO_4$), filtered, and evaporated to dryness, to yield a pale yellow solid (0.154 g), which was identified by GC−MS and ^{1}H NMR spectroscopy as **8** (48%) and [2-(bromomercurio)-1,3-phenylene]-16-crown-5 (52%). Compound **8** was obtained pure (0.027 g clear colorless crystals, 0.036 mmol, 15%). MS (EI, direct inlet): *m/z* (relative intensity) 736 ($M^{\bullet +}$, $C_{28}H_{38}O_{10}{}^{202}Hg$, 1.6), 469 (100), 268 (2.5), 161 (1.5), 149 (2.5), 135 (5), 107 (7), 91 (5). HRMS: calcd for $C_{28}H_{38}O_{10}{}^{202}Hg$ 732.212, found 732.2134 ± 0.003. ^{1}H NMR (200 MHz, $CDCl_3$, ref C*H*Cl_3 at 7.27 ppm): δ 3.31−3.50, 3.63−3.72, 3.79−3.95, and 4.23−4.39 (4 × m, 32H, CH_2), 6.68 (dd, $^3J = 7.8$ Hz, $^4J(Hg-H) = 19.6$ Hz, 2H, aryl H4 and H6), 7.05 (t, $^3J = 7.8$ Hz, 2H, aryl H5).

Synthesis of 19-Benzyl-2,5,8,11,14-pentaoxabicyclo-[13.3.1]nonadeca-1(19),15,17-triene ((2-Benzyl-1,3-phenylene)-16-crown-5; 9). At −30 °C, *n*-BuLi (0.48 mmol in 0.30 mL of hexane) was added to a solution of **1** (0.086 g, 0.32 mmol) in 5 mL of THF under a nitrogen atmosphere. After the mixture was stirred for 1 h at −30 °C, benzyl bromide (0.29 g, 1.7 mmol) was added, after which the solution was slowly warmed to room temperature. Subsequently, some water was added and the THF was removed by evaporation. The organic material was extracted with diethyl ether and the ether layer was dried ($MgSO_4$), filtered, and evaporated to dryness, to yield a pale yellow oil (0.417 g), which was identified by GC−MS. Apart from benzyl bromide and 1,2-diphenylethane, the oil contained the two crown ethers **1** (37%) and **9** (63%). After evaporation under high vacuum (10^{-3} mbar) for 10 h at 55 °C, the residue is a white solid, containing only **1** (34%) and **9** (66%). After crystallization from acetone at −20 °C, compound **9** was obtained pure (0.017 g of white crystals, 0.047 mmol, 15%). GC−MS (EI): *m/z* (relative intensity) 358 ($M^{\bullet +}$, $C_{21}H_{26}O_5$, 100), 267 (27), 226 (52), 209 (38), 197 (76), 153 (41), 91 (96), 45 (73). ^{1}H NMR (200 MHz, $CDCl_3$, ref C*H*Cl_3 at 7.27 ppm): δ 3.34−3.80 (m, 12H, 2 × A_2B_2 and 2 × B_2 part of A_2B_2, CH_2), 4.22 (s, 2H, benzyl CH_2), 4.22−4.49 (m, 4H, 2 × A_2 part of A_2B_2, phenylene−OCH_2) 6.67 (d, $^3J = 8.2$ Hz, 2H, aryl H4 and H6), 7.07−7.35 (m, 6H, aryl H5 and 5 × benzyl H).

Synthesis of Bromo(2,5,8,11,14-pentaoxabicyclo-[13.3.1]nonadeca-1(19),15,17-trien-19-yl)magnesium ([2-(Bromomagnesio)-1,3-phenylene]-16-crown-5; 10). An excess of magnesium dibromide (2 mmol) in 5 mL of THF was added at −30 °C to the suspension of **2** (1.06 mmol in 10 mL of THF), under nitrogen. Subsequently, the reaction mixture was warmed slowly to room temperature, after which the reaction mixture was transferred to a reaction vessel coupled to a vacuum line. The solution was degassed and frozen with liquid nitrogen. After high-vacuum pumping, the reaction vessel was sealed off. Product **10** was not soluble in toluene and had a very low solubility in THF (according to titration, <5 mmol/L). The solubility was too low for ^{1}H NMR spectroscopy. The solid product was dissolved in 180 mL of THF, and upon storage at −20 °C, crystals formed on the wall of the vessel. They were introduced into a nitrogen-filled glovebox to select crystals suitable for a structure determination. A deuterium oxide quench of part of these crystals yielded **3**.

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Supporting Information Available: Tables giving full details of the structure determinations of **6**, **7**, and **10**, including crystal data and structure determination details, atomic coordinates, bond lengths, bond angles, and anisotropic displacement parameters (15 pages). Ordering information is given on any current masthead page.

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