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Intra-annular reactions of the (1,3-xylylene)-18-crown-5 system: synthesis and crystal structure of [2-(bromomagnesio)-1,3-xylylene]-18-crown-5, [2-(bromomercurio)-1,3-xylylene]-18-crown-5 and bis[(1,3-xylylene-18-crown-5)-2-yl]mercury

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Abstract

The Grignard compound [2-(bromomagnesio)-1,3-xylylene]-18-crown-5 (**4**) was prepared from the aryllithium compound (2-lithio-1,3-xylylene)-18-crown-5 (**9**) and magnesium bromide. The crystal structure of **4** shows that it crystallizes without solvent and is coordinatively saturated (distorted octahedral) by complexation of the magnesium with four of the five crown ether oxygens.

The 1:1 reaction of **9** with $HgBr_2$ yielded the corresponding organomercury compound [2-(bromomercurio)-1,3-xylylene]-18-crown-5 (**10**), which crystallizes without solvent. Its crystal structure reveals that intramolecular Hg–O coordination occurs with two of the five oxygens, and only weak interaction with a third crown ether oxygen. Reaction of **10** with metallic magnesium lead to the symmetric compound bis[(1,3-xylylene-18-crown-5)-2-yl]mercury (**11**). The centrosymmetric crystal structure of **11** shows that the mercury is intramolecularly coordinated with only four of the ten oxygens; the mercury atom is completely shielded by the crown ether rings. This shielding is probably the reason for the failure to bring about reaction of **11** with magnesium to give the corresponding diarylmagnesium compound.

The crown ether Grignard **4** was treated with deuterium oxide, chlorotrimethylstannane, iodine and benzophenone to give the products (2-D-1,3-xylylene)-18-crown-5 (**14a**), (2-trimethylstannyl-1,3-xylylene)-18-crown-5 (**15**), (2-iodo-1,3-xylylene)-18-crown-5 (**16**) and 2-(diphenylhydroxy)methyl-1,3-xylylene)-18-crown-5 (**17**) (the latter being converted into its methyl ether (2-(1,1-diphenyl-2-oxapropyl)-1,3-xylylene)-18-crown-5 (**17a**) for identification), respectively. The lithium compound **9** was treated with benzophenone, chlorotrimethylgermane, chlorodiphenylphosphine and 4,4′-dimethoxybenzophenone to give intra-annularly substituted crown ether derivatives **17**, (2-trimethylgermyl-1,3-xylylene)-18-crown-5 (**18**), (2-diphenylphosphinyl-1,3-xylylene)-18-crown-5 (**19**) (the latter undergoing slow oxidation to (2-oxodiphenylphosphinyl-1,3-xylylene)-18-crown-5 (**20**)) and (2-(4,4′-dimethoxydiphenylhydroxymethyl)-1,3-xylylene)-18-crown-5 (**21**) (which was converted under acidic conditions to {2-[(4-methoxyphenyl)(4′-oxo-2′,5′-cyclohexylidene)methyl]-1,3-xylylene}-18-crown-5 (**22**)), respectively.

1. Introduction

In a previous paper [1], we discussed the reactions of (2-bromo-1,3-xylylene)-15-crown-4 (**1**) and (2-bromo-1,3-xylylene)-18-crown-5 (**2**) with magnesium, performed to prepare the Grignard reagents [2-(bromomagnesio)-1,3-xylylene]-15-crown-4 (**3**) and [2-(bromomagnesio)-1,3-xylylene]-18-crown-5 (**4**) (Scheme 1).

During these reactions, two major by-products were formed in a 1:1 stoichiometry, *viz.* the "hydrolysis" product of the Grignard compound and a Grignard compound in which the crown ether ring was cleaved at a specific site. When the reaction was performed in a deuterated solvent, the same, *i.e.* undeuterated, products were formed, indicating that the "hydrolysis" product did not arise from proton abstraction from the solvent. Owing to these side reactions, isolation from the reaction mixture of pure **4** (17% yield following a Me_3SnCl quench) was not possible. However, during

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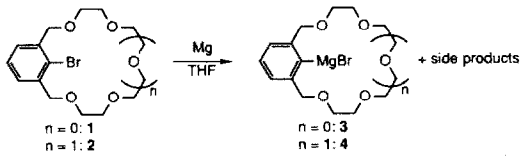


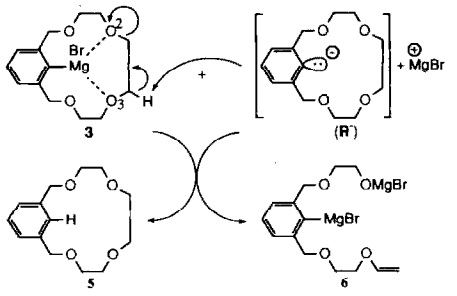
Scheme 1.

the reaction of **1** with magnesium in a relatively high concentration, part of the formed Grignard **3** crystallized out, owing to its low solubility in THF (< 4 mmol l^{-1}). The X-ray crystal structure of **3** showed that the magnesium coordinates most strongly with the two central, adjacent, oxygens O2 and O3 of the polyether ring, thereby activating the hydrogens of the ethylene unit between these oxygens. Assuming that the Grignard formation occurs, at least in part, *via* an anionic intermediate (R^- in Scheme 2), which abstracts an activated proton from a previously formed Grignard molecule **3**, the "hydrolysis" product **5** is released as **3** undergoes cleavage of the crown ether ring to give **6**.

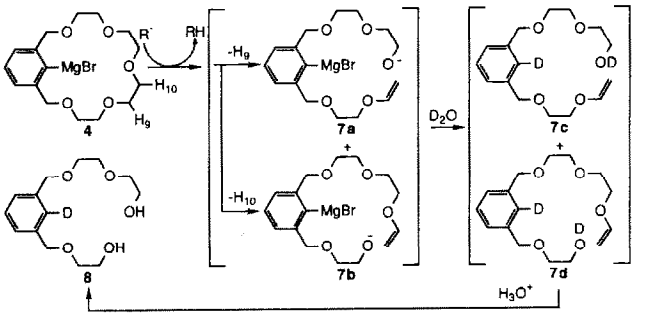
The 400 MHz ^{1}H NMR spectra of the mixture produced by reaction **2** with magnesium showed that two different cleavage products (**7a** and **7b**) were present, indicating that in an intact molecule of **4**, coordination similar to that in **3** must be present. On deuterolysis followed by acidic work-up, both cleavage products yielded diol **8** (Scheme 3).

For comparative studies with **3**, it was essential to have available the crystal structure of **4**. Since **4** could not be isolated from the Grignard reaction mixture, an alternative synthesis had to be developed.

An obvious candidate as the starting material for the synthesis of **4** was the corresponding aryllithium compound (2-lithio-1,3-xylylene)-18-crown-5 (**9**), first synthesized by Reinhoudt *et al.* [2,3]. For the conversion of **9** into **4**, two routes can be envisaged (Scheme 4): (i) reaction of **9** with 1 equiv. of mercuric bromide to give the air-stable [2-(bromomercurio)-1,3-xylylene]-18-crown-5 (**10**), which can be purified under "normal" laboratory conditions, before being converted into **4** by



Scheme 2.

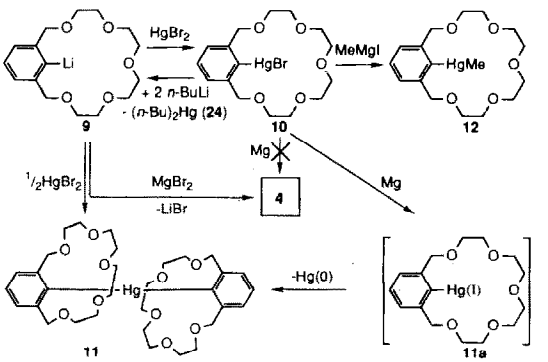


Scheme 3.

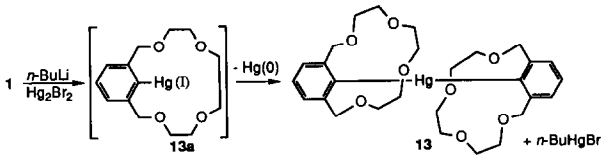
the exchange reaction with magnesium; and (ii) reaction of **9** with magnesium bromide (Scheme 4) in which case **4** would have to be separated from lithium bromide.

2. Results and discussion

The lithium compound **9** was prepared by halogen-metal exchange of **2** with n-butyllithium at low temperature [2,3]. The 1:1 reaction of **9** with mercuric bromide yielded **10**, the crystal structure of which was determined (*vide infra*). Reaction of **10** with methylmagnesium iodide gave **12**, a stable compound that disproportionated to dimethylmercury and the diarylmercury compound **11** only very slowly (< 5% after 1 month in the solid state, *vide infra*). Disappointingly, treatment of **10** with magnesium in THF did not yield the Grignard reagent **4**. Instead, under rather drastic conditions (50°C, 10 days), **11** was formed (Scheme 4). Apparently, the magnesium acts as a reducing agent, giving the unstable mercury(I) compound **11a** as initial product, which loses Hg^0 (which forms an amalgam with the excess of magnesium) to give **11**, a compound that was also formed in the 2:1 reaction of **9** with $HgBr_2$. It is noteworthy that **11** does not undergo the



Scheme 4.



Scheme 5.

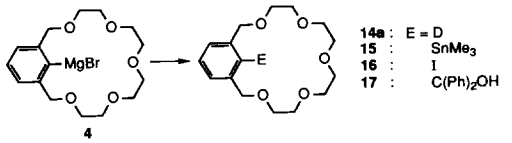
expected consecutive reaction with magnesium to give the magnesium analogue of **11** (vide infra).

Support for the intermediacy of the mercury(I) compound **11a** comes from the reaction of the lithium derivative of **1**, prepared by its reaction with n-butyllithium in the presence of Hg_2Br_2. Apparently, in this case also, elimination of mercury(0) from the primary intermediate **13a**, the crown-4 analogue of **11a**, gave **13** in reasonable yield (57%), together with n-butylmercuric bromide (Scheme 5).

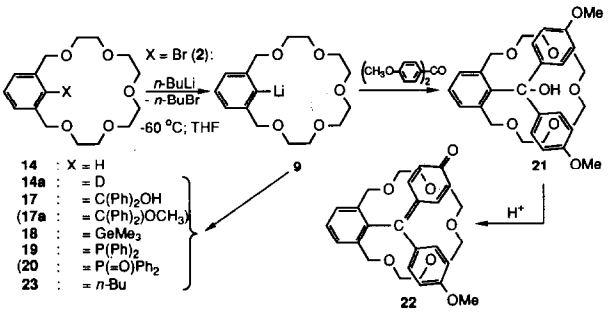
The crystal structure of **11** (*vide infra*) shows that the mercury atom is only intramolecularly coordinated by four of the ten oxygens and is completely encapsulated by both crown ether rings, making it inaccessible to the magnesium and thus completely inhibiting the normally expected metal/metal exchange.

The successful method for the preparation of **4** was found to be the second alternative, the reaction of lithium compound **9** with magnesium bromide (Scheme 4). This gave the Grignard reagent in high yield and purity, and in crystalline form. Its X-ray crystal structure was determined and is discussed later. The compound was further identified by reactions with D_2O, Me_3SnCl, iodine, and benzophenone, which gave **14a** and **15–17**, respectively, in high yield (see Scheme 6).

The availability of **9** prompted us to examine some more of its reactions (Scheme 7). Some of the reactions were straightforward and analogous to those of **4**, giving **14a**, **17** (which was converted to its methyl ether **17a** for identification), **18** and **19**; the latter compound was oxidized slowly to **20**. Of special interest is the formation of **22**. It was expected that from **9** and 4,4′-dimethoxybenzophenone and subsequent treatment of the initially formed carbinol **21** with HCl, a crown ether stabilized carbocationic species would be formed. However, under the reaction conditions employed, **21** lost methanol to give the quinone methine **22**. Initially, this subsequent reaction was thought to



Scheme 6.



Scheme 7.

result from the coordinating power and/or steric interaction of the crown ether ring. However, exploratory reactions of 4,4′-dimethoxybenzophenone with Grignard reagents bearing only small alkyl substituents in the *ortho* positions revealed that the presence of the crown ether ring is not essential for occurrence of this elimination reaction; *e.g.* with 2,6-dimethylphenylmagnesium bromide, the analogous quinone methine was formed. The results of these latter investigations will be published elsewhere.

When a solution of **9** was warmed to room temperature, appreciable amounts (up to 67%) of the 2-n-butylated product **23** were formed from **9** and n-butyl bromide (*cf.* [3]). An alternative synthesis of **9**, resulting in a product not contaminated with n-butyl bromide, involved reaction of **10** with n-butyllithium; the yield of **9** was nearly quantitative, but the compound necessarily contained a molar equivalent of di(n-butyl)mercury (**24**; Scheme 4).

2.1. Preparation and crystal structure of [2-(bromomercurio)-1,3-xylylene]-18-crown-5 (10)

The mercury compound **10** was synthesized by the reaction of **9** and $HgBr_2$ in a 1:1 ratio (Scheme 4); its identity was confirmed by the crystal structure shown in Fig. 1. No external solvent molecules are involved in the coordination of the mercury atom. A selection of bond lengths and bond angles is given in Table 1. The bond lengths Hg–O1 (2.754(6) Å) and Hg–O5 (2.855(6) Å) indicate that there are weak coordinative bonds to these oxygens, while the Hg–O4 bond distance of 3.060(6) Å, clearly shorter than the sum of the van der Waals radii of about 4.00 Å, suggests a further, rather weak, interaction. Probably because of these mercury–oxygen interactions, the C1–Hg–Br bond angle, 175.0(2)°, deviates slightly from the linear geometry of non-coordinated, sp-hybridized mercury, the Hg and Br moving away from these oxygens. All the oxygens, the three interacting ones included, lie above the plane of the aromatic ring. As indicated by the torsion angle Hg–C1–C2–C3 (177.4(7)°), the Hg–C1 bond is slightly

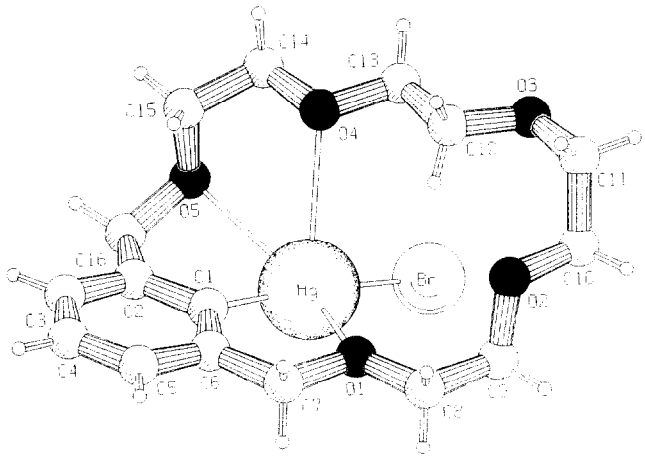


Fig. 1. PLUTON drawing of **10**, with the atom labeling.

bent down from the plane of the aromatic ring. The C1–Hg–O angles in the two five-membered rings, resulting from the coordination of the mercury with O1 and O5, are 72.5(3)° and 71.9(3)°, respectively; they are determined by the rigidity of the five-membered rings. The O4–Hg–O5 angle is small: 57.81(16)°. The O1–Hg–O5 bond angle, 136.6(2)°, is rather large.

2.2. Preparation and crystal structure of bis[(1,3-xylylene-18-crown-5)-2-yl]mercury (11)

Compound **11** was synthesized from **9** and $HgBr_2$ in a 2:1 ratio (Scheme 4); its identity was confirmed by the crystal structure shown in Fig. 2. A selection of bond lengths and bond angles is given in Table 2. Like **10**, the compound crystallizes without solvent molecules. The structure is centrosymmetric around the mercury, which means that the oxygens O1, O5, O1a and O5a lie in one plane on the corners of a parallelogram with mercury in its center; for these oxygens, weak coordination is apparent: Hg–O1 (= Hg–O1a) 3.064(3) Å and Hg–O5 (= Hg–O5a) 2.984(3). These bond lengths are slightly larger than those found in the mercury bromide compound **10** (*vide supra*). This may in part be the result of the presence of the

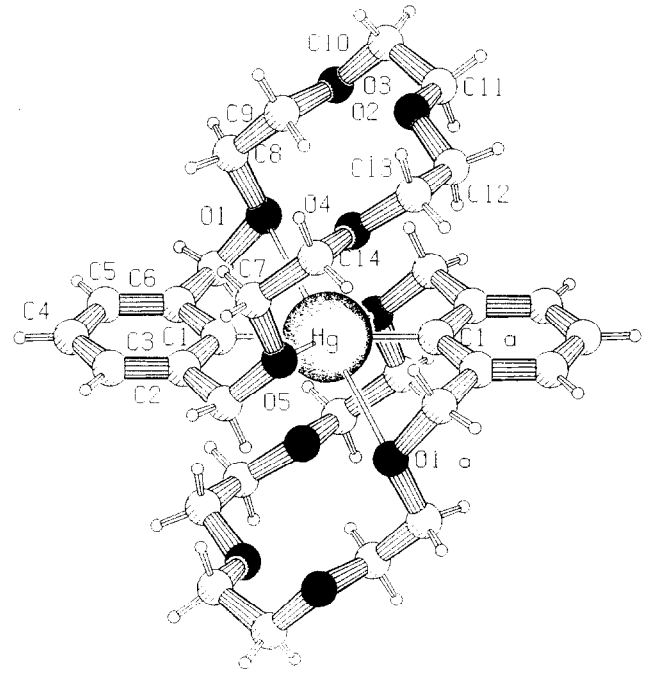


Fig. 2. PLUTON drawing of **11**, with the atom labeling.

relatively strongly electronegative bromine attached to the metal atom in **10**, increasing its Lewis acidity and thereby the strength of the coordination bonds. Coordinative saturation and steric interactions may also play a role. The O1–Hg–O5 angle is 119.09(8)° and thus the angle O1–Hg–O5a equals 60.91(8)°. From the value of the Hg–O4 bond length (3.540(3) Å) the existence of a rather weak interaction with this oxygen seems likely. Oxygens O2 (Hg · · · O2 4.881(4)) and O3 (Hg · · · O3 4.775(5)) do not interact with the mercury. The Hg–C1 bond is elongated (2.070(4) Å) in **11** compared with that in **10** (2.057(9) Å), probably as a result of the steric interaction of the crown ether rings. The sixfold coordination of the mercury can be regarded as strongly distorted octahedral.

As mentioned above, treatment of **11** with metallic magnesium did not yield the expected magnesium analogue. The crystal structure clearly shows that the mercury atom is encapsulated by the two crown ether

TABLE 1. Relevant distances (Å) and angles (°) for **10**

Hg–C1	2.057(9)	Hg–O1	2.754(6)	Hg · · · O2	4.247(6)
Hg–Br	2.430(1)	Hg–O4	3.060(6)	Hg–O5	2.855(6)
C1–C2–C3	119.8(8)	C1–Hg–Br	175.0(2)		
C2–C3–C4	121.1(9)	C1–Hg–O1	72.5(3)		
C3–C4–C5	119.3(10)	C1–Hg–O4	95.4(3)		
C4–C5–C6	122.3(9)	C1–Hg–O5	71.9(3)		
C5–C6–C1	119.2(8)	O1–Hg–O4	102.2(2)		
C2–C1–C6	118.1(8)	O1–Hg–O5	136.6(2)		
O4–Hg–O5	57.81(16)				

TABLE 2. Relevant distances (Å) and angles (°) for **11**

Hg–O1	3.064(3)	Hg · · · O2	4.881(4)	Hg · · · O3	4.775(5)
Hg–O4	3.540(3)	Hg–O5	2.984(3)	Hg–C1	2.070(4)
C1–Hg–C1a	180	C1–C2–C3	120.2(4)		
O1–Hg–O1a	180	C2–C3–C4	121.3(4)		
O5–Hg–O5a	180	C3–C4–C5	119.8(4)		
O1–Hg–O5	119.09(8)	C4–C5–C6	120.4(4)		
O1–Hg–O5a	60.91(8)	C5–C6–C1	120.8(4)		
C1–Hg–O5	69.17(13)	C2–C1–C6	117.4(3)		

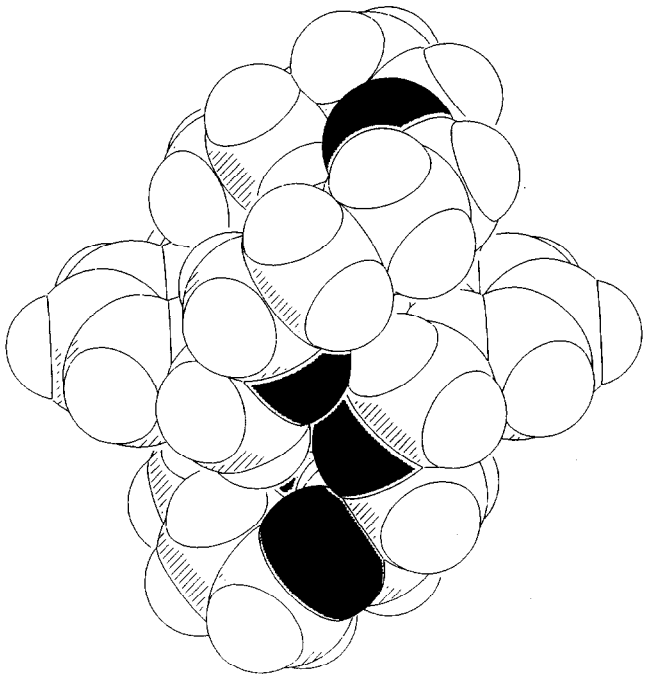


Fig. 3. Space-filling model of **11**; oxygens are shown in black, the mercury is invisible.

rings, which inhibits the approach of the magnesium to the active site of the molecule. This steric shielding is shown even more convincingly in the space filling model of **11** in Fig. 3.

2.3. *Preparation and crystal structure of [2-(bromomagnesio)-1,3-xylylene]-18-crown-5) (4)*

The Grignard reagent **4** was obtained by the addition of 1 molar equivalent of magnesium bromide to a solution of **9** in THF at −60°C (Scheme 4). Owing to its low solubility in THF at this temperature, the magnesium bromide was present in suspension; warming to room temperature during about 15 min resulted in formation of a clear supersaturated mixture from which crystals of **4** separated on standing.

According to the ^{1}H NMR spectrum in THF-d_8, the product **4** contained no solvent of crystallization, indicating that the magnesium was only intramolecularly coordinated. The crystalline product was transferred into a glovebox with nitrogen atmosphere to allow selection of the best crystals. The remaining crystals were treated with water, titration confirmed a "total base" to Mg^{2+} ratio of 1:1. The identity as completely intramolecularly coordinated **4** was confirmed by its X-ray crystal structure.

The unit cell of **4** contains two chemically identical residues which differ only slightly in their conformations. Since both residues are very similar, only one is

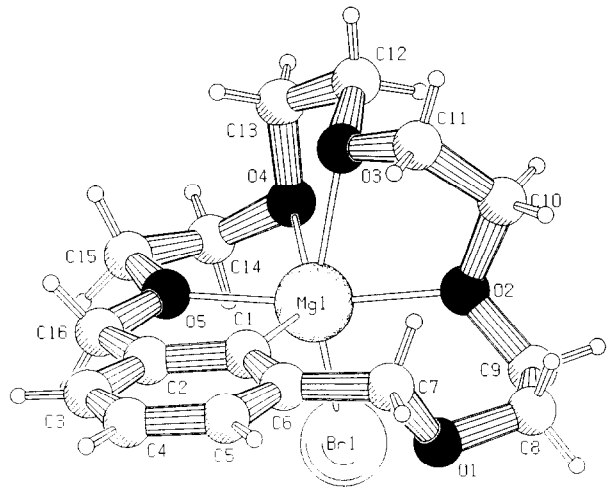


Fig. 4. PLUTON drawing of one of the two similar crystallographically independent molecules of **4**, with the atom labeling.

shown in Fig. 4; bond angles and distances for this molecule are presented in Table 3. The distorted-octahedrally coordinated magnesium atom has interactions with four of the five crown ether oxygens. The low symmetry of the structure and the presence of a non-coordinating oxygen indicates an "unfavorable" (too large) size of the crown ether ring in **4**. In particular, the angles involving the MgBr bond show notable deviations from ideal octahedral coordination: Br–Mg–C1 110.6(1)°, Br–Mg–O2 93.1(1)°, Br–Mg–O3 148.0(1)°, Br–Mg–O4 88.0(1)°, Br–Mg–O5 93.1(1)°. As expected, the angles inside the five-membered chelation rings are relatively small (O2–Mg–O3 72.6(2)°, O3–Mg–O4 69.5(2)°, O4–Mg–O5, 69.9(2)°, C1–Mg–O5 77.5(2)°). There is a large variation in Mg–O bond distances (Mg–O2 2.170(4) Å, Mg–O3 2.235(4) Å, Mg–O4 2.331(4) Å, Mg–O5 2.126(4) Å), while the Mg–C and Mg–Br bonds have quite normal lengths (2.176(5) and 2.597(23) Å, respectively).

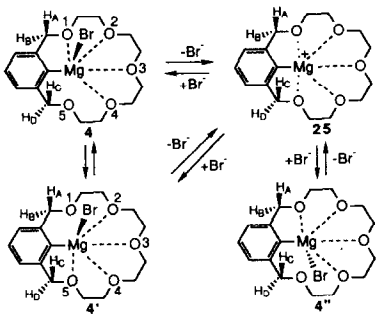
In order to relate the crystal structure of **4** to the ether cleavage reaction occurring during its formation from **2** and magnesium, this latter reaction was reinvestigated. From our earlier work [1], it was known that a

TABLE 3. Relevant bond distances (Å) and angles (°) for **4** (molecule 1)

Mg–C(1)	2.176(5)	Mg–O(2)	2.170(4)
Mg–Br	2.597(2)	Mg–O(3)	2.235(4)
Mg–O(4)	2.331(4)		
Mg–O(5)	2.126(4)		
Br–Mg–C(1)	110.6(1)	O(2)–Mg–O(3)	72.6(2)
Br–Mg–O(2)	93.1(1)	O(3)–Mg–O(4)	69.5(2)
Br–Mg–O(3)	148.0(1)	O(4)–Mg–O(5)	69.9(2)
Br–Mg–O(4)	88.0(1)	C(1)–Mg–O(5)	77.5(2)
Br–Mg–O(5)	93.1(1)		

deuterium oxide quench of the reaction mixture and subsequent acidic workup yielded the ether-cleavage product **8** (Scheme 3). This product must originate from a precursor carrying a vinyl ether group at the end of one of the "side-arms", which is lost during acidic hydrolysis. Since the hydroxylic positions in **8** are not identical two intermediate compounds (**7a** and **7b**) can be imagined, both of which will give **8** upon acidic hydrolysis. When the mixture formed from reaction of **2** with magnesium was quenched with deuterium oxide and worked up under slightly basic conditions, two different vinyl ether groups (ratio roughly 1 : 1) could be distinguished in the ^{1}H NMR spectrum (see Experimental section), in agreement with the presence of **7c** and **7d**. Thus, the ether-cleavage reaction occurring during the formation of **4** is slightly less specific than in the case of **3**, for which only one cleavage product was observed (see Introduction). However, it should be pointed out that in view of the *a priori* larger number of possible modes of cleavage (in total, five different products are conceivable), this cleavage reaction is also far from random.

We suggest that these observations can be rationalized as follows. The Grignard reagent **4**, which is the substrate for the ether cleavage by the intermediate carbanionic species (in analogy to Scheme 2), is asymmetric in the crystal, but not in solution. Its ^{1}H NMR spectrum (THF-d_8, 250 MHz) suggests a much higher symmetry: apparently C_{2v}. This implies that O1 and O5 are equally coordinated, as indicated by the structures **4** and **4′** (C_s symmetry, Scheme 8); this (fast) exchange leads to the equivalence of the methylene pairs H_A/H_B and H_C/H_D. But the two protons of each of the benzylic methylene groups are also equivalent (as was also found for **3** [1]). This is in sharp contrast to observations on other derivatives of 1,3-xylylene-18-crown-5, which mostly show an AB pattern for the benzylic methylene group because the crown ether bridge cannot swing around to the other side of the aromatic ring; this holds even for compounds such as **2** which carry smaller groups than MgBr at position 2. The high symmetry of **4** in solution can be accounted for assuming a fast ionic dissociation and recombination of the Mg–Br bond, leading to an equilibrium between **4** and its mirror image **4″** via cation **25** (C_{2v} symmetry); this equilibrium, which leads to the equivalence of H_A and H_B as well as H_C and H_D, must be rapid on the NMR time scale. (Note that **4′** and **4″** are structurally identical, but differ by the exchange of the methylene pairs H_A/H_B and H_C/H_D.) As O1 and O5 are weakly bound to magnesium, this leaves oxygens 2, 3 and 4 available for strong coordination. Consequently, only the ethylene protons between these latter three oxygens are activated for cleavage, as envisaged in the mechanism proposed in Scheme 3; as there are two different types of such protons, *i.e.* protons 9 and 10, their abstraction by the intermediate anionic species leads to the two cleavage products **7a** and **7b** in about equal amounts.



Scheme 8.

The crystal structures of bromomercurio compound **10** and Grignard 4 clearly illustrate the differing behaviors of magnesium and mercury in the aryl-metal bromide system. Magnesium tends to attain high coordination numbers, resulting in a (distorted) octahedral environment in **4**, in which the C–Mg–Br angle is 110.6(1)°, but the situation in the analogous mercury compound is quite different. Although weak coordination with the crown ether oxygens is discernable, this hardly influences the C–Hg–Br angle; in **10**, this angle is 175.0(2). The deviation from 180°, expected in an uncomplexed and undistorted mercury compound, may result either from a slight rehybridization of mercury as a result of coordination or from the steric interaction of the crown ether ring on one side of the molecule. Probably, both effects operate.

3. Experimental details

The crown ether bromides **1** and **2** were made by the known multistep procedure [2], starting from 2,6-dimethylaniline. Lithiation reactions were performed in standard glassware with ground joints under an argon atmosphere. THF was dried by distillation from $LiAlH_4$ prior to use. In order to prevent contamination by hydrolysis or oxidation, the synthesis of **4** and its quench reactions were performed in sealed and evacuated glass apparatus. For these experiments, the ethereal solvents were dried by distillation from a Na/K alloy. Concentrations of "total base" and Mg^{2+} of organomagnesium solutions were determined by titration of a hydrolyzed sample with acid-base or EDTA complexon, respectively [4].

NMR spectra were recorded with a Bruker WH-90 (^{1}H, 90 MHz) or a Bruker WM-250 (^{1}H, 250 MHz; ^{13}C,

62.89 MHz). GLC-MS analyses were performed on a HP 5890 GC/5970 MS combination, operating at 70 eV and equipped with a Chrompack CP Sil 19CB 51 m/0.21 mm column. Elemental analyses were carried out at the TNO Institute For Applied Chemistry and Elemental Analyses (Zeist, The Netherlands). The starting materials 2,6-dimethylaniline (Janssen), tetraethyleneglycol (Merck), chlorotrimethylgermane (Ventron), chlorotrimethylstannane (Janssen), benzophenone, 4,4'-dimethoxybenzophenone (Janssen) and mercuric bromide (Merck, z.A.) were commercially available. The magnesium used was triply sublimed. Mercurous bromide was precipitated from an aqueous mercurous nitrate solution by the addition of potassium bromide, washed with water and acetone, and vacuum dried. A solution of dry magnesium bromide in THF was prepared *via* the exchange reaction of mercuric bromide and magnesium metal [5].

3.1. (2-Bromomagnesio-1,3-xylylene)-18-crown-5 (4)

In a fully sealed glass apparatus, a suspension of magnesium bromide (1 mmol) in THF (7 ml) was added to a solution of 1 mmol of **9** (*vide infra*) in 100 ml of THF at −60°C. The reaction mixture was slowly warmed with shaking to room temperature. The magnesium bromide dissolved and a clear solution was obtained. Slow crystallization of **4** occurred when the solution was set aside for 24 h. The crystals, which have a very low solubility in THF (according to titration, about 3 mmol l^{-1}) were separated from their mother liquor. After identification by ^{1}H NMR spectroscopy in THF-d_8 (see below), some well-shaped crystals were selected for a X-ray structure determination. The remaining solid was hydrolysed, and the solution titrated to confirm the "total base" to Mg^{2+} ratio of 1:1.

3.2. Larger scale synthesis of 4

A solution of **2** (10 mmol, 3.75 g) in THF (70 ml) was treated with n-butyllithium (10 mmol, in 6 ml of n-hexane) at −60°C. The solution of the lithiation product **9**, still at −60°C, was immediately quenched, with stirring, with a magnesium bromide suspension (10 mmol) in THF (40 ml). When the mixture was allowed to warm to room temperature, a clear solution was obtained.

An aliquot (4.76 ml) was quenched with an excess of deuterium oxide (about 0.5 ml), diluted ammonium chloride solution was added, and the organic material was extracted with dichloromethane. The extract was dried, filtered, and analyzed by GLC-MS. Apart from the expected deuterated product **14a**, only about 10% of the starting material **2** was found to be present.

Crystallization of the remaining solution was induced by seeding with solid **4**. An amorphous colorless solid separated and was separated from the mother liquor by decantation then washed with 25 ml of THF which was distilled back on to the solid. Finally all solvent was distilled on to the solid material. Titration of a suspension of the solid in THF showed a "total base"/Mg^{2+} ratio of 1.03:1, in accordance with a Grignard reagent. The residue of the mother liquor (a light yellowish oil) contained 2.02 mmol "total base" and 4.30 mmol Mg^{2+} indicating a total yield of about 70% of **4** in both fractions.

4: ^{1}H NMR (250 MHz, THF-d_8, ref. THF-d_7 = 1.75 ppm): δ 3.86 (m, 12H, C_2H_4); 3.97–4.01 (m, 4H, C_2H_4); 4.69 (s, 4H, xylyl-CH_2); 6.76 (d, ^3J = 7 Hz, xylyl-H(4,6)); 6.86 (t, ^3J = 7 Hz, 1 H, xylyl-H(5)). Due to the very low solubility of **4** in THF, signals of hydrolysis product (**14**, 0.4 equiv.) were discernible [6].

The solid, containing **4**, was subjected to several quench reactions. Each time, a suspension of **4** (0.5–1 mmol, in 5 ml THF) was treated in a sealed ampoule with an excess of the pure quenching reagent. After 24 h the mixture was poured into water, and the organic material was extracted with dichloromethane. The extract was dried, filtered, and evaporated to dryness. In all cases a single product was formed. Quenching of **4** with an excess of deuterium oxide followed by the standard workup described above gave a colorless oil which crystallized upon standing: examination by ^{1}H NMR spectroscopy and GLC-MS revealed that the product was pure **14a** (*vide infra*).

The mixture formed from **2** with magnesium in THF was quenched with deuterium oxide and worked up under neutral to slightly basic conditions. The ^{1}H NMR spectrum of the residue revealed the presence of **14/14a** (66%) and two ether cleavage products bearing a vinylic ether group (**7a/7b**, 34%). ^{1}H NMR (400 MHz, $CDCl_3$, ref. $CHCl_3$ = 7.27 ppm) for **7a**: δ 4.024 (dd, $^3J_{cis}$ = 7 Hz, $^2J_{gem}$ = 2 Hz, 1 H, =CH_2Z); 4.203 (dd, $^3J_{trans}$ = 14 Hz, $^2J_{gem}$ = 2 Hz, 1 H, =CH_2E); 6.519 (dd, $^3J_{trans}$ = 14 Hz, $^2J_{cis}$ = 7 Hz, 1 H, OCH=). **7b**: δ 4.0164 (dd, $^3J_{cis}$ = 7 Hz, $^2J_{gem}$ = 2 Hz, 1 H, =CH_2Z); 4.195 (dd, $^3J_{trans}$ = 14 Hz, $^2J_{gen}$ = 2 Hz, 1 H, =CH_2E); 6.509 (dd, $^3J_{trans}$ = 14 Hz, $^2H_{cis}$ = 7 Hz, 1 H, OCH=). Due to extensive overlap, the C_2H_4, aryl-CH_2 and aryl-H signals of **14/14a** and **7a/7b** could not be assigned separately.

3.3. (2-Lithio-1,3-xylylene)-18-crown-5 (9)

The reported halogen-lithium exchange reaction of (2-bromo-1,3-xylylene)-18-crown-5 (**2**) [2] was slightly modified. To a solution of **2** (751 mg, 2 mmol) in THF (25 ml), cooled to −60°C (CO_2/acetone), was added within 1 min, 1.25 ml (2.1 equiv.) of a 1.6 M solution of n-butyllithium in n-hexane. After 2 min stirring, the quenching reagent was added. Subsequently, the mix-

ture was warmed during 1 h to room temperature and the solvent evaporated off. After addition of H_2O (0.5 ml) to the residue, the organic material was extracted with dichloromethane. The extract was dried ($MgSO_4$), filtered, and evaporated to dryness and the residue characterized by ^1H NMR spectroscopy (90 MHz) and/or GLC-MS.

*3.4. Preparation of **9** free of n-butyl bromide*

A solution of **10** (0.5 mmol, 288 mg) in THF (25 ml) was cooled to −60°C, and 2 equiv. of n-butyllithium (1 mmol in 0.7 ml of n-hexane) were added. After 15 min, an excess of EtOD (250 μl) was added and the mixture was warmed to room temperature. Water (200 ml) was added, and the organic products were extracted with dichloromethane. The extract was dried and filtered, and the solvent distilled off to give a colorless oil (0.44 g), the ^1H NMR spectrum (90 MHz, $CDCl_3$) of which revealed the presence of **14a** and di(n-butyl)mercury (**24**) in a 1:1 stoichiometry, together with about 3 equiv. of residual THF. GLC-MS analysis confirmed the presence of fully deuterated **14a** and of **24** without further side products. The spectral data of **14a** were in accordance with those reported previously [1].

24: GLC-MS mass spectrum: m/z (rel. intensity) 316 (M^+, 1), 202 (1, Hg^+), 57 (100).

*3.5. (2-Bromomercurio-1,3-xylylene)-18-crown-5 (**10**) and bis[(1,3-xylylene-18-crown-5)-2-yl]mercury (**11**) from **9** and mercuric bromide*

To a solution of **9** (2 mmol, in 50 ml THF) at −60°C was added during *ca.* 15 min, a molar equivalent of $HgBr_2$ in 10 ml of THF; during the addition a white suspension was formed. The mixture was slowly warmed to room temperature and evaporated to dryness. After the addition of water, the organic material was extracted with dichloromethane. The extract was dried, filtered, and evaporated to dryness, to give an amorphous white solid. As indicated by ^1H NMR spectroscopy (90 MHz, $CDCl_3$), two crown ether organomercury products were present. They were separated by means of fractional crystallization from acetone, and characterized by various spectroscopic techniques. The least soluble compound proved to be bis[(1,3-xylylene-18-crown-5)-2-yl]mercury (**11**, 0.30 g, 38%, m.p. 162–163°C); from the mother liquor, the more soluble (2-bromomercurio-1,3-xylylene)-18-crown-5 (**10**) was isolated (0.44 g, 37%).

Upon rapid addition (within 1 min) of the mercuric bromide solution to **9** by the procedure described above, only **10** was formed. After evaporation of the organic phase to dryness, crude **10** (1.07 g, 93% yield, > 95% pure according to ^1H NMR spectroscopy, $CDCl_3$, 90 MHz) was isolated as a colorless viscous oil, which crystallized upon standing. The product was recrystallized from acetone (0.67 g = 58% yield, m.p. 90–92°C).

10: ^1H NMR (250 MHz, $CDCl_3$, ref. $CHCl_3$ = 7.27 ppm): δ 3.50–3.94 (m, 16H, C_2H_4); 4.57 (2 × d, AB, $\delta\Delta$ = 0.19 ppm, ^2J = 12 Hz, 4H, xylyl–CH_2); 7.12–7.19 (m, 3H, xylyl–H). ^{13}C NMR (250 MHz, $CDCl_3$, ref. $CDCl_3$ = 77 ppm): δ 69.0 (t, ^1J(C–H) = 140 Hz, 2C, C_2H_4); 70.0 (t, ^1J(C–H) = 140 Hz, 2C, C_2H_4); 70.3 (t, ^1J(C–H) = 141 Hz, 2 C, C_2H_4); 70.3 (t, ^1J(C–H) = 142 Hz, 2C, C_2H_4); 74.4 (t, ^1J(C–H) = 139 Hz, Hg satellites ^3J(C–^{199}Hg) = 101 Hz, 2Cm, xylyl–CH_2); 127.6 (d, ^1J(C–H)-156 Hz, Hg satellites ^3J(C–^{199}Hg) = 177 Hz, 2C, xylyl(4,6)); 127.9 (d, ^1J(C–H) = 161 Hz, Hg satellites ^4J(C–^{199}Hg) = 13 Hz, 1C, xylyl(5)); 144.2 (s, Hg satellites ^2J(C–^{199}Hg) = 76 Hz, 2C, xylyl(1,3)); 152.6 (s, low intensity, 1C, xylyl(2)). MS (direct inlet, Varian CH5 DF): m/z (rel. intensity) 497 (100, M^+ – Br, $C_{16}H_{23}O_5Hg$), 295 (52, M^+ – HgBr), 177(15), 133(21), 119(63), 103(84), 89(57), 77(30). Parent ion mass calcd. for $C_{16}H_{23}O_5Hg$: 497.125; found 497.126. Melting point after repeated recrystallization from acetone: 94°C. Anal. Found: C, 33.34, H, 4.08; Hg, 34.80. $C_{16}H_{23}O_5HgBr$ calcd.: C, 33.37; H, 4.03; Hg, 34.83%.

11: ^1H NMR (250 MHz, $CDCl_3$, ref. $CHCl_3$ = 7.27 ppm): δ 2.81–2.89 (m, 4 H, C_2H_4); 3.16–3.23 (m, 4H, C_2H_4); 3.30–3.89 (m, 24H, C_2H_4); 4.80 (2 × d, AB, $\Delta\delta$ = 1.14 ppm, ^2J = 12 Hz, 8H, xylyl–CH_2); 7.12 (t, ^3J = 7 Hz, 2 H, xylyl–H(5)); 7.24 (d, ^3J = 7 Hz, 4H, xylyl–H(4,6)). ^{13}C NMR (250 MHz, $CDCl_3$, ref. $CDCl_3$ = 77 ppm): δ 67.4 (t, ^1J(C–H) = 139 Hz, 4C, C_2H_4); 70.4 (t, ^1J(C–H) = 140 Hz, 4C, C_2H_4); 70.6 (t, ^1J(C–H) = 140 Hz, 4C, C_2H_4); 71.0 (t, ^1J(C–H) = 131 Hz, 4C, C_2H_4); 75.7 (t, ^1J(C–H) = 151 Hz, Hg satellites ^3J(C–^{199}Hg) = 64 Hz, 4C, xylyl–CH_2); 126.3 (d, ^1J(C–H) = 159 Hz, 2C, xylyl(5)); 128.4 (d, ^1J(C–H) = 157 Hz, Hg satellites ^3J(C–^{199}Hg) = 90 Hz, 4C, xylyl(4,6)); 146.5 (s, Hg satellites ^2J(C–^{199}Hg) ~ 50 Hz, 4C, xylyl(1,3)); 172.7 (s, Hg satellites ^1J(C–^{199}Hg) = 1794 Hz, 2C, xylyl(2)). ^{199}Hg NMR (44.77 MHz, $CDCl_3$, ref. Ph_2Hg = 0 ppm): δ 49.75 (s, broad, 1 Hg). MS (CI, NH_3, Finnigan MAT 90): m/z (rel. intensity) 810 (78, M · NH_4^+, $C_{32}H_{50}O_{10}$-HgN); 514 (5, aryl–$Hg^+ \cdot NH_3$); 497 (15, aryl–Hg^+); 314 (100, aryl–H · NH_4^+). Anal. Found: C, 48.51, H, 5.86; Hg, 25.33; m.p. 162–163°C (acetone). $C_{32}H_{46}O_{10}$ Hg calcd.: C, 48.57; H, 5.86; Hg, 25.35%.

*3.6. Formation of **11** by the reaction of **10** with magnesium*

In a sealed glass apparatus, **10** (1.16 g, 2 mmol in 50 ml of THF) was stirred with magnesium (0.5 g, 20 mmol) at 50°C for 10 days. After settling of the magnesium(amalgam), the clear and colorless supernatant liquid was decanted. Titration of an aliquot (6.90 ml) showed the presence of 0.5 equiv. Mg^{2+} and no basic

material (< 0.01 mmol), suggesting a complete symmetrization of **10** to **11**. The remaining solution was quenched with D_2O (about 1 ml) and evaporated to dryness. After the addition of water the organic material was extracted with dichloromethane. The extract was dried, filtered and evaporated to dryness to give solid **11** (*vide supra*, > 95% pure according to ^1H NMR spectroscopy, $CDCl_3$, 90 MHz), in almost quantitative yield.

3.7. (2-Methylmercurio-1,3-xylylene)-18-crown-5 (12)

A mixture of a solution of **10** (1 mmol, 576 mg) in THF (25 ml, distilled from $LiAlH_4$) with magnesium metal (200 mg, about 8 mmol) was stirred under argon and methyl iodide (300 μl, about 5 mmol) was added from a syringe. After formation of the Grignard reagent, the colorless and clear solution was stirred for 60 h. The mixture was evaporated to dryness, water (50 ml) and 1 g of NH_4Cl were added, and the organic material extracted with dichloromethane. The extract was dried, filtered, and evaporated to dryness. The product (0.35 g, colorless oil) crystallized out slowly upon standing. According to ^1H NMR spectroscopy ($CHCl_3$, 90 MHz), a mixture of (2-methylmercurio-1,3-xylylene)-18-crown-5 (**12**, 80 mmol%, 61% yield relative to **10**) and hydrolysis product (**14**, 20 mol%) was obtained. Compound **12** could be purified to some extent by crystallization from diethyl ether at −20°C (m.p. 56–57°C), although a complete removal of **14** was not achieved.

Compound **12** proved to be quite stable at room temperature towards disproportionation to **11** and dimethylmercury. After 1 month, solid **12** was contaminated with < 5% of **11** according to ^1H NMR spectroscopy ($CDCl_3$, 90 MHz).

12: ^1H NMR (250 MHz, $CDCl_3$, ref. $CHCl_3$ = 7.27 ppm): δ 0.51 (s, $^2J(^{199}Hg–H)$ = 122 Hz, 3H, Me); 3.53–3.76 (m, 16H, C_2H_4); 4.33 (2 × d, A part of AB, ^2J = 12 Hz, 2H, xylyl–CH_2); 4.76 (d, B part of AB, ^2J = 12 Hz, 2H, xylyl–CH_2); 7.10 (t, ^3J = 7 Hz, 1H, xylyl–H(5)); 7.20 (d, ^3J = 7 Hz, 2H, xylyl–H(4,6)). ^{13}C NMR (250 MHz, $CDCl_3$, ref. $CDCl_3$ = 77 ppm): δ 1.20 (q, ^1J(C–H) = 130 Hz, 1C, Me); 68.4 (t, ^1J(C–H) = 140 Hz, 2C, C_2H_4); 70.5 (t, ^1J(C–H) = 140 Hz, 6C, C_2H_4); 75.7 (t, ^1J(C–H) = 141 Hz, 2C, xylyl–CH_2); 126.2 (d, ^1J(C–H) = 160 Hz, 1C, xylyl(5)), 127.7 (d, ^1J(C–H) = 155 Hz, 2C, xylyl(4,6)); 146.0 (s, 2C, xylyl(1,3)), 178 (s, low intensity, 1C, xylyl(2)). GLC-MS mass spectrum: *m/z* (rel. intensity) 497 (100, $C_{16}H_{23}O_5Hg$, M^+ − Me), 321(3), 307(18), 217(10), 145(21), 119(26), 103(77), 91(26), 77(44), 45(52).

3.8. Bis[(1,3-xylylene-15-crown-4)-2-yl]mercury (13)

To a stirred suspension of mercurous bromide (2 mmol, 0.56 g) in a solution of **1** (2 mmol, 0.66 g) in THF (50 ml) at −60°C, n-butyllithium (2 mmol, in 1.56 ml of n-hexane) was added within 2 min. The mixture gradually turned black owing to the formation of dispersed mercury. After stirring for a further 0.5 h at −60°C, the mixture was warmed to room temperature and filtered through a small Al_2O_3 column (Merck 90, activity II–III, 1 × 10 cm). The filtrate was evaporated to dryness to leave a colorless solid (0.64 g). According to ^1H NMR spectroscopy ($CDCl_3$, 90 MHz) this contained **13** together with crown ether hydrolysis product **5** and n-butylmercury bromide. Pure **13** was obtained by recrystallization from acetone (0.40 g, 57% yield).

13: Colorless crystalline solid, m.p. 210°C, sublimation (1 bar) starting at about 200°C. ^1H NMR (250 MHz, $CDCl_3$, ref. $CHCl_3$ = 7.27 ppm): δ 3.28–3.36 (m, 4H, C_2H_4); 3.46–3.75 (m, 20H, C_2H_4); 4.80 (2 × d, AB, Δδ = 1.13 ppm, ^2J = 12 Hz, 8H, xylyl–CH_2); 7.14 (t, ^3J = 7 Hz, 2H, xylyl–H(5)); 7.28 (d, ^3J = 7 Hz, 4H, xylyl–H(4,6)). ^{13}C NMR (62.89 MHz, $CDCl_3$, ref. $CDCl_3$ = 77 ppm): δ 68.1 (t, ^1J(C–H) = 141 Hz, 4C, C_2H_4); 70.3 (t, ^1J(C–H) = 141 Hz, 4C, C_2H_4); 70.5 (t, ^1J(C–H) = 141 Hz, 4C, C_2H_4); 75.8 (t, ^1J(C–H) = 142 Hz, Hg satellites $^3J(C–^{199}Hg)$ = 66 Hz, 4C, xylyl–CH_2); 125.3 (d, ^1J(C–H) = 159 Hz, 2C, xylyl(5)); 128.9 (d, ^1J(C–H) = 158 Hz, Hg satellites $^3J(C–^{199}Hg)$ = 92 Hz, 4C, xylyl(4,6)); 145.9 (s, Hg satellites $^2J(C–^{199}Hg$ = 51 Hz, 4C, xylyl(1,3)); 173.8 (s, 2C, xylyl(2)). MS (CI, NH_3, Finnigan MAT 90); *m/z* (rel. intensity) 722 (17, M · NH_4^+, $C_{28}H_{42}O_8HgN$); 470 (37, aryl–$Hg^+ \cdot NH_3$); 453 (10, aryl–Hg^+); 270 (100, aryl–H · NH_4^+). Anal. Found: C, 47.73, H, 5.55; Hg, 28.38. $C_{28}H_{38}O_8Hg$ calcd.: C, 47.83; H, 5.45; Hg, 28.53%.

3.9. (2-D-1,3-Xylylene)-18-crown-5 (14a)

A solution of **4** (2 mmol, 25 ml THF) was treated with a large excess (250 μL) of EtOD. Standard workup gave a colorless oil (0.65 g), which crystallized upon standing. Analysis by ^1H NMR spectroscopy (90 MHz, $CDCl_3$) and GLC-MS revealed the quantitative formation of the deuterated compound **14a**. The solid material was recrystallized from diethyl ether at −20°C (m.p. 43–44°C, 0.51 g). The spectroscopic data for **14a** were in accord with those reported previously [1].

3.10. (2-Trimethylstannyl-1,3-xylylene)-18-crown-5 (15)

Upon mixing a suspension of **4** in THF with a small excess of chlorotrimethylstannane the insoluble starting material disappeared within 10 s. Aqueous sodium hydroxide was added to destroy the residual chlorotrimethylstannane before the usual workup. The product, a colorless oil, was identified by ^1H NMR ($CDCl_3$ 250 MHz) as pure **15**; the ^1H NMR spectrum was in accord with data obtained before [1]. The product solidified on standing; recrystallization from ethanol gave material of m.p. 42–43°C.

3.11. (2-Iodo-1,3-xylylene)-18-crown-5 (16)

A slight excess of iodine was added to a suspension of **4** in THF. Prior to extraction with dichloromethane, sodium hydroxide solution was added to destroy the excess of iodine. The crude product was an almost colorless oil, which solidified upon cooling (+5°C); it was identified as pure (> 95%) (2-iodo-1,3-xylylene)-18-crown-5 (**16**); crystallization from ethanol (−60°C) gave material of m.p. 45°C. ^{1}H NMR (250 MHz, $CDCl_3$, ref. $CHCl_3$ = 7.27 pm): δ 3.5–3.56 (m, 8H, C_2H_4); 3.62 (s, 8H, C_2H_4); 4.67 (s, 4H, xylyl-CH_2); 7.26 (s, 3H, xylyl-H). The ^{1}H NMR spectrum of **16** differs only slightly from that of the corresponding bromide **2**. Mass spectrum (direct inlet): *m/z* (rel. intensity) 422 (M^+, 13), 295 ($M^+ - I$, 26), 230(46), 177(41), 133(30), 119(32), 103(42), 89(100), 77(15), 56(19).

3.12. (2-(Diphenylhydroxy)methyl-1,3-xylylene(-18-crown-5 (17)

A solution of 1 mmol (0.18 g) of benzophenone in THF (5 ml) was added during 5 min to a solution of **9** (2 mmol, in 25 ml THF) at −60°C. The greenish mixture was allowed to warm to room temperature overnight, during which a white precipitate was formed. The mixture was diluted with water (250 ml), and the organic material extracted with dichloromethane. After evaporation of the solvent, crude (2-(diphenylhydroxymethyl)-1,3-xylylene)-18-crown-5 (**17**) was obtained as a cloudy oil (1.15 g). Crystallization from acetone yielded a colorless solid (0.77 g, m.p. 106°C, yield 80%).

17: ^{1}H NMR (250 MHz): δ 3.08–3.29 (m, A_2B_2, 4H, C_2H_4); 3.41–3.69 (m, 10H, C_2H_4); 3.89 (m, AB, $\Delta\delta$ = 0.53, ^2J = 13 Hz, 4H, xylyl-CH_2); 5.26 (s, broad, 1H, OH); 7.07–7.37 (m, 9H, phenyl-H and xylyl-H); 7.52 (d, ^3J = 7 Hz, 4H, phenyl-H(2,6)). ^{13}C NMR (62.89 MHz): δ 67.4 (t, ^1J(C–H) = 139 Hz, 4C, C_2H_4); 69.4 (t, ^1J(C–H) = 140 Hz, 4C, C_2H_4); 70.2 (t, ^1J(C–H) = 141 Hz, 4C, C_2H_4); 70.4 (t, ^1J(C–H) = 141 Hz, 4C, C_2H_4); 72.0 (t, ^1J(C–H) = 144 Hz, 4C, xylyl-CH_2); 79.9 (s, 1C, $C_{quat.}$); 125.6 (d, ^1J(C–H) = 159 Hz, 6C, aryl-C); 126.7 (d, ^1J(C–H) = 161 Hz, 1C, xylyl-C(5)); 127.6 (d, ^1J(C–H) = 159 Hz, 4C, phenyl-C); 130.2 (d, ^1J(C–H) = 160 Hz, 2C, xylyl-C(4,6)); 139.9 (s, 2C, aryl-C); 145.2 (s, 1C, xylyl-C(2)); 149.8 (s, 2C, aryl-C). MS (direct inlet, Varian MAT CH5 DF): extensive fragmentation occurred; no parent ion was observed.

The identity of **17** was confirmed by conversion into its methyl ether. In a three-necked flask (50 ml) under nitrogen, potassium hydride (8 mmol) was washed free from paraffin with THF (three portions of 5 ml) and suspended in THF (25 ml). To the stirred mixture, solid **17** (1 mmol, 478 mg) was added in one portion. When the evolution of hydrogen had ceased (0.5 h), methyl iodide (2 mmol, 0.28 g, 125 μl) was added from a syringe. After a further 1.5 h stirring, water (1 ml) was added and the mixture evaporated to dryness. After the addition of 25 ml of water, the organic products were extracted with dichloromethane. The extract was dried, filtered, and evaporated to dryness to yield a yellowish oil (0.49 g). According to ^{1}H NMR spectroscopy, the conversion of **17** into (2-(1,1-diphenyl-2-oxapropyl)-1,3-xylylene)-18-crown-5 (**17a**) was almost complete. Recrystallization from diethyl ether (−20°C) yielded 0.39 g of **17a** (79%, colorless solid, m.p. 85°C).

17a: ^{1}H NMR (250 MHz, $CDCl_3$, ref. $CHCl_3$ = 7.27 ppm): δ 2.98–3.05 (m, 2H, C_2H_4); 3.20–3.43 (m, 14H, C_2H_4); 3.21 (s, 3H, OMe); 4.10 (m, AB, $\Delta\delta$ = 0.09 ppm, ^2J = 13 Hz, 4H, aryl-CH_2); 7.24–7.42 (m, 11H, aryl-H); 7.59 (d, ^3J = 8 Hz, 2H, xylyl-H(4,6)). ^{13}C NMR (62.89 MHz, $CDCl_3$, ref. $CDCl_3$ = 77 ppm): δ 52.2 (q, ^1J(C–H) = 142 Hz, 1C, OMe); 69.7 (t, ^1J(C–H) = 142 Hz, 2C, C_2H_4); 70.0 (t, ^1J(C–H) = 139 Hz, 2C, C_2H_4); 70.3 (t, ^1J(C–H) = 142 Hz, 4C, C_2H_4); 71.4 (t, ^1J(C–H) = 148 Hz, 2C, aryl-CH_2); 87.2 (s, 1C, $C_{quat.}$); 127.0 (d, ^1J(C–H) = 160 Hz, 2C, aryl-C); 127.1 (d, ^1J(C–H) = 161 Hz, 1C, xylyl-C(5)); 127.8 (d, ^1J(C–H) = 165 Hz, 4C, phenyl-C); 128.0 (d, ^1J(C–H) = 160 Hz, 4C, phenyl-C); 129.1 (d, ^1J(C–H) = 165 Hz, 2C, aryl-C); 140.0 (s, 1C, xylyl-C(2)); 140.4 (s, 2C, aryl-C); 144.5 (s, 2C, aryl-C). Anal. Found: C, 72.40; H, 7.26. $C_{30}H_{36}O_6$ calcd.: C, 73.15; H, 7.37%.

3.13. Preparation of (2-(diphenylhydroxy)methyl-1,3-xylylene)-18-crown-5 (17) from 4

In a fully sealed glass ampoule, a suspension of *ca.* 2 mmol of **4** in 5 ml of THF was treated with benzophenone (0.36 g, 2 mmol) at 80°C for 5 h, during which the insoluble **4** gradually disappeared. Before all the **4** had dissolved, a new colorless product suddenly crystallized out. After cooling to room temperature, the contents of the ampoule were quenched with an excess (about 1 ml) of deuterium oxide. Diluted hydrochloric acid was added, and the organic products were extracted with dichloromethane. The extract was dried, filtered and evaporated to dryness to leave 1.40 g of a colorless oil. According to ^{1}H NMR spectroscopy (90 MHz, $CDCl_3$), a mixture of **17** (*vide supra*, about 75%) and **14a** (about 25%, free of **14**) was present. Titration of the aqueous phase of the extraction showed the presence of 2.76 mmol Mg^{2+}, indicating that the amount of **4** used was larger than intended. Crystallization of **17** was from diethyl ether at −20°C gave material of m.p. 106°C (0.73 g, 76% yield).

3.14. (2-Trimethylgermyl-1,3-xylylene)-18-crown-5 (18)

A solution of **9** (2 mmol in 25 ml of THF) was treated with chlorotrimethylgermane (250 μl, 0.31 g, 2

mmol) at −60°C. The mixture was allowed to warm up slowly (about 2 h), quenched with water. The product was isolated by the standard workup as a colorless oil (0.90 g). According to ^{1}H NMR spectroscopy ($CDCl_3$, 90 MHz), about 90% of **18** had been formed, together with 10% of **14**. Recrystallization from n-pentane at −20°C yielded pure **18** as a white solid (0.68 g, 82%, m.p. 35–36°C).

18: ^{1}H NMR (250 MHz): δ 0.58 (s, 9H, Me); 3.39–3.60 (m, 16H, C_2H_4); 4.63 (M, AB, $\Delta\delta = 0.80$ ppm, $^2J = 12$ Hz, 4H, aryl–CH_2); 7.20–7.22 (m, 3H, aryl–H). ^{13}C NMR (62.89 MHz): δ 3.4 (q, ^1J(C–H) = 125 Hz, 3C, Me); 68.4 (t, ^1J(C–H) = 139 Hz, 2C, C_2H_4); 70.1 (t, ^1J(C–H) = 142 Hz, 2C, C_2H_4); 70.3 (t, ^1J(C–H) = 142 Hz, 4C, C_2H_4); 74.1 (t, ^1J(C–H) = 141 Hz, 2C, aryl–CH_2); 127.3 (d, ^1J(C–H) = 160 Hz, 1C, aryl–C(5)); 129.6 (dm, ^1J(C–H) = 158 Hz, 2C, aryl–C(4,6)); 142.6 (s, 1C, aryl–C(2)); 144.7 (s, 2C, aryl–C(1,3)). GLC-MS mass spectrum: *m/z* (rel. intensity) 414 (2, M^+), 399 (100, $M^+ - Me$), 237(10), 223(46), 207(19), 193(10), 177(8), 163(8), 147(8), 133(13), 117(82), 104(43), 91(21), 89(26), 87(39), 45(82). Anal. Found: C, 55.32; H, 7.71. $C_{19}H_{32}O_5Ge$ calcd.: C, 55.25; H, 7.81%.

3.15. (2-Diphenylphosphinyl-1,3-xylylene)-18-crown-5 (19) and (2-oxodiphenylphosphinyl-1,3-xylylene)-18-crown-5 (20)

To a solution of **9** (2 mmol in 25 ml of THF) at −60°C, chlorodiphenylphosphine (1.2 equiv., 0.54 g, 459 μl) was added within 2 min; during which the mixture turned yellow. When the mixture was allowed to warm to room temperature during several hours, the color disappeared. After standing overnight, the mixture was evaporated to dryness, water was added, and the organic material extracted with dichloromethane. The extract was dried and filtered, and the solvent distilled off. A colorless oil (1.45 g) obtained contained about 60% of (2-diphenylphosphinyl-1,3-xylylene)-18-crown-5 (**19**) according to the ^{1}H NMR spectrum ($CDCl_3$, 90 MHz). Purification was performed by gradient column separation (Al_2O_3, Merck 90, 1.5 × 30 cm, eluent pentane/Et_2O/THF). An unknown byproduct was eluted first with 200 ml of a 1:1 Et_2O/pentane mixture. Subsequently, the main product was eluted with Et_2O containing 10% of THF. After evaporation of the eluent, **19** was obtained as a colorless oil (0.68 g, 71% yield) and characterized by ^{1}H NMR spectroscopy. In spite of several attempts, **19** could not be crystallized.

19: ^{1}H NMR (250 MHz, $CDCl_3$, ref. $CHCl_3 = 7.27$ ppm): δ 3.18–3.50 (m, 16H, C_2H_4): 4.10 (d, A part of AB, $^2J = 12$ Hz, 2H, xylyl–CH_2); 4.93 (dd, B part of AB, $^2J = 12$ Hz, $^4J(^{31}P–H) = 3$ Hz, 2H, xylyl–CH_2); 7.27–7.53 (m, 13H, aryl–H). Due to its low volatility, GLC-MS analysis was not possible.

In contact with air, both pure and in solution, **19** was slowly oxidized (in about 1 year) quantitatively to the corresponding oxide (2-oxodiphenylphosphinyl-1,3-xylylene)-18-crown-5 (**20**), a water-soluble colorless oil.

20: ^{1}H NMR (250 MHz, $CDCl_3$, ref. $CHCl_3 = 7.27$ ppm): δ 3.11–3.18 (m, 2H, C_2H_4); 3.24–3.46 (m, 14H, C_2H_4); 4.11 (d, A part of AB, $^2J = 13$ Hz, 2H, xylyl–CH_2); 4.51 (d, B part of AB, $^2J = 13$ Hz, 2H, xylyl–CH_2); 7.44–7.55 (m, 9H, phenyl–H(2,6) and xylyl–H); 7.75–7.84 (m, 4H, phenyl–H(3,5)).

^{13}C NMR (62.89 MHz, $CDCl_3$, ref. $CDCl_3 = 77$ ppm): δ 69.5 (t, ^1J(C–H) = 141 Hz, 2C, C_2H_4); 70.0 (t, ^1J(C–H) = 141 Hz, 2C, C_2H_4); 70.4 (t, ^1J(C–H) = 141 Hz, 2C, C_2H_4); 70.7 (t, ^1J(C–H) = 141 Hz, 2C, C_2H_4); 72.1 (td, ^1J(C–H) = 144 Hz, $^3J(C–^{31}P) = 4$ Hz, 2C, xylyl–CH_2); 128.4 (dd, ^1J(C–H) = 151 Hz, $^3J(C–^{31}P) = 12$ Hz, 4C, phenyl(3)); 129.7 (dd, ^1J(C–H) = 147 Hz, $^3J(C–^{31}P) = 10$ Hz, 2C, xylyl(4,6)); 131.1 (dd, ^1J(C–H) = 161 Hz, $^4J(C–^{31}P) = 2$ Hz, 1C, xylyl(5)); 131.5 (dd, ^1J(C–H) = 159 Hz, $^4J(C–^{31}P) = 2$ Hz, 2C, phenyl(4)); 131.9 (dd, ^1J(C–H) = 157 Hz, $^2J(C–^{31}P) = 10$ Hz, 4C, phenyl(2)); 134.8 (d, $^1J(C–^{31}P) = 103$ Hz, 2C, phenyl(1)); 144.7 (d, $^2J(C–^{31}P) = 9$ Hz, 2C, xylyl(1,3)). Probably due to a very long relaxation time, xylyl(2) is not visible. ^{31}P NMR (101.2 MHz, BB, $CDCl_3$, ref. 85% H_3PO_4 external = 0 ppm): δ 30.52. MS (direct inlet, Finnigan CH5): *m/z* (relative intensity) 496 (52, M^+, $C_{28}H_{33}O_6P$), 335(10), 320(89), 318(100), 303(20), 291(13), 165(20), 105(20), 89(25), 78(22). Molecular ion mass calcd. for $C_{28}H_{33}O_6P$: 496.201. Found: 496.202.

3.16. (2-(4,4'-Dimethoxydiphenylhydroxymethyl)-1,3-xylylene)-18-crown-5 (21)

To a solution of **9** (2 mmol in 50 ml of THF) at −60°C, a solution of 4,4'-dimethoxybenzophenone (2 mmol, 0.48 g) in THF (10 ml) was added during 5 min. The mixture was allowed to warm overnight to room temperature, and subsequently evaporated to dryness. The residue was transferred to a separatory funnel containing water and dichloromethane. Brine was added, and all the organic material was extracted into the dichloromethane. After evaporation of the solvent, crude [2-(4,4'-dimethoxy-diphenylhydroxymethyl)-1,3-xylylene]-18-crown-5 (**21**) was obtained as a waxy solid (1.20 g) that slowly turned slightly red on contact with air. The solid was washed with diethyl ether; 0.62 g of **21** remained (m.p. 126°C, yield 58%). According to ^{1}H and ^{13}C NMR spectroscopy, its purity was > 95%. Recrystallization proved to be impossible due to interference by the methanol-elimination reaction (*vide infra*).

TABLE 4. Crystal data and details of the structure determination

	4	**10**	**11**
Crystal data			
Empirical formula	$C_{16}H_{23}BrMgO_5$	$C_{16}H_{23}BrHgO_5$	$C_{32}H_{46}HgO_{10}$
Formula weight	399.56	575.85	791.30
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, b, c (Å)	10.016(1), 12.804(1), 15.172(1)	12.249(2), 8.5030(10), 17.461(3)	9.6230(10), 8.831(5), 19.400(10)
α, β, γ (°)	77.77(1), 76.16(1), 70.48(1)	90, 91.390(10), 90	90, 96.52(3), 90
V (Å^3)	1762.1(3)	1818.1(5)	1638.0(13)
z	4	4	2
$D_{calc.}$ (g cm^{-3})	1.506	2.104	1.604
$F(000)$ (electrons)	824	1096	796
μ (cm^{-1})	37.4	106.6	47.5
Crystal size (mm)	0.50 × 0.62 × 0.88	0.25 × 0.45 × 0.55	0.30 × 0.45 × 0.50
Data collection			
Temperature (K)	295	295	295
Radiation (Å)	Cu Kα(Ni) 1.54184	Mo Kα(Zr) 0.71073	Mo Kα(Zr) 0.71073
Theta min–max (°)	3.0, 70.0	1.17, 27.5	1.05, 27.5
Scan type	ω–2 θ	ω–2θ	ω–2θ
Scan (°)	0.50 + 0.15 tan(θ)	0.40 + 0.35 tan(θ)	0.60 + 0.35 tan(θ)
Horizontal and vertical aperture (mm)	3.00, 5.00	4.00, 6.00	3.00, 3.00
Reference reflection(s)	2 −2 −2, 3 3 1 (decay 8%)	5 0 7, 3 3 −4 (13% decay)	1 0 3; 1 1 0; 0 1 7 (no decay)
Dataset	−12:11, −15:15, −18:0	0:15, 0:11, − − 22:22	0:12; 0:11, −25:25
Total unique data	6953, 6682	4646, 4154	4246, 3760
Observed data [$I > 2.5\ \sigma(I)$] refinement	4857	3111	2579
N_{ref}, N_{par}	4857, 436	3110, 209	2577, 198
R, wR, S	0.0552, 0.0723, 1.40	0.042, 0.040, 3.28	0.0219, 0.0244, 1.15
Weighting scheme	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$
Max. and ave-shift/error	0.005, 0.001	0.10, 0.02	0.10, 0.01
Min. and max. residual density (e A^{-3})	−1.21, 0.54	−1.24, 1.31	−1.27, 0.86

21: ^{1}H NMR (250 MHz, $CDCl_3$, ref. $CHCl_3$ = 7.27 ppm): δ 3.11–3.30 (m, 4H, C_2H_4); 3.40–3.84 (m, 12H, C_2H_4); 3.75 (s, 6H, OMe); 3.57 (d, A part of AB, ^2J = 13 Hz, 2H, aryl–CH_2); 4.21 (d, B part of AB, ^2J = 13 Hz, 2H, aryl–CH_2); 5.12 (s, 1H, OH); 6.76 (d, A part of AB, ^3J = 9 Hz, 4H, aryl–H); 7.37 (d, B part of AB, ^3J = 9 Hz, 4H, aryl–H); 7.24–7.35 (m, 3H, xylyl–H). ^{13}C NMR (62.89 MHz, $CDCl_3$, ref. $CDCl_3$ = 77 ppm): δ 55.0 (q, ^1J(C–H) = 144 Hz, 2C, OMe); 67.7 (t, ^1J(C–H) = 138 Hz, 2C, CH_2); 69.6 (t, ^1J(C–H) = 141 Hz, 2C, CH_2); 70.4 (t, ^1J(C–H) = 141 Hz, 2C, CH_2); 70.5 (t, ^1J(C–H) = 141 Hz, 2C, CH_2); 72.1 (t, ^1J(C–H) = 145 Hz, 2C, xylyl–CH_2); 79.6 (s, 1C, C–OH); 113.1 (d, ^1J(C–H) = 159 Hz, 4C, aryl–C(3,5)); 126.7 (d, ^1J(C–H) = 158 Hz, 1C, xylyl–C(5)); 126.8 (d, ^1J(C–H) = 158 Hz, 4C, aryl–C(2,6)); 130.2 (d, ^1J(C–H)) = 162 Hz, 2C, xylyl–C(4,6)); 140.0 (s, 2C); 142.5 (s, 2C); 145.6 (s, 1C, xylyl–C(2)); 157.6 (s, 2C). MS (DCI, NH_3, Finnigan MAT 90): *m/z* (relative intensity) 556 (100, $C_{31}H_{42}NO_8$, M · NH_4^+), 540(23), 521(10, $C_{31}H_{37}O$, M^+ − OH), 391(11), 314(30), 283(24), 243(27). Anal. Found: C, 68.05, H, 7.03. $C_{31}H_{38}O_8$ calcd.: C, 69.13; H, 7.11%.

3.17. {2-[(4-Methoxyphenyl)(4'-oxo-2',5'-cyclohexylidene)methyl]-1,3-xylylene}-18-crown-5 (22)

In a separatory funnel, a solution of **21** (0.10 g) in dichloromethane (10 ml) was shaken for several minutes with dilute HCl (5%). During this operation, the mixture rapidly turned deep red. Upon neutralization by the addition of solid $NaHCO_3$, the color changed to a less intense orange. The organic layer was separated, dried, filtered, and evaporated to dryness to leave a dark-orange powder (about 0.10 g), which was shown to be almost pure (> 95%) **22** by ^{1}H NMR spectroscopy ($CDCl_3$, 90 MHz). The compound was recrystallized from methanol; m.p. 181–182°C.

22: ^{1}H NMR (250 MHz, $CDCl_3$, ref. TMS = 0 ppm): δ 3.30–3.51 (m, 14H, C_2H_4): 3.63–3.75 (m, 2H, C_2H_4); 3.82 (s, 3H, OMe); 4.20 (d, A part of AB, ^2J = 13 Hz, xylyl–CH_2); 4.36 (d, B part of AB, ^2J = 13 Hz, xylyl–CH_2); 6.44–6.52 (m, 2H, chin–H(3,5)); 6.97 (2 × d, AB, $\Delta\delta$ = 0.22 ppm, ^3J = 9 Hz, aryl–H); 7.40–7.4975 (m, 3H, xylyl–H(4–6)); 7.52–7.64 (m, 2H, chin-H(2,6)). ^{13}C NMR (62.89 MHz, DMSO-d_6, ref. TMS = 0 ppm): δ 55.5 (q, ^1J(C–H) = 143 Hz, 1C, OMe); 68.8 (t, ^1J(C–H)

= 142 Hz, 2C, C_2H_4); 69.9 (s, 1C, $C_{quat.}$); 70.1 (t, ^1J(C–H) = 141 Hz, 4C?, C_2H_4); 70.2 (t, ^1J(C–H) = 141 Hz, 2C?, C_2H_4); 70.4 (t, ^1J(C–H) = 143 Hz, 2C, xylyl–CH_2); 114.3 (d, ^1J(C–H) = 163 Hz, 2C, phenyl–C(3,5)); 126.6 (d, ^1J(C–H) = 166 Hz, 1C, arom. C–H); 128.0 (d, ^1J(C–H) = 162 Hz, 1C, arom. C–H), 128.5 (d, ^1J(C–H) = 162 Hz, 1C, arom. C–H); 129.8 (d, ^1J(C–H) = 160 Hz, 2C, arom. C–H); 130.5 (s, 1C?, arom. $C_{quat.}$); 130.7 (s, 1C?, arom. $C_{quat.}$); 132.8 (d, ^1J(C–H) = 161 Hz, 2C, arom. C–H); 136.5 (s, 2C, xylyl–C(1,3)); 137.9 (d, ^1J(C–H) = 161 Hz, 1C, arom. $C_{quat.}$); 139.2 (s, 1C, arom. $C_{quat.}$); 142.8 (d, ^1J(C–H) = 168 Hz, 1C, chin.–C); 154.9 (s, 1C, phenyl–C(4)); 160.7 (s, 1C, chin.–C(1)); 186.6 (s, 1C, C=O). MS (direct inlet, Finnigan CH5); *m/z* (relative intensity) 506 (M^+, $C_{30}H_{34}O_7$), 329(28), 312(24), 299(7), 283(18), 269(9), 252(15), 239(10), 221(11), 208(10), 194(7), 178(6), 165(10), 135(12), 121(14). Parent ion mass calcd. for $C_{30}H_{34}O_7$: 506.230. Found: 506.233. Anal. Found: C, 69.85, H, 6.76; O, 22.38. $C_{30}H_{34}O_7$ calcd.: C, 71.13; H, 6.76; O, 22.11%.

TABLE 5. Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for $C_{16}H_{23}BrMgO_5$ (**4**)

Atom	*x*	*y*	*z*	U_{eq} (Å^2) [a]
Br(1)	0.08051(6)	0.31256(4)	0.16079(4)	0.0551(2)
Mg(1)	0.04344(17)	0.18007(12)	0.31382(11)	0.0414(5)
O(1)	−0.0669(4)	0.4211(3)	0.4188(3)	0.0633(14)
O(2)	−0.1772(3)	0.2805(3)	0.3549(2)	0.0472(11)
O(3)	−0.0768(4)	0.0647(3)	0.4017(3)	0.0539(11)
O(4)	0.0305(4)	0.0532(3)	0.2287(3)	0.0595(14)
O(5)	0.2497(4)	0.0625(3)	0.2819(3)	0.0630(14)
C(1)	0.1593(5)	0.1991(4)	0.4109(3)	0.0433(17)
C(2)	0.3027(5)	0.1340(4)	0.3989(4)	0.0504(19)
C(3)	0.4007(6)	0.1338(5)	0.4513(5)	0.066(2)
C(4)	0.3555(7)	0.2003(5)	0.5184(5)	0.072(3)
C(5)	0.2140(7)	0.2679(5)	0.5335(4)	0.064(2)
C(6)	0.1195(6)	0.2688(4)	0.4799(3)	0.0479(17)
C(7)	−0.0310(6)	0.3464(5)	0.4984(4)	0.060(2)
C(8)	−0.2134(6)	0.4538(5)	0.4111(4)	0.061(2)
C(9)	−0.2314(6)	0.4019(4)	0.3376(4)	0.0512(17)
C(10)	−0.2770(6)	0.2316(4)	0.4206(4)	0.0564(19)
C(11)	−0.1892(6)	0.1261(5)	0.4679(4)	0.064(2)
C(12)	−0.1290(7)	0.0022(5)	0.3573(5)	0.073(3)
C(13)	−0.0070(7)	−0.0424(5)	0.2837(5)	0.073(3)
C(14)	0.1658(7)	0.0217(5)	0.1646(4)	0.069(2)
C(15)	0.2877(7)	−0.0120(5)	0.2172(5)	0.071(2)
C(16)	0.3604(6)	0.0599(5)	0.3250(4)	0.065(2)
Br(2)	0.41676(7)	0.68189(5)	0.34002(4)	0.0572(2)
Mg(2)	0.44578(16)	0.61545(12)	0.18563(11)	0.0396(5)
O(6)	0.2327(4)	0.6027(3)	0.2077(3)	0.0579(14)
O(7)	0.4373(4)	0.4390(3)	0.2688(3)	0.0583(14)
O(8)	0.5540(4)	0.4826(3)	0.0978(2)	0.0508(11)
O(9)	0.6741(3)	0.6038(3)	0.1505(2)	0.0492(11)
O(10)	0.5800(4)	0.8337(3)	0.0973(3)	0.0613(14)
C(17)	0.3489(5)	0.7472(3)	0.0833(3)	0.0387(14)
C(18)	0.4031(5)	0.8274(4)	0.0176(3)	0.0435(16)
C(19)	0.3215(6)	0.9028(4)	−0.0457(4)	0.0571(19)
C(20)	0.1867(7)	0.8994(5)	−0.0462(5)	0.069(2)
C(21)	0.1265(6)	0.8263(5)	0.0186(5)	0.061(2)
C(22)	0.2075(5)	0.7528(4)	0.0819(4)	0.0454(17)
C(23)	0.1351(5)	0.6770(5)	0.1517(4)	0.0554(19)
C(24)	0.1825(7)	0.5171(5)	0.2683(5)	0.071(2)
C(25)	0.2963(7)	0.4557(5)	0.3256(4)	0.069(3)
C(26)	0.4768(7)	0.3530(5)	0.2136(5)	0.066(2)
C(27)	0.6015(8)	0.3690(5)	0.1415(5)	0.075(3)
C(28)	0.6668(7)	0.5137(5)	0.0322(4)	0.072(2)
C(29)	0.7643(6)	0.5419(5)	0.0781(4)	0.0583(19)
C(30)	0.7360(6)	0.6774(5)	0.1754(4)	0.059(2)
C(31)	0.7270(6)	0.7821(5)	0.1070(5)	0.063(2)
C(32)	0.5532(6)	0.8321(4)	0.0110(4)	0.0534(17)

[a] U_{eq} = one-third of the trace of the orthogonalized *U*.

TABLE 6. Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for $C_{16}H_{23}BrHgO_5$ (**10**)

Atom	*x*	*y*	*z*	U_{eq} (Å^2) [a]
Hg	0.91814(3)	−0.17870(4)	−0.07961(2)	0.0316(1)
Br	0.83361(9)	0.00297(12)	0.00855(6)	0.0519(4)
O(1)	0.8373(5)	−0.4724(7)	−0.0463(3)	0.049(3)
O(2)	0.6166(5)	−0.3764(7)	−0.0129(3)	0.048(2)
O(3)	0.5314(5)	−0.0727(7)	−0.0863(3)	0.048(2)
O(4)	0.7607(5)	−0.0670(6)	−0.2070(3)	0.042(2)
O(5)	0.9918(5)	−0.0187(7)	−0.2125(3)	0.044(2)
C(1)	0.9984(7)	−0.3387(10)	−0.1464(5)	0.033(3)
C(2)	1.0681(7)	−0.2868(10)	−0.2031(5)	0.039(3)
C(3)	1.1253(8)	−0.3952(13)	−0.2458(6)	0.053(4)
C(4)	1.1133(9)	−0.5541(13)	−0.2341(6)	0.058(4)
C(5)	1.0457(8)	−0.6042(11)	−0.1811(6)	0.050(4)
C(6)	0.9852(8)	−0.5013(11)	−0.1368(5)	0.037(3)
C(7)	0.9096(8)	−0.5788(10)	−0.0821(5)	0.047(3)
C(8)	0.7686(8)	−0.5439(11)	0.0062(5)	0.048(4)
C(9)	0.6967(9)	−0.4244(11)	0.0422(5)	0.050(3)
C(10)	0.5456(9)	−0.2609(12)	0.0183(6)	0.059(4)
C(11)	0.4776(8)	−0.1912(12)	−0.0456(6)	0.053(3)
C(12)	0.6119(7)	−0.1320(10)	−0.1346(5)	0.042(3)
C(13)	0.6665(7)	−0.0002(10)	−0.1742(5)	0.040(3)
C(14)	0.8143(8)	0.0319(10)	−0.2574(5)	0.043(3)
C(15)	0.9209(7)	−0.0382(10)	−0.2783(4)	0.036(3)
C(16)	1.0887(8)	−0.1122(10)	−0.2168(5)	0.042(3)

[a] U_{eq} = one-third of the trace of the orthogonalized *U*.

3.18. (2-n-Butyl-1,3-xylylene)-18-crown-5 (23)

A solution of **9** (2 mmol) in THF (25 ml), prepared at −60°C from **2** and n-butyllithium, was allowed to warm to room temperature overnight then was quenched with D_2O (0.5 ml). The mixture was evaporated to dryness, an excess of water was added, and the organic products were extracted with dichloromethane. The crude product (0.72 g of a slightly yellowish oil) was analyzed with ^{1}H NMR spectroscopy and GLC-MS. In addition to the deuterolysis product **14a** (26%), an appreciable amount (67%) of (2-n-butyl-1,3-xylylene)-18-crown-5 (**23**, *cf.* [2]) was present, formed by alkylation of **9** by n-butyl bromide. The remaining products (about 7%, possibly ether cleavage products) could not be identified. Purification of **23** was performed by

crystallization from diethyl ether/n-pentane (m.p. about 43°C), although complete separation from **14a** was not possible.

23: ^{1}H NMR (250 MHz, $CDCl_3$, ref. $CHCl_3$ = 7.27 ppm): δ 0.98 (t, ^3J = 7 Hz, 3H, alkyl-CH_3); 1.47–1.51 (m, 4H, CH_2CH_2); 3.06 (t, broad, ^3J = 9 Hz, 2H, CH_2–C_3H_7); 3.50–3.70 (m, 16H, C_2H_4); 4.29 (d, A part of AB, ^2J = 11 Hz, 2H, xylyl-CH_2); 4.90 (d, B part of AB, ^2J = 11 Hz, 2H, xylyl-CH_2); 7.10 (t, ^3J = 7 Hz, 1H, xylyl-H(5)); 7.20 (d, ^3J = 7 Hz, 2H, xylyl-H(4,6)). ^{13}C NMR (62.89 MHz, $CDCl_3$, ref. $CDCl_3$ = 77 ppm): δ 14.1 (q, ^1J(C–H) = 124 Hz, 1C, Me); 23.5 (t, ^1J(C–H) = 125 Hz, 1C, CH_2–Me), 27.2 (t, ^1J(C–H) = 128 Hz, 1C, CH_2–Et); 33.4 (t, ^1J(C–H) = 127 Hz, 1C, aryl-CH_2–Pr); 69.2 (t, ^1J(C–H) = 140 Hz, 2C, C_2H_4); 70.3 (t, ^1J(C–H) = 141 Hz, 2C, C_2H_4); 70.5 (t, ^1J(C–H) = 141 Hz, 2C, C_2H_4); 70.6 (t, ^1J(C–H) = 141 Hz, 2C, C_2H_4); 72.1 (t, ^1J(C–H) = 141 Hz, 2C, xylyl-CH_2); 124.9 (d, ^1J(C–H) = 161 Hz, 1C, xylyl(5)); 130.8 (d, ^1J(C–H) = 158 Hz, 2C, xylyl(4,6)); 136.2 (s, 2C, xylyl(1,3)); 143.5 (s, 1C, xylyl(2)). GLC-MS mass spectrum: *m/z* (rel. intensity) 352 (4, M^+, $C_{20}H_{32}O_5$), 175(30), 158(38), 143(22), 131(16), 129(28), 119(30), 105(15), 89(37), 45(100).

3.19. Crystal structure determinations

X-Ray data were collected on an Enraf–Nonius CAD4 diffractometer. All calculations were carried out on a MicroVAX-II cluster. Details of the structure determinations are given in Table 4. Supplementary data have been deposited with the Cambridge Crystallographic Data Centre. Geometrical calculations were carried out with PLATON [7], and molecular drawings are by PLUTON [8]. Scattering factors were taken from [9] and corrected for anomalous dispersion [10].

For **4**, ($C_{16}H_{23}BrMgO_5$), reflections were collected from a transparent colorless crystal glued on top of a glass fibre. Unit cell parameters were derived from the SET4 setting of 12 reflections in the range $13 < \theta < 19°$. The data were corrected for Lp decay and absorption (DIFABS [11] correction range 0.87–1.20). The structure was solved by direct methods with SHELXS-86 [12] and refined on F with SHELX-76 [13]. Hydrogen atoms were fixed at calculated positions with a common U_{iso}. Final positions of all non H-atoms are given in Table 5.

For **10** ($C_{16}H_{23}BrHgO_5$) reflection data were collected from a block-shaped transparent colorless crystal. Unit cell parameters were derived from the SET4 setting of 25 reflections in the range $9 < \theta < 15°$. The data were corrected for Lp, decay and absorption (DIFABS [11] correction range 0.74–1.63). The structure was solved by standard Patterson and Fourier methods with SHELXS-86 [12] and refined on F with SHELX-76 [13]. Hydrogen atoms were fixed at calculated positions with a common U_{iso}. Final positions of all non H-atoms are given in Table 6.

For **11** ($C_{32}H_{46}HgO_{10}$), reflection data were collected from a colorless block-shaped crystal glued on top of a glass fiber. Unit cell parameters were derived from the SET4 setting angles of 12 reflections in the range $11 < \theta < 14°$. The data were corrected for Lp, decay and absorption (DIFABS [11] correction range 0.78–1.41). The structure was solved with standard Patterson and Fourier techniques with SHELXS-86 [12] and refined with SHELX-76 [13]. Hydrogen atoms were fixed at calculated positions. Final positions of all non H-atoms are given in Table 7.

TABLE 7. Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for $C_{32}H_{46}HgO_{10}$ (**11**)

Atom	*x*	*y*	*z*	U_{eq} (Å^2) [a]
Hg	1	1	0	0.0338(1)
O(1)	0.7962(3)	0.7679(3)	0.04924(13)	0.0426(8)
O(2)	0.5799(4)	0.6952(3)	−0.05823(17)	0.0668(11)
O(3)	0.5865(4)	0.9559(4)	−0.15987(18)	0.0670(12)
O(4)	0.7298(3)	1.2097(3)	−0.09557(15)	0.0544(10)
O(5)	0.9313(3)	1.3289(3)	0.00616(14)	0.0428(9)
C(1)	0.9417(4)	1.0567(5)	0.09616(18)	0.0348(10)
C(2)	0.9477(4)	1.2072(4)	0.1202(2)	0.0387(12)
C(3)	0.9095(4)	1.2416(5)	0.1849(2)	0.0490(14)
C(4)	0.8639(5)	1.1322(6)	0.2266(2)	0.0560(16)
C(5)	0.8539(4)	0.9851(6)	0.20396(19)	0.0520(13)
C(6)	0.8924(4)	0.9464(5)	0.1396(2)	0.0377(11)
C(7)	0.8808(5)	0.7827(5)	0.1138(2)	0.0434(12)
C(8)	0.6510(4)	0.7893(5)	0.0546(2)	0.0508(16)
C(9)	0.5788(5)	0.8257(5)	−0.0152(2)	0.0588(17)
C(10)	0.5071(6)	0.7158(6)	−0.1253(3)	0.0723(19)
C(11)	0.5916(7)	0.7991(6)	−0.1730(3)	0.0737(19)
C(12)	0.6884(6)	1.0383(6)	−0.1896(3)	0.0692(19)
C(13)	0.6820(6)	1.2004(6)	−0.1667(2)	0.0682(19)
C(14)	0.7260(5)	1.3596(5)	−0.0719(2)	0.0564(14)
C(15)	0.7878(4)	1.3668(5)	0.0029(2)	0.0497(14)
C(16)	0.9990(4)	1.3292(4)	0.0755(2)	0.0470(14)

[a] U_{eq} = one-third of the trace of the orthogonalized U.

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